Articles

Phosphonium-Bridged Alkali and Alkaline-Earth Metallocene Complexes[1]

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Chiral metallocene complexes with a dialkylphosphonium bridge and different main-group metal (Li, K, Ba) centers have been synthesized from phosphonium-bridged bis(cyclopentadienyl) ligands in their mono- and diprotonated forms. NMR studies in solution and crystal structures of the kalocene $Me_2P(2\text{-}Me\text{-}4\text{-}t\text{Bu-}C_5H_2)_2K$ and of the barocene $Me_2P(2\text{-}Me\text{-}4\text{-}t\text{Bu-}C_5H_2)_2Ba(THF)_3^+BPh_4^-$ show that these metallocenes are obtained in form of their racemic diastereomers.

Introduction

Since the first preparations of carbon-bridged chiral *ansa*-metallocenes,[2,3] the kind of interannular bridge has been widely varied. Silyl-bridged complexes have been most extensively developed because of their application to α-olefin polymerization. Other heteroatom-bridged metallocenes synthesized include germanium-,[4] nitrogen-,[5,6] oxygen-,[7] and, more recently, boron-bridged complexes.[8,9] So far, the phosphorus bridge has not found comparable attention. Only one phenylphosphine-bridged representative has been described, each for the titanocene[10] and the zirconocene[11] series. Except for a phosphonium-bridged ferrocene, $MePhP(C_5H_4)_2Fe^+I^-$, which has not been completely characterized,[12] no phosphonium-bridged metallocene complexes have yet been described in the literature.

The phosphorus atom has a covalent radius of 106 pm and is only slightly smaller than the silicon atom with 111 pm. The difference between these two heteroatom bridges will thus be mainly of electronic origin. Phosphonium-bridged metallocenes such as $R_2P(C_5H_4)_2YX_2$ and $R_2P(C_5H_4)_2BaX$ (X = halogen, alkyl, amide) would be isoelectronic to the silyl-bridged species $R_2Si(C_5H_4)_2ZrX_2$ and $R_2Si(C_5H_4)_2YX$, respectively, and would thus provide an opportunity to study the electronic effects of the positively charged phosphorus atom, e.g., on the reactivities of these metallocene complexes in stoichiometric and catalytic reactions.

Results and Discussion

Ligand Syntheses. The synthesis of the phosphine-bridged ligands $MeP(2\text{-}Me\text{-}4\text{-}t\text{Bu-}C_5H_3)_2$ (**1A**) and $n\text{BuP}(2\text{-}Me\text{-}4\text{-}t\text{Bu-}C_5H_3)_2$ (**1B**) was achieved by adding $MePCl_2$ or $n\text{BuPCl}_2$, respectively, to the lithium salt $Me\text{-}3\text{-}t\text{Bu-}C_5H_3^-Li^+$ in pentane/THF solution at temperatures below 0 °C (see Experimental Section). Reaction of the phosphine ligands **1A** and **1B** with an excess of MeI or *n*BuI, respectively, afforded the phosphonium-bridged ligands $Me_2P(2\text{-}Me\text{-}4\text{-}t\text{Bu-}C_5H_3)_2^+I^-$ (**2A**) and $n\text{Bu}_2P(2\text{-}Me\text{-}4\text{-}t\text{Bu-}C_5H_3)_2^+I^-$ (**2B**). Reaction with 1 equiv of KH transforms the iodide salts **2A** and **2B** to the ylides $Me_2P(2\text{-}Me\text{-}4\text{-}t\text{Bu-}C_5H_2)(2'\text{-}Me\text{-}4'\text{-}t\text{Bu-}C_5H_3)$ (**3A**) and $n\text{Bu}_2P(2\text{-}Me\text{-}4\text{-}t\text{Bu-}C_5H_2)(2'\text{-}Me\text{-}4'\text{-}t\text{Bu-}C_5H_3)$ (**3B**). For the synthesis of the tetraphenylborate salt $Me_2P(2\text{-}Me\text{-}4\text{-}t\text{Bu-}C_5H_3)_2^+BPh_4^-$ (**4A**), the ylide **3A** is reacted with 1 equiv of $NHMe_3^+BPh_4^-$ (Scheme 1).

The ^1H NMR spectra of the iodide and tetraphenylborate salts indicate that only the racemic form of the phosphonium-bridged ligand is present in solution.

In the ^1H NMR spectra of all phosphonium-bridged ligands, the PMe_2 group appears as a doublet with a coupling constant of $^2J(P,H) = 11.8{-}13.8$ Hz. The phosphorus atom couples also with the protons of each cyclopentadienyl ring and with the Me group in the 2-position at the protonated rings in **2A**, **2B**, **3A**, **3B**, and **4A**. The latter coupling is not observed for the deprotonated cyclopentadienyl ring of the ylides **3A** and **3B**. In these cases, the 2-methyl substituent gives rise to a singlet ^1H NMR signal.

Syntheses of Metal Complexes. Lithium salts of the phosphonium-bridged *ansa*-ligands were obtained by adding 2 equiv of *n*BuLi to **2A** or to **2B**. Since it

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[1] *ansa*-Metallocene Derivatives. Part 44. For Part 43, see: Hüttenhofer, M.; Brintzinger, H.-H. *Angew. Chem.*, in press.

