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The synthesis of substituted bis[(diarylphosphinomethyl)cyclopentadienyl]zirconocene dichloride complexes for the preparation of heterodimetallic complexes containing early/late transition metal combinations¹

Boris Bosch, Gerhard Erker *, Roland Fröhlich

Organisch-Chemisches Institut der Universität Münster, Corrensstraße 40, D-48149 Münster, Germany

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Abstract

Fulvenes (1a-e) derived from condensation of cyclopentadiene with acetone or a variety of aldehydes were treated with LiPAr₂ (Ar = phenyl, *p*-tolyl) to yield the respective substituted (diarylphosphinomethyl)cyclopentadienides (2, 3). Subsequent reaction with $Z_rCl_4(THF)_2$ gave the respective bis[(diarylphosphinomethyl)cyclopentadienyl]zirconium dichlorides (Ar = phenyl (4), *p*-tolyl (5)). The complex *rac*-[C₅H₄-CH(CH₃)-PPh₂]₂ZrCl₂ (*rac*-4b) was characterized by X-ray diffraction. The reaction of complexes 4a and 5a [(Cp-CMe₂-PAr₂)₂ZrCl₂] with PdCl₂(NCPh)₂ or PtCl₂(NCPh)₂ leads to the formation of the *trans*-(metallocene-chelate-phosphane)metal complexes 6-9 (e.g. *trans*-Cl₂Pd(Ph₂P-CMe₂-Cp)₂ZrCl₂]. Chloride abstraction from the reaction product of [Cp-CH(CMe₃)PPh₂]₂ZrCl₂ with PdCl₂(NCPh)₂ eventually gave the cationic complex [*meso*, *trans*-(Cp-CH(CMe₃)PPh₂)₂(Cl)Zr(μ -Cl)Pd(Cl)]⁺ (10) that was also characterized by X-ray diffraction. It features a dimetallabicyclic framework with two Cp-CHR-PPh₂ ligands and a chloride bridging between the early and the late transition metal center. © 1998 Elsevier Science S.A.

Keywords: Zirconocene complexes; Chelate phosphane complexes; Heterodimetallic complexes; Crystal structures

1. Introduction

Various catalytic applications are known that make specific use of the characteristic features of the transition elements with regard to their positions in the Periodic Table [1]. Early and late transition metals in a number of cases exhibit complementary properties that may lead to useful novel future applications if they could become combined. One way of combining early and late transition metals lies in the selective preparation of heterodimetallic systems that contain bifunctional ligand systems. From a variety of selected examples it appears that cyclopentadienides that contain phosphane functionalities as substituents [2] are well suited for this purpose [2,3]. The Cp ligand binds strongly to the electrophilic early metal whereas phosphane ligands are known to be the favored ligands of many late transition elements. Several types of such systems have been reported so far. Many examples involve Cp-PR₂ type ligands [2a]. A variety of other systems contain tethered phosphane moieties at the Cp ligands, i.e. are of the $Cp-(CH_2)_n PR_2$ type [2c]. Only very little is known so far to our knowledge about early/late transition metal heterodimetallic systems that contain phosphinomethyl side chains attached at the Cp ligands (i.e. $Cp-CR^{1}R^{2}-PR_{2}$) [2b], although such complexes might combine a number of advantageous properties such as easy synthetic availability, high thermodynamic as well as kinetic stabilities of both the early transition metal complex precursor and the final heterodimetallic system, and a very good chance of a close electronic interaction of the pair of transition metals in the dimetallic complex. We have now prepared and characterized a number of such Cp–CR¹R²–PAr₂ ligand systems, their respective zirconocene dichloride complexes, and used them in preliminary experiments for the synthesis of rather stable early/late heterodimetallic systems, one example of which showed some interesting interaction between the pair of metals involved.

^{*} Corresponding author. Tel.: +49-251 833 3221; fax: +49-251 833 9772; e-mail: erker@uni-muenster.de

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2. Results and discussion

2.1. Preparation and characterization of the $(Cp-CR^{T}R^{2}-PAr_{2})_{2}ZrCl_{2}$ complexes (Scheme 1)

We have chosen to synthesize the (phosphinomethyl)cyclopentadienide ligand systems used in this study by means of the fulvene route. Fulvenes are in some respect regarded as the all carbon analogues of the organic carbonyl compounds. A great variety of nucleophiles can be added at their positively polarized C6 carbon atoms. This typical reaction mode has previously been used extensively for the generation of substituted cyclopentadienides [4].

In this study the fulvenes 1(a,c-e) were prepared by variations of the method introduced by Stone and Little, i.e. by condensation of cyclopentadiene with the respective ketone or aldehyde in methanol solution with the aid of pyrrolidine [5]. Fulvene 1b was obtained by a variant of the Thiele method. These fulvenes were then treated with equimolar amounts of lithiodiphenylphosphide [6]. A clean addition reaction was observed and the corresponding (diphenylphosphinomethyl)cyclopentadienyl lithium compounds 2a-e obtained. These were usually isolated in the form of very viscous oils but with some effort could be solidified by prolonged treatment with pentane and then recovered as solid materials. The reagents 2 were characterized spectroscopically. As a typical example, lithio(1-methyl-1-diphenylphosphinoethyl)cyclopentadienide (2a) shows a ⁷Li NMR resonance in a benzene-d₆/THF-d₈ solvent mixture at $\delta - 5.9$ ppm [7]. Its ³¹P NMR signal is observed at δ 21.5 ppm. The ¹H NMR resonance of the system is observed as a doublet at δ 1.65 due to coupling with the adjacent phosphorus nucleus $({}^{3}J_{PH} = 12 \text{ Hz})$, and so is the corresponding ${}^{13}C$ NMR methyl resonance (δ 29.4, $^{2}J_{PC} = 18$ Hz). The adjacent quaternary carbon signal of the $-CMe_2PPh_2$ substituent is observed at δ 36.3 as a doublet (${}^{1}J_{PC} = 18 \text{ Hz}$), and the Cp-methine carbon atom signals are found at δ 103.1 (s, C3) and δ 102.7 (d, ${}^{3}J_{PC} = 5 \text{ Hz}, \text{ C2}$).



The addition of the LiPPh₂ reagent to the fulvenes **1b**–e, that are derived from the condensation reaction of cyclopentadiene with the respective aldehydes, results in the formation of a chiral center in the α -position of the cyclopentadienyl ring system (products **2b–e**). This leads to a diastereotopic splitting of the respective pairs of aryl groups at phosphorus due to the persistent non-planar coordination geometry at phosphorus on the NMR time scale. The general appearance of the –CpLi resonances remains unaffected by this stereochemical feature because of the apparent symmetric coordination behavior of this lithioorganic system under rapid exchange conditions as they typically prevail in THF-containing solutions at the NMR monitoring temperatures applied.

A typical example is lithio-(1-tert-butyldiphenylphosphinomethyl)cyclopentadienide (2c). It shows two ¹H NMR C_5H_4 multiplets, each of relative intensity two, in benzene d_6 solution containing stoichiometric quantities of THF, at δ 6.25 and 6.06 ppm. The substituent CH group resonance appears at δ 3.86 ppm as a doublet (${}^{2}J_{PH} = 7$ Hz). In the ${}^{13}C$ NMR spectrum there is a pair of signals corresponding to the ipso-carbon atoms of the diastereotopic phenyl groups at phosphorus (δ 150.9, ${}^{1}J_{PC} = 31$ Hz; 142.6, ${}^{1}J_{PC} = 35$ Hz), and there are corresponding signals of diastereotopic pairs of o-phenyl (δ 134.6, ${}^{2}J_{PC} = 21$ Hz; 133.8, ${}^{2}J_{PC} = 21$ Hz), mphenyl (δ 131.9, ${}^{3}J_{PC} = 16$ Hz; 128.5, ${}^{3}J_{PC} = 15$ Hz) and p-phenyl carbon centers (127.8, s; 122.2, s). The cyclopentadienide ¹³C NMR C_5H_4 -methine resonances appear at δ $106.2 ({}^{3}J_{PC} = 8 \text{ Hz}, \text{C3}) \text{ and } 103.5 (s, \text{C2}). \text{ The substituent-}$ CH ¹³C NMR signal is observed at δ 50.3 as a doublet $({}^{1}J_{PC} = 17 \text{ Hz}; \delta \text{ C} = 119.3, {}^{2}J_{PC} = 8 \text{ Hz}).$

In order to achieve an increased solubility of the metallocene complexes derived from these phosphinomethylsubstituted cyclopentadienides the corresponding di-*p*-tolylphosphino derivatives **3a-c** were prepared analogously by treatment of the fulvenes **1a-c** with lithio-di-*p*-tolylphosphide. The substituted cyclopentadienide reagents **3a-c** exhibit analogous spectroscopic properties as described above for their Ph₂P-parent compounds (for details see Section 3).

The lithio(phosphinomethyl)cyclopentadienides 2a-e and 3a-c were then reacted with zirconium tetrachloride (see Scheme 1 and Table 1). As a typical example lithio-(1-methyl-1-diphenylphosphinoethyl)cyclopentadienide was treated with 0.5 molar equiv. of ZrCl₄·2THF in toluene/ pentane at low temperature ($\sim -30^{\circ}$ C). After conventional workup the bis[(1-methyl-1-diphenylphosphinoethyl)cyclopentadienyl]zirconiumdichloride product (4a) was isolated as a white solid in > 60% yield. The complex exhibits a single ³¹P NMR resonance at δ 33.2 ppm (in CDCl₃). It shows two Cp-methine ¹H NMR multiplets at $\delta 6.18$ and 6.02ppm (in CD₂Cl₂) and a methyl doublet at δ 1.60 (³J_{PH} = 14 Hz, 12H). The ¹³C NMR signals of the $-C(CH_3)_2$ -[P] section of the substituent are observed at δ 39.0 (quat C, d, ${}^{1}J_{PC} = 22$ Hz) and $\delta 25.5$ (methyl groups, d, ${}^{2}J_{PC} = 18$ Hz) and there are three resonances originating from the η^5 -C₅H₄

Table 1 Preparation of the $(Cp-CR^{1}R^{2}-PAr_{2})_{2}ZrCl_{2}$ complexes 4 and 5

Complex	Ar	R ¹	R ²	Yield (%)	δ ³¹ Ρ ª
4a	Ph	CH ₃	CH ₃	66	33.2
4b	Ph	CH ₃	Н	72	9.8, 9.7
4c	Ph	CMe ₃	н	82 ^b	12.0, 11.8
4d	Ph	Ph	н	93 ^b	7.0, 5.5
4e	Ph	<i>p</i> -tolyl	Н	76 ^b	6.0, 4.5
5a	p-tolyl	CH ₃	CH ₃	68	31.8
5b	p-tolyl	CH ₃	н	34 °	8.1, 8.0
5c	p-tolyl	CMe ₃	Н	49 °	10.9, 10.5

^a Two diastereomers except for 4a and 5a.

^b 1:1 mixture of diastereomers.

^c One diastereomer enriched during workup.

carbon atoms at δ 139.3 (*ipso*-C, ² J_{PC} =7 Hz), 118.0 (³ J_{PC} =4 Hz, C2) and 111.5 (s, C3). The corresponding di*p*-tolylphosphino derivative **5a** was prepared analogously, and it exhibits similar spectroscopic characteristics.

The coordination of the chiral Cp–CR¹R²–PAr₂– reagents 2b–e (and 3b–c) employed as racemates produces in each case a pair of diastereotopic metallocene complexes *rac*-4 and *meso*-4 (and *rac*-5 and *meso*-5, respectively). The reactions between ZrCl₄ and 2b–e (and 3b–c) showed no diastereoselectivity under the reaction conditions employed. In all cases 1:1 mixtures of the respective metallocene diastereoisomers were formed. In several cases it was, however, possible to achieve a significant enrichment of one of the diastereomers in the course of the workup procedure or by subsequent crystallization. In one case, namely the complex 4b, a single diastereomer was obtained pure as single crystals.

In the case of the bis[(1-tert-butyldiphenylphosphinomethyl)cyclopentadienyl]zirconium dichloride complex (4c), which is a typical example of this class of compounds, the rac-4c and meso-4c diastereoisomers can be distinguished from their ¹H NMR C_5H_4 resonances. Coordination of the chiral C_5H_4 –C(R)H– PPh_2 ligand to zirconium makes each of the $(C_5H_4-X)M$ units prochiral and thus leads to the occurrence of diastereotopic pairs of α -CH and β -CH methine units within each $(\eta - C_5 H_4 - X)M$ building block [8]. Due to the overall C_2 symmetry of the substituted metallocene dihalide rac-4c the two Cp-C(R)H-PPh₂ units in this complex are symmetry-equivalent, and so are the corresponding ligand systems in *meso-4c*, in this case due to the C_s symmetry of this complex. Therefore, each of the $[Cp-C(CMe_3)H PPh_2]_2ZrCl_2$ complexes, rac-4c and meso-4c, should exhibit a set of four cyclopentadienyl CH signals. This is in fact observed. In the ¹H NMR spectrum of the 1:1 mixture of the diastereomers four pairs of CH signals of the C₅H₄-X groups are observed. Enrichment of one of the diastereoisomers by fractionating crystallization from a dichloromethane/pentane solvent mixture resulted in a 5:1 enrichment of one of the isomers. This allowed a distinction between the two diastereoisomers and their corresponding ¹H NMR sets of signals, although an absolute assignment of the meso- and rac-4c diastereoisomers was not possible. The two sets of Cp-methine signals of *rac-* and *meso-***4c** occur at δ 6.13, 5.48, 5.37 and 5.31 ppm (isomer **A**) and δ 5.97, 5.53, 5.37 and 5.21 ppm (isomer **B**, in benzene-d₆).

