

# Structural Characterization of Heterodimetallic Zr/Pd and Zr/Rh Catalyst Precursors Containing the C<sub>5</sub>H<sub>4</sub>PPh<sub>2</sub> Ligand

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(Cp-PPh<sub>2</sub>)<sub>2</sub>ZrCl<sub>2</sub> (**5**) reacts with (PhCN)<sub>2</sub>PdCl<sub>2</sub> to yield the early–late heterodimetallic complex [(Cp-PPh<sub>2</sub>)<sub>2</sub>ZrCl<sub>2</sub>/PdCl<sub>2</sub>], **7**, which was characterized by an X-ray crystal structure analysis. The phosphine-substituted bent metallocene moiety in **7** serves as a conformationally flexible chelate phosphine ligand (angle P–Pd–P: 96.46(3)°). Complex **7** is an active catalyst for the cross-coupling of *sec*-butylmagnesium bromide with bromobenzene, leading to excellent regioselectivity and moderate reactivity. Complex **5** reacts with dicarbonylrhodium chloride dimer (0.5 equiv) to yield the triply bridged complex **12**, [ClZr(μ-Cp-PPh<sub>2</sub>)<sub>2</sub>(μ-Cl)Rh(CO)Cl], which was also characterized by X-ray diffraction (the angle P–Rh–P is 158° at the distorted square-pyramidal pentacoordinated rhodium center). (Cp-PPh<sub>2</sub>)<sub>2</sub>Zr(CH<sub>3</sub>)<sub>2</sub> (**13**) reacts with [H(CO)Rh(PPh<sub>3</sub>)<sub>3</sub>] (**14**) with loss of two PPh<sub>3</sub> ligands and instantaneous liberation of methane to form complex **15**, [CH<sub>3</sub>Zr(μ-Cp-PPh<sub>2</sub>)<sub>2</sub>Rh(CO)PPh<sub>3</sub>](Zr–Rh), which probably contains a metal–metal bond between the early and late transition metal. Complex **15** is a very active 1-hexene hydroformylation catalyst (TOF > 600, n/iso ≈ 3 at 80 °C).

## Introduction

Phosphine ligands are extensively used in homogeneous catalysis, and especially chelate phosphines are of enormous importance.<sup>1</sup> Phosphines that are attached at organometallic frameworks have been very useful for a number of catalytic applications, with 1,1'-bis(diphenylphosphino)ferrocene and its derivatives being very typical examples.<sup>2</sup> One might envisage that the analogous phosphine derivatives of the group 4 bent metallocenes may become of a similar usefulness as chelate ligands in catalysis,<sup>3</sup> especially since their central MX<sub>2</sub> moiety may open additional possibilities for catalyst activation, offering ways of coordinative or electronic support of the catalytic process and the action of the active catalyst center.

The organometallic chemistry of the Cp-PPh<sub>2</sub> ligand at group 4 metal complexes is developed to a significant extent. There are a variety of examples of the complex type **1** and **2** (see Chart 1)<sup>4,5</sup> and related systems<sup>6,7</sup> known, although surprisingly few examples of the heterodimetallic metallocene systems were character-

ized by X-ray diffraction, and only a few of these and the related Cp<sub>2</sub>M[–(CR<sub>2</sub>)<sub>n</sub>PR<sub>2</sub>]<sub>2</sub>-type systems **3** were employed in the development of catalytic reactions.<sup>8,9</sup> We have now prepared a few novel (Cp-PPh<sub>2</sub>)ZrX<sub>2</sub>/palladium and rhodium complexes, characterized two

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<sup>†</sup> X-ray crystal structure analyses.

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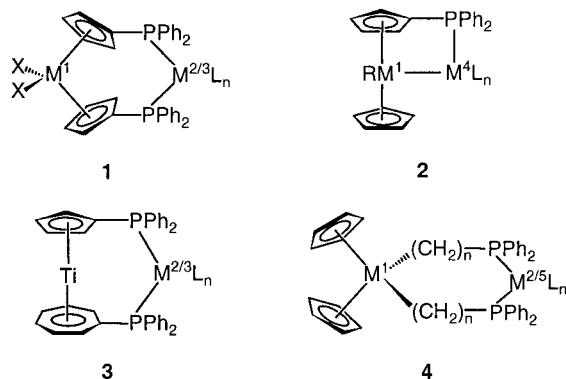
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**Chart 1. Selection of Previously Reported Types of Phosphine-Containing Early(group 4)–Late Heterodimetallic Complexes**

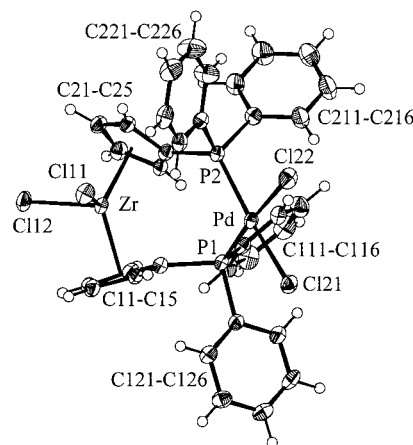
(M<sup>1</sup> = Zr, Ti; e.g. M<sup>2</sup> = Cr, Mo; M<sup>3</sup> = W, Mn, Pd, Pt, Ru, Cu;  
M<sup>4</sup> = Co, Fe; M<sup>5</sup> = Ni, Rh)

examples by X-ray crystal structure analyses, and found that such early–late heterodimetallic systems may have quite some potential in homogeneous catalysis.

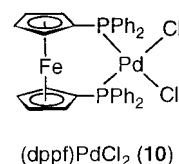
## Results and Discussion

**Synthesis, Structure, and Catalytic Features of a Zirconium/Palladium System.** Bis(diphenylphosphinocyclopentadienyl)zirconium dichloride (**5**) was prepared by treatment of ZrCl<sub>4</sub>(thf)<sub>2</sub> with (Cp-PPh<sub>2</sub>)Li, analogously as described by W. Tikkanen et al.<sup>10</sup> The organometallic chelate phosphine ligand **5** was obtained as a colorless solid in 80% yield. It was then treated with bis(benzonitrile)palladium dichloride (**6**) in dichloromethane (−78 °C to room temperature). Two equivalents of benzonitrile were cleaved off, and the adduct κ<sup>2</sup>P,P′-[(Cp-PPh<sub>2</sub>)<sub>2</sub>ZrCl<sub>2</sub>]PdCl<sub>2</sub> (**7**) was isolated as a pale yellow solid (85% yield). It shows a <sup>31</sup>P NMR resonance at δ 29.0 ppm (**5**: δ −17.0 ppm) and two C<sub>5</sub>H<sub>4</sub> <sup>1</sup>H NMR multiplets at δ 6.91 and 6.34 ppm [corresponding <sup>13</sup>C NMR methine resonances of the Ph<sub>2</sub>P-substituted Cp-ligand at δ 127.5 (<sup>1</sup>J<sub>PC</sub> = 6.9 Hz) and δ 121.4 (<sup>1</sup>J<sub>PC</sub> = 8.6 Hz)].