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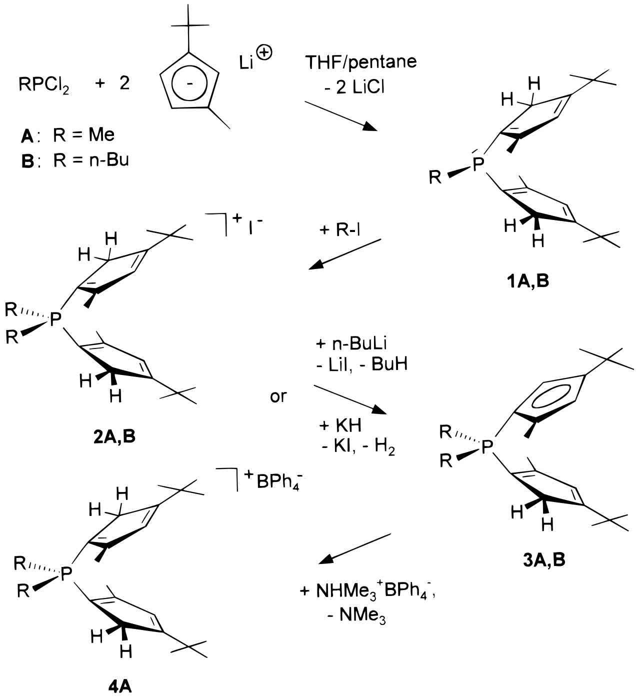
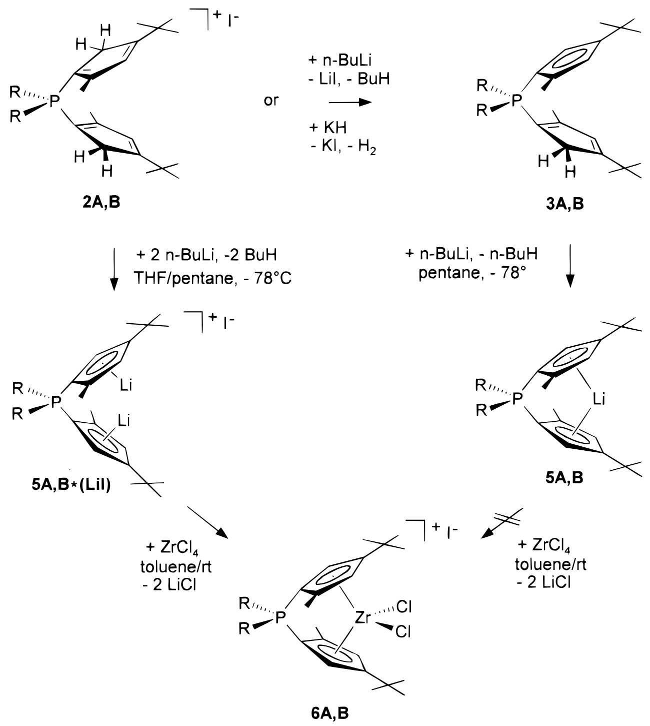
Scheme 1



Scheme 2



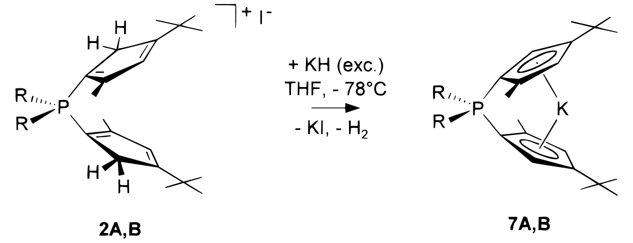
proved impossible to separate these salts from the resulting LiI in any way, we assume that the products contain one Li^+ ion at each cyclopentadienyl ring; they will thus be formulated as $Me_2P(2\text{-}Me\text{-}4\text{-}tBu\text{-}C_5H_2\text{-}Li)_2{}^+I^-$ (**5A**-LiI) and $nBu_2P(2\text{-}Me\text{-}4\text{-}tBu\text{-}C_5H_2Li)_2{}^+I^-$ (**5B**-LiI), respectively.

The LiI-free lithium salts $Me_2P(2\text{-}Me\text{-}4\text{-}tBu\text{-}C_5H_2)_2Li$ (**5A**) and $nBu_2P(2\text{-}Me\text{-}4\text{-}tBu\text{-}C_5H_2)_2Li$ (**5B**), on the other hand, were prepared by reacting the ylides **3A** and **3B,** respectively, with 1 equiv of *n*BuLi (Scheme 2). In THF-d_8 solution, all four Li compounds give rise to simple ^1H NMR spectra which indicate that only the C_2-symmetric, racemic isomers are present. Even at −60 °C, no additional signals or signal broadenings are apparent which would indicate the presence of other isomers in these solutions.

When the lithium salts **5A** or **5B** were treated with $ZrCl_4$ or $HfCl_4$, only the unchanged reactants were recovered. Reaction of their LiI adducts **5A**-LiI or **5B**-LiI with $ZrCl_4$, on the other hand, gave product mixtures with ^1H NMR spectra that indicate the presence of zirconocene complexes of the type $Me_2P(2\text{-}Me\text{-}4\text{-}tBu\text{-}C_5H_2)_2ZrCl_2{}^+I^-$ (**6A**) and $nBu_2P(2\text{-}Me\text{-}4\text{-}tBu\text{-}C_5H_2)_2\text{-}ZrCl_2{}^+I^-$ (**6B**), respectively. Each of these product mixtures gave rise to two NMR signal sets (see Experimental Section), which indicate the presence of two *ansa*-metallocene species in varying ratios. Unfortunately, it proved impossible to separate or to isolate any one of them. It remains undetermined, therefore, whether the two product species of **6A** and **6B** are the racemic and meso isomers of the metallocene dichlorides with iodide as counterion or ligand-exchange isomers in which one of the chlorides at the metal center is replaced by iodide.

Reaction of either the Li salt **5A** or its LiI adduct **5A**-LiI with $YCl_3(THF)_{3.5}$ did not afford the expected phosphonium-bridged yttrocene. Instead, the ylide **3A** was formed, probably by proton transfer from a coordinated THF molecule.

Scheme 3



Synthesis of the kalocenes $Me_2P(2\text{-}Me\text{-}4\text{-}tBu\text{-}C_5H_2)_2K$ (**7A**) and $nBu_2P(2\text{-}Me\text{-}4\text{-}tBu\text{-}C_5H_2)_2K$ (**7B**) was achieved, with raw yields of ca. 90%, by reaction of the ligand salts **2A** and **2B** with an excess of KH in THF at −78 °C (Scheme 3). Removal of excess KH and of the KI precipitate and evaporation of the solvent gave complex **7A** in form of reddish crystals, complex **7B** as a yellow powder.

