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## An Unprecedented $[C_2+C_1+C_1]$ Coupling of an Alkynyl, an Allenylidene, and a CO Unit: The Formation of a Highly Unsaturated Cyclobutenone Derivative in the Coordination Sphere of Rhodium()\*\*

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Dedicated to Professor Heinrich Vahrenkamp on the occasion of his 60th birthday

Metal-assisted C–C coupling reactions belong to the most important processes in organometallic chemistry.<sup>[1]</sup> Following our work on the synthesis of metal vinylidene compounds from alkynes, we recently reported that the square-planar rhodium complexes *trans*-[RhR(=C=CR<sup>1</sup>R<sup>2</sup>)(PiPr<sub>3</sub>)<sub>2</sub>] (R = methyl, vinyl, phenyl, alkynyl) undergo an intramolecular C–C coupling reaction in the presence of CO to give *trans*-[Rh{C(R)=CR<sup>1</sup>R<sup>2</sup>}(CO)(PiPr<sub>3</sub>)<sub>2</sub>].<sup>[2]</sup> A related reaction occurs between the allenylidene compounds *trans*-[RhX(=C=C= CR<sup>1</sup>R<sup>2</sup>)(PiPr<sub>3</sub>)<sub>2</sub>] (X = OAr, OC(O)Me, N<sub>3</sub>) and CO to give the alkynyl complexes *trans*-[Rh(C=C–CXR<sup>1</sup>R<sup>2</sup>)(CO)-(PiPr<sub>3</sub>)<sub>2</sub>], resulting from the migration of the group X to the  $\gamma$ -C atom of the allenylidene ligand.<sup>[3]</sup> While earlier attempts from our laboratory to obtain alkyl, vinyl, or arylrhodium(i) complexes of the general composition *trans*-[RhR(=C=C= CR<sup>1</sup>R<sup>2</sup>)(P*i*Pr<sub>3</sub>)<sub>2</sub>] failed,<sup>[4]</sup> we have now succeeded with the preparation of the corresponding alkynyl(allenylidene) compounds *trans*-[Rh(C=CPh)(=C=C=CR<sup>1</sup>R<sup>2</sup>)(P*i*Pr<sub>3</sub>)<sub>2</sub>], one of which undergoes an unprecedented [ $C_2+C_1+C_1$ ] coupling reaction with CO to give a highly unsaturated cyclobutenone derivative.

The synthetic route to the new alkynylrhodium(I) complexes 5 and 6 is outlined in Scheme 1. In order to coordinate the  $C_2$  unit to the metal center, the key to success was the use



Scheme 1. Synthesis of mono- and dinuclear rhodium(1) complexes 5-8.

of the mild transmetalating reagent PhC=CSnPh<sub>3</sub><sup>[5]</sup> and the highly reactive fluoro compounds **3** and **4**. While the latter could not be prepared by salt metathesis from *trans*-[RhCl{=C=C=C(R)Ph}(PiPr<sub>3</sub>)<sub>2</sub>] and KF or TlF, respectively, they were obtained in excellent yield by treatment of the hydroxo derivatives **1** and **2** with one equivalent of NEt<sub>3</sub> · 3 HF in benzene. The fluoro complexes are green-yellow (**3**) and green (**4**) crystalline solids that can be stored at room temperature under argon and are stable for several days in solution in C<sub>6</sub>D<sub>6</sub>. The <sup>19</sup>F NMR spectra of **3** and **4** show the expected pattern of signals with <sup>103</sup>Rh-<sup>19</sup>F and <sup>31</sup>P-<sup>19</sup>F couplings, the <sup>2</sup>J(P,F) values of about 19 Hz being characteristic for a *cis* disposition of the fluoro and the phosphane ligands.<sup>[6]</sup>