In the case of the [(1-diphenylphosphinoethyl)cyclopentadienyl]zirconium dichloride complex (**4b**) it was possible to obtain one of the diastereoisomers as single crystals (X-ray crystal structure analysis see below) and thus assign the spectral data of the *rac*-**4b** diastereomer directly. The complex *rac*-**4b** is characterized by a set of four ¹H NMR η^5 -C₅H₄ resonances at δ 5.91, 5.65, 5.39 and 5.25 (in benzene-d₆). The CH(CH₃) group of the substituent exhibits ¹H NMR signals at δ 4.23 (dq, ³J_{HH} = 7.1 Hz, ²J_{PH} = 1.8 Hz) and 1.53 (dd, ³J_{HH} = 7.1 Hz, ³J_{PH} = 14.5). The corresponding CH(CH₃) ¹³C NMR signals are observed at δ 33.6 (¹J_{PC} = 17 Hz, CH) and 16.5 (²J_{PC} = 17 Hz), and a set of four ¹³C NMR c₅H₄-X methine resonances appears at δ 116.5, 116.0, 114.2 and 106.0 ppm.

Single crystals for the X-ray crystal structure analysis were obtained by crystallization from the mixture of diastereoisomers from a dichloromethane solution. The obtained crystals contained the pure *rac*-4b diastereoisomer.

Complex *rac*-4b in the crystal is chiral and C_2 symmetric. The zirconium center is pseudotetrahedrally coordinated by two η^5 -Cp–CHMe–PPh₂ ligands and two chlorides. The zirconium–chloride distance is 2.4405(12) Å (i.e. Zr–Cl8, see Fig. 1) [9]. The Cl8–Zr–Cl8* angle is 98.85(6)°. The Cpring systems are very uniformly η^5 -coordinated to the metal



Fig. 1. A view of the molecular structure of the metallocene complex **4b** with (unsystematical) atom numbering scheme. Selected bond lengths (Å) and angles (°): Zr-Cl8 2.4405(12), Zr-Cl 2.545(4), Zr-C2 2.535(4), Zr-C3 2.505(4), Zr-C4 2.453(4), Zr-C5 2.491, C1-C6 1.510(5), C6-C61 1.534(6), C6-P7 1.867(4), P7-C71 1.829(5), P7-C77 1.849(4); C18*-Zr-Cl8 98.85(6), C2-C1-C6 125.8(6), C5-C1-C6 126.2(4), C2-C1-C5 107.6(4), C1-C6-P7 105.5(3), C1-C6-C61 114.7(3), P7-C6-C61 108.1(3), C6-P7-C71 102.3(2), C6-P7-C77 104.1(2), C71-P7-C77 100.0(2).

atom, the individual Zr-C(Cp) bond lengths are 2.545(4) (Zr-C1), 2.535(4) (Zr-C2), 2.505(4) (Zr-C3), 2.453(4) (Zr-C4) and 2.491(4) (Zr-C5) Å. The D1- $Zr-D1^*$ angle is 130.6° (D1 and D1* denote the centroids of the Cp-ring systems).

The metallocene conformation of complex rac-4b is bislateral:anti, i.e. the bulky Ph₂P-substituted secondary alkyl groups at the Cp rings are oriented toward the opposite lateral sectors at the bent metallocene moiety (dihedral angle C6-D1-D1*-C6* 178.6°) [10]. The C6-H vector is oriented coplanar with the Cp-ring plane, the C-H bond at C6 points toward the open front side of the bent metallocene wedge $(C1-C6: 1.510(5) \text{ Å}, \text{ angles } C5-C1-C6 126.2(4)^{\circ}, C2-C1-C6 126.2(4)^{\circ}, C2-C1-C1-C6 126.2(4)^{\circ}, C2-C1-C1-C6 126.2(4)^{\circ}, C2-C1-C1-C6 126.2(4)^{\circ}, C2-C1-C1-C6 126.2(4)^$ $C6 125.8(4)^{\circ}$, C2–C1–C5 107.6(4)°). Thus, the sum of the bond angles around the Cp-ring carbon atom C1 is 359.6° as expected for a distorted trigonally planar arrangement. The sum of the angles between the linkages of the heavy atoms at C6 is 328.3° (i.e. C1-C6-C61 114.7(3)°, C1-C6-P7 $105.5(3)^{\circ}$, C61–C6–P7 108.1(3)°) which is very close to the expected value of 327° for an ideal tetrahedral geometry. The corresponding sum of bonding angles at the adjacent phosphorus center is markedly smaller at 306.4° (i.e. C6-P7-C77 104.1(2)°, C6-P7-C71 102.3(2)°, C71-P7-C77 $100.0(2)^{\circ}$) which is as expected for this third row main group element. A distinct conformational arrangement of the -CHMe-PPh₂ Cp substituent is observed that features one of the phenyl groups at phosphorus (C77-C82) antiperiplanar to the C6--C1 vector and the other (C71--C76) antiperiplanar to the methyl group (i.e. the C6-C61 vector). The corresponding dihedral angles are θ (C1–C6–P7– $(C77) = 177.0(3)^{\circ}$ and $(C61-C6-P7-C71) = 63.2(3)^{\circ}$. In this arrangement, the C6-H vector and the space available for bonding of any electrophilic reagent to the lone pair at phosphorus are also in an antiperiplanar orientation. The bulky Ph₂P group is oriented away from zirconium toward the periphery of the organometallic system, whereas the methyl group at C6 is directed toward the central plane of the bent metallocene framework.

It is possible that the conformation that is observed in the crystal may also represent the favored rotational isomer of rac-4b in solution, but we must assume that conformational changes and equilibrations can easily be achieved [10]. This is necessary when reactions with transition metal complexes are carried out employing the metallocene complexes 4 (or 5) as chelating ligand systems. Some preliminary experiments concerning such use of the complexes 4 (and 5) were carried out that were directed toward the synthesis of heterodimetallic compounds containing pairs of early and late transition metals.

2.2. Synthesis of heterodimetallic systems (Scheme 2)

In the preliminary experiments carried out in this study the metallocene complexes **4a**, **5a** and **4c** were employed. First, we have treated the bis[(1-methyldiarylphosphinomethyl)cyclopentadienyl]zirconium dichloride complexes **4a**



(Ar = phenyl) and 5a (Ar = p-tolyl) with equimolar amounts of bis(benzonitrile)dichloropalladium at low temperature $(-45^{\circ}C)$ in tetrahydrofuran. The reaction between these reagents occurs instantaneously and a precipitate of the heterodimetallic complexes 6 (Ar = phenyl) and 7 (Ar = ptolyl), respectively, is formed. The products are generated by displacement of the benzonitrile ligands by the organometallic chelate phosphane ligand system. The dimetallic structure of complex 7 follows from the elemental analysis and its typical spectroscopic properties. The ³¹P NMR resonance of the system is observed at δ 45.7 (in dichloromethane-d₂) which corresponds to a ³¹P NMR coordination shift of $\Delta = +14.5$ ppm relative to the ³¹P NMR resonance of the free ligand 5a (δ 31.2 ppm, measured in benzene-d₆). According to Shaw and co-workers [11] there is a linear relationship between the ³¹P NMR shift of free phosphane ligands (δ_{lig}) with the coordination shift Δ which is markedly different for the series of cis- and trans-L₂PdCl₂ complex systems. Thus, the stereochemistry of the system investigated can be deduced by comparing the calculated respective values with the actually observed ³¹P NMR shifts using the relationships δ_{cis} 38 + 0.69 δ_{lig} and δ_{trans} 28 + 0.64 δ_{lig} [11a]. For the system of complex 7/free ligand 5a the respective calculated values are δ_{cis} 59.5 and δ_{trans} 47.9 ppm. With an observed ³¹P NMR chemical shift of δ_{obs} 45.7 ppm this clearly indicates a trans-coordination of the organometallic chelate phosphane to palladium in the heterodimetallic complex 7.

Trans-coordinated phosphanes are also indicated by the appearance of the ¹H NMR methyl signals at the bridging $-C(CH_3)_2-[P]$ -groups [12]. Coupling with both phosphorus nuclei occurs only in the *trans*-complex, where both P atoms commonly share an orbital at Pd for bonding, as is observed here: a 'pseudotriplet' (as part of an A₆XX' spin system) is observed for the CH₃ resonance with a 'virtual' coupling constant of ${}^{3}J_{PH} + {}^{5}J_{PH} \approx 8$ Hz. The remaining ¹H and ¹³C NMR signals show that the intact framework of the ligand system **5a** is retained in complex **7**. Complex **6** has an

analogous structure as is evident from the very similar spectroscopic features.

The heterodimetallic zirconium--platinum complexes 8 (Ar = phenyl) and 9 (Ar = p-tolyl) were prepared similarly. They have structures analogous to the Pd complexes (6, 7, 7)see above). This follows from their characteristic NMR spectra. The Zr/Pt complex 9 thus exhibits a ³¹P NMR resonance at δ 37.9 ppm. Due to the presence of the ¹⁹⁵Pt isotope (33.7%) natural abundance, I = 1/2) a splitting due to ³¹P-¹⁹⁵Pt coupling is observed. It is well known that the magnitude of the ${}^{1}J_{PtP}$ coupling constant in L₂PtCl₂ complexes is very diagnostic for their identification as the cis- or trans-isomers [13] (e.g. cis-PtCl₂(PMe₃)₂: ${}^{1}J_{PtP} = 3480$ Hz, trans- $PtCl_2(PMe_3)_2$: ${}^{1}J_{PtP} = 2379 Hz$ [14] or *cis-/trans*-PtCl_2[Pp-tolyl)₃]₂: ¹ J_{PtP} = 3694 Hz/2595 Hz [15]). The observed ${}^{1}J_{\text{PtP}}$ coupling constants in our systems are 2605 (9) and 2631 (8) Hz, respectively, and thus indicate the presence of trans-structures. This is supported by the observation of a ¹H NMR $-C(CH_3)_2 - [P]$ 'pseudotriplet' (A₆ part of an A₆XX' system) for the same reasons as discussed above for examples 6 and 7.

Eventually, the organometallic chelate phosphane system **4c** was treated with $PdCl_2(PhCN)_2$. After 1 day at ambient temperature a rather complicated mixture of products resulted, from which a single heterodimetallic complex (**10**) was obtained by crystallization. The isolated material shows four cyclopentadienyl ¹H NMR resonances in dichloromethane solution at δ 7.11, 6.90, 6.51 and 6.33 ppm (each 2H), a single tert-butyl ¹H NMR singlet at δ 0.63 ppm (18H), and a single ³¹P NMR resonance at 25.5 ppm.

The X-ray crystal structure analysis of **10** has revealed that a salt was obtained. It contains a heterodimetallic cation of composition $[(Cp-CHCMe_3-PPh_2)_2(Cl)Zr(\mu-Cl)Pd(Cl)]^+$. The salt contains an $[MCl_5(THF)^-]$ counteranion with M probably being zirconium. This is consistent with the refinement of the X-ray crystal structure analysis [16] and is supported by the observation of a pronounced $[ZrCl_5^-]$ feature of the sample in a MALDI-TOF-MS experiment in the negative ion mode. A mechanistic description of the formation of **10** must await further studies, but it could be that some excess $ZrCl_4$ present in the sample from the preparation or formed by decomposition may have served as a suitable chloride abstractor.

Cations and anions of **10** are well separated in the solid. The cation of **10** contains a zirconocene unit that is slightly distorted. The zirconium center is pseudotetrahedrally surrounded by two cyclopentadienyl ligands and two chlorides. The Cp ligands are rather uniformly η^5 -coordinated to zirconium (Zr–C10 to C14: 2.482(12), 2.478(12), 2.460(12), 2.529(12), 2.538(11) Å; Zr–C20 to C24: 2.519(12), 2.464(12), 2.501(12), 2.497(12), 2.527(11) Å). The D1– Zr–D2 angle is 134.7° (D1 and D2 denote the centroids of the Cp-ring systems). The two zirconium to chloride linkages are very different. The bond between the metal to the terminal Cl ligand (Zr–C111) is in the usual range at 2.471(3) Å. The other chloride is bridging between zirconium and palladium. This zirconium to chloride bond (Zr–Cl12) is much longer at 2.567(3) Å. This situation is rather different from that found at the adjacent Pd center. Here the difference between the terminal Pd–Cl21 bond length (2.290(3) Å) and the Pd– Cl12 distance to the bridging chloride ligand (2.295(3) Å) is only marginally different. It should also be noted that the Cl12–Zr–Cl11 angle is rather large at 121.92(10)°. It thus appears that this section of the complex should be described by a situation where a Pd–Cl moiety just coordinates through its nucleophilic halide atom to a Cp₂Zr–Cl⁺ cation [17] inside the framework of the bridged heterodimetallic system. The Pd…Zr distance is 2.946 Å, which is probably dictated by the framework geometry [18]. A view of the molecular structure of **10** is given in Fig. 2.