^1H NMR spectra of **7A** and **7B** in THF-d_8 solution, which remain unchanged even at temperatures down to −60 °C, indicate that the phosphonium-bridged kalocenes are obtained again exclusively in form of their racemic isomers. The $^2J(P,H)$ coupling between the P atom and the protons of the P-bound Me substituents remains in the expected range (12.6 and 14.4 Hz). The coupling between the P atom and the 2-Me group at the C_5 ring, which was observed for protonated cyclopentadienyl compounds, is not apparent in complexes **7A** and **7B**.

The crystal structure of **7A** (Figure 1, Table 1) documents the racemic configuration of this complex. The potassium atom is coordinated to both cyclopentadienyl rings of one ligand molecule, as well as to a third C_5 ring, which is part of a second complex molecule. The planes of the phosphonium-bridged cyclopentadienyl rings, E(1) and E(2), are almost perpendicular to each other; the resulting very open structure allows coordi-

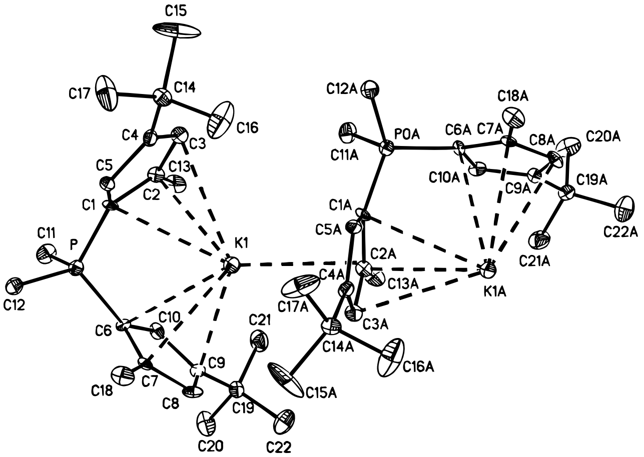


Figure 1. ORTEP drawing of $Me_2P(2\text{-}Me\text{-}4\text{-}tBu\text{-}C_5H_2)_2K$ (**7A**) with 30% probability ellipsoids.

Table 1. Selected Distances (pm) and Angles (deg) for Compound 7A

K(1)−C(1)	312.1(9)	K(1)−C(9)	339.8(8)
K(1)−C(2)	292.7(9)	K(1)−C(10)	333.8(8)
K(1)−C(3)	321.7(9)	K(1)−C(1A)	322.7(8)
K(1)−C(4)	356.3(9)	K(1)−C(2A)	311.1(10)
K(1)−C(5)	347.1(9)	K(1)−C(3A)	301.2(9)
K(1)−C(6)	310.0(8)	K(1)−C(4A)	309.5(8)
K(1)−C(7)	299.9(8)	K(1)−C(5A)	324.0(8)
K(1)−C(8)	316.9(9)		
C(1)−C(2)	143.0(13)	C(6)−C(7)	140.3(10)
C(2)−C(3)	137.6(12)	C(7)−C(8)	140.2(14)
C(3)−C(4)	142.4(13)	C(8)−C(9)	142.1(11)
C(4)−C(5)	139.8(12)	C(9)−C(10)	138.6(12)
C(5)−C(1)	143.3(12)	C(10)−C(6)	142.3(13)
P(1)−C(1)	175.6(8)	P(1)−C(6)	174.6(9)
P(1)−C(11)	179.5(8)	P(1)−C(12)	178.5(11)
K(1)−P(1)	371.1(3)		
P(1)−C(1)−E(1)	10.5	P(1)−C(6)−E(2)	12.0
C(1)−P(1)−C(6)	112.8(4)	C(11)−P(1)−C(12)	105.8(4)
C(1)−P(1)−C(12)	108.5(4)	C(6)−P(1)−C(11)	108.2(4)
C(1)−P(1)−C(11)	109.7(4)	C(6)−P(1)−C(12)	111.7(4)
E(1)−E(2)	88.8		

nation of a third cyclopentadienyl ring. The alkali metal appears to prefer another aromatic ring to saturate its coordination sphere rather than a solvent molecule, although the crystallization took place in the presence of THF.

Only a few structures of potassium cyclopentadienyl compounds have appeared in the literature so far; most of them crystallize in polymeric chain structures, e.g., $C_5Me_5K(py)_2$[13] and $C_5H_4SiMe_3K$.[14] Formation of a polymeric chain has also been observed for a complex $[(C_5Me_4)SiMe_2(N(H)tBu)]K(THF)$ obtained by Bercaw and co-workers from a reaction of $(C_5Me_4H)SiMe_2(N(H)\text{-}tBu)$ with KH.[15] Here again, the potassium atom is situated in a polymeric chain, between cyclopentadienyl rings of two different ligand molecules without interacting with the nitrogen atom.

The $K-C_{Cp}$ distances in complex **7A** vary between 293 and 356 pm. The shortest of these bonds connects the K atom to a C atom next to the bridgehead position, but the remaining $K-C_{Cp}$ distances are not grouped into distinct sets which would allow a clear-cut hapticity classification (Table 1). K−C bond lengths in η^5-coordinated K−cyclopentadienyl compounds have been found to vary between 295 and 310 pm.[13−16] Depending on the limiting distance used, the K atom can be considered to be either η^1- or η^3-coordinated to the C_5 rings of the first *ansa*-ligand and either η^3- or η^5-coordinated to the third C_5 ring donated by a neighboring complex molecule.

The $P-C_{Cp}$ distances of P(1)−C(1) = 174.6(9) pm and P(1)−C(6) = 174.6(9) pm in **7A** are intermediate between a double-bond distance of 166 pm, as in $Ph_3P{=}CH_2$,[17] and a single-bond distance of 183 pm, as found for Ph−P in $Ph_3P{=}CH_2$.[17] As in other related species,[18−20] the P−Cp bonding in complex **7A** appears to be intermediate between an ylide and ylene limiting case.