Diffusion of pentane into a dichloromethane solution of **7** furnished single crystals for the X-ray crystal structure analysis. In the structure of **7** the zirconium and palladium atoms are well separated (Zr...Pd 4.723(1) Å).<sup>7c,11</sup> They are connected by means of the bridging Cp-PPh<sub>2</sub> ligands, the Cp-parts of which are coordinated to zirconium and the phosphorus atoms to palladium. The bent metallocene moiety of **7** shows unexceptional bonding parameters. The Cp(centroid)–Zr–Cp(centroid) angle is 130.3°, the Cl(11)–Zr–Cl(12) angle amounts to 96.25(4)° (*d*(Zr–Cl(11)) = 2.416(1) Å; *d*(Zr–Cl(12)) = 2.419(1) Å). These values are in the typical range of Cp<sub>2</sub>ZrCl<sub>2</sub> complexes.<sup>12</sup> The substituted zirconocene unit exhibits a staggered metallocene conformation. Both Ph<sub>2</sub>P-substituents are oriented toward the backside of the bent metallocene wedge. They are located there in close conformational proximity at adjacent staggered positions.



**Figure 1.** Molecular structure of the Zr/Pd complex **7** (with unsystematical atom-numbering scheme). Selected bond lengths (Å) and angles (deg) (additional values are given in the text): Zr–Cl11 2.416(1), Zr–Cl12 2.419(1), Zr–C<sub>Cp1</sub> 2.514(4), Zr–C<sub>Cp2</sub> 2.515(4), Pd–Cl21 2.330(1), Pd–Cl22 2.346(1), Pd–P1 2.279(1), Pd–P2 2.278(1), P1–C11 1.811(4), P1–C111 1.814(3), P1–C121 1.829(4), P2–C21 1.804(3), P2–C211 1.826(4), P2–C221 1.825(3); Cl11–Zr–Cl12 96.25(4), Zr–Cl11–P1 131.9(2), Zr–C21–P2 128.9(2), C11–P1–Pd 115.3(1), C111–P1–Pd 112.4(1), C121–P1–Pd 115.5(1), C11–P1–C111 110.1(2), C11–P1–C121 101.3(2), C111–P1–C121 100.8(2), C21–P2–Pd 122.0(1), C211–P2–Pd 113.1(1), C221–P2–Pd 112.1(1), C21–P2–C211 101.4(2), C21–P2–C221 101.4(2), C211–P2–C221 104.9(2), Cl21–Pd–Cl22 88.12(4), P1–Pd–P2 96.46(3), Cl21–Pd–P1 89.42(3), Cl21–Pd–P2 174.11(3), Cl22–Pd–P1 175.21(4), Cl22–Pd–P2 86.03(3).

**Chart 2. Structure of the (dppf)PdCl<sub>2</sub> Catalyst Precursor**(dppf)PdCl<sub>2</sub> (**10**)

The coordination geometry at palladium is distorted square-planar (see Figure 1). The chelate phosphine ligand binds to adjacent cis-positions at Pd (*d*(P(1)–Pd) = 2.279(1) Å, *d*(P(2)–Pd) = 2.278(1) Å, *d*(Cl(21)–Pd) = 2.330(1) Å, *d*(Cl(22)–Pd) = 2.346(1) Å). These bond distances are very similar to those found in (dppf)PdCl<sub>2</sub> (**10**) (see Chart 2; *d*(P–Pd) = 2.301(1), 2.283(1) Å; *d*(Cl–Pd) = 2.347(1), 2.348(1) Å<sup>13</sup>). The “bite angle” of a bent metallocene is in principle variable; it will adjust favorably to the stereoelectronic needs of the coordinated late transition metal. In **7** this leads to a P(1)–Pd–P(2) angle of 96.46(3)°, which is noticeably smaller than the P–Pd–P bite angle in **10** of 99.07(5)°.<sup>13</sup> The remaining bond angles around palladium in **7** are 89.42(3)° (P(1)–Pd–Cl(21)), 88.12(4)° (Cl(21)–Pd–Cl(22)), and 86.03(3)° (P(2)–Pd–Cl(22)). The C(Cp)–P–Pd coordination angles amount to 115.3(1)° (at P(1)) and 122.0(1)° (at P(2)). The remaining bond angles at the tetravalent phosphorus atoms are markedly smaller as expected (see Figure 1).

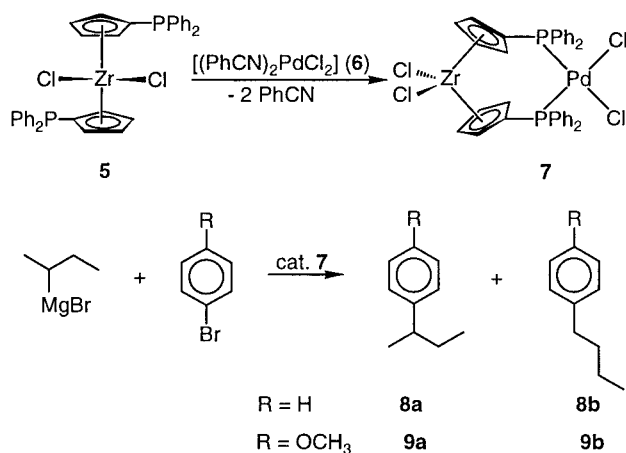
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Scheme 1



**Table 1. Pd-Catalyzed Cross-Coupling Reactions between *sec*-Butylmagnesium Bromide and Bromobenzene or *p*-Bromoanisole<sup>a</sup>**

cat.	temp	rxn time	% <b>8a</b>	<b>8b</b> <sup>b</sup>
<b>7</b>	rt	1 h	11	<1
		4.5 h	33	<1
		16 days	53	<1
<b>7</b>	-30 °C	26 h	40	<1
<b>10</b>	rt	0.5 h	35	<1
		2 h	78	<1
		5.25 h	98	<1
PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> <sup>c</sup>	rt	24 h	5	6
PdCl <sub>2</sub> (dppe) <sup>c</sup>	40 °C	48 h		
PdCl <sub>2</sub> (dppp) <sup>c</sup>	r.t.	24 h	43	19
PdCl <sub>2</sub> (dppp) <sup>c</sup>	r.t.	8 h	51	25
cat.	temp	rxn time	% <b>9a</b>	<b>9b</b> <sup>d</sup>
<b>7</b>	rt	19 h	16	<1 <sup>e</sup>
<b>10</b>	rt	19 h	75	1
PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	rt	18 h	3	2

<sup>a</sup> Reactions in ether employing 5 mol % of the respective catalyst. Structures of the products are depicted in Scheme 1.