The reactions of **3** and **4** with PhC=CSnPh<sub>3</sub> resulted in the formation of the alkynyl complexes **5** and **6** together with a white, poorly soluble by-product which was identified as Ph<sub>3</sub>SnF by comparison of its IR spectrum with that of an authentic sample prepared from Ph<sub>3</sub>SnCl and KF.<sup>[7]</sup> Although compounds **5** and **6** (which are violet and brown crystalline solids, respectively) are more sensitive than the related fluoro or hydroxo derivatives, they have been fully characterized on the basis of their analytical and spectroscopic data. Besides the single resonance in the <sup>31</sup>P NMR spectra with a <sup>1</sup>*J*(Rh,P) coupling constant that is typical for a *trans* disposition of both phosphorus atoms, the most characteristic features are the

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low-field signals for the allenylidene and the alkynyl ligands in the <sup>13</sup>C NMR spectra of **5** and **6**. In particular, the resonances for the  $\alpha$ -carbon atoms of the allenylidene and the alkynyl units (both doublets of triplets) can be clearly assigned owing to the large <sup>1</sup>*J*(Rh,C) coupling constants of about 53 and 40 Hz, respectively.

The high reactivity of the fluororhodium(i) compounds 3 and 4 is not only illustrated by the formation of 5 and 6 but also by the synthesis of the dinuclear complexes 7 and 8 (Scheme 1). However, these compounds were not only formed by treatment of **3** and **4** with Ph<sub>3</sub>SnC=CC=CSnPh<sub>3</sub>, but even more conveniently by using the hydroxo derivatives 1 and 2 as starting materials. In this case the by-product is Ph<sub>3</sub>SnOH, which can be easily separated from the less soluble complexes 7 and 8 by washing with acetone. The <sup>13</sup>C NMR spectrum of compound 8 (which is more soluble in organic solvents than 7) displays the expected signals for the allenylidene and butadiynediyl ligands with the chemical shifts and coupling constants similar to those of 6. Additional structural support is provided by the mass spectra of 7 and 8, which show in both cases the peaks of the molecular ions and the fragments  $[Rh{C_3(R)Ph}(PiPr_3)_2]^+$ , respectively. In this context we note that dinuclear transition metal complexes containing a "naked" C4 bridge were recently prepared by Gladysz et al.,<sup>[8]</sup> Lapinte et al.,<sup>[9]</sup> Bruce et al.,<sup>[10]</sup> and others (including us)<sup>[5, 11]</sup> and investigated as promising candidates for use in material science.<sup>[12]</sup>

Since we knew that reactions of the vinylidene complexes trans-[Rh(C=CR)(=C=CR<sup>1</sup>R<sup>2</sup>)(PiPr<sub>3</sub>)<sub>2</sub>] with CO give rise to a migratory insertion of the vinylidene ligand into the Rh–C  $\sigma$ bond,<sup>[2]</sup> we were interested to find out whether an analogous reaction of 6 with CO would also occur. However, when a stream of CO was passed through a suspension of 6 in hexane at room temperature, a quantitative conversion of the alkynyl derivative to the cyclic compound 9 took place (Scheme 2). The result of the single-crystal X-ray diffraction study of 9 confirmed (Figure 1)<sup>[13]</sup> that quite unexpectedly two CO molecules were involved in the formation of the novel C-C coupling product. One carbonyl group is coordinated to the metal, while the other forms a four-membered ring together with the two alkynyl carbon atoms and the  $\alpha$ -carbon atom of the allenylidene unit. The cyclobutenone ring is  $\sigma$ -bonded to the rhodium center by the  $\alpha$ -C atom of the original alkynyl ligand. The phenyl group at C3, the cyclobutenone ring, and the cumulene unit are nearly coplanar, defining a plane which lies almost perpendicular to the coordination plane around the metal center. The dihedral angle between the two planes [P1,P2,Rh,C1,C2] and [C2,C3,C4,C5] amounts to 89.7(1)°. Owing to the molecular symmetry and the slow rotation around the Rh–C  $\sigma$  bond, the two phosphorus nuclei are chemically inequivalent and thus the <sup>31</sup>P NMR spectrum of 9 displays a multiplet corresponding to the AB part of an ABX system. We therefore assume that the molecular structure of **9** which was found in the crystal is also preserved in solution.