Bridging of the μ -Cl ligand and the two Cp–CH(CMe₃)– PPh₂ ligands between zirconium and palladium results in the formation of a dimetallabicyclic framework with the metals serving as bridgehead atoms. The carbon centers C15 and C25 are chiral, and they exhibit opposite absolute configurations. Thus, complex **10** is a *meso*-compound. The bulky tert-butyl substituents are both oriented in pseudo-equatorial positions at the dimetallabicyclic framework. They point



Fig. 2. A view of the molecular structure of the salt 10 with (unsystematical atom numbering scheme). Selected bond lengths (Å) and angles (°): Zr1-Cl11 2.471(3), Zr-Cl12 2.567(3), Pd2-Cl12 2.295(3), Pd2-Cl21 2.290(3), Pd2-P1 2.337(4), Pd2-P2 2.347(4), P1-Caryl 1.808(12), P1-C15 1.894(12), P2-Caryl 1.808(12), P2-C25 1.872(12), Zr3-Cl31 2.401(3), Zr3-Cl32 2.427(4), Zr3-Cl33 2.425(4), Zr3-Cl34 2.445(4), Zr3-Cl35 2.451(3), Zr3-O91 2.219(9), Cl11-Zr1-Cl12 121.92(10), Zr1-Cl12-Pd2 74.34(9), Cl12-Pd2-Cl21 173.79(12), Cl12-Pd2-P1 86.61(11), Cl12-Pd2-P2 86.26(11), Cl21-Pd2-P1 92.67(12), Cl21-Pd2-P2 92.98(12), P1-Pd2-P2 164.83(12), Pd2-P1-C15 114.2(4), Pd2-P2-C25114.4(4), O91-Zr-Cl31177.3(3), O91-Zr3-Cl3288.6(3), O91-Zr3-Cl3385.4(3), O91-Zr3-Cl3485.1(3), O91-Zr3-Cl3585.7(3), Cl31-Zr3-Cl32 94.2(2), Cl31-Zr3-Cl33 94.43(13), Cl31-Zr3-Cl34 95.24(14), Cl31-Zr3-Cl35 91.58(13), Cl32-Zr3-Cl33 88.7(2), Cl32-Zr3-Cl34 88.0(2), Cl32-Zr3-Cl35 174.20(14), Cl33-Zr3-Cl34 169.98(14), Cl33-Zr3-Cl35 91.76(13), Cl34-Zr3-Cl35 90.60(14); for additional data see text.

away from the center of the complex framework toward opposite directions.

The palladium center exhibits a 'square-planar' coordination geometry with a sum of σ -bond angles of 358.5° (individual bond angles Cl21–Pd2–P1 92.67(12)°, Cl12–Pd2–P1 86.61(11)°, Cl21–Pd2–P2 92.98(12)°, Cl12–Pd2–P2 86.26(11)°). The Cl21–Pd2–Cl12 angle thus is 173.79(12)° and the P1–Pd2–P2 angle is 164.83(12)°. The palladiumphosphorus distances are 2.337(4) (Pd2–P1) and 2.347(4) (Pd2–P2) Å, and the Pd2–Cl12–Zr angle is small at 74.34(9)°.

We conclude from the results obtained in this study that bent metallocene complexes containing substituted diarylphosphinomethyl side-chains at their Cp-ring systems can readily be synthesized by means of the fulvene route applied here. In the reaction with L2PdCl2 and L2PtCl2 reagents they may serve as organometallic bis-phosphane chelating ligands that have a high tendency of forming the respective transchelate bis-phosphane complexes at the late transition metal component of the resulting early-late heterodimetallic product. There is also some indication (see the formation of 10) that the phosphane-containing zirconocene complexes described here can do more than just serve as flexible chelating donor ligands but that they are suited to serve as functionalized metallocene components (e.g. zirconocene cations) that closely and directly interact with the ligand sphere at the adjacent late transition metal. Whether these features might lead to novel catalytic applications of related heterodimetallic systems will be studied in our laboratory.

3. Experimental

All compounds described are air- and moisture-sensitive. They were prepared in an argon atmosphere using Schlenk type glassware or in a glove-box. Solvents (including deuterated solvents) were dried and distilled under argon prior to use. NMR spectra were recorded on a Bruker AC 200 P (¹H, 200 MHz; ³¹P, 81 MHz, H₃PO₄ external standard; ⁷Li, 77.8 MHz, LiCl in D₂O external standard; ¹³C, 50.3 MHz), a Bruker ARX 300 (¹³C, 75.5 MHz) or a Varian Unity plus (¹H, 600 MHz, ¹³C, 150 MHz) NMR spectrometer; the latter spectrometer was also used for measuring the GHSQC- and GHMBC-2D NMR spectra (for a description see Ref. [19]). IR spectroscopy: Nicolet 5 DXC FT-IR spectrometer (KBr). Elemental analyses: Foss Heraeus CHNO-Rapid. DSC: Dupont 2910 DSC (STA intruments). X-ray-crystal structure analyses: Enraf-Nonius MACH 3 diffractometer (programs used: SHELX 86, SHELX 93 XP and SCHAKAL). A selfconstructed (H. Luftmann) time of flight mass spectrometer was used for carrying out the MALDI-TOF-MS measurements. The following reagents were prepared according to literature procedures: bis(tetrahydrofuran)tetrachlorozirconium [20], 6,6-dimethylfulvene (1a), 6-tert-butylfulvene (1c), 6-phenylfulvene (1d), 6-tolylfulvene (1e) [5], 6methylfulvene (1b) [21], bis(benzonitril)dichloropalladium(II) and bis(benzonitril)dichloroplatinum(II) [22], lithiodiphenylphosphide and di-*p*-tolylphosphine [6].

3.1. Lithio(1-methyl-1-diphenylphosphinoethyl)cyclopentadienide (**2a**) and general procedure

6.70 ml (10.7 mmol) of n-butyllithium (1.6 M in hexane) were added to a vigorously stirred solution of 2.09 g (10.7 mmol) of diphenylphosphine in 30 ml of THF at -78° C. The dark red solution was allowed to warm to room temperature within 2 h. Subsequently, a solution of 1.28 ml (1.13 g, 10.7 mmol) of 6,6-dimethylfulvene (1a) in 30 ml of pentane was added slowly from a dropping funnel at $-78^{\circ}C$ within 1 h. The reaction mixture was then stirred at room temperature overnight. The solvent was evaporated until a highly viscous orange-red foam was formed. Repeated addition of pentane, shaking of the Schlenk flask in an ultrasonic bath for several minutes and evaporation of the solvent eventually allowed the product to be isolated as a powdery solid on a Schlenk frit. Washing with two 15 ml portions of pentane and drying in vacuo yielded 2.40 g (75%) of white powdery **2a**. ¹H NMR (benzene- d_6 /THF- d_8 , 200.1 MHz): δ 7.63 (m, 4H, o-Ph-H), 7.2-7.0 (m, 6H, m-Ph-H, p-Ph-H), 6.16 (s, 4H, C₅H₄), 1.65 (d, ${}^{3}J_{PH} = 12.1$ Hz, 6H, CH₃). ${}^{31}P$ NMR (benzene- d_6 /THF- d_8 , 81.0 MHz): δ 21.5. ⁷Li NMR (ben $zene-d_6/THF-d_8$, 77.8 MHz): $\delta - 5.9$.

3.2. Lithio(1-methyl-1-di-p-tolylphosphinoethyl)cyclopentadienide (**3a**)

In an analogous procedure 2.65 g (12.4 mmol) of di-ptolylphosphine were deprotonated with 7.7 ml (12.3 mmol) of n-butyllithium (1.6 M) and then reacted with 1.6 g (15.1 m)mmol) of 6,6-dimethylfulvene (1a) yielding 4.18 g (85%) of the pale yellow mono-THF adduct of 3a. ¹H NMR (ben $zene-d_6/THF-d_8$, 200.1 MHz): δ 7.50 (pt, 4H, o-Ph-H), 6.96 $(pd, 4H, m-Ph-H), 6.09 (s, 4H, C_5H_4), 3.54 (m, 4H, \alpha-H of$ THF), 2.08 (s, 6H, tolyl-CH₃), 1.63 (d, ${}^{3}J_{PH} = 12.2$ Hz, 6H, CH₃), 1.42 (m, 4H, β -H of THF). ¹³C NMR (benzene-d₆/ THF-d₈, 50 MHz): C1 not observed. δ 137.3 (s, *p*-tolyl), 136.5 (d, ${}^{1}J_{PC} = 22$ Hz, *ipso*-C of tolyl), 135.6 (d, ${}^{2}J_{PC} = 20$ Hz, o-tolyl), 128.5 (d, ${}^{3}J_{PC} = 5$ Hz, m-tolyl), 103.1 (d, $J_{PC} = 7$ Hz, C_5H_4), 102.7 (s, C_5H_4), 36.2 (d, ${}^{1}J_{PC} = 17$ Hz, C1'), 29.7 (d, ${}^{2}J_{PC} = 18$ Hz, CH₃), 21.1 (s, tolyl-CH₃). ${}^{31}P$ NMR (benzene- $d_6/THF-d_8$): δ 19.9. ⁷Li NMR (benzene d_6 /THF- d_8 , 77.8 MHz): δ - 7.5.

3.3. Lithio(1-diphenylphosphinoethyl)cyclopentadienide (2b)

Deprotonation of 2.58 g (13.9 mmol) of diphenylphosphine with 8.6 ml (13.8 mmol) of n-butyllithium (1.6 M) in 40 ml of THF (-78° C, analogously as described above) and reaction with an excess of 6-methylfulvene (**1b**) (containing 1 equiv. of pentane) (2.8 g, 17 mmol) in 40 ml of pentane yielded 3.2 g (11.3 mmol) (81%) of **2b** within 12 h reaction time. ¹H NMR (benzene-d₆/THF-d₈): δ 7.64 (m, 2H, o-Ph-H), 7.43 (m, 2H, o-Ph-H), 7.12–6.95 (m, 6H, m,p-Ph-H), 6.01 (s, 4H, C₅H₄), 3.80 (dq, ²J_{HH} = 7.1 Hz, ²J_{PH} = 7.1 Hz, 1H, 1'H), 1.48 (dd, ²J_{HH} = 7.1 Hz, ²J_{PH} = 14.7 Hz, 3H, CH₃). ³¹P NMR (benzene-d₆/THF-d₈, 81.0 MHz): δ 0.2.

3.4. Lithio(1-di-p-tolylphosphinoethyl)cyclopentadienide (3b)

Reaction of 1.94 g (9.06 mmol) of di-*p*-tolylphosphine in 40 ml of THF with 5.7 ml (9.1 mmol) of 1.6 M n-butyllithium followed by treatment with 1.1 g (9.5 mmol) of 6-methyl-fulvene (**1b**) (containing 0.33 equiv. of pentane) in 40 ml of pentane yielded 2.18 g (77%) of off-white **3b**. ¹H NMR (benzene-d₆/THF-d₈, 200.1 MHz): δ 7.63 (pt, 2H, *o*-tolyl-H), 7.50 (pt, 2H, *o*-tolyl-H), 6.99 (pd, 2H, *m*-tolyl-H), 6.91 (pd, 2H, *m*-tolyl-H), 6.01 (s, 4H, C₅H₄), 3.90 (dq, ²J_{HH} = 7.2 Hz, ²J_{PH} = 7.2 Hz, 1H, 1'H), 2.08, 2.02 (each s, each 3H, tolyl-CH₃), 1.59 (dd, ²J_{HH} = 7.1 Hz, ²J_{PH} = 14.6 Hz, 3H, CH₃).