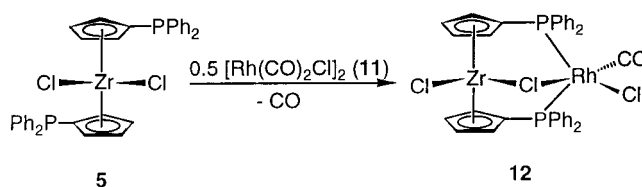
<sup>b</sup> Total conversion determined by GPC with internal standard *n*-dodecane, rest to 100% is starting material. <sup>c</sup> From ref 14a.

<sup>d</sup> Products derived from *p*-bromoanisole. <sup>e</sup> Contains traces of anisole.

Complex **7** catalyzes the cross-coupling between *sec*-butylmagnesium bromide and bromobenzene to give *sec*-butylbenzene very selectively with only trace admixtures of the isomeric *n*-butylbenzene coupling product. In view of the regioselective outcome the catalyst **7** (employed in 5 mol % concentration in these experiments) equals the conventionally used (dppf)PdCl<sub>2</sub> catalyst **10**, but is considerably less active.<sup>13a,14</sup> Typically, the catalysis by **7** gives ca. 33% of **8a** (with only a <1% trace of **8b**, see Scheme 1 and Table 1) after ca. 4.5 h at ambient temperature; in a comparison, complex **10** has catalytically transformed this mixture of the starting materials to an extent of 95% after 2 h at ambient temperature (**8a:8b** > 80:1). In turn, complex **7** catalyzes the *sec*-butylmagnesium bromide plus bromobenzene cross-coupling reaction considerably better than the conventional catalysts PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, PdCl<sub>2</sub>(dppe), PdCl<sub>2</sub>(dppp), or PdCl<sub>2</sub>(dppb) (i.e., with the chelate ligands bis(diphenylphosphino)ethane, -propane, or -butane), with regard to both activity and selectivity.<sup>14a</sup>

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Scheme 2



A similar overall trend was observed in the cross-coupling reaction between *sec*-butylmagnesium bromide and *p*-bromoanisole, catalyzed by **7**, **10**, and PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>.

**Zirconium/Rhodium Complexes.** Treatment of (Cp-PPh<sub>2</sub>)<sub>2</sub>ZrCl<sub>2</sub> (**5**) with 0.5 molar equiv of [(CO)<sub>2</sub>RhCl]<sub>2</sub> (**11**) gave the 1:1 adduct **12**, which was isolated in close to 90% yield. The product shows a single <sup>31</sup>P NMR resonance at δ 8.1 ppm with a <sup>1</sup>J<sub>Rh-P</sub> coupling constant of 93 Hz. Together with the observation of a set of four C<sub>5</sub>H<sub>4</sub>-methine <sup>1</sup>H NMR signals at δ 6.60, 6.45, 6.05, and 5.84 (corresponding <sup>13</sup>C NMR resonances at δ 121.1, 116.4, 116.1, 105.3 ppm) this points to a distorted pentacoordinated geometry at rhodium.<sup>15</sup> Complex **12** exhibits an IR ν(CO) band at 1990 cm<sup>-1</sup> (in KBr) [RhCl(CO)(PR<sub>3</sub>)<sub>2</sub>: ν = 1969 cm<sup>-1</sup> (PEtPh<sub>2</sub>); 1974 cm<sup>-1</sup> (PMe-Ph<sub>2</sub>)<sup>16</sup>]. Single crystals of **12** were obtained from tetrahydrofuran. The yellow needles contained four molecules of disordered solvent THF in the unit cell. In the solid state, the molecules of **12** are C<sub>s</sub>-symmetric, with the symmetry plane lying in the zirconocene σ-ligand plane. The two metal centers are connected again by two κP,η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>-PPh<sub>2</sub> ligands, and in addition they are bridged by a μ-chloride ligand. The Cp(centroid)-Zr-Cp(centroid) angle at zirconium is 131.6°, which is in the typical group 4 bent metallocene range. However, the Cl(1)-Zr-Cl(2) angle is at 80.3(1)°, much smaller than usually observed (e.g., **7**: ~96°). Also the Zr-Cl(1) (2.556(3) Å) and Zr-Cl(2) (2.504(4) Å) bond lengths are increased from the typical zirconocene dichloride values.<sup>12,17</sup> Both these features may indicate some zirconium/rhodium interaction; the Zr...Rh separation in **12** is 2.997(2) Å, which is just outside the sum of the covalent radii.<sup>18</sup>

The rhodium coordination is distorted square-pyramidal. The two phosphorus atoms and the CO and Cl(1) ligand mark the basis of this coordination polyhedron, and Cl(3) is at its apex. The apical Rh-Cl(3) bond (2.574(4) Å), oriented trans to zirconium, is significantly longer than the basal Rh-Cl(1) linkage (2.398(3) Å), which may further indicate a weak electronic Rh...Zr interaction making use of the empty lateral metallocene acceptor orbital in the heterodimetallic complex **12**.

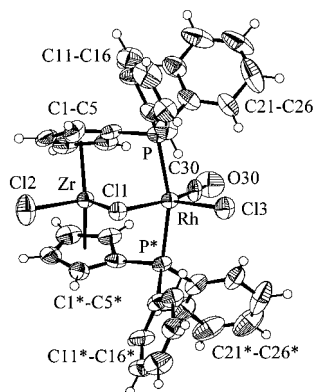
(15) Tetracoordinated Cl(CO)<sub>2</sub>Rh(PPh<sub>2</sub>)<sub>2</sub> complexes typically show larger <sup>31</sup>P NMR δ-values (ca. 13–26 ppm) and substantially increased <sup>1</sup>J<sub>Rh-P</sub> coupling constants (ca. 115–130 Hz), see ref 7b and: Mann, B. E.; Masters, C.; Shaw, B. L. *J. Chem. Soc. (A)* **1971**, 1104.