Phosphonium-bridged metallocenes with Ba centers were synthesized by two routes, using either the ylide **3A** or the protonated ligands **2A**, **2B**, and **4A** as starting compounds. Reaction of the ylide **3A** with 1 equiv of $Ba[N(SiMe_3)_2]_2$ in toluene at room temperature gave a barium compound with a ^1H NMR spectrum in accord with the expected composition $Me_2P(2\text{-}Me\text{-}4\text{-}tBu\text{-}C_5H_2)_2\text{-}BaN(SiMe_3)_2$ (**8A**). When the same starting reagents were used in a 2:1 ratio, we observed a new set of NMR signals assignable to $[Me_2P(2\text{-}Me\text{-}4\text{-}tBu\text{-}C_5H_2)_2]_2Ba$ (**9A**). When the protonated ligand salt **2A**, **2B**, and **4A** were reacted with 1 equiv of $Ba[N(SiMe_3)_2]_2$, we obtained the cationic barocene derivatives $Me_2P(2\text{-}Me\text{-}4\text{-}tBu\text{-}C_5H_2)_2\text{-}Ba^+I^-$ (**10A**), $nBu_2P(2\text{-}Me\text{-}4\text{-}tBu\text{-}C_5H_2)_2Ba^+I^-$ (**10B**), and $Me_2P(2\text{-}Me\text{-}4\text{-}tBu\text{-}C_5H_2)_2Ba^+\ BPh_4^-$ (**11A**), respectively. Here again, NMR spectra indicate that each product was obtained as the pure racemic isomer (Scheme 4). ^1H NMR spectra of complex **8A**, both at room temperature and at −60 °C, likewise indicate a C_2-symmetic, racemic structure.

2D-ROESY spectra of complex **8A** showed cross signals between the ^1H NMR signals of the Me group in 2-position of the cyclopentadienyl ring (2.09 ppm) and the protons of the trimethylsilyl group of the amido substituent (0.3 ppm). This indicates that at least one amido substituent is still coordinated to the barium center. In accord with this, reaction of **8A** with another equivalent of **3A** led to the formation of the 2:1 complex **9A**. No formation of **9A** and $Ba[N(SiMe_3)_2]_2$ in equilibrium with **8A** is observed, however, when solutions of **8A** are measured over a period of 1 day. The mixed ligand barocene complex **8A** thus appears to be substantially more stable than its homoleptic dismutation products.

In the case of the barocene iodide salts **10A** and **10B**, the results deviate from expectation in that we observe in both cases two racemic metallocene species. Positive cross signals in the 2D-ROESY spectra, which connect ^1H NMR signals assignable to the signal sets for each of the compounds **10A** and **10B**, document an exchange between the corresponding protons of *rac1*-**10A** with

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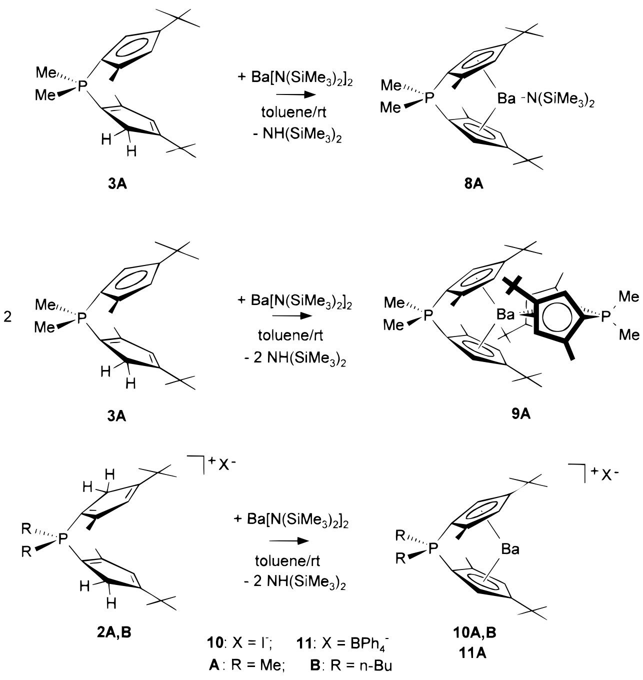
Scheme 4



those of *rac2*-**10A** and of *rac1*-**10B** with *rac2*-**10B** in solution at room temperature. We assume that this exchange involves two racemic barocene complexes differing by the coordination or noncoordination of the iodide anion.

This assumption is supported by reaction of Ba[N(SiMe$_3$)$_2$]$_2$ with 1 equiv of **4A**, which contains the noncoordinating tetraphenyl borate as counteranion. Here, only one racemic barocene species, **11A**, was obtained from reaction of equivalent amounts of ligand **4A** and Ba[N(SiMe$_3$)$_2$]$_2$.

The ^{1}H NMR spectra of all barocene complexes studied here show a doublet with coupling constants ^2J(P,H) in the expected range of 13.2−13.7 Hz. In addition, the P atom couples with the protons in the 3- and 5-positions at the cyclopentadienyl rings.

While several examples of unbridged barocenes have been described in the literature,[21−24] only one *ansa*-barocene complex, Me$_2$Si(fluorenyl)$_2$Ba(THF)$_4$,[25] has been reported so far. The phosphonium-bridged barocenes **8A**, **9A**, **10A**, **10B**, and **11A** described above, which were obtained in the form of their pure racemic isomers, are the first examples of chiral *ansa*-barocene derivatives.

Barocene complex **11A** was crystallized from a THF/pentane mixture. A crystal structure determination of **11A** (Figure 2, Table 2) proves the racemic configuration. The unit cell (space group $P\bar{1}$) contains a pair of enantiomers of **11A**. Three THF molecules are bound to the barium center to saturate its coordination sphere. As expected, the tetraphenyl borate counterion is noncoordinating.

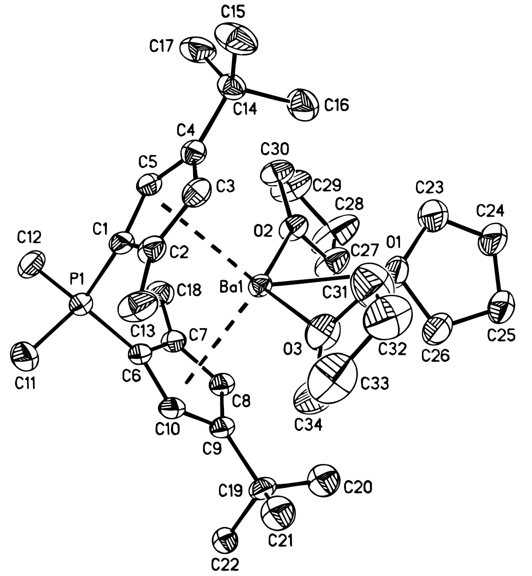


Figure 2. ORTEP drawing of the cation of Me$_2$P(2-Me-4-tBu-C$_5$H$_2$)$_2$Ba(THF)$_3$$^+BPh_4$$^-$ (**11A**) with 30% probability ellipsoids.