3.5. Lithio(1-tert-butyldiphenylphosphinomethyl)cyclopentadienide (2c)

8.00 ml (8.41g, 45.2 mmol) of diphenylphosphine in 100 ml of THF/pentane was reacted at -50° C with 28.4 ml (45.2 mmol) of 1.59 M n-butyllithium followed by a slow addition of an excess of tert-butylfulvene (1c) (9.22 g, 60.5 mmol), dissolved in 30 ml of pentane. Work-up similar to 2a after 2 h reaction time at ambient temperature gave 10.6 g (59%) of 2c as a mono-THF-adduct. Additional slightly less pure product (1.5 g) could be precipitated from the mother liquid by concentration and cooling to -20° C. ¹H NMR (benzened₆, 200.1 MHz): δ7.80–7.63 (m, 4H, *o*-Ph-H), 7.10–6.90, $6.88-6.80, 6.74-6.66 \text{ (m, 6H, Ph-H)}, 6.25 \text{ (br s, 2H, C_5H_4)},$ 6.06 (m, 2H, C_5H_4), 3.86 (d, ${}^{2}J_{PH} = 7.3$ Hz, 1H, 1'H), 2.73 $(m, 4H, \alpha$ -THF-H), 1.20 (s, 9H, 'Bu-CH₃), 0.98 (m, 4H, β -THF-H). ¹³C NMR (benzene-d₆, 50.3 MHz): δ 150.9 (d, ${}^{1}J_{PC} = 31$ Hz, *ipso-C* of Ph), 142.6 (d, ${}^{1}J_{PC} = 35$ Hz, *ipso-C* of Ph), 134.6 (d, ${}^{2}J_{PC} = 21$ Hz, o-Ph), 133.8 (d, ${}^{2}J_{PC} = 21$ Hz, o-Ph), 131.9 (d, ${}^{3}J_{PC} = 16$ Hz, m-Ph), 128.5 (d, ${}^{3}J_{PC} = 15$ Hz, m-Ph), 127.8 (s, p-Ph), 122.2 (s, p-Ph), 119.3 (d, $^{2}J_{PC} = 10 \text{ Hz}, ipso-C \text{ of } C_{5}H_{4}), 106.2 \text{ (d, } J_{PC} = 8 \text{ Hz}, C_{5}H_{4}),$ 103.5 (s, C_5H_4), 68.3 (THF), 50.3 (d, ${}^{1}J_{PC} = 17$ Hz, C1'), 36.6 (d, ${}^{2}J_{PC} = 17$ Hz, $C(CH_{3})_{3}$), 31.0 (d, ${}^{3}J_{PC} = 7$ Hz, $C(CH_3)_3$, 25.3 (THF). ³¹P NMR (benzene-d₆, 81.0 MHz): δ 12.7.

3.6. Lithio(1-tert-butyldi-p-tolylphosphinomethyl)cyclopentadienide (**3c**)

Reaction of 4.08 g (19.1 mmol) of di-*p*-tolylphosphine in 50 ml of THF with 11.8 ml (18.9 mmol) of 1.6 M n-butyllithium and 3.45 g (22.6 mmol) of 6-tert-butylfulvene (1c) (containing 0.25 equiv. of diethyl ether) in 40 ml of pentane yielded after 12 h reaction time 6.48 g (80%) of **3c** as a bright yellow powdery mono-THF adduct. ¹H NMR (benzene-d₆/ THF-d₈, 200.1 MHz): δ 7.70 (pt, 2H, *o*-tolyl-H), 7.61 (pt, 2H, *o*-tolyl-H), 6.91 (pd, 2H, *m*-tolyl-H), 6.72 (pd, 2H, *m*tolyl-H), 6.22 (br s, 2H, C₅H₄), 6.03 (m, 2H, C₅H₄), 3.87 (d, ²J_{PH} = 7.2 Hz, 1H, 1'H), 3.47 (m, 4H, *α*-THF-H), 2.01, 1.86 (each s, each tolyl-CH₃), 1.39 (m, 4H, *β*-THF-H), 1.20 (s, 9H, 'Bu-CH₃).

3.7. Lithio(1-phenyldiphenylphosphinomethyl)cyclopentadienide (2d)

Reaction of 2.52 g of diphenylphosphine (13.0 mmol), dissolved in 25 ml of THF, with 8.15 ml (13.0 mmol) of 1.6 M n-butyllithium and 2.02 g (13.1 mmol) of 6-phenylfulvene (1d) in 30 ml of pentane yielded after work-up 4.16 g of 2d containing 0.75 equiv. of THF (yield 80%). ¹H NMR (benzene-d₆, 200.1 MHz): δ 7.57–7.47, 7.44–7.31 (2 m, 6H, Ph-H), 7.11–6.75 (m, 9H, Ph-H), 6.28 (br s, 2H, C₅H₄), 6.12 (m, 2H, C₅H₄), 4.89 (d, ²J_{PH}=7.5 Hz, 1H, 1'H). ³¹P NMR (toluene-d₈, 81.0 MHz, 250 K): δ 3.6. ⁷Li NMR (benzened₆, 77.8 MHz): δ 11.5 (s, br).

3.8. Lithio(1-p-tolyldiphenylphosphinomethyl)cyclopentadienide (2e)

6.8 g (40.5 mmol) of 6-*p*-tolylfulvene (**1e**), dissolved in 50 ml of pentane, was added to a stirred solution of lithiodiphenylphosphide (in situ generated from 5.6 g (30.1 mmol) of diphenylphosphine in 50 ml of THF and 18.8 ml (30.1 mmol) of 1.6 M n-butyllithium within 3 h and stirred overnight at room temperature. Yield: 9.0 g (83%) of **2e**. ¹H NMR (benzene-d₆/THF-d₈, 200.1 MHz): δ 7.3–6.9 (m, 12H, Ph-H, *o*-tolyl-H), 6.86 (pd, 2H, *m*-tolyl-H), 5.83 (m, 2H, C₅H₄), 5.64 (m, 2H, C₅H₄), 4.64 (d, ²J_{PH}=7.8 Hz, 1H, 1'H), 2.19 (s, 3H, CH₃).

3.9. General procedure for the preparation of the metallocene dichloride complexes **4a–e** and **5a–c**

10 mmol of the respective lithiumcyclopentadienide (2ae, 3a-c) and 5 mmol of zirconium tetrachloride (or its THF adduct) were separately suspended in toluene or 1:1 mixtures of toluene and pentane (50–100 ml). At -78° C the suspension of the lithiumcyclopentadienide was siphoned into the vigorously stirred ZrCl₄ suspension. After a given reaction time (usually 12 h) the solvent was evaporated in vacuo and the residue taken up in 100 ml of dichloromethane. Subsequent filtration through a 3 cm bed of celite removed finely suspended lithium chloride yielding a clear yellow solution of the metallocene dichloride. The solvent was removed in vacuo, the residue suspended in various amounts of pentane (depending on the solubility of the product) and transferred onto a Schlenk frit. The crude product was washed twice with pentane and dried in vacuo yielding the white to off-white metallocene dichlorides 4a-e and 5a-c, respectively.

3.10. Bis[(1-methyl-1-diphenylphosphinoethyl)cyclopentadienyl]zirconium dichloride (4a)

2a (2.21 g, 7.42 mmol) in 50 ml of toluene was reacted at -78°C with 1.40 g (3.71 mmol) of bis(tetrahydrofuran)tetrachlorozirconium in 50 ml of toluene and stirred at that temperature for 4 h. Subsequent work-up yielded 1.82 g (66%) of analytically pure white microcrystalline 4a. M.p. 201°C. Anal. Calc. for C₄₀H₄₀Cl₂P₂Zr (744.83): C, 64.50; H, 5.41. Found: C, 64.77; H, 5.48%. ¹H NMR (dichloromethane- d_2 , 200.1 MHz): δ 7.4–7.1 (m, 20H, Ph–H), 6.18 (m, 4H, C_5H_4), 6.02 (4H, C_5H_4), 1.60 (d, ${}^{3}J_{PH} = 14.3$ Hz, 12H, CH₃). ¹³C NMR (benzene- d_6 /THF- d_8 , 50.3 MHz): δ 139.3 $(d, {}^{2}J_{PC} = 7 \text{ Hz}, C1), 135.8 (d, {}^{1}J_{PC} = 23 \text{ Hz}, ipso-C \text{ of Ph}),$ 135.4 (d, ${}^{2}J_{PC} = 21$ Hz, o-Ph), 129.2 (s, p-Ph), 128.1 (d, ${}^{3}J_{PC} = 6$ Hz, m-Ph), 118.0 (d, ${}^{3}J_{PC} = 4$ Hz, C2), 111.5 (s, C3), 39.0 (d, ${}^{1}J_{PC} = 22$ Hz, C1'), 25.5 (d, ${}^{2}J_{PC} = 18$ Hz, CH₃). ³¹P NMR (chloroform-d₁, 81.0 MHz): δ 33.2. IR (KBr): $\tilde{\nu} = 3099, 3087, 2961, 2934, 2868, 1475, 1434$ (s), 1366, 1262, 1120, 1088, 1074, 1054, 1044, 1027, 829 (vs), 822 (vs), 805, 748 (s), 740, 700 (s), 499 cm⁻¹. MALDI-TOF-MS (positive ion mode): m/z 742 (M^+ – H), 635.

3.11. Bis[(1-methyl-1-di-p-tolylphosphinoethyl)cyclopentadienyl]zirconium dichloride (5a)

3.65 g (9.15 mmol) of 3a and 1.72 g (4.57 mmol) of bis(tetrahydrofuran)tetrachlorozirconium, in 50 ml of toluene each, were brought to reaction at -78° C. The resulting mixture was allowed to warm to room temperature overnight and the product isolated analogously as described above. Yield: 2.4 g (68%) of off-white 5a. M.p. 235°C (decomp.). Anal. Calc. for C₄₄H₄₈Cl₂P₂Zr (800.94): C, 65.98; H, 6.04. Found: C, 65.65, H, 6.45%. ¹H NMR (dichloromethane-d₂, 200.1 MHz): δ 7.2-7.0 (m, 16H, tolyl-H), 6.18 (m, 4H, C_5H_4), 6.01 (4H, C_5H_4), 2.34 (s, 12H, tolyl-CH₃), 1.57 (d, ${}^{3}J_{\rm PH} = 14.3$ Hz, 12H, CH₃). ${}^{13}C$ NMR (benzene-d₆, 50.3) MHz): $\delta 139.5$ (d, ${}^{2}J_{PC} = 7$ Hz, C1), 138.9 (s, *p*-tolyl), 135.4 $(d, {}^{2}J_{PC} = 21 \text{ Hz}, o\text{-tolyl}), 132.9 (d, {}^{1}J_{PC} = 21 \text{ Hz}, ipso-C \text{ of}$ *p*-tolyl), 128.1 (d, ${}^{3}J_{PC} = 7$ Hz, *m*-tolyl), 117.6 (d, ${}^{3}J_{PC} = 5$ Hz, C2), 111.0 (s, C3), 39.0 (d, ${}^{1}J_{PC} = 21$ Hz, C1'), 25.9 $(d, {}^{2}J_{PC} = 18 \text{ Hz}, \text{CH}_{3}), 21.2 \text{ (s, tolyl-CH}_{3}). {}^{31}\text{P} \text{ NMR} \text{ (dich$ loromethane-d₂, 81.0 MHz): δ 31.8. IR (KBr) $\tilde{\nu}$ = 3014, 2962, 2918, 2865, 1598, 1496, 1478, 1458, 1447, 1395, 1379, 1361, 1310, 1262, 1186, 1121, 1089, 1040, 1019, 932, 877, 805 (vs), 712, 698, 646, 625, 545, 509 cm⁻¹.

3.12. Bis[(1-diphenylphosphinoethyl)cyclopentadienyl]zirconium dichloride (4b)

2.72 g (9.58 mmol) of **2b** in 100 ml of pentane/toluene was reacted with 1.81 g (4.79 mmol) of bis(tetrahydrofuran)tetrachlorozirconium in 30 ml of pentane. Yield: 2.48 g (72%) of a 1:1 mixture of diastereomers. Cooling of a saturated dichloromethane solution of **4b** to -20° C yielded colorless single crystals suitable for X-ray crystal structure analysis. M.p. 156°C (dec.). Anal. Calc. for C₃₈H₃₆Cl₂P₂Zr (716.78): C, 63.68; H, 5.06. Found: C, 63.37; H, 5.18%. The ¹H NMR resonances of the two diastereomers are almost identical. ¹H NMR (benzene-d₆, 200.1 MHz); diastereomer rac-4b: δ 7.52, 7.35 (each m, each 8H, o-Ph-H), 7.03 (m, 12H, m-Ph-H, p-Ph-H), 5.91, 5.65, 5.39, 5.25 (each m, each 2H, C₅H₄), 4.23 (dq, ${}^{2}J_{PH} = 1.8$ Hz, ${}^{3}J_{HH} = 7.1$ Hz, 2H, 1'H), 1.51 (dd, ${}^{3}J_{HH} = 7.0 \text{ Hz}$, ${}^{3}J_{PH} = 14.5 \text{ Hz}$, 2H, CH₃). ${}^{13}C \text{ NMR}$ (benzene-d₆, 50.3 MHz): diastereomer rac-4b: δ 137.3-136.7 (2C, not unambiguously assignable due to PC coupling), 134.6 (d, ${}^{2}J_{PC} = 20$ Hz, o-Ph), 133.6 (d, ${}^{2}J_{PC} = 20$ Hz, o-Ph), 129.1, 128.9 128.7, 128.6 (m- and p-Ph), 116.5, 116.0, 114.2, 106.0 (each s, C_5H_4), 33.6 (d, ${}^{1}J_{PC} = 17$ Hz, C1'), 16.5 (d, ${}^{2}J_{PC} = 17$ Hz, CH₃). ${}^{13}C$ NMR (dichloromethane-d₂, 50.3 MHz) 1:1 mixture of the diastereoisomers, most of the resonances of the two diastereomers are at close to identical δ values, δ 137.1 (d, $J_{PC} = 18$ Hz, C), 134.6 (d, ${}^{2}J_{PC} = 20$ Hz, o-Ph), 133.7 (d, ${}^{2}J_{PC} = 19$ Hz, o-Ph), 129.5, 129.2 (each s, p-Ph), 128.8 (d, ${}^{3}J_{PC} = 6$ Hz, m-Ph), 128.5 $(d, {}^{3}J_{PC} = 6 \text{ Hz}, m\text{-Ph}), 117.2, 117.0, 116.5, 116.2, 114.3 (2)$ CH), 107.7, 107.0 (each s, C_5H_4), 33.6 (2 d, ${}^1J_{PC} = 17$ Hz, C1'), 16.5 (2 d, CH₃). ³¹P NMR (benzene- d_6 /THF- d_8 , 81.0 MHz): δ 9.8, 9.7. IR (KBr): $\tilde{\nu} = 3103, 3067, 2970, 2911,$ 1481, 1433, 1374, 1262, 1155, 1094, 1060, 1037, 1027, 999, 911, 887, 831 (sh), 826 (v br), 749, 740, 697, 504, 487 cm⁻¹. Formula $C_{38}H_{36}Cl_2P_2Zr$, M = 716.73, 0.30×0.30 $\times 0.10 \text{ mm}, a = 18.029(3), b = 6.418(1), c = 30.736(3) \text{ Å},$ $\beta = 101.90(1), V = 3480.0(9) \text{ Å}^3, \rho_{\text{calc}} = 1.368 \text{ g cm}^{-3},$ $\mu = 5.87 \text{ cm}^{-1}$, empirical absorption correction via ψ -scan data $(0.979 \le C \le 0.999)$, Z=4, monoclinic, space group C2/c (No. 15), $\lambda = 0.71073$ Å, T = 223 K, $\omega/2\theta$ scans, 3625 reflections collected $(+h, +k, \pm l)$, $[(\sin \theta)/\lambda] = 0.62$ $Å^{-1}$, 3516 independent and 2368 observed reflections $[I \ge 2\sigma(I)]$, 196 refined parameters, R = 0.044, $wR^2 = 0.090$, max. residual electron density 0.43 (-0.35) e Å⁻³, hydrogens calculated and riding.