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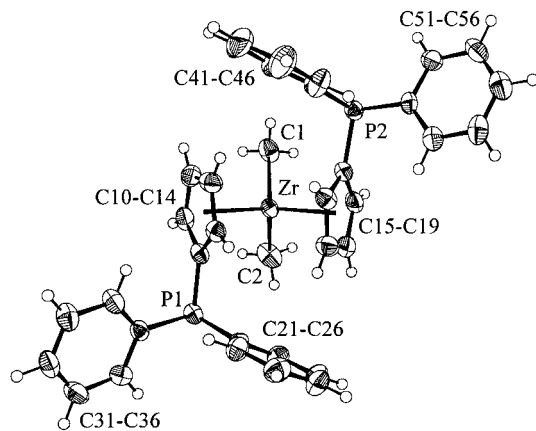




**Figure 2.** Molecular structure of the Zr/Rh complex **12** (with unsystematical atom-numbering scheme). Selected bond lengths (Å) and angles (deg) (for additional values see text): Rh–Zr 2.997(2), Rh–P 2.311(3), Rh–Cl1 2.398(3), Rh–Cl3 2.574(4), Rh–C30 1.84(2), C30–O30 1.13(2), P–C1 1.812(10), P–C11 1.820(10), P–C21 1.820(10), Zr–Cl1 2.556(3), Zr–Cl2 2.504(4), Zr–C<sub>CP</sub> 2.503(10); P–Rh–P\* 158.4(1), P–Rh–Cl1 87.5(1), P–Rh–Cl3 100.7(1), Cl1–Rh–Cl3 96.1(1), P–Rh–C30 88.6(1), Cl1–Rh–C30 159.4(4), Cl3–Rh–C30 104.5(4), Rh–C30–O30 179.7(12), Rh–P–C1 100.3(3), Rh–P–C11 120.3(3), Rh–P–C21 119.2(4), C1–P–C11 106.7(5), C1–P–C21 106.9(5), C11–P–C21 102.1(5), Rh–Cl1–Zr 74.4(1), Cl1–Zr–Cl2 80.3(1).

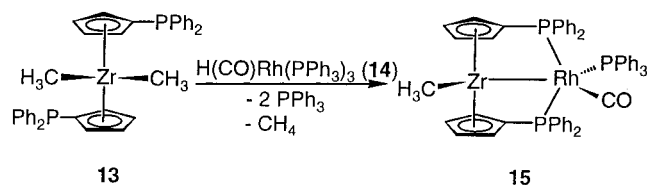
The phosphines are coordinated trans to each other at Rh ( $d(\text{Rh}–\text{P}) = 2.311(3)$  Å).<sup>19,20</sup> The corresponding bond angles at the base of the distorted square pyramid are 158.4(1)° (P–Rh–P\*), 87.5(1)° (P–Rh–Cl(1)), 159.4(4)° (Cl(1)–Rh–C(30)), and 88.6(1)° (P–Rh–C(30)). The remaining bond angles to the apical chloride ligand amount to 96.1(1)° (Cl(1)–Rh–Cl(3)), 100.7(1)° (P–Rh–Cl(3)), and 104.5(4)° (C(30)–Rh–Cl(3)). The Rh–C(30) bond length of the rhodium–carbonyl moiety is 1.84(2) Å; the C(30)–O(30) bond is short at 1.13(2) Å.

Complex **5** was then converted to  $(\text{Cp}–\text{PPh}_2)_2\text{Zr}(\text{CH}_3)_2$  (**13**) by treatment with 2 equiv of methylolithium analogously as described in the literature.<sup>10</sup> We have characterized complex **13** by an X-ray crystal structure analysis (see Figure 3). It was then reacted with hydrido(carbonyl)tris(triphenylphosphine)rhodium (**14**) in toluene solution at 0 °C. A dark red solution is formed instantaneously with evolution of methane. The liberated triphenylphosphine was difficult to separate from the resulting organometallic product (**15**). Eventually a clean microcrystalline sample of **15** was obtained from toluene/ether (1:1). We assume that a Cp–PPh<sub>2</sub>-bridged zirconium, rhodium ( $\text{Zr}–\text{Rh}$ ) complex containing a metal–metal bond was formed, similar to the [(alkoxy)phosphine] $\text{Zr}–\text{Rh}$  systems previously reported by P. Wolczanski et al.<sup>21</sup> Complex **15** exhibits a IR  $\tilde{\nu}(\text{CO})$  band at 1977 cm<sup>−1</sup> in dichloromethane solution. The <sup>13</sup>C NMR resonance of the Rh–C≡O moiety is observed at  $\delta$  195.5 ppm (ddt, with coupling constants of <sup>1</sup> $J_{\text{RhC}} = 80$  Hz and



**Figure 3.** Molecular structure of **13** (with unsystematical atom-numbering scheme). Selected bond lengths (Å) and angles (deg) (for additional values see text): Zr–C1 2.250(4), Zr–C2 2.268(5), Zr–C<sub>CP1</sub> 2.526(5), Zr–C<sub>CP2</sub> 2.535(5), P1–C10 1.821(4), P1–C21 1.841(4), P1–C31 1.840(4), P2–C15 1.820(4), P2–C41 1.839(4), P2–C51 1.821(4); C1–Zr–C2 92.9(2), Zr–C10–P1 122.5(2), Zr–C15–P2 122.8(2), C10–P1–C21 101.6(2), C10–P1–C31 100.3(2), C21–P1–C31 100.9(2), C15–P2–C41 101.4(2), C15–P2–C51 101.2(2), C41–P2–C51 100.9(2).

### Scheme 3



<sup>2</sup> $J_{\text{PC}} = 9$  and 12 Hz). There is a single <sup>1</sup>H NMR Zr–CH<sub>3</sub> resonance at  $\delta$  −0.83 ppm (corresponding <sup>13</sup>C NMR signal at  $\delta$  29.1 ppm). Complex **15** exhibits two <sup>31</sup>P NMR resonances in a 2:1 intensity ratio at  $\delta$  27.2 ppm (C<sub>5</sub>H<sub>4</sub>–PPh<sub>2</sub>, <sup>1</sup> $J_{\text{RhP}} = 162$  Hz) and  $\delta$  45.5 ppm (Rh–PPh<sub>3</sub>, <sup>1</sup> $J_{\text{RhP}} = 111$  Hz) with a geminal coupling constant of <sup>2</sup> $J_{\text{PP}} = 37$  Hz. Complex **15** exhibits four separate C<sub>5</sub>H<sub>4</sub> <sup>1</sup>H NMR resonances at  $\delta$  6.61, 6.40, 5.40, and 4.11 (with corresponding <sup>13</sup>C NMR signals at  $\delta$  116.31, 116.29, 108.3, and 103.4; ipso-carbon atom signal of the symmetry-equivalent C<sub>5</sub>H<sub>4</sub>–PPh<sub>2</sub> ligands at  $\delta$  107.8 ppm).