A possible mechanism for the conversion of 6 to 9 is shown in Scheme 2. In the initial step, the starting material 6 reacts with one molecule of CO to give the intermediate 10, which contains a  $C_5$  chain resulting from the coupling of the allenylidene and the alkynyl ligands. By carrying out the



Scheme 2. Synthesis and mechanism of the formation of 9.  $L = PiPr_3$ .



Figure 1. Molecular structure of **9** in the crystal. Selected bond lengths [Å] and angles [°]: Rh-C1 1.840(3), Rh-C2 2.030(3), Rh-P1 2.3439(9), Rh-P2 2.3347(9), O2-C4 1.209(3), C2-C3 1.392(4), C2-C5 1.511(4), C3-C4 1.458(4), C3-C6 1.459(4), C4-C5 1.523(4), C5-C12 1.298(4), C12-C13 1.320(4); C1-Rh-C2 173.38(13), C2-Rh-P1 90.83(8), C1-Rh-P2 89.06(10), C1-Rh-P1 89.72(10), C2-Rh-P2 91.51(8), P2-Rh-P1 170.14(3), C2-C3-C4 93.6(2), O1-C1-Rh 175.6(3), C3-C2-Rh 132.7(2), C5-C2-Rh 135.8(2), C3-C2-C5 91.5(2), O2-C4-C3 137.4(3), O2-C4-C5 134.0(3), C3-C4-C5 88.5(2), C12-C5-C2 140.9(3), C12-C5-C4 132.7(3), C2-C5-C4 86.4(2), C5-C12-C13 172.2(3).

reaction of **6** with one equivalent of CO at low temperature, **10** could be isolated as a yellow, thermally unstable solid. The IR and <sup>13</sup>C NMR data of **10** are similar to those of the related four-coordinate compound *trans*-[Rh{ $\eta^1$ -C(CH=CH\_2)=C= CPh<sub>2</sub>}(CO)(PiPr<sub>3</sub>)<sub>2</sub>] which was obtained by treatment of [Rh( $\eta^3$ -CH<sub>2</sub>CHC=C=CPh<sub>2</sub>)(PiPr<sub>3</sub>)<sub>2</sub>] with CO.<sup>[4]</sup> The intermediate **10** (which in C<sub>6</sub>D<sub>6</sub> in the presence of CO affords quantitatively the cyclobutenone derivative **9**) could inter-

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convert with the isomer 11 through the interaction of the C=Cbond with the rhodium center. An analogous equilibrium has recently been observed between *trans*-[Rh{ $\eta^1$ -C(C=CH)=  $CH_2$ (CO)(PiPr\_3)<sub>2</sub>] and trans-[Rh{ $\eta^1$ -CH=C=C=CH\_2(CO)- $(PiPr_3)_2$ .<sup>[14]</sup> In a subsequent step, the reaction of **11** with a second molecule of CO could give the acyl complex 12 which undergoes an isomerization to 13 by an 1,3-shift of the  $[Rh(CO)(PiPr_3)_2]$  fragment. The cyclobutenone derivative 9 could finally be generated by an intramolecular [2+2] cycloaddition from 13. Although to the best of our knowledge there is no precedent in organometallic chemistry for such an isomerization reaction of 12 to 13, an analogous rearrangement has been observed in the thermal interconversion of acylallenes to vinylketenes by flash vacuum thermolysis.<sup>[15]</sup> Regarding the formation of unsaturated four-membered rings which are connected to an organometallic entity, we note that the groups of Davison,<sup>[16]</sup> Kolobova,<sup>[17]</sup> Hughes,<sup>[18]</sup> and Fischer<sup>[19]</sup> already reported the synthesis of cyclobutenylidene complexes by [2+2] cycloaddition of either cationic or neutral vinylidene-metal precursors and metal alkynyl complexes. However, in this case the generated four-membered ring does not contain an exocyclic C-C double bond.

#### **Experimental Section**

All experiments were carried out under argon. The NMR data of the phenyl and *tert*-butyl groups are ommitted for clarity. Abbreviations: v = virtual coupling;  $N = {}^{3}J(PH) + {}^{5}J(PH)$  or  ${}^{1}J(PC) + {}^{3}J(PC)$ ; w = weak; m = medium; s = strong.