3.13. Bis[(1-di-p-tolylphosphinoethyl)cyclopentadienyl]zirconium dichloride (5b)

Reaction of 1.95 g (6.25 mmol) of 3b in 100 ml of toluene with 1.18 g (3.12 mmol) of bis(tetrahydrofuran)tetrachlorozirconium in 30 ml of pentane at -78°C yielded after work-up 810 mg (34%) of 5b. M.p. 65°C. ¹H NMR (benzene-d₆, 200.1 MHz): δ 7.50, 7.37 (each pt, each 8H, o-tolyl-H), 6.89 (m, 16H, m-tolyl-H), 5.97, 5.69, 5.48, 5.31 $(each m, each 4H, C_5H_4), 4.27 (m, 4H, 1'H), 2.03 (s, 24H, 1'H)$ tolyl-CH₃), 1.52 (pq, 12H, CH₃). ¹H NMR (dichloromethane-d₂, 600 MHz, 1:1 mixture of two diastereoisomers A and **B**): δ 7.36 (m, 8H, o-tolyl-H), 7.16 (m, 16H, o, m-tolyl-H), 7.08 (m, 8H, *m*-tolyl-H), 6.25 (m, 2H, C_5H_4 -A), 6.21-6.19 (m, 4H, C_5H_4 -B), 6.15 (m, 2H, C_5H_4 -A), 6.00 (m, 4H, C_5H_4 -**A**+**B**), 5.344 (**B**), 5.335 (**A**) (each 2H, C_5H_4), 3.88 (m, 4H, 1'H), 2.36 (s, 12H, tolyl-CH₃), 2.332, 2.326 (each s, each 6H, tolyl-CH₃), 1.34-1.28 (2 dd, each 6H, CH₃, coupling not unambiguously assignable). ¹³C NMR (dichloromethane-d₂, 150 MHz, APT) & 139.67, 139.65, 139.33, 139.32 (each s, *p*-tolyl-C), 137.49 (d, ${}^{2}J_{PC} = 12 \text{ Hz}$, C1), 136.9 (d, ${}^{2}J_{PC} = 13$ Hz, C1), 134.52 (d, ${}^{2}J_{PC} = 20$ Hz, *o*-tolyl), 134.50 (d, ${}^{2}J_{PC} = 20$ Hz, *o*-tolyl), 133.55 (d, $^{2}J_{PC} = 19$ Hz, *o*-tolyl), 133.52 (d, $^{2}J_{PC} = 19$ Hz, *o*-tolyl), 133.46 (d, ${}^{1}J_{PC} = 17$ Hz, *ipso-C* of tolyl), 133.43 (d, ${}^{1}J_{PC} = 16 \text{ Hz}, ipso-C \text{ of tolyl}, 133.16 (d, C, ipso-C \text{ of tolyl}),$ ${}^{1}J_{PC} = 15 \text{ Hz}$, 133.11 (d, C, *ipso*-C of tolyl, ${}^{1}J_{PC} = 15 \text{ Hz}$), 129.53 (d, CH, *m*-tolyl, ${}^{3}J_{PC} = 7$ Hz) (double intensity), 129.25 (d, CH, *m*-tolyl, ${}^{3}J_{PC} = 7$ Hz), 129.24 (d, CH, *m*tolyl, ${}^{3}J_{PC} = 7$ Hz), 117.34 (s, CH, $C_{5}H_{4}$), 116.78 (d, CH, C_5H_4 , ${}^3J_{PC} = 3Hz$), 116.51 (s, CH, C_5H_4), 115.86 (d, CH, C_5H_4 , ${}^{3}J_{PC} = 3$ Hz), 114.35 (d, CH, C_5H_4 , ${}^{3}J_{PC} = 4$ Hz), 114.34 (d, CH, C_5H_4 , ${}^{3}J_{PC} = 3$ Hz), 107.72, 107.04 (each s, CH, C_5H_4), 33.69 (d, CH, C1', ${}^{1}J_{PC} = 16 \text{ Hz}$), 33.67 (d, CH, C1', ${}^{1}J_{PC} = 16$ Hz), 21.41 (s, CH₃, tolyl-CH₃), 21.37 (s, CH₃, tolyl-CH₃), 16.50 (d, CH₃, ${}^{2}J_{PC} = 15$ Hz), 16.39 (d, CH_{3} , ${}^{2}J_{PC} = 17$ Hz). GHSQC-NMR: (dichloromethane-d₂, 150 MHz): δ [139.67, 139.65, 139.33, 139.32 (*p*-tolyl), quaternary], [137.49, 136.98 (C1), quaternary], [134.52, 134.50/7.16 (*o*-tolyl)], [133.55, 133.52/7.36 (*o*-tolyl)], [133.46, 133.43, 133.16, 133.11 (ipso-C of tolyl), quaternary], [129.53 (double intensity), 129.25, 129.24/7.08, 7.16 (m-tolyl)], $[117.34/6.25 (C_5H_4-A)]$, [116.78], 116.51/6.21–6.19 $(C_5H_4$ -**B**)], [115.86/6.15 $(C_5H_4$ -**A**)], $[114.35, 114.34/5.344, 5.335 (C_5H_4-A+B)], [107.72]$ $107.04/6.00 (C_5H_4-A+B)$], [33.69, 33.67/3.88 (C1')], [21.41, 21.37/2.36 (double intensity), 2.332, 2.326 (tolyl-CH₃)], [16.50, 16.39/1.30, 1.29 (CH₃)]. GHMBC-NMR: (dichloromethane-d₂, 150 MHz): δ only strong cross-peaks are listed [139.67, 139.65, 139.33, 139.32 (p-tolyl-C)/7.36 (o-tolyl-H), 7.16 (o,m-tolyl-H), 2.36 (double intensity), 2.332, 2.326 (tolyl-CH₃)], [137.49, 136.98 (C1)/6.21-6.19, 6.00, (C_5H_4-A+B) , 3.88 (1'H), 1.30, 1.29 (CH₃)], [134.52, 134.50, 133.55, 133.52 (o-tolyl-H)/7.36, 7.16, 7.08 (*o*,*m*-tolyl-H)], [133.16, 133.11 (*ipso*-C of tolyl)/7.08 (*m*-tolyl-H), 3.88 (1'H)], [129.53 (double intensity), 129.25, 129.24 (m-tolyl)/7.36, 7.16, 7.08 (o,m-tolyl-H), 2.36 (double intensity), 2.332, 2.326 (tolyl-CH₃)], [117.34 $(C_{5}H_{4}-A)/6.15$ $(C_{5}H_{4}-A)$], [116.78 $(C_{5}H_{4}-B)/5.34$ (C_5H_4-B)], [116.51 $(C_5H_4-B)/6.21-6.19$ (C_5H_4-B)], 115.86 $(C_5H_4-A)/6.25$ (C_5H_4-A) , 6.00 (C_5H_4-A) , 5.335 (C_5H_4-A)], [114.35, 114.34 $(C_5H_4-A+B)/6.00$ $(C_5H_4-A+B)/6.00$ A+B), 6.15 (C_5H_4-A), 6.21–6.19 (C_5H_4-B)], [107.72 $(C_5H_4-B)/6.21-6.19(C_5H_4-B), 5.344(C_5H_4-B)], [107.04$ $(C_{5}H_{4}-A)/6.15(C_{5}H_{4}-A), 5.335(C_{5}H_{4}-A)], [33.69, 33.67]$ (C1')/1.30, 1.29 (CH₃)], [21.41, 21.37 (tolyl-CH₃)/7.16 (o,m-tolyl-H), 7.08 (m-tolyl-H)], [16.50, 16.39 $(CH_3)/$ 3.88 (1'H)]. ³¹P NMR (benzene- d_6 /THF- d_8 , 81.0 MHz): δ 8.1, 8.0. IR (KBr): $\tilde{\nu}$ 3067, 3013, 2962, 2919, 2868, 1598, 1497, 1482, 1450, 1395, 1373, 1309, 1259, 1213, 1185, 1120, 1092, 1063, 1038, 1019, 912, 872, 805 (vs), 716, 642, 625, 614, 534, 513, 503 cm⁻¹. HRMS, calc. for $C_{42}H_{44}P_2Cl_2Zr$ 772.1337, found 772.1359.

3.14. Bis[(1-tert-butyldiphenylphosphinomethyl)cyclopentadienyl]zirconium dichloride (4c)

3.85 g (9.67 mmol) of 2c in 50 ml toluene and 1.82 g (4.84 mmol) of bis(tetrahydrofuran)tetrachlorozirconium in 50 ml of pentane were reacted at -78° C and stirred overnight at room temperature. It is necessary to wash the product only with small amounts of precooled $(-30^{\circ}C)$ pentane. Due to the different solubilities in pentane of the two diastereomers of 4c that were primarily formed in 1:1 ratio, it is possible to obtain one diastereomer 80% enriched in the pentane washing phase. Recrystallization from dichloromethane/pentane at -20° C yields an enrichment of the other diastereomer in a 5:1 ratio. Yield: 3.16 g (82%, 1:1 ratio of the diastereomers A, B). M.p. 113°C (decomp.), 160°C (decomp.). Anal. Calc. for C₄₄H₄₈Cl₂P₂Zr (800.93): C, 65.98; H, 6.04. Found: C, 65.54; H, 5.78%. ¹H NMR (dichloromethane-d₂, 200.1 MHz): δA and B: 7.6–7.1 (m, 32H, Ph-H); A: 6.90 (m, 4H, Ph-H), 6.28, 5.95, 5.89, 5.26 (each m, each 2H, C_5H_4), 4.08 $(d, {}^{2}J_{PH} = 2.9 \text{ Hz}, 2H, 1'H), 1.26 (s, 18H, {}^{1}Bu-CH_{3}); B: 6.87$ (m, 4H, Ph-H), 6.18, 6.00, 5.89, 5.21 (each m, each 2H, C_5H_4), 4.14 (d, ${}^2J_{PH} = 2.7$ Hz, 2H, 1'H), 1.27 (s, 18H, 'Bu-CH₃). ¹H NMR (benzene-d₆, 200.1 MHz): δ 7.68 A and B: (pt, 8H, o-Ph-H), 7.13-6.85 (m, 32H, Ph-H); A: 6.13, 5.48, 5.37, 5.31 (each m, each 2H, C_5H_4), 4.42 (d, ${}^2J_{PH} = 3.0$ Hz, 2H, 1'H), 1.39 (s, 18H, 'Bu-CH₃). B: 5.97, 5.53, 5.37, 5.21 (each m, each 2H, C_5H_4), 4.47 (d, ${}^2J_{PH} = 2.7$ Hz, 2H, 1'H), 1.40 (s, 18H, 'Bu-CH₃). ¹³C NMR (dichloromethane-d₂, 50.3 MHz): δ 138.9–136.6 (C), 135.2 (d, ² J_{PC} = 23 Hz, o-Ph), 134.8 (d, ${}^{2}J_{PC} = 22$ Hz, o-Ph), 133.2 (d, ${}^{2}J_{PC} = 17$ Hz, o-Ph), 132.9 (d, ${}^{2}J_{PC} = 17$ Hz, o-Ph), 129.1–128.0 (m, m,p-Ph), 118.7 (A), 117.5 (B), 116.4 (B), 115.8 (A), 112.9 (**B**), 112.2 (**A**), 109.2 (**A**), 106.5 (**B**) (all s, C_5H_4), 52.5 $(d, {}^{1}J_{PC} = 25 \text{ Hz}, C1'), 52.3 (d, {}^{1}J_{PC} = 31 \text{ Hz}, C1'), 35.7 (d,$ ${}^{2}J_{PC} = 18 \text{ Hz}, C(CH_{3})_{3}), 35.2, (d, {}^{2}J_{PC} = 19 \text{ Hz}, C(CH_{3})_{3}),$ 30.9 (2 isochronous d, ${}^{3}J_{PC} = 13$ Hz, ${}^{4}Bu-CH_{3}$). ${}^{31}P$ NMR (dichloromethane-d₂, 81.0 MHz): δ 12.0, 11.8. IR (KBr): $\tilde{\nu} = 3069, 3052, 2961, 2918, 2868, 1635, 1584, 1478, 1434,$ 1395, 1364, 1261, 1094, 1067, 1048, 1027, 803, 741, 697, 501 cm^{-1} .