Table 2. Selected Distances (pm) and Angles (deg) for Compound 11A

Ba(1)−C(1)	300.1(4)	Ba(1)−C(6)	297.4(5)
Ba(1)−C(2)	306.0(4)	Ba(1)−C(7)	300.2(5)
Ba(1)−C(3)	312.5(4)	Ba(1)−C(8)	312.5(5)
Ba(1)−C(4)	313.4(4)	Ba(1)−C(9)	320.1
Ba(1)−C(5)	302.8(4)	Ba(1)−C(10)	306.4(4)
C(1)−C(2)	140.5(7)	C(6)−C(7)	140.1(7)
C(2)−C(3)	138.4(7)	C(7)−C(8)	138.4(6)
C(3)−C(4)	139.8(6)	C(8)−C(9)	140.9(6)
C(4)−C(5)	138.2(6)	C(9)−C(10)	139.0(6)
C(5)−C(1)	141.9(6)	C(10)−C(6)	143.0(6)
P(1)−C(1)	174.1(5)	P(1)−C(6)	175.0(4)
P(1)−C(11)	178.4(6)	P(1)−C(12)	178.1(6)
Ba(1)−P(1)	363.3		
P(1)−C(1)−E(1)	13.6 (endo)	P(1)−C(6)−E(2)	12.0 (endo)
C(1)−P(1)−C(6)	109.5(2)	C(11)−P(1)−C(12)	106.2(3)
C(1)−P(1)−C(11)	111.8(3)	C(6)−P(1)−C(12)	112.1(3)
C(1)−P(1)−C(12)	108.6(2)	C(6)−P(1)−C(11)	108.6(2)

Both cyclopentadienyl rings can be considered to be η^5-coordinated to the barium center, as all Ba−C$_{Cp}$ bond lengths are in the range of 297−320 pm, comparable to previously reported distances of 284−294 pm for Cp*$_2$-Ba[26] and of 300−344 pm for Me$_2$Si(fluro)$_2$Ba(THF)$_4$.[25]

The P−C$_{Cp}$ bond lengths in **11A** are significantly shorter (174.1(5) and 175.0(4) pm) than the P−C$_{Me}$ distances (178.4(6) and 178.1(6) pm), presumably because of a partial double-bond character of the P−C$_{Cp}$ bond. The P−C$_{Cp}$ bond lengths in **11A** are also significantly shorter, by about 12 pm, than the Si−C$_{Cp}$ distances in the otherwise analogous dimethylsilyl-bridged zirconocene Me$_2$Si(2-Me-4-tBu-C$_5$H$_2$)$_2$ZrCl$_2$ (Si−C$_{Cp}$ = 187,6 pm).[27] The cyclopentadienyl rings are bent away from the P−C$_{Cp}$ bond toward the metal with P(1)−C(1)−E(1) and P(1)−C(6)−E(2) angles of 13.6° and 12.0°, respectively. The shortening of the P−C$_{Cp}$ distances relative to the Si−C$_{Cp}$ distances in silyl-bridged complexes, together with a comparable degree of bending

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of the P−C_{Cp} and Si−C_{Cp} bonds,[28] position the α-substituents of a meso-configurated *ansa*-ligand much closer to each other in a phosphonium-bridged metallocene than in a comparable silyl-bridged metallocene. The short P−C_{Cp} distances in the phosphonium-bridged ligands might thus be the cause for the exclusive formation of racemic complexes.

Conclusions

Our results show that phosphonium-bridged metallocenes of group IV and III transition metals are substantially less easily accessible than their silyl-bridged analogues. This is most likely caused by repulsion between the positive charge at the bridge atom and the highly charged central ion. In accord with this notion is the formation of stable and well-characterized complexes with di- and monovalent central metals from groups I and II, which give rise to the first examples of chiral kalocene and barocene derivatives. Interestingly, only the racemic isomers of these complexes are observed in the crystalline state as in solution, probably due to increased repulsions between the α-positioned ring substituents. An extension of this work to related alkaline-earth complexes which might be utilized as chiral synthons, e.g., for metallocenes containing other metals, is presently under study.

Experimental Section

General Procedures. All reactions were carried out under Ar or N_2 atmosphere using standard Schlenk and glovebox techniques. NMR spectra were recorded on Bruker WM (250 MHz), Bruker AC (250 MHz), and Bruker DRX (600 MHz) spectrometers with residual C_6HD_5 (7.15 ppm), C_4HD_7O (3.58 ppm), and $CHCl_3$ (7.24 ppm) as internal standards. Mass spectra were recorded on Finnigan MAT 312 and Kratos Analytic Kompac MALDI 1 without matrix. All solvents used were thoroughly dried and degassed. $MePCl_2$ was obtained from Strem Chemicals. nBuPCl_2[29] and Ba[N(SiMe$_3$)$_2$]$_2$[25] were prepared according to literature procedures.

1. $Me_2P(2\text{-}Me\text{-}4\text{-}t Bu\text{-}C_5H_3)_2{}^+I^-$ (2A). To a suspension of 4.85 g of Me-3-*t*Bu-$C_5H_3{}^-Li^+$ (34 mmol) in a mixture of 30 mL of THF and 10 mL of pentane at −40 °C was added, dropwise over a period of 20 min, 1.5 mL of $MePCl_2$ (16 mmol) in 6 mL of THF. The suspension was stirred overnight and allowed to warm to room temperature. After evaporation to dryness, extraction of the phosphine with pentane, and renewed evaporation to dryness, **1A** was obtained as a yellow oily product. Yield: 4.76 g (15.05 mmol); 94% of theory. Compound **1A**, the ^{1}H NMR spectrum of which shows the presence of several tautomers, was used for the next reaction step without further purification.