**3**: A solution of **1** (458 mg, 0.73 mmol) in benzene (20 mL) was treated with NEt<sub>3</sub> · 3 HF (40 µL, 0.25 mmol) at room temperature. The reaction mixture was stirred for 1 h and evaporated to dryness in vacuo. The residue was extracted four times with 20 mL-portions of pentane. The extract was concentrated to about 4 mL in vacuo and then stored for 2 h at -25 °C. A green-yellow microcrystalline solid precipitated which was washed three times with 3 mL-portions of pentane (-50 °C) and dried; yield 386 mg (84 %); m.p. 112 °C (decomp); IR (nujol):  $\tilde{\nu} = 1871$  (C=C=C), 475, 458 (Rh–F) cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = 2.74$  (m, 6H, PCHCH<sub>3</sub>), 1.34 (dvt, N = 13.5, <sup>3</sup>J(H,H) = 6.4 Hz, 36H, PCHCH<sub>3</sub>); <sup>13</sup>C[<sup>1</sup>H] NMR (100.6 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = 254.3$  (dt, <sup>2</sup>J(Rh,C) = 14.2, <sup>3</sup>J(P,C) = 6.4 Hz, Rh=C=C), 230.6 (m, Rh=C), 154.7 (s, Rh=C=C=C), 23.5 (vt, N = 19.3 Hz, PCHCH<sub>3</sub>); 20.2 (s, PCHCH<sub>3</sub>); <sup>19</sup>F NMR (188.3 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = -188.8$  (dt, <sup>1</sup>J(Rh,F) = 23.0, <sup>2</sup>J(P,F) = 20.2 Hz); <sup>31</sup>P[<sup>1</sup>H] NMR (162.0 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = 41.5$  (dd, <sup>1</sup>J(Rh,P) = 140.7, <sup>2</sup>J(P,F) = 18.7 Hz).

Compound **4** was prepared in a similar way from **2** (274 mg, 0.45 mmol) and NEt<sub>3</sub> · 3 HF (24.4 µL, 0.15 mmol); green crystals; yield 245 mg (89%); m.p. 102 °C (decomp); IR (nujol):  $\tilde{\nu} = 1890$ , 1879 (C=C=C), 473, 467, 449 (Rh–F) cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = 2.55$  (m, 6H, PCHCH<sub>3</sub>), 1.29 (dvt, N = 13.5, <sup>3</sup>*J*(H,H) = 6.4 Hz, 36H, PCHCH<sub>3</sub>); <sup>13</sup>C[<sup>1</sup>H] NMR (100.6 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = 250.5$  (m, Rh=C=C), 239.0 (m, Rh=C), 154.9 (s, Rh=C=C=C), 23.1 (vt, N = 18.1 Hz, PCHCH<sub>3</sub>), 20.1 (s, PCHCH<sub>3</sub>); <sup>19</sup>F NMR (376.4 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = -181.7$  (dt, <sup>1</sup>*J*(Rh,F) = <sup>2</sup>*J*(P,F) = 20.3 Hz); <sup>31</sup>P[<sup>1</sup>H] NMR (162.0 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = 43.1$  (dd, <sup>1</sup>*J*(Rh,P) = 141.6, <sup>2</sup>*J*(P,F) = 19.5 Hz).

**5**: A solution of **3** (285 mg, 0.45 mmol) in pentane (25 mL) was treated with PhC=CSnPh<sub>3</sub> (203 mg, 0.45 mmol) and stirred for 2 h at room temperature. A dark red-violet suspension was formed, which was filtered through a cotton pad. The filtrate was evaporated to dryness in vacuo and the residue was extracted four times with 10 mL-portions of pentane. The combined extracts were concentrated to about 8 mL in vacuo and then stored for three days at -25 °C. A dark red-violet microcrystalline solid precipitated which was washed three times with 3 mL-portions of pentane (-78 °C) and dried; yield 260 mg (81%); m.p. 128 °C (decomp); IR (nujol):  $\tilde{\nu} = 2059$  (C=C), 1869 (C=C=C) cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = 3.01$  (m, 6H,