3.15. Bis[(1-tert-butyl-di-p-tolylphosphinomethyl)cyclopentadienyl]zirconium dichloride (5c)

2.26 g (5.31 mmol) of **3c** in 40 ml of toluene were added at -78° C to a suspension of 1.00 g (2.65 mmol) of bis(tetrahydrofuran)tetrachlorozirconium in 20 ml of pentane and the reaction mixture was allowed to warm to room temperature overnight. Separation of side-products from the 1:1 mixture of diastereomers of the crude metallocene dichloride was achieved by stirring the dichloromethane extract in 50 ml of precooled heptane and subsequent isolation of the product on a cooled frit. Drying in vacuo gave 1.1 g (49%) of a light tanned solid in a diastereomeric ratio of 2:1. M.p. 150°C (decomp.). Anal. Calc. for C₄₈H₅₆Cl₂P₂Zr (857.05): C, 67.27; H, 6.04. Found: C, 66.94, H, 6.76%. ¹H NMR

(dichloromethane-d₂, 600 MHz): δ A and B: 7.34 (m, 4H, o-tolyl-H), 7.18 (pd, 2H, m-tolyl-H), 7.17 (pd, 2H, *m*-tolyl-H), 6.95 (pd, 2H, *m*-tolyl-H), 6.92 (pd, 2H, *m*-tolyl-H); A: 6.80 (pt, 2H, o-tolyl-H), 6.26, 5.99, 5.94, 5.30 (each m, each 2H, C_5H_4), 3.95 (d, ${}^2J_{PH} = 2.4$ Hz, 2H, 1'H), 2.36, 2.29 (each s, each 6H, tolyl-CH₃), 1.22 (s, 18H, 'Bu-CH₃); B: 6.76 (pt, 2H, o-tolyl-H), 6.16, 6.04, 5.94, 5.21 (each m, each 2H, C_5H_4), 4.00 (d, ${}^2J_{PH} = 2.2$ Hz, 2H, 1'H), 2.37, 2.26 (each s, each 6H, tolyI-CH₃), 1.23 (s, 18H, 'Bu-CH₃). ¹³C NMR (dichloromethane-d₂, 150 MHz, APT) δ 139.2 (d, ${}^{2}J_{PC} = 5$ Hz, C1-B), [139.1, 138.9, 138.5, 138.2, (each s, ptolyl-C)], 137.93 (d, C1-A), 135.4 (d, ${}^{1}J_{PC} = 16$ Hz, *ipso*-C of tolyl-B), 135.3 (d, ${}^{1}J_{PC} = 17$ Hz, *ipso*-C of tolyl-A), 133.0 (d, ${}^{1}J_{PC} = 19$ Hz, *ipso-C* of tolyl-A), 132.8 (d, ${}^{1}J_{PC} = 20$ Hz, *ipso-C* of tolyl-**B**), 135.3 (d, ${}^{2}J_{PC} = 23$ Hz, *o*tolyl-**B**), 135.0 (d, ${}^{2}J_{PC} = 23$ Hz, *o*-tolyl-**A**), 133.1 (d, ${}^{2}J_{PC} = 19$ Hz, o-tolyl-A), 132.6 (d, ${}^{2}J_{PC} = 18$ Hz, o-tolyl-B), 129.80 (d, ${}^{3}J_{PC} = 5$ Hz, *m*-tolyl), 129.76 (d, ${}^{3}J_{PC} = 5$ Hz, *m*tolyl), 128.87 (d, ${}^{3}J_{PC} = 6$ Hz, *m*-tolyl), 128.83 (d, ${}^{3}J_{PC} = 7$ Hz, m-tolyl), 118.7 (A), 117.6 (B), 116.2 (B), 115.8 (A), 112.7 (**B**), 112.2 (**A**), 109.8 (**A**), 106.6 (**B**) (each C_5H_4), 53.0 (d, ${}^{1}J_{PC}$ = 33 Hz, C1'-A), 52.8 (d, ${}^{1}J_{PC}$ = 35 Hz, C1'-**B**), 35.6 (d, ${}^{2}J_{PC} = 17$ Hz, CMe₃-A), 35.1 (d, ${}^{2}J_{PC} = 19$ Hz, *C*Me₃-**B**), 30.86 (d, ${}^{3}J_{PC} = 13$ Hz, 'Bu), 30.85 (d, ${}^{3}J_{PC} = 12$ Hz, 'Bu), 21.3 (s, tolyl-CH₃). GHSQC-NMR (dichloromethane-d₂, 600 MHz): δ [135.3 (o-tolyl-B), 135.0 (o-tolyl-A)/7.34 (o-tolyl-H)], 133.1/6.80 (o-tolyl-A), 132.6/6.76 (*o*-tolyl-**B**), [129.80, 129.76/7.20, 7.17 (*m*-tolyl)], [128.87, 128.83/6.95, 6.92 (m-tolyl)], [118.7/6.26 (A),117.6/6.04 (**B**), 116.2/6.16 (**B**), 115.8/5.99 (**A**), 112.7/ 5.21 (**B**), 112.2/5.30 (**A**), 109.8/5.94 (**A**), 106.6/5.94 (**B**) $(each C_5H_4)$], 53.0/3.95 (1'H-A), 52.8/4.00 (1'H-B), [30.86, 30.85/1.23, 1.22 ('Bu)], [21.3/2.37, 2.29, 2.26] $(tolyl-CH_3)$]. GHMBC-NMR (dichloromethane-d₂, 600 MHz): δ [139.2 (C1-B)/6.16, 6.04, 5.93 (C₅H₄-B, 4.00 (1'H)], [139.1, 138.9, 138.5, 138.2, (*p*-tolyl-C)], [137.93 $(C1-A)/6.26, 5.31 (C_5H_4-A, 3.95 (1'H-A)), [[135.4]$ (ipso-C of tolyl-B), 135.3 (ipso-C of tolyl-A), 133.0 (ipso-C of tolyl-A), 132.8 (*ipso*-C of tolyl-B), 135.3 (*o*-tolyl-B), 135.0 (o-tolyl-A), 133.1 (o-tolyl-A), 132.6 (o-tolyl-B)}/ 4.00, 3.95 (C1'H)], [129.80, 129.76 (m-tolyl)/6.80, 6.76 (o-tolyl-H), 2.37, 2.36 (tolyl-CH₃)], [128.87, 128.83 (mtolyl)/7.34 (o-tolyl-H), 2.26, 2.29 (tolyl-CH₃)], [118.7 $(C_{5}H_{4})/6.26$ (C₅H₄), 3.95 (1'H) (A)], [117.6 (C₅H₄)/ 6.16 (C_5H_4) (**B**)], [116.2 $(C_5H_4)/4.00$ (1'H) (**B**)], $[115.8 (C_5H_4)/6.26 (C_5H_4) (A)], [112.7 (C_5H_4)/6.16]$ (C_5H_4) , 4.00 (1'H) (B)], [112.2 $(C_5H_4)/6.26$ (C_5H_4) , 3.95 (1'H) (A), [109.8 (C_5H_4)/6.26, 5.30 (C_5H_4) (A)], $[106.6 (C_5H_4)/6.16, 5.21 (C_5H_4) (\mathbf{B})], [53.0, 52.8 (C1')/$ 1.23, 1.22 ('Bu-CH₃)], [35.6, 35.1 (CMe3)/4.00, 3.95 (1'H), 1.23, 1.22 ('Bu-CH₃)], [30.86 30.85 ('Bu)/4.00, 3.95 (1'H)], [21.3 (tolyl-CH₃)/7.18, 7.17, 6.95, 6.93 (mtolyl-H)]. IR (KBr): $\tilde{\nu} = 2952, 2919, 2866, 1635, 1599,$ 1497, 1476, 1395, 1364, 1261, 1187, 1111, 1090, 1045, 1018, $804 (vs), 509, 500 cm^{-1}$.

3.16. Bis[(1-phenyldiphenylphosphinomethyl)cyclopentadienyl]zirconium dichloride (4d)

Solid 2d (1.27 g, 3.17 mmol) and bis(tetrahydrofuran)tetrachlorozirconium (0.59 g, 1.56 mmol) were mixed, 100 ml of toluene were added at -78° C and the temperature was maintained for an additional 30 min. Then the cooling bath was removed and the reaction mixture was worked up after 5 h of stirring at ambient temperature. 4d was isolated as a white solid in a 1:1 ratio of diastereomers in 93% yield (1.22 g). M.p. 169°C. Anal. Calc. for C₄₈H₄₀Cl₂P₂Zr (840.92): C, 68.56; H, 4.79. Found: C, 68.03; H, 4.68%. ¹H NMR (benzene-d₆, 200.1 MHz): δ 7.7–7.3, 7.1-6.8 (2 m, 60H, Ph-H), A: 6.09, 5.66, 5.44, 4.18 (each m, each 2H, C_5H_4), 5.27 (d, ${}^2J_{PH} = 4.0$ Hz, 2H, 1'H), **B**: 5.88 5.63, 5.50, 4.88 (each m, each 2H, C_5H_4), 5.40 (d, ${}^2J_{PH} = 4.1$ Hz, 2H, 1'H). ¹H NMR (chloroform-d₁, 200.1 MHz): δ 7.6– 7.0 (m, 60H, Ph-H), 6.08 (m, 2H, C_5H_4), 5.98 (m, 2H, C_5H_4 , 5.90–5.81 (m, 4H, C_5H_4), 5.27 (m, 2H, C_5H_4), 5.22– 5.10 (m, 4H, C₅ H_4), 5.02 (d, 2H, 1'H, ${}^2J_{PH}$ = 4.2 Hz), 4.91 $(d, 2H, 1'H, {}^{2}J_{PH} = 4.2 \text{ Hz}), 4.11 (m, 2H, C_{5}H_{4}). {}^{13}\text{C NMR}$ (dichloromethane-d₂, 50.3 MHz): not all resonances assigned due to the complexity of the aromatic region of the spectrum, δ 139.5 (2d, ${}^{1}J_{PC} = 10$ Hz, C), 137.5–136.5 (4d, C), 135.3 (d, ${}^{2}J_{PC} = 22$ Hz, o-Ph), 135.1 (d, ${}^{2}J_{PC} = 22$ Hz, o-Ph), [133.7 (d, J_{PC} = 19 Hz, CH), 133.4 (d, J_{PC} = 19 Hz, CH), 132.9 (s, C), 130.9 (d, $J_{PC} = 10$ Hz, CH), 130.7 (d, $J_{PC} = 9 \text{ Hz}, \text{CH}$, 130.1 (s, CH), 130.0 (s, CH), 129.1–128.4 (m, CH), 127.6, 127.2, (2s, CH) (all Ph)], 125.8 (s, C₅H₄), 118.1 (s, 2 C_5H_4), 116.9 (s, C_5H_4), 116.4 (d, $J_{PC}=4$ Hz, C_5H_4), 111.9 (d, $J_{PC} = 2$ Hz, C_5H_4), 109.0, 106.0 (C_5H_4), 47.4 (d, ${}^{1}J_{PC} = 17 \text{ Hz}, C1'$), 46.8 (d, ${}^{1}J_{PC} = 17 \text{ Hz}, C1'$). ³¹P NMR (chloroform- d_1 , 81.0 MHz): δ 7.0, 5.5. IR (KBr): $\tilde{\nu} = 2963, 1480, 1474, 1452, 1432, 1262$ (s), 1094 (s), 1058, 1025 (s), 802 (vs), 740, 713, 695, 509 cm⁻¹.