To a solution of 3.71 g of **1A** (11.8 mmol) in THF (20 mL) at −78 °C was added dropwise 2 mL of MeI (32 mmol). The reaction mixture was stirred overnight, allowed to come to room temperature, and evaporated to dryness. After washing the solid three times with pentane, to remove residual MeI, **2A** was obtained as a light yellow solid. Yield: 5.21 g (11.4 mmol); 97% of theory. ^{1}H NMR ($CDCl_3$, 600 MHz, δ in ppm): 6.13 (m, 2H, H−C_3), 3.64 (br m, 4H, H_2−C_5), 2.45 (d, 6H, P(CH_3)$_2$, ^2J(P,H) = 13.5 Hz), 1.98 (q, 6H, CH_3−C_2), 1.22 (s, 18H, C(CH_3)$_3$−C_4). ^{13}C NMR ($CDCl_3$, 151 MHz, δ in ppm): 171 (d, C_4, ^3J(P,C) = 8 Hz), 162 (d, C_2, ^2J(P,C) = 11 Hz), 129 (d, C_3, ^3J(P,C) = 15 Hz), 112 (d, C_1, ^1J(P,C) = 99 Hz), 44 (d, C_5, ^2J(P,C) = 15 Hz), 33.7 (C(CH$_3$)$_3$), 30.3 (C(CH$_3$)$_3$), 15.7 (d, CH$_3$−C_2, ^3J(P,C) = 4 Hz), 12.7 (d, P(CH$_3$)$_2$, ^1J(P,C) = 60 Hz).

2. $n Bu_2P(2\text{-}Me\text{-}4\text{-}t Bu\text{-}C_5H_3)_2{}^+I^-$ (2B). To a suspension of 6.3 g of Me-3-*t*Bu-$C_5H_3{}^-Li^+$ (44.4 mmol) in a 2:1 mixture of pentane and THF (100 mL) at −78 °C was added dropwise, over a period of 30 min, 3 mL of nBuPCl_2 (22.02 mmol) in 10 mL of pentane/THF (2:1). The resulting suspension was stirred overnight and allowed to warm to room temperature. After evaporation to dryness, extraction of the phosphine with pentane, and renewed evaporation to dryness, **1B** was obtained as a yellow solid, which was used for the next reaction step without further purification. Yield: 9.28 g (17.12 mmol); 94% of theory.

To a solution of 6.5 g of **1B** (18.15 mmol) in 80 mL of toluene was added 3 mL of nBuI (26 mmol). The reaction mixture was stirred for 15 h under reflux, evaporated to dryness, and washed with pentane. In this manner, **2B** was isolated as a yellow solid. Yield: 9.28 g (17.12 mmol); 94% of theory. ^{1}H NMR ($CDCl_3$, 600 MHz, δ in ppm): 6.16 (m, 2H, H−C_3), 3.54 (m, 4H, H_2−C_5), 2.7 (m, 4H, H_2−C_6), 1.96 (q, 6H, CH_3−C_2), 1.7−1.4 (2m, 4H each, H_2−C_7 and H_2−C_8), 1.22 (s, 18H, C(CH_3)$_3$), 0.9 (t, 6H, H_3−C_9). ^{13}C NMR ($CDCl_3$, 151 MHz, δ in ppm): 171.7, 163 (2d, C_4 and C_2, J(P,C) = 9 and 7.5 Hz), 130 (d, C_3,^3J(P,C) = 14.5 Hz), 110.1 (d, C_1,^1J(P,C) = 94.5 Hz), 45.3 (d, C_5, ^1J(P,C) = 14 Hz), 34.1 (C(CH$_3$)$_3$), 30.5 (C(CH$_3$)$_3$, 24.2 (d, C_8, ^3J(P,C) = 4 Hz), 23.6 (d, C_7, ^2J(P,C) = 19.5 Hz), 23.4 (d, C_6, ^1J(P,C) = 20 Hz), 16.4 (d, CH$_3$−C_2, ^3J(P,C) = 4 Hz), 13.7 (C_9). Anal. Calcd for $C_{28}H_{48}IP$: C, 61.98; H, 8.92. Found.: C, 62.20; H, 9.14.

3. $Me_2P(2\text{-}Me\text{-}4\text{-}t Bu\text{-}C_5H_2)(2'\text{-}Me\text{-}4'\text{-}t Bu\text{-}C_5H_3)$ (3A). To a suspension of 0.165 g of KH (4.12 mmol) in 20 mL of THF at −78 °C was added dropwise, over a period of 30 min, a solution of 1.89 g of **2A** (4.12 mmol) in 20 mL of THF. The reaction mixture was stirred and allowed to warm to room temperature. The KI formed during the reaction was removed by filtration. The clear solution, evaporated to dryness, afforded **3A** as a yellow solid. Yield: 0.79 g (2.4 mmol); 58% of theory. ^{1}H NMR ($CDCl_3$, 600 MHz, δ in ppm): 6.11, 6.02 (2m, 1H each, H−C_3 and H−$C_{3'}$) 5.90 (m, 1H, H−C_5), 3.25 (m, 2H, H_2−$C_{5'}$), 2.3 (s, 3H, CH_3−C_2), 1.86 (q, 3H, CH_3−$C_{2'}$), 2.00 (d, 6H, P(CH_3)$_2$, ^2J(P,H) = 12.5 Hz), 1.30, 1.25 (2s, 9H each, C(CH_3)$_3$−C_4 and C(CH_4)$_3$−$C_{4'}$). ^{13}C NMR ($CDCl_3$, 151 MHz, δ in ppm): 165.9, 158.5, 137.9, 121.9, 119.4, 118.8 (C_q), 132.2, 112.4 (2d, C_3 and $C_{3'}$, ^3J(P,C) = 14 and 16 Hz), 107.6 ($C_{5'}$), 42.8 (d, C_5, ^2J(P,C) = 13 Hz), 32.4, 30.4 (C(CH$_3$)$_3$−C_4 and C(CH$_3$)$_3$−$C_{4'}$), 15.65 (CH$_3$−C_2; CH$_3$−$C_{2'}$), 14.3 (d, P(CH$_3$)$_2$, ^2J(P,C) = 62 Hz).