Complex **15** is an active hydroformylation catalyst.<sup>22</sup> It was shown to catalyze the formation of heptanals from 1-hexene in a temperature range of ca. 22–120 °C. Above ca. 50 °C excellent activities are obtained. The maximum *initial* turnover frequency of >600 mol aldehyde/(mol catalyst·h) for 1-hexene hydroformylation was found at 80 °C, 20 bar CO/H<sub>2</sub> (1:1) pressure with a substrate-to-catalyst ratio of 400. This is in the very high activity range and equals or exceeds some of the best Rh/chelate phosphine systems (see Chart 3)<sup>23</sup> operating in organic solvents. *n*/iso ratios of about 3 are obtained at the catalyst system **15**. This is in the range

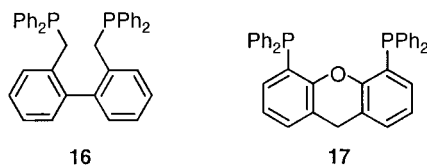
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**Chart 3. Structures of the Chelate Phosphines 16 and 17**

observed for many other Rh hydroformylation systems, but it is far away from the optimum,<sup>24</sup> such as, for example, achieved with the ligand examples **16** and **17** shown in Chart 3.

### Conclusions

In the monometallic ligand systems (Cp-PPh<sub>2</sub>)<sub>2</sub>ZrX<sub>2</sub> (X = Cl or CH<sub>3</sub>), the bulky Ph<sub>2</sub>P-substituents are oriented far away from each other in the lateral sectors of the bent metallocene wedge (bis-lateral:anti-conformation). However, rotation about the Zr–Cp vector is a low activation energy process<sup>25</sup> and thus allows for an adjustment of the actual bite angle over a very broad range, when these systems function as organometallic chelate phosphines in early–late heterodimetallic complexes. In this respect, the bent metallocene chelate phosphines are fundamentally different from their ordinary “linear” metallocene chelate phosphine relatives, such as, for example, dppe<sup>13</sup> (**10**, see Chart 2). This great variability and adjustment of the P–M–P angle is illustrated by the two structurally characterized systems described in this study: the Zr/Pd complex **7** exhibits a P–Pd–P angle of 96°, whereas the Zr/Rh complex **15** shows a 158° angle. The pronounced conformational flexibility of the group 4 bent metallocenes makes an a priori adjustment of the optimal chelate bite angle difficult, but this high conformational freedom apparently allows some systems to adjust to achieve either a high selectivity (observed in cross-coupling at the catalyst originating from the Zr/Pd system **7**) or high reactivity (Zr/Rh hydroformylation catalyst **15**). Carefully adding a few conformational restraints by using ansa-metallocene frameworks may lead to a way to generate novel catalyst systems of this type with much improved reactivity/selectivity profiles.

The selected examples **7**, **12**, and **15** also illustrate nicely the broad range of support that the group 4 bent metallocene unit can provide for the adjacent late transition metal in such early–late heterodimetallic complexes. In **7** the (Cp-PPh<sub>2</sub>)<sub>2</sub>ZrCl<sub>2</sub> unit merely serves as a flexible chelate phosphine ligand, but in **12** and **15** it actively interacts by means of additional bridging or the formation of a metal–metal bond with the Rh-center and alters and determines its coordinative and electronic features substantially. Such effects will probably be very useful in catalyst design and control of catalyst action, as indicated by the high hydroformylation activity found with the heterodimetallic Zr/Rh catalyst **15**.

### Experimental Section

All reactions were carried out under argon using Schlenk-type glassware or in a glovebox. Solvents were dried and distilled under argon prior to use. For further general information including a list of instrumentation used for the spectroscopic and physical characterization of the compounds see ref 26. The complexes (Cp-PPh<sub>2</sub>)<sub>2</sub>ZrCl<sub>2</sub> (**5**) and (Cp-PPh<sub>2</sub>)<sub>2</sub>Zr(CH<sub>3</sub>)<sub>2</sub> (**13**) were prepared analogously as described in the literature.<sup>10</sup>

**Reaction of (Cp-PPh<sub>2</sub>)<sub>2</sub>ZrCl<sub>2</sub> (**5**) with (PhCN)<sub>2</sub>PdCl<sub>2</sub>, Synthesis of **7**.** Two separate solutions of (Cp-PPh<sub>2</sub>)<sub>2</sub>ZrCl<sub>2</sub> (**5**, 572 mg, 0.87 mmol) and (PhCN)<sub>2</sub>PdCl<sub>2</sub> (**6**, 333 mg, 0.87 mmol), each in 30 mL of dichloromethane, were cooled to –78 °C and then slowly added dropwise simultaneously to 20 mL of dichloromethane at –78 °C. The mixture was stirred at –78 °C for 1 h and then warmed to room temperature. After 12 h the reaction mixture was reduced to a volume of 10 mL in vacuo, and the product precipitated by the addition of pentane (20 mL). The pale yellow solid was collected by filtration and dried in vacuo to yield 620 mg (85%) of **7**. Mp: 260 °C. Anal. C<sub>34</sub>H<sub>28</sub>P<sub>2</sub>Cl<sub>4</sub>ZrPd (838.0): calcd C 48.73, H 3.37; found C 48.75, H 3.46. <sup>1</sup>H NMR (dichloromethane-*d*<sub>2</sub>, 600 MHz): δ = 7.63 (m, 8H), 7.56 (pt, 4H), 7.43 (pt, 8H) (o,p,m-Ph), 6.91 (m, 4H), 6.34 (m, 4H) (C<sub>5</sub>H<sub>4</sub>). <sup>13</sup>C NMR (dichloromethane-*d*<sub>2</sub>, 150 MHz): δ = 131.1 (d, <sup>1</sup>J<sub>PC</sub> = 60 Hz), 135.0 (d, <sup>2</sup>J<sub>PC</sub> = 11 Hz), 132.5 (s), 129.0 (d, <sup>3</sup>J<sub>PC</sub> = 12 Hz; ipso-, o-, p-, m-PPh<sub>2</sub>), 127.5 (d, <sup>2</sup>J<sub>PC</sub> = 7 Hz), 121.4 (d, <sup>3</sup>J<sub>PC</sub> = 9 Hz), 114.8 (dd, <sup>1</sup>J<sub>PC</sub> = 46 Hz, <sup>3</sup>J<sub>PC</sub> = 7 Hz; α-, β-, ipso-C of C<sub>5</sub>H<sub>4</sub>). <sup>31</sup>P NMR (dichloromethane-*d*<sub>2</sub>, 81 MHz): δ = 29.0. IR (KBr): ν̄ = 3086, 2917, 2851, 1482, 1435, 1182, 1095, 1041, 828 cm<sup>–1</sup>. X-ray crystal structure analysis of **7**: single crystals from dichloromethane, formula C<sub>34</sub>H<sub>28</sub>P<sub>2</sub>Cl<sub>4</sub>ZrPd·2/2CH<sub>2</sub>Cl<sub>2</sub>, *M* = 922.85, light yellow crystal 0.35 × 0.10 × 0.05 mm, *a* = 9.443(1) Å, *b* = 14.478(1) Å, *c* = 14.517(1) Å, α = 100.42(1)°, β = 99.47(1)°, γ = 93.59(1)°, *V* = 1916.6(3) Å<sup>3</sup>, ρ<sub>calc</sub> = 1.599 g cm<sup>–3</sup>, μ = 12.67 cm<sup>–1</sup>, empirical absorption correction via SORTAV (0.666 ≤ *T* ≤ 0.939), *Z* = 2, triclinic, space group *P* $\bar{1}$  (No. 2), λ = 0.71073 Å, *T* = 198 K, ω and φ scans, 25 158 reflections collected (±*h*, ±*k*, ±*l*), [(sin θ)/λ] = 0.72 Å<sup>–1</sup>, 11 066 independent (*R*<sub>int</sub> = 0.043) and 8862 observed reflections [*I* ≥ 2 σ(*I*)], 433 refined parameters, *R* = 0.047, *wR*<sub>2</sub> = 0.114, max. residual electron density 1.36 (–0.87) e Å<sup>–3</sup>, occupancies for the solvent molecules refined and then fixed to 0.5, hydrogens calculated and refined as riding atoms, data set collected with a Nonius Kappa CCD on a rotating anode generator FR591.<sup>26</sup>