3.17. Bis{(1-tolyldiphenylphosphinomethyl)cyclopentadienyl]zirconium dichloride (**4e**)

Reaction of 2.64 g (7.33 mmol) of 2e in 75 ml of pentane/ toluene 1:1 with 1.36 g of (3.61 mmol) bis(tetrahydrofuran)tetrachlorozirconium in 30 ml of pentane yielded 2.38 g (76%) of 4e as a 1:1 mixture of diastereomers. A sample with a 4:1 excess of the less soluble diastereomer could be obtained by precipitation from a concentrated toluene solution. M.p. 112°C (decomp.). Anal. Calc. for C₅₀H₄₄Cl₂P₂Zr (868.97): C, 69.11; H, 5.10. Found: C, 69.64; H, 5.38%. ¹H NMR (benzene-d₆, 200.1 MHz): δ 7.61, 7.45, 7.1–6.7 (m, 56H, Ph-H, tolyl-H), major isomer A: 6.16, 5.73, 5.43, 4.25 (each m, each 2H, C_5H_4), 5.28 (d, ${}^2J_{PH}$ = 4.3 Hz, 2H, 1'H), 1.98 (s, 6H, tolyl-CH₃); minor isomer **B**: 5.91, 5.67, 5.49 $(each m, each 2H, C_5H_4), 5.45-5.39 (m, 2H, 1'H), 4.91 (m,$ 2H, C_5H_4), 1.96 (s, 6H, tolyl-CH₃). ¹H NMR (dichloromethane-d₂, 200.1 MHz): δ 7.4-7.0 (m, 56H, Ph-H, tolyl-H), 6.06 (m, 2H, C_5H_4), 5.98 (m, 2H, C_5H_4), 5.91–5.85 (m, 4H, C_5H_4), 5.21 (m, 4H, C_5H_4), 5.08 (m, 2H, C_5H_4), 5.01

(d, ${}^{2}J_{PH}$ = 4.2 Hz, 2H, 1'H), 4.91 (d, ${}^{2}J_{PH}$ = 4.3 Hz, 2H, 1'H), 4.22 (m, 2H, C₅H₄), 2.32, 2.29 (each s, each 6H, tolyl-CH₃). 13 C NMR (dichloromethane-d₂, 50.3 MHz): not all resonances assigned due to the complexity of the spectrum, δ 137.5–136 (4d, C), 135.3 (d, ${}^{2}J_{PC}$ = 22 Hz, *o*-Ar), 135.1 (d, ${}^{2}J_{PC}$ = 21 Hz, *o*-Ar), 133.7 (d, ${}^{2}J_{PC}$ = 19 Hz, *o*-Ar), 133.3 (d, ${}^{2}J_{PC}$ = 24 Hz, *o*-Ar), 131–128 (m, CH, Ar), 126.1 (s, C₅H₄), 118.2 (s, C₅H₄), 118.0 (s, C₅H₄), 116.7 (d, J_{PC} = 3 Hz, C₅H₄), 116.3 (d, J_{PC} = 4 Hz, C₅H₄), 111.8 (s, C₅H₄), 109.0, 106.0 (2 C₅H₄), 46.9 (d, ${}^{1}J_{PC}$ = 16 Hz, C1'), 46.3 (d, ${}^{1}J_{PC}$ = 16 Hz, C1'), 21.2 (s, CH₃, tolyl-CH₃). 31 P NMR (benzene-d₆, 81.0 MHz): δ 6.0, 4.5. IR (KBr): $\tilde{\nu}$ = 3070, 3051, 3018, 2920, 2855, 1585, 1511, 1479, 1434 (s), 1184 (w), 1094, 1069, 1044, 1026, 1000, 818 (s), 735 (s), 695 (vs), 514 (s), 503, 474 cm⁻¹.

3.18. Trans-dichlorobis{[(1-methyl-1-diphenylphosphinoethyl)cyclopentadienyl]dichlorozirconium(IV)- κ^2 -P,P'}palladium(II) (6)

Samples of 745 mg (1.00 mmol) of 4a and 384 mg (1.00 mmol) of PdCl₂(PhCN)₂ were separately dissolved in 30 ml of THF. At -40° C the cooled solutions were added dropwise and simultaneously transferred per cannula to 25 ml of THF. The solution turned yellow and a yellow precipitate was formed that was collected by filtration, washed twice with each 10 ml of THF and dried in vacuo. Yield: 680 mg (74%) of poorly soluble 6. Anal. Calc. for C₄₀H₄₀Cl₄P₂PdZr (922.16), recrystallized from pentane/dichloromethane: C, 52.10; H, 4.37. Found: C, 50.64; H, 4.49%. ¹H NMR (dichloromethane-d₂, 200.1 MHz): δ 7.67 (br, 8H, Ph-H), 7.6–7.2 (m, br, 12H, Ph-H), 6.15 (m, 4H, C₅H₄), 5.97 (m, 4H, C₅H₄), 1.85 (pt, ³⁺⁵J_{PH}=7.6 Hz, 12H, CH₃). ³¹P NMR (chloroform-d₁, 81.0 MHz): δ 46.4.

3.19. Trans-dichlorobis{[(1-methyl-1-diphenylphosphinoethyl)cyclopentadienyl]dichlorozirconium(IV)- κ^2 -P,P'}platinum(II)(8)

75 mg (0.1 mmol) of **4a** and 47 mg (0.1 mmol) of PtCl₂(PhCN)₂ were reacted analogously as described above in 30 ml of THF. After 2 h a pale yellow solid was isolated on a frit, washed with two portions of pentane and dried in vacuo; yield 90 mg (89%) of sparingly soluble **8**. Anal. Calc. for C₄₀H₄₀Cl₄P₂PtZr (1010.83), recrystallized from pentane/dichloromethane: C, 47.53; H, 3.99. Found: C, 48.39; H, 4.22%. ¹H NMR (dichloromethane-d₂, 200.1 MHz): δ 7.7 (m, 8H, Ph-H), 7.4 (m, 12H, Ph-H), 6.12 (m, 4H, C₅H₄), 5.91 (m, 4H, C₅H₄), 1.85 (pt, ³⁺⁵J_{PH}=7.4 Hz, 12H, CH₃). ¹³C NMR (dichloromethane-d₂, 150 MHz): δ 136.1, 131.0, 129.0 (pseudo-t, J_{PC} = 24 Hz), 127.7 (phenyl), 136.9, 119.7, 112.2 (Cp), 43.9 (pseudo-t, J_{PC} = 12 Hz, CMe₂), 24.7 (C(CH₃)₂). ³¹P NMR (dichloromethane-d₂, 81.0 MHz): δ 38.7 (¹J_{PtP} = 2631 Hz).

3.20. Trans-dichlorobis{[(1-methyl-1-di-p-tolylphosphinoethyl)cyclopentadienyl]dichlorozirconium(IV)- κ^2 -P,P'}palladium(II)(7)

98 mg (0.122 mmol) of 5a and 47 mg (0.123 mmol) of $PdCl_2(PhCN)_2$ were separately dissolved in 10 ml of toluene each, cooled to -78° C and were cannula-transferred into a Schlenk flask containing 10 ml of toluene at -78° C. The reaction mixture was stirred for 2 h at room temperature, concentrated to 10 ml and the product precipitated by addition of 10 ml of pentane. Red crystalline 7 was collected by filtration and washed with additional 10 ml of pentane. Yield: 100 mg of 7, containing 2 molar equiv. of toluene (70%). Anal. Calc. for $C_{44}H_{48}Cl_4P_2PdZr \cdot 2C_7H_8$ (1162.55): C, 59.92; H, 5.55. Found: C, 57.31; H, 5.42%. ¹H NMR (dichloromethane- d_2 , 200.1 MHz): δ 7.6–7.1 (2 m, 16H + 10H, tolyl-H, toluene-H), 6.13 (m, 4H, C₅H₄), 5.93 (m, 4H, C₅H₄), 2.40 (s, 12H, tolyl-CH₃), 2.34 (s, 6H, toluene-CH₃), 1.78 (pt, $^{3+5}J_{PH} = 8.1$ Hz, 12H, CH₃). ^{13}C NMR (dichloromethaned₂, 150 MHz): δ141.4 (s, p-tolyl), 138.3 (toluene-C), 136.4 (br, C), 136.0 (br, tolyl-CH), 129.3 (toluene), 128.5 (br, tolyl-CH), 126.2 (pt, J = 20 Hz, C), 125.6 (toluene) 119.6 (br, C_5H_4), 112.3 (br, C_5H_4), 44.6 (pt, $J_{PC}=9$ Hz, C1'), 24.8 (br, C2'), 21.6 (pt, $J_{PC} = 10$ Hz, CH₃). ³¹P NMR (dichloromethane- d_2 , 81.0 MHz): δ 45.7.

3.21. Trans-dichlorobis{[(1-methyl-1-di-p-tolylphosphinoethyl)cyclopentadienyl]dichlorozirconium(IV)- κ^2 -P,P'}platinum(II)(9)

248 mg (0.31 mmol) of 5a and 146 mg (0.31 mmol) of $PtCl_2(PhCN)_2$ were reacted in toluene analogously as described above, stirred for about 12 h at room temperature, followed by concentration of the mixture to half of its original volume in vacuo. Addition of 20 ml of pentane precipitated the product, which was then collected by filtration on a Schlenk frit. Complex 9 was washed with 2 ml of toluene, 5 ml of pentane and dried in vacuo yielding 210 mg (63%) of 9. M.p. 184°C (decomp.). Anal. Calc. for C₄₄H₄₈Cl₄P₂PtZr (1066.94): C, 49.53; H, 4.53. Found: C, 47.33; H, 4.43%. ¹H NMR (dichloromethane-d₂, 200 MHz): δ 7.54 (m, 8H, tolyl-H), 7.18 (m, 8H, tolyl-H), 6.11 (m, 4H, C₅H₄), 5.90 $(m, 4H, C_5H_4)$, 2.39 (s, 12H, tolyl-CH₃), 1.81 (pt, $^{3+5}J_{PH} = 8.1$ Hz, 12H, CH₃). ^{31}P NMR ([D₂]-dichloromethane, 81.0 MHz): δ 37.9 (¹J_{PtP} = 2605 Hz). IR (KBr): $\tilde{\nu} = 3106, 3085, 3020, 2977, 2919, 2868, 1600, 1562, 1499,$ 1474, 1447, 1398, 1383, 1366, 1315, 1262, 1191, 1125 (s), 1094 (s), 1046, 1018, 932, 883, 805 (vs), 755, 732, 709, 652, 632, 551, 514 (vs), 480, 442 cm⁻¹.

3.22. Chlorobis{[(1-tert-butyldiphenylphosphinomethyl)cyclopentadienyl]chlorozirconium(IV)- κ^2 -P,P']}- μ -chloropalladium(II)pentachlorotetrahydrofuranozirconate(IV) (10)

Samples of 800 mg of 4c (1 mmol) and 384 mg of PdCl₂(PhCN)₂ (1 mmol) were separately dissolved in 30

ml THF each and at -40° C slowly added to a Schlenk flask containing 30 ml of THF. The solvent was removed from the clear orange solution after 10 h. Some THF and 10 ml of pentane were added in succession and a yellow solid was collected by filtration after 1 h. 90 mg of yellow 10 were isolated. The mother liquid contained several other palladium complexes, probably mainly the neutral trans complexes. Yellow single crystals suitable for X-ray structure determination were obtained by cooling a dichloromethane solution of 10 to -20° C. ¹H NMR (dichloromethane-d₂, 200.1 MHz): δ 8.17, 7.74 (each m, each 4H, Ph-H), 7.55, 7.28 (each m, each 6H, Ph-H), 7.11, 6.90, 6.51, 6.33 (each m, each 2H, C_5H_4), 4.62 (pt, ²⁺⁴ J_{PH} =5.5 Hz, 2H, 1'H), 4.62 $(m, 4H, THF-Pd-H), 3.71 (m, 4H, \beta-THF-H), 2.07 (m, 4H,$ THF-Pd-H), 1.82 (m, 4H, α-THF-H), 0.63 (s, 18H, 'Bu-CH₃). ³¹P NMR (dichloromethane-d₂, 81.0 MHz): δ 25.5. NMR of the mother liquid: tert-butyl-resonances of other isomers: (1.15, 1.13) weak, (0.93, 0.70) strong. X-ray crystal structure analysis of 10: formula C48H56OP2Cl8Pd- $Zr_2 \cdot CH_2Cl_2$, M = 1580.55, $0.40 \times 0.20 \times 0.10$ mm, a =14.6523(8), b = 15.7113(13), c = 16.5192(13) Å, $\alpha =$ 77.656(7), $\beta = 81.503(6)$, $\gamma = 62.375(6)^{\circ}$, V = 3286.2(4)Å³, $\rho_{calc} = 1.597 \text{ g cm}^{-3}$, $\mu = 12.75 \text{ cm}^{-1}$, empirical absorption correction via ψ -scan data (0.864 $\leq C \leq 0.999$), Z=2, triclinic, space group P1 (No. 2), $\lambda = 0.71073$ Å, T = 223 K, $\omega/2\theta$ scans, 9197 reflections collected $(\pm h, \pm k, \pm l)$, [(sin $(\theta)/\lambda = 0.54 \text{ Å}^{-1}$, 8800 independent and 4758 observed reflections $[I \le 2\sigma(I)]$, 661 refined parameters, R = 0.063, $wR^2 = 0.157$, max. residual electron density 1.42 (-1.09) e $Å^{-3}$ close to the disordered CH₂Cl₂, hydrogens calculated and riding, CH2Cl2 molecules refined with restraints (distances, angles, and displacement parameters). All data sets were collected with an Enraf Nonius MACH3 diffractometer. Programs used: data reduction MolEN, structure solution SHELXS-86, structure refinement SHELXL-93, graphics SCHAKAL-92.