PCHCH<sub>3</sub>), 1.40 (dvt, *N* = 13.5, <sup>3</sup>*J*(H,H) = 7.0 Hz, 36H, PCHCH<sub>3</sub>); <sup>13</sup>C[<sup>1</sup>H] NMR (100.6 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 249.1 (dt, <sup>2</sup>*J*(Rh,C) = 10.2, <sup>3</sup>*J*(P,C) = 5.1 Hz, Rh=C=C), 233.5 (dt, <sup>1</sup>*J*(Rh,C) = 53.9, <sup>2</sup>*J*(P,C) = 17.3 Hz, Rh=C), 158.6 (d, <sup>2</sup>*J*(Rh,C) = 8.1 Hz, Rh-C=C), 156.0 (t, <sup>4</sup>*J*(P,C) = 2.6 Hz, Rh=C=C=C), 118.6 (dt, <sup>1</sup>*J*(Rh,C) = 40.7, <sup>2</sup>*J*(P,C) = 19.0 Hz, Rh–C=C), 25.9 (vt, *N* = 19.3 Hz, PCHCH<sub>3</sub>), 20.8 (s, PCHCH<sub>3</sub>); <sup>31</sup>P[<sup>1</sup>H] NMR (162.0 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 41.5 (d, <sup>1</sup>*J*(Rh,P) = 134.0 Hz).

Compound **6** was prepared in a similar way from **4** (296 mg, 0.48 mmol) and PhC=CSnPh<sub>3</sub> (218 mg, 0.48 mmol); brown crystals; yield 242 mg (72%); m.p. 79 °C (decomp); IR (nujol):  $\tilde{\nu} = 2064$  (C=C), 1890 (C=C=C) cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = 2.82$  (m, 6H, PCHCH<sub>3</sub>), 1.34 (dvt, N = 13.2, <sup>3</sup>*J*(H,H) = 6.2 Hz, 36H, PCHCH<sub>3</sub>); <sup>13</sup>C[<sup>1</sup>H] NMR (100.6 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = 257.6$  (dt, <sup>1</sup>*J*(Rh,C) = 51.9, <sup>2</sup>*J*(P,C) = 16.8 Hz, Rh=C), 236.1 (dt, <sup>2</sup>*J*(Rh,C) = 12.2, <sup>3</sup>*J*(P,C) = 5.8 Hz, Rh=C=C), 156.3 (t, <sup>4</sup>*J*(P,C) = 3.0 Hz, Rh=C=C=C), 153.5 (d, <sup>2</sup>*J*(Rh,C) = 9.2 Hz, Rh=C=C), 123.4 (dt, <sup>1</sup>*J*(Rh,C) = 39.7, <sup>2</sup>*J*(P,C) = 19.3 Hz, Rh=C=C), 25.8 (vt, N = 19.3 Hz, PCHCH<sub>3</sub>), 20.8 (s, PCHCH<sub>3</sub>); <sup>31</sup>P[<sup>1</sup>H] NMR (162.0 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = 43.9$  (d, <sup>1</sup>*J*(Rh,P) = 133.9 Hz).

7: A solution of 1 (251 mg, 0.40 mmol) in THF (10 mL) was treated with Ph<sub>3</sub>SnC=CC=CSnPh<sub>3</sub> (149 mg, 0.20 mmol) at -78 °C. Under continuous stirring, the mixture was slowly allowed to warm to room temperature and stirred for 7 h. The resulting dark blue suspension was concentrated to about 0.5 mL in vacuo and acetone (5 mL) was added. The solution was filtered and the filtrate was evaporated to dryness in vacuo. The residue was washed five times with 5 mL-portions of acetone and dried; yield 217 mg (85 %); m.p. 50 °C (decomp); IR (nujol):  $\tilde{\nu} = 1947$  (C=C), 1860 (C=C=C) cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta = 2.77$  (m, 12 H, PCHCH<sub>3</sub>), 1.21 (dvt, N = 13.4, <sup>3</sup>/(H,H) = 6.4 Hz, 72 H, PCHCH<sub>3</sub>); <sup>31</sup>P[<sup>4</sup>H] NMR (81.0 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta = 42.5$  (d, <sup>1</sup>/(Rh,P) = 132.9 Hz); ESI MS (CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>CN): m/z: 1275 [*M*H<sup>+</sup>], 613 [Rh{C<sub>3</sub>Ph<sub>2</sub>}](PiPr<sub>3</sub>)<sub>2</sub><sup>+</sup>].