**Catalytic Cross-Coupling Reaction, Formation of **8** and **9**.** A sample of the Zr/Pd complex **7** (0.04 mmol) was dissolved in 10 mL of diethyl ether. *n*-Dodecane (0.5 mL) was added as an internal standard for the GLC analysis and 4.0 mmol of bromobenzene or *p*-bromoanisole, respectively. The mixture was cooled to –78 °C, and 8.8 mL (8.0 mmol) of a 0.91 M ethereal *sec*-butylmagnesium bromide solution was added. The mixture was then quickly heated to the reaction temperature and the progress of the reaction monitored by analyzing aliquots of the solution. For that purpose 1 mL samples of the mixture were quenched by treatment with 10% aqueous HCl (1 mL), the phases separated, and the organic phases dried over Na<sub>2</sub>SO<sub>4</sub>. The remaining inorganic products were removed by filtration through a 5 × 0.3 cm silica gel column. The clear solution was then analyzed by gas chromatography (25 m HP5 column, temp program 40–280 °C, 10 °C min<sup>–1</sup>). The adduct/product ratio and the product isomer ratio were determined

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by integration relative to the internal standard *n*-dodecane. The results from a series of representative experiments are listed in Table 1.

**Reaction of (Cp-PPh<sub>2</sub>)<sub>2</sub>ZrCl<sub>2</sub> (5) with [Rh(CO)<sub>2</sub>Cl]<sub>2</sub> (11), Preparation of 12. (a) Preparation in Dichloromethane.** A solution of complex 5 (340 mg, 0.51 mmol) in 30 mL of dichloromethane was added dropwise at 0 °C to a solution of 11 (100 mg, 0.254 mmol) in dichloromethane. The reaction mixture was allowed to warm to room temperature and then stirred for 24 h. The mixture was concentrated in vacuo to a volume of 5 mL, and then pentane (20 mL) was added to precipitate further product. The solid was collected by filtration and dried in vacuo to yield 375 mg (89%) of 12. The poorly soluble complex was recrystallized from tetrahydrofuran at -20 °C to give single crystals for the X-ray crystal structure analysis of 12: formula C<sub>35</sub>H<sub>28</sub>OP<sub>2</sub>Cl<sub>3</sub>ZrRh·4C<sub>4</sub>H<sub>8</sub>O, *M* = 1115.41, yellow crystal 1.20 × 0.25 × 0.10 mm, *a* = 10.220(1) Å, *b* = 18.962(4) Å, *c* = 13.161(1) Å, β = 103.09(1)°, *V* = 2484.2(6) Å<sup>3</sup>, ρ<sub>calc</sub> = 1.491 g cm<sup>-3</sup>, μ = 8.13 cm<sup>-1</sup>, no empirical absorption correction due to the shape of the used crystal, *Z* = 2, monoclinic, space group *P*2<sub>1</sub>/*m* (No. 11), λ = 0.71073 Å, *T* = 223 K, ω/2θ scans, 4787 reflections collected (-*h*, -*k*, ±*l*), [(sin θ)/λ] = 0.59 Å<sup>-1</sup>, 4521 independent (*R*<sub>int</sub> = 0.083) and 2520 observed reflections [*I* ≥ 2 σ(*I*)], 344 refined parameters, *R* = 0.069, *wR*<sub>2</sub> = 0.171, max. residual electron density 1.09 (-0.94) e Å<sup>-3</sup>, hydrogens calculated and refined as riding atoms, cutting of the crystal leads to a extreme broadening of the profiles in the ω-scans, data set collected with an Enraf-Nonius CAD4 with a sealed-tube generator.<sup>26</sup>