4. Supplementary material

Further details of the X-ray crystal structures analyses can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, on quoting the depository numbers CSD 407266 and 407267, the names of the authors, and the journal citation.

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References

- [2] (a) C.P. Casey, R.M. Bullock, W.C. Fultz and A.L. Rheingold, Organometallics, 1 (1982) 1591; C.P. Casey, R.M. Bullock and F. Nief, J. Am. Chem. Soc., 105 (1983) 7574; M.D. Rausch, B.H. Edwards, R.D. Rogers and J.L. Atwood, J. Am. Chem. Soc., 105 (1983) 3882; W. Tikkanen, Y. Fujita and J.L. Petersen, Organometallics, 5 (1986) 888; R.M. Bullock and C.P. Casey, Acc. Chem. Res., 20 (1987) 167; G.K. Anderson and M. Lin, Organometallics, 7 (1988) 2285; D. Morcos and W. Tikkanen, J. Organomet. Chem., 371 (1989) 15; J. Szymoniak, M.M. Kubicki, J. Besançon and C. Moïse, Inorg. Chim. Acta, 180 (1991) 153; W.A. Schenk and C. Labude, Chem. Ber., 122 (1989) 1489; Z. Naturforsch., Teil B, 46 (1991) 573; W. Tikkanen and J.W. Ziller, Organometallics, 10 (1991) 2266; K.A. Fallis, G.K. Anderson and N.P. Rath, Organometallics, 11 (1992) 885; I.M. Lorković, M.S. Wrighton and W.M. Davis, J. Am. Chem. Soc., 116 (1994) 6220; F.T. Ladipo, G.K. Anderson and N.P. Rath, Organometallics, 13 (1994) 4741; L. Spadoni, C.L. Sterzo, R. Crescenzi and G. Frachey, Organometallics, 14 (1995) 3149; J.M. Brown, J.J. Pérez-Torrente, N.W. Alcock and H.J. Clase, Organometallics, 14 (1995) 207; M. Viotte, B. Gautheron, M.M. Kubicki, Y. Mugnier and R.V. Parish, Inorg. Chem., 34 (1995) 3465; E. Delgado, J. Forniés, E. Hernández, E. Lalinde, N. Mansilla and M.T. Moreno, J. Organomet. Chem., 494 (1995) 261; G. Herberich and S. Moss, Chem. Ber., 128 (1995) 689; W. Tikkanen, A.L. Kim, K.B. Lam and K. Ruekert, Organometallics, 14 (1995) 1525; E. Delgado, J. Forniés, E. Hernández, E. Lalinde, N. Mansilla and M.T. Moreno, J. Organomet. Chem., 494 (1995) 261; D. Baudry, A. Dormond, M. Visseaux, C. Monnot, H. Chardot, Y. Lin and V.I. Bakhmutov, New J. Chem., 19 (1995) 921; I. Ara, E. Delgado, J. Forniés, E. Hernandez, E. Lalinde, N. Mansilla and M.T. Moreno, J. Chem. Soc., Dalton Trans., (1996) 3201; V.I. Bakhmutov, M. Visseaux, D. Baudry, A. Dormond and P. Richard, Inorg. Chem., 35 (1996) 7316; P.J. Stang, B. Olenyuk, J. Fan and A.M. Arif, Organometallics, 15 (1996) 904; S. Rigny, V.I. Bakhmutov, B. Nuber, J.-C. Leblanc and C. Moïse, Inorg. Chem., 35 (1996) 3202. (b) C. Charrier and F. Mathey, Tetrahedron Lett., (1978) 2407; F. Edelmann, P. Behrens, S. Behrens and U. Behrens, J. Organomet. Chem., 310 (1986) 333; D.M. Bensley, Jr. and E.A. Mintz, J. Organomet. Chem., 353 (1988) 93; R.T. Kettenbach, W. Bonrath and H. Butenschön, Chem. Ber., 126 (1993) 1657; Y. Yamamoto, T. Tanase, I. Mori and Y. Nakamura, J. Chem. Soc., Dalton Trans., (1994) 2191; M. Sawamura, R. Kuwano and Y. Ito, Angew. Chem., 106 (1994) 92; Angew. Chem., Int. Ed. Engl., 33 (1994) 111; H.C.L. Abbenhuis, U. Burckhardt, V. Gramlich, A. Togni, A. Albinati and B. Müller, Organometallics, 13 (1994) 4481. (c) C. Charrier and F. Mathey, J. Organomet. Chem., 170 (1979) C41; N.E. Schore, J. Am. Chem. Soc., 101 (1979) 7410; T. Kauffmann, J. Ennen, H. Lhotak, A. Rensing, F. Steinseifer and A. Woltermann, Angew. Chem., 92 (1980) 1255; Angew. Chem., Int. Ed. Engl., 19 (1980) 328; N.E. Schore, L.S. Benner and B.E. LaBelle, Inorg. Chem., 20 (1981) 3200; J.C. LeBlanc, C. Moïse, A. Maisonnat, R. Poilblanc, C. Charrier and F. Mathey, J. Organomet. Chem., 231 (1982) C43; D.R. Tueting, S.R. Iyer and N.E. Schore, J. Organomet. Chem., 320 (1987) 349.
- [3] N.E. Schore and H. Hope, J. Am. Chem. Soc., 102 (1980) 4251; R. Choukron and D. Gervais, J. Chem. Soc., Chem. Commun., (1982) 1300; N.E. Schore, S.J. Young and M.M. Olmstead, Organometallics, 2 (1983) 1769; T.S. Targos, R.P. Rosen, R.R. Whittle and G.L. Geoffroy, Inorg. Chem., 24 (1985) 1375; R.T. Baker, T.H. Tulip and S.S. Wreford, Inorg. Chem., 24 (1985) 1379; L. Gelmino, L.C. Matassa and D.W. Stephan, Inorg. Chem., 24 (1985) 1499; J. Ho, Z. Hou, R.J. Drake and D.W. Stephan, Organometallics, 12 (1993) 3145; P. Scott, U. Rief, J. Diebold and H.H. Brintzinger, Organometallics, 12 (1993) 3094; J.R. Pinkes, B.D. Steffey, J.C. Vites and A.R. Cutler, Organometallics, 13 (1994) 21; R. Broussier, A. DaRold, M. Kubicki and B. Gautheron, Bull. Soc. Chim. Fr., 131 (1994) 951; G.M. Diamond, M.L.H. Green, N.A. Popham and A.N. Chernega, J. Chem. Soc., Chem. Commun., (1994) 727; P. Veya, P.G. Cozzi, C. Floriani,

B. Cornils and W.A. Herrmann (eds.), Applied Homogeneous Catalysis with Organometallic Compounds, Vols. 1 and 2, VCH, Weinheim, 1996, and Refs. therein.

F.P. Rotzinger, A. Chiesi-Villa and C. Rizzoli, Organometallics, 14 (1995) 4101; C. Elschenbroich, E. Schmidt, B. Metz and K. Harms, Organometallics, 14 (1995) 4043; A.M. Baranger, T.A. Hanna and R.G. Bergman, J. Am. Chem. Soc., 117 (1995) 10041; D.H. Gibson, J.M. Mehta, B.A. Sleadd, M.S. Mashuta and J.F. Richardson, Organometallics, 14 (1995) 4886; D.J. Schwartz, G.E. Ball and R.A. Anderson, J. Am. Chem. Soc., 117 (1995) 6027; F. Lindenberg, T. Shribman, J. Sieler, E. Hey-Hawkins and M.S. Eisen, J. Organomet. Chem., 515 (1996) 19; D.W. Stephan, Coord. Chem. Rev., 95 (1989) 41.

- [4] G.R. Knox and P.C. Pauson, J. Chem. Soc., (1961) 4610; F. Le Moigne, A. Dormond, J.C. Leblanc, C. Moise and J. Tirouflet, J. Organomet. Chem., 54 (1973) C13; C. Moise, J.C. Leblanc and J. Tirouflet, J. Am. Chem. Soc., 97 (1975) 6272; J. Leblanc and C. Moise, J. Organomet. Chem., 120 (1976) 65; 131 (1977) 35; P. Renaut, G. Tainturier and B. Gautheron, J. Organomet. Chem., 148 (1978) 35; G. Erker, R. Nolte, R. Aul, S. Wilker, C. Krüger and R. Noe, J. Am. Chem. Soc., 113 (1991) 7594; M.S. Erickson, J.M. Cronan, J.G. Garcia and M.L. McLaughlin, J. Org. Chem., 57 (1992) 2504; G. Erker, S. Wilker, C. Krüger and M. Nolte, Organometallics, 12 (1993) 2140; G. Erker, C. Psiorz, C. Krüger and M. Nolte, Chem. Ber., 127 (1994) 1551; C. Psiorz, G. Erker, R. Fröhlich and M. Grehl, Chem. Ber., 128 (1995) 357; G. Erker, C. Psiorz, R. Fröhlich, M. Grehl, C. Krüger, R. Noe and M. Nolte, Tetrahedron, 51 (1995) 4347.
- [5] K.J. Stone and R.D. Little, J. Org. Chem., 49 (1984) 1849.
- [6] K. Issleib and A. Tzschach, Chem. Ber., 92 (1959) 1118; S.O. Grim and A.W. Yankowsky, J. Org. Chem., 42 (1977) 1236.
- [7] L.A. Paquette, W. Bauer, M.R. Sivik, M. Bühl, M. Feigel and P.v.R. Schleyer, J. Am. Chem. Soc., 112 (1990) 8776; W. Bauer, G.A. O'Doherty, P.v.R. Schleyer and L.A. Paquette, J. Am. Chem. Soc., 113 (1991) 7093.
- [8] C. Krüger, F. Lutz, M. Nolte, G. Erker and M. Aulbach, J. Organomet. Chem., 452 (1993) 79; G. Erker, M. Aulbach, M. Knickmeier, D. Wingbermühle, C. Krüger, M. Nolte and S. Werner, J. Am. Chem. Soc., 115 (1993) 4590.
- [9] A.G. Orpen, L. Brammer, F.H. Allen, O. Kennard, D.G. Watson and R. Taylor, J. Chem. Soc., Dalton Trans., (1989) S1.

- [10] C. Krüger, M. Nolte, G. Erker and S. Thiele, Z. Naturforsch., Teil B, 47 (1992) 995; G. Erker, F. Zaegel, B. Gautheron, P. Meunier and L.A. Paquette, Organometallics, 14 (1995) 5446; M. Knickmeier, G. Erker and T. Fox, J. Am. Chem. Soc., 118 (1996) 9623, and Refs. therein.
- [11] (a) B.E. Mann, B.L. Shaw and R.M. Slade, J. Chem. Soc. A, (1971) 2976; (b) B.E. Mann, C. Masters and B.L. Shaw, J. Chem. Soc., Dalton Trans., (1972) 704; J. Chem. Soc. A, (1971) 1104; P.E. Garrou, Chem. Rev., 81 (1981) 229, and Refs. therein.
- [12] J.M. Jenkins and B.L. Shaw, J. Chem. Soc. A, (1966) 770.
- [13] P.S. Pregosin, in J.G. Verkade and L.D. Quin (eds.), Stereochemistry of Metal Complexes: Unidentate Phosphorus Ligands, Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis; Organic Compounds and Metal Complexes, VCH, Weinheim, 1987, pp. 465–530.
- [14] P.L. Goggin, R.J. Goodfellow, S.R. Haddock, J.R. Knight, F.J.S. Reed and B.F. Taylor, J. Chem. Soc., Dalton Trans., (1974) 523.
- [15] R. Favez, R. Roulet, A.A. Pinkerton and D. Schwarzenbach, Inorg. Chem., 19 (1980) 1356.
- [16] M. Polamo and M. Leskelä, Acta Chem. Scand., 51 (1997) 44; J. Scholz, B. Richter, R. Goddard and C. Krüger, Chem. Ber., 126 (1993) 57; H. Prinz, S.G. Bott and J.L. Atwood, J. Am. Chem. Soc., 108 (1986) 2113.
- [17] R.F. Jordan, Adv. Organomet. Chem., 32 (1991) 325; R.F. Jordan and A.S. Guram, in E.W. Abel, F.G.A. Stone and G. Wilkinson (eds.), Comprehensive Organometallic Chemistry, Vol. 4, Pergamon, London, 1995, p. 589; S.C. Sockwell, P.S. Tanner and T.P. Hanusa, Organometallics, 11 (1992) 2634; S.K. Brownstein, E.J. Gabe, N.F. Han, F.L. Lee, Y. Le Page, A.M. Piotrowski and J.J. Eisch, J. Chem. Res. S, (1992) 214.
- [18] P. Cianfriglia, V. Narducci, C.L. Sterzo, E. Viola, G. Bocelli and T.A. Kodenkandath, Organometallics, 15 (1996) 5220.
- [19] S. Braun, H. Kalinowski and S. Berger, 100 and More Basic NMR Experiments, VCH, Weinheim, 1996, and Refs. therein.
- [20] L.E. Manzer, Inorg. Synth., 21 (1982) 136.
- [21] D.W. Macomber, W.C. Spink and M.D. Rausch, J. Organomet. Chem., 250 (1983) 311.
- [22] G.K. Anderson and M. Lin, Inorg. Synth., 28 (1989) 60.