Compound **8** was prepared in a similar way from **2** (310 mg, 0.51 mmol) and Ph<sub>3</sub>SnC=CC=CSnPh<sub>3</sub> (190 mg, 0.25 mmol) in benzene (10 mL) at room temperature; blue-violet solid; yield 202 mg (65%); m.p. 59°C (decomp); IR (nujol):  $\bar{\nu} = 1952$  (C=C), 1888, 1878 (C=C=C) cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, [D<sub>8</sub>]THF):  $\delta = 2.69$  (m, 12 H, PCHCH<sub>3</sub>), 1.21 (dvt, N = 13.5, <sup>3</sup>*J*(H,H) = 6.4 Hz, 72 H, PCHCH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz, [D]<sub>8</sub>THF):  $\delta = 254.2$  (dt, <sup>1</sup>*J*(Rh,C) = 51.9, <sup>2</sup>*J*(P,C) = 17.3 Hz, Rh=C), 235.3 (dt, <sup>2</sup>*J*(Rh,C) = 11.2, <sup>3</sup>*J*(P,C) = 6.1 Hz, Rh=C=C), 156.0 (t, <sup>4</sup>*J*(P,C) = 3.1 Hz, Rh=C=C=C), 149.8 (m, Rh–C=C), 133.7 (dt, <sup>1</sup>*J*(Rh,C) = 39.7, <sup>2</sup>*J*(P,C) = 19.3 Hz, Rh–C=C), 25.9 (vt, N = 20.3 Hz, PCHCH<sub>3</sub>), 20.8 (s, PCHCH<sub>3</sub>); <sup>31</sup>P{<sup>1</sup>H} NMR (162.0 MHz, [D<sub>8</sub>]THF):  $\delta = 44.4$  (d, <sup>1</sup>*J*(Rh,P) = 133.9 Hz). ESI MS (CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>CN): *m*/*z*: 1234 [*M*<sup>+</sup>], 593 [Rh{C<sub>3</sub>(*t*Bu})Ph}(PiPr<sub>3</sub>)<sub>2</sub>+].

9: A slow stream of CO was passed through a suspension of 6 (168 mg, 0.24 mmol) in hexane (6 mL) for 30 s at room temperature. The flask was sealed and the mixture was stirred for 3 h. The resulting yellow-orange suspension was concentrated to about 3 mL in vacuo and stored at  $-25\,^{\circ}\text{C}$ for 3.5 h. A yellow solid precipitated which was washed twice with 2-mL portions of pentane (-78 °C) and dried; yield 172 mg (90 %); m.p. 161 °C (decomp); IR (nujol):  $\tilde{\nu} = 1955$  (s), 1908 (w) (CO and C=C=C), 1734 (s), 1717 (s) (C=O), 1596 (m), 1512 (m) (C=C) cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ ):  $\delta = 2.17, 1.94$  (both m, 6H, PCHCH<sub>3</sub>), 1.26, 1.00, 0.92, 0.88 (all m, 36 H, PCHCH<sub>3</sub>);  ${}^{13}C{}^{1}H$  NMR (100.6 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = 241.7$  (dt,  ${}^{1}J(Rh,C) = 33.2, {}^{2}J(P,C) = 15.3 \text{ Hz}, Rh-C), 198.1 (dt, {}^{1}J(Rh,C) = 53.9,$  $^{2}J(P,C) = 15.0 \text{ Hz}, \text{ Rh}-CO), 189.9 \text{ (s, } C=O), 181.3 \text{ (d, } ^{3}J(Rh,C) = 2.7 \text{ Hz},$ C=C=C), 163.4 (t,  ${}^{3}J(P,C) = 3.6$  Hz, Rh-C=CPh), 129.5 (d,  ${}^{2}J(Rh,C) =$ 1.8 Hz, C=C=C), 122.0 (s, C=C=C), 27.0, 26.6 (both vdd, J=15.3 and 5.4 Hz, PCHCH<sub>3</sub>), 20.9, 20.4, 19.6, 19.5 (all s, PCHCH<sub>3</sub>); <sup>31</sup>P{<sup>1</sup>H} NMR (162.0 MHz, C<sub>6</sub>D<sub>6</sub>): AB part of an ABX system,  $\delta_A = 47.3$ ,  $\delta_B = 48.2$  $({}^{1}J(\text{Rh},\text{P}_{\text{A}}) = {}^{1}J(\text{Rh},\text{P}_{\text{B}}) = 135.7 \text{ Hz}, {}^{2}J(\text{P}_{\text{A}},\text{P}_{\text{B}}) = 235.7 \text{ Hz}).$ 