**(b) Preparation in Toluene.** A solution of 5 (220 mg, 0.33 mmol) in toluene (20 mL) was added dropwise at -60 °C to a solution of 11 (65 mg, 0.167 mmol) in 20 mL of toluene. The mixture was stirred for 1 day at room temperature. Pentane (10 mL) was added to the reaction mixture that contained a bright yellow solid. The precipitate was collected by filtration, washed with toluene and pentane, and dried in vacuo to give 262 mg (86%) of 12. Mp: 177 °C (decomp). Isolated samples of complex 12 always contained some solvent (here ca. 1 equiv of toluene). It was, therefore, difficult to get 12 analytically pure. Anal. C<sub>35</sub>H<sub>28</sub>P<sub>2</sub>OCl<sub>3</sub>ZrRh·C<sub>7</sub>H<sub>8</sub> (919.2): calcd C 54.88, H 3.95; found C 53.94, H 3.72. <sup>1</sup>H NMR (dichloromethane-*d*<sub>2</sub>, 200 MHz): δ = 8.26 (m, 4H), 8.11 (m, 4H), 7.5 (br m, 12H) (Ph), 6.60, 6.45, 6.05, 5.84 (m, each 2H, C<sub>5</sub>H<sub>4</sub>). <sup>13</sup>C NMR (dichloromethane-*d*<sub>2</sub>, 150 MHz): δ = 135.1, 132.2, 129.6–129.3 (several signals, Ph), 121.1, 116.4, 116.1, 105.3 (C<sub>5</sub>H<sub>4</sub>), ipso-C resonances of the poorly soluble complex 12 were not observed. <sup>31</sup>P NMR (dichloromethane-*d*<sub>2</sub>, 81 MHz): δ = 8.1 (d, <sup>1</sup>*J*<sub>RhP</sub> = 93 Hz). IR (KBr): ν̄ = 1990 cm<sup>-1</sup> (Rh–C≡O).

**X-ray Crystal Structure Analysis of (Cp-PPh<sub>2</sub>)<sub>2</sub>Zr-(CH<sub>3</sub>)<sub>2</sub> (13).** Complex 13 was prepared analogously as described by W. Tikkanen et al.<sup>10</sup> by treatment of 5 (4.65 g, 7.1 mmol) in 150 mL of toluene with 30 mL of a 0.47 M solution of methylolithium (14.1 mmol) in ether at -78 °C. After 4 h the mixture was filtered at room temperature and the filtrate concentrated in vacuo to a volume of 10 mL. Pentane (50 mL) was added. The product was collected by filtration, washed with pentane, and dried in vacuo to yield 3.72 g (85%) of 13. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 600 MHz): δ = 7.3 (m, 20H, Ph), 6.12 and 5.97 (m, each 4H, C<sub>5</sub>H<sub>4</sub>), -0.41 (br t, <sup>4</sup>*J*<sub>PH</sub> = 0.5 Hz, Zr–CH<sub>3</sub>). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 150 MHz): δ = 138.7 (d, <sup>1</sup>*J*<sub>PC</sub> = 11 Hz), 134.0 (d, <sup>2</sup>*J*<sub>PC</sub> = 21 Hz), 129.2 (s), 128.7 (d, <sup>3</sup>*J*<sub>PC</sub> = 8 Hz; ipso-, o-, p-, m-PPh<sub>2</sub>), 117.9 (d, <sup>1</sup>*J*<sub>PC</sub> = 11 Hz), 116.1 (d, <sup>2</sup>*J*<sub>PC</sub> = 12 Hz), 113.9 (br s; ipso-, α- and β-C<sub>5</sub>H<sub>4</sub>), 32.4 (t, <sup>3</sup>*J*<sub>PC</sub> = 6 Hz, Zr–CH<sub>3</sub>). <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ = -18.9. Single crystals were obtained from a solution of 13 in toluene containing a supernatant pentane solvent phase. Diffusion of the two phases overnight at -20 °C gave large crystals of 13: formula C<sub>36</sub>H<sub>34</sub>P<sub>2</sub>Zr, *M* = 619.79, colorless crystal 0.50 × 0.40 × 0.10 mm, *a* = 9.273(1) Å, *b* = 12.326(1) Å, *c* = 14.344(2) Å, α = 102.33(1)°, β = 97.48(1)°, γ = 102.94(1)°, *V* = 1533.5(3) Å<sup>3</sup>, ρ<sub>calc</sub> = 1.342 g cm<sup>-3</sup>, μ = 4.86 cm<sup>-1</sup>, empirical absorption

correction via ψ-scan data (0.964 ≤ *C* ≤ 0.999), *Z* = 2, triclinic, space group *P*1̄ (No. 2), λ = 0.71073 Å, *T* = 223 K, ω/2θ scans, 6583 reflections collected (-*h*, ±*k*, ±*l*), [(sin θ)/λ] = 0.62 Å<sup>-1</sup>, 6187 independent (*R*<sub>int</sub> = 0.031) and 4889 observed reflections [*I* ≥ 2 σ(*I*)], 354 refined parameters, *R* = 0.054, *wR*<sub>2</sub> = 0.171, max. residual electron density 1.08 (-0.94) e Å<sup>-3</sup>, hydrogens calculated and refined as riding atoms, data set collected with an Enraf-Nonius CAD4 with a sealed-tube generator.<sup>26</sup>