4. $n Bu_2P(2\text{-}Me\text{-}4\text{-}t Bu\text{-}C_5H_2)(2'\text{-}Me\text{-}4'\text{-}t Bu\text{-}C_5H_3)$ (3B). To a suspension of 2.06 g of **2B** (3.8 mmol) in 50 mL of pentane was added dropwise, over a period of 15 min, 2.38 mL of 1.6 M nBuLi (3.8 mmol) in hexane at −78 °C. The reaction mixture was stirred overnight, allowed to warm to room temperature, and evaporated to dryness. The product **3B** was extracted with pentane and the extract again evaporated to dryness, to leave **3B** as a green-yellow solid. Yield: 1.54 g (3.72 mmol); 98% of theory. ^{1}H NMR ($CDCl_3$, 250 MHz, δ in ppm): 6.09, 6.00, 5.89 (3m, 1H each, H−C_3, H−C_5, and H−$C_{3'}$), 3.25 (m, 2H, H_2−$C_{5'}$), 2.26 (m, 4H, H_2−C_6), 2.00 (s, 3H, CH_3−C_2), 1,83 (q, 3H, CH_3−$C_{2'}$), 1.53 (m, 4H, H_2−C_7), 1.29 (m, 4H, H_2−C_8), 0.92 (m, 6H, H_2−C_9), 1.23, 1.19 (2s, 9H each, C(CH_3)$_3$−C_4 and C(CH_3)$_3$−$C_{4'}$).

5. $Me_2P(2\text{-}Me\text{-}4\text{-}t Bu\text{-}C_5H_3)_2{}^+BPh_4{}^-$ (4A). To a mixture of 0.68 g of **3A** (2.06 mmol) and 0.78 g of $NHMe_3{}^+BPh_4{}^-$ (2.06 mmol) was added 20 mL of THF/pentane (1:1). The yellow suspension was stirred for 12 h at room temperature and evaporated to dryness and the solid residue washed three times with pentane to give **4A** as a white solid. Yield: 1.32 g (2.03 mmol); 99% of theory. ^{1}H NMR ($CDCl_3$, 250 MHz, δ in ppm): 7.48 (bm, 8H, o-H−phenyl), 7.03 (t, 8H, m-H−phenyl), 6.86 (m, 4H, p-H−phenyl), 6.14 (m, 2H, H−C_3), 2.99 (m, 4H,

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[28] A comparable angle Si(1)−C(1)−E(1) of 15.8° has been reported for the zirconocene complex $Me_2Si(2\text{-}Me\text{-}4\text{-}t Bu\text{-}C_5H_2)_2ZrCl_2$.[27]

[29] Weil, Th.; Prijs, B.; Erlenmeyer, H.*Helv. Chim. Acta* **1952**, *35*, 1412. Weil, Th.; Prijs, B.; Erlenmeyer, H. *Helv. Chim. Acta* **1953**, *36*, 1314.

H_2-C_5), 1.79 (q, 6H, CH_3-C_2), 1.23 (s, 18H, $C(CH_3)_3$), 0.9 (d, 6H, $P(CH_3)_2$, $^2J(P,H) = 11.9$ Hz). Anal. Calcd for $C_{46}H_{56}BP$: C, 84.9; H, 8.67. Found: C, 84.67; H, 8.97.

6. $Me_2P(2\text{-}Me\text{-}4\text{-}tBu\text{-}C_5H_2Li)_2{}^+I^-$ (5A-LiI). To a suspension of 5 g of **2A** (10 mmol) in 40 mL of diethyl ether/THF (1:2) at −78 °C was added, dropwise over a period of 1 h, 13.8 mL of 1.6 M *n*BuLi (20 mmol) in hexane. After 20 min, the reaction mixture is a deep red. After stirring overnight and allowing the reaction mixture to warm to room temperature, the product was evaporated to dryness and washed with pentane. Compound **5A**-LiI was obtained as a light red solid. Yield: 4.58 g (9 mmol); 91% of theory. ^1H NMR (THF-d_8, 250 MHz, δ in ppm): 5.7, 5.67 (2m, 2H each, $H-C_3$ and $H-C_5$), 2.08 (s, 6H, CH_3-C_2), 1.81 (d, 6H, $P(CH_3)_2$, $^2J(P,H) = 13.5$ Hz), 1.18 (s, 18H, $C(CH_3)_3$).

7. $nBu_2P(2\text{-}Me\text{-}4\text{-}tBu\text{-}C_5H_2Li)_2{}^+I^-$ (5B-LiI). To a suspension of 0.5 g of **2B** (0.9 mmol) in 20 mL of pentane at −78 °C was added dropwise over a period of 10 min 1.15 mL of 1.6 M *n*BuLi (1.8 mmol) in hexane. The reaction mixture was stirred, allowed to warm to room temperature, and then evaporated to dryness. As the product is soluble even in pentane, it cannot be purified by washing or recrystallization. Compound **5B**-LiI was obtained as a light yellow solid, which was used as such for further reactions. Yield: quantitative. ^1H NMR (THF-d_8, 250 MHz, δ in ppm): 5.74, 5.65 (2m, 2H each, $H-C_3$ and $H-C_5$), 2.07 (s, 4H, H_2-C_6), 1.99 (s, 6H, CH_3-C_2,), 1.35−1.1 (m, 8H, H_2-C_7 and H_2-C_8), 1.18 (s, 18H, $C(CH_3)_3$), 0.88 (m, 6H, H_3-C_9).