**10**: Gaseous CO (ca. 0.1 mmol) was introduced into a schlenk flask containing a suspension of **6** (69 mg, 0.01 mmol) in pentane (10 mL) at -78 °C. Under continuous stirring, the mixture was allowed to warm to -45 °C, stirred for 25 min and then evaporated to dryness in vacuo to give a yellow solid; IR (nujol):  $\tilde{\nu} = 2159$  (m) (C=C), 1969 (w), 1947 (s), 1902 (w), 1875 (w) (CO and C=C=C) cm<sup>-1</sup>; <sup>13</sup>C[<sup>1</sup>H] NMR (100.6 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = 208.3$  (t, <sup>3</sup>*J*(P,C) = 5.1 Hz, C=C=C), 195.6 (dt, <sup>1</sup>*J*(Rh,C) = 60.0, <sup>2</sup>*J*(P,C) = 15.8 Hz, Rh–CO), 104.3 (s, Rh–C=C=C), 97.9 (dt, <sup>1</sup>*J*(Rh,C) = 25.4, <sup>2</sup>*J*(P,C) = 12.2 Hz, Rh–C), 94.8, 92.0 (both s, C=C), 26.0 (br.m, PCHCH<sub>3</sub>), 20.7, 20.1 (both br.m, PCHCH<sub>3</sub>).

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### Dialkylaminoethyl-Functionalized *ansa*-Zirconocene Dichlorides: Precatalysts for the Regulation of the Molecular Weight Distribution of Polyethylene\*\*

Christian Müller, Dieter Lilge, Marc Oliver Kristen,\* and Peter Jutzi\*

#### Dedicated to Professor Reinhard Schmutzler on the occasion of his 65th birthday

The synthesis of metallocene derivatives which can be used as precatalysts in the methylalumoxane (MAO)-activated polymerization of  $\alpha$ -olefins is a rapidly growing research area. Special attention is directed to the design of the metal coordination sphere: variations in the substitution pattern and in the connection of cyclopentadienyl (Cp) ligands may be utilized for synthesizing tailor-made single-site catalysts. Thus, polymer parameters such as stereochemical microstructure (tacticity), molecular weight distribution, crystallinity, and copolymer incorporation can be influenced systematically.<sup>[1, 2]</sup> This new generation of catalysts therefore is playing an important role in the development of new polyolefin-based materials.

The molecular weights of polymers produced with  $[Cp_2ZrCl_2]/MAO$  catalysts range between 100000 and 1000000 gmol<sup>-1</sup> for polyethylenes and between 200 and 1000 gmol<sup>-1</sup> for polypropylenes. Polymers made by the conventional Ziegler–Natta process have broad molecular weight distributions with high polydipersities of  $M_w/M_n = 5-10$ , whereas single-site metallocene catalysts usually produce polyolefins with a unimodal molecular weight distribution and polydispersities of about 2. With respect to these features, there are no differences between unbridged, bridged, or Cp-substituted systems.<sup>[1a, 3]</sup>

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