**Reaction of (Cp-PPh<sub>2</sub>)<sub>2</sub>Zr(CH<sub>3</sub>)<sub>2</sub> (13) with H(CO)Rh-(PPh<sub>3</sub>)<sub>3</sub> (14), Formation of 15.** Toluene (50 mL) was added at 0 °C to a solid mixture of 13 (930 mg, 1.5 mmol) and 14 (1.38 g, 1.5 mmol). The solution turned dark red immediately. After 1 h a yellowish precipitate was removed by filtration and the solvent removed from the remaining clear solution in vacuo. Workup of the product turned out to be very problematic since removal of the PPh<sub>3</sub> was severely hampered by the sensitivity of 15. Several attempts resulted in complete decomposition to yield a black oil or a dark brown powder of an unknown composition. In a successful experiment a part of the crude product (300 mg), which still contained 2 molar equiv of PPh<sub>3</sub>, was dissolved in a toluene/diethyl ether (1:1) mixture and crystallized at -20 °C. To remove the phosphine, the precipitated red-brown microcrystalline solid was quickly collected by filtration and dried in vacuo. Mp: 134 °C (decomp). Due to small amounts of PPh<sub>3</sub> that remained, it was difficult to obtain the very sensitive complex 15 completely analytically pure. Anal. C<sub>54</sub>H<sub>46</sub>P<sub>3</sub>ORhZr (998.0): calcd C 64.99, H 4.65; found C 64.03, H 4.77. <sup>1</sup>H NMR (dichloromethane-*d*<sub>2</sub>, 600 MHz): δ = 7.38, 7.35, 7.28, 7.18, 7.16, 7.05, 6.86 (m, 35H, PPh<sub>2</sub>, PPh<sub>3</sub>), 6.61, 6.40, 5.40, 4.11 (m, each 2H, C<sub>5</sub>H<sub>4</sub>), -0.83 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (dichloromethane-*d*<sub>2</sub>, 150 MHz): δ = 195.5 (ddt, <sup>1</sup>*J*<sub>RhC</sub> = 80 Hz, <sup>2</sup>*J*<sub>PC</sub> = 12 and 9 Hz, C≡O), 140.3 (dt, <sup>1</sup>*J*<sub>PC</sub> = 19.8 Hz, <sup>3</sup>*J*<sub>PC</sub> = 3.9 Hz, ipso C of PPh<sub>2</sub>), 139.7 (td, <sup>1</sup>*J*<sub>PC</sub> = 24.2 Hz, <sup>3</sup>*J*<sub>PC</sub> = 3.9 Hz, ipso-C of PPh<sub>3</sub>), 139.2 (t, <sup>1</sup>*J*<sub>PC</sub> = 9.6 Hz, ipso-C of PPh<sub>2</sub>), 134.4 (t, *J*<sub>PC</sub> = 8.4 Hz, PPh<sub>2</sub>), 134.3 (d, *J*<sub>PC</sub> = 13.4 Hz, PPh<sub>3</sub>), 132.7 (t, *J*<sub>PC</sub> = 7.5 Hz, PPh<sub>2</sub>), 129.4 (s, p-C of PPh<sub>3</sub>), 128.5 (s, p-C of both PPh<sub>2</sub>), 127.4 (d, *J*<sub>PC</sub> = 9.0 Hz, PPh<sub>3</sub>), 116.3 (t, *J*<sub>PC</sub> = 3.2 Hz, C<sub>5</sub>H<sub>4</sub>), 116.3 (t, *J*<sub>PC</sub> = 5.7 Hz, C<sub>5</sub>H<sub>4</sub>), 108.3 (t, *J*<sub>PC</sub> = 3.8 Hz, C<sub>5</sub>H<sub>4</sub>), 107.8 (ddd, *J* = 20.4, 18.5, and 9.6 Hz, ipso-C of C<sub>5</sub>H<sub>4</sub>), 103.4 (t, *J* = 4.5 Hz, C<sub>5</sub>H<sub>4</sub>), 29.1 (s, CH<sub>3</sub>) ppm. GHMBC NMR (dichloromethane-*d*<sub>2</sub>, 600 MHz): δ = [195.5 (Rh–C≡O)]/-0.83 (Zr–CH<sub>3</sub>), [116.3 (C<sub>5</sub>H<sub>4</sub>)/6.61, 5.40, 4.11 (C<sub>5</sub>H<sub>4</sub>), -0.83 (Zr–CH<sub>3</sub>)], [108.3 (C<sub>5</sub>H<sub>4</sub>)/6.61 (C<sub>5</sub>H<sub>4</sub>)], [107.8 (ipso C of C<sub>5</sub>H<sub>4</sub>)/4.11 (C<sub>5</sub>H<sub>4</sub>), 7.3 (Ph–H)], [103.4 (C<sub>5</sub>H<sub>4</sub>)/6.61, 6.40, 5.40 (C<sub>5</sub>H<sub>4</sub>)], [29.1 (Zr–CH<sub>3</sub>)]/-0.83 (Zr–CH<sub>3</sub>). <sup>31</sup>P NMR (dichloromethane-*d*<sub>2</sub>, 81 MHz): δ = 46.5 (dt, <sup>1</sup>*J*<sub>RhP</sub> = 111 Hz, <sup>2</sup>*J*<sub>PP</sub> = 37 Hz, Rh–PPh<sub>3</sub>), 27.2 (dd, <sup>1</sup>*J*<sub>RhP</sub> = 162 Hz, <sup>2</sup>*J*<sub>PP</sub> = 37 Hz, PPh<sub>2</sub>). IR (CH<sub>2</sub>Cl<sub>2</sub>): ν̄ = 1977 cm<sup>-1</sup> (Rh–C≡O).

**Hexene Hydroformylation Catalyzed by the Zr/Rd Complex 15.** 1-Hexene was purified by stirring over Na/K alloy and then distilled. The *n*-dodecane used as an internal standard for the GLC analysis was dried over 4 Å molecular sieves and distilled prior to use. The hydroformylation reaction was carried out in a special steel autoclave fitted with a pressurized dropping funnel and a capillary and valve for taking samples at any chosen time during the reaction. A 1:1 mixture of CO and H<sub>2</sub> was employed.

**General Procedure.** In a typical experiment 0.08 mmol of the catalyst 15 was employed with 4.0 mL (32.0 mmol) of 1-hexene (i.e., a substrate-to-catalyst ratio of 400:1) in the presence of 0.5 mL (4.4 mmol) of the internal standard *n*-dodecane. The autoclave was charged with a THF solution (5–10 mL) of the Zr/Rh catalyst. The system was then pressurized (20 bar) and the autoclave thermostated at the chosen temperature. 1-Hexene and *n*-dodecane dissolved in ca. 10 mL of THF was then added through the dropping funnel, and the reaction started with stirring. Samples of ca. 1 mL were taken from time to time under pressure. The system was repressurized as soon as the pressure had dropped by 5 bar during the reaction. The samples were quenched by treatment

with 1 mL of a saturated aqueous  $\text{NH}_4\text{Cl}$  solution. The phases were separated and the organic phase dried over  $\text{MgSO}_4$ . Remaining inorganic products were removed by filtration through a  $5 \times 0.4$  cm silica gel column. The products and the progress were analyzed by gas chromatography (25 m HP5 column, 3 min at  $40^\circ\text{C}$ , temperature programmed  $10^\circ\text{C min}^{-1}$  to  $150^\circ\text{C}$ , followed by  $20^\circ\text{C min}^{-1}$  to  $280$  min. The product ratios were determined by integration relative to the *n*-dodecane standard, and the response factors of the single components were separately determined. 1-Hexene/2-hexene and *n*-hexane were not baseline separated under these conditions and monitored together. The accuracy of the values at higher conversions was estimated at ca.  $\pm 10\%$ . Series of experiments were carried out at four temperatures. The initial TOF (mol product/(mol cat. $\cdot$ h)) was determined in each case at the early stages of the reaction using the increase of the relative product yield between the second and third samples taken. The following results were obtained: expt 1,  $43^\circ\text{C}$ , TOF

24, n/iso 3.1; expt 2,  $55^\circ\text{C}$ , TOF 305, n/iso 2.8; expt 3,  $80^\circ\text{C}$ , TOF 630, n/iso 3.0; expt 4,  $120^\circ\text{C}$ , TOF 465, n/iso 3.2. Further details about these experiments are given in the Supporting Information.

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**Supporting Information Available:** Details of the X-ray crystal structure analyses including complete listings of bond lengths and angles, thermal parameters, atomic positional parameters, and the hydroformylation experiments using complex **15** as a catalyst. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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