8. $Me_2P(2\text{-}Me\text{-}4\text{-}tBu\text{-}C_5H_2)_2Li$ (5A). To a solution of 0.79 g of **3A** (2.4 mmol) in 30 mL of pentane at −78 °C was added 1.5 mL of 1.6 M *n*BuLi (2.4 mmol) in hexane. The reaction mixture was stirred overnight and allowed to warm to room temperature. After evaporation to dryness, the solid residue was washed three times with pentane to give **5A** as a light yellow solid. Yield: 0.39 g (1.17 mmol); 49% of theory. ^1H NMR (THF-d_8, 250 MHz, δ in ppm): 5.8−5.6 (m, 4H, $H-C_3$ and $H-C_5$), 2.22 (s, 6H, CH_3-C_2), 1.87 (d, 6H, $P(CH_3)_2$, $^2J(P,H) = 13.1$ Hz), 1.17 (s, 18H, $C(CH_3)_3$). A low-temperature NMR spectrum (−90 °C) of **5A** in THF-d_8 solution did not show any signals other than those of the racemic isomer.

9. $nBu_2P(2\text{-}Me\text{-}4\text{-}tBu\text{-}C_5H_2)_2Li$ (5B). To a solution of 1.54 g of **3B** (3.72 mmol) in 40 mL of pentane were added dropwise 2.33 mL of 1.6 M *n*BuLi (3.72 mmol) in hexane and 20 mL of pentane at −78 °C. The reaction mixture was allowed to warm to room temperature while being stirred and then evaporated to dryness in vacuo to give **5B** as a yellow solid. Yield: 1.41 g (3.35 mmol); 90% of theory. ^1H NMR (THF-d_8, 250 MHz, δ in ppm): 5.76, 5.65 (2m, 2H each, $H-C_3$ and $H-C_5$), 2.21 (s, 4H, H_2-C_6), 2.1 (s, 6H, CH_3-C_2), 1.42−1.1 (m, 8H, H_2-C_7 and H_2-C_8), 1.18 (s, 18H, $C(CH_3)_3$), 0.96 (m, 6H, H_3-C_9).

10. $Me_2P(2\text{-}Me\text{-}4\text{-}tBu\text{-}C_5H_2)_2ZrCl_2{}^+I^-$ (6A). To a mixture of 0.78 g of **5A**-LiI (2.26 mmol) and 0.53 g of $ZrCl_4$ (2.26 mmol) was added 20 mL of toluene at room temperature. The light yellow suspension soon became darker. The ^1H NMR spectrum in $CDCl_3$ showed **6A** with a rac:meso ratio of about 1.3: 1. The product could not be isolated, and the yield could not be determined. ^1H NMR ($CDCl_3$, 250 MHz, δ in ppm): 6.82, 6.72, 6.42, 6.04 (4m, 1H each, $H-C_3$ and $H-C_5$), 3.42, 3.03 (2d, 3H each, $P(CH_3)_2$ of *meso*-**6A**, $^2J(P,H) = 15$ Hz), 3.22 (d, 6H, $P(CH_3)_2$ of *rac*-**6A**, $^2J(P,H) = 15$ Hz), 2.38, 2.34 (2s, 6H, CH_3-C_2), 1.35, 1.32 (2s, 18H, $C(CH_3)_3$).

11. $nBu_2P(2\text{-}Me\text{-}4\text{-}tBu\text{-}C_5H_2)_2ZrCl_2{}^+I^-$ (6B). To a solution of 0.35 g of **5B**-LiI (0.63 mmol) in 5 mL of toluene at −5 °C was added a cooled suspension of 0.15 g of $ZrCl_4$ (2.26 mmol) in 5 mL of toluene. The reaction mixture was stirred and allowed to warm to room temperature. The complex was extracted with toluene, evaporated to dryness, and washed with pentane. The resulting solid obtained in this manner consisted of a mixture of zirconocene **6B** and protonated ligand **2B**. These products could not be separated, and a yield could not be determined. ^1H NMR ($CDCl_3$, 250 MHz, δ in ppm): 7.66; 6.92; 6.70; 6.39 (4m, 1H each, $H-C_3$ and $H-C_5$), 3.89−2.45 (several m, 4H, H_2-C_6), 2.42; 2.35 (s, 6H, CH_3-C_2), 1.87 (m, 8H, H_2-C_7 and H_2-C_8), 1.4−0.8 (several m, 6H, H_3-C_9), 1.36; 1.34 (s, 9H each, $C(CH_3)_3$).

12. $Me_2P(2\text{-}Me\text{-}4\text{-}tBu\text{-}C_5H_2)_2K$ (7A). To a suspension of 2.5 g of KH (62 mmol) in 40 mL of THF at −78 °C was added dropwise a solution of 6.4 g of **2A** (14 mmol) in 20 mL of THF. The reaction mixture was stirred and allowed to warm to room temperature. The KI formed during the reaction and the KH excess were removed by filtration. After evaporation to dryness, the solid residue was washed with pentane to give **7A** as a yellow solid. Yield: 4.54 g (12 mmol); 88% of theory. ^1H NMR (THF-d_8, 600 MHz, δ in ppm): 5.77 (m, 2H, $H-C_5$), 5.56 (m, 2H, $H-C_3$), 2.28 (m, 6H, CH_3-C_2), 2.03 (d, 6H, $P(CH_3)_2$, $^2J(P,H) = 12.6$ Hz), 1.14 (s, 18H, $C(CH_3)_3$). ^{13}C NMR (THF-d_8, 151 MHz, δ in ppm): 136.2, 118.5 (2d, C_4 and C_2, $J(P,C) = 15$ and 14 Hz), 110.9, 104.1 (d, C_3 and C_5, $J(P,C) =$ 15.1 and 15.3 Hz), 92.8 (d, C_1, $^1J(P,C) = 99.9$ Hz), 33.7 ($C(CH_3)_3$), 33.5 ($C(CH_3)_3$), 16.6 (s, CH_3-C_2), 13.5 (d, $P(CH_3)_2$, $^1J(P,C) = 61$ Hz).

13. $nBu_2P(2\text{-}Me\text{-}4\text{-}tBu\text{-}C_5H_3)_2K$ (7B). To a suspension of 1 g of KH (25 mmol) in 30 mL of THF at −78 °C was added dropwise a solution of 0.36 g of **2B** (0.73 mmol) in 15 mL of THF. The reaction mixture was stirred overnight and allowed to warm to room temperature. Excess KH and KI precipitate were removed by filtration. The solution was evaporated to dryness and the solid residue washed with pentane, to give **7B** as a yellow solid. Yield: 0.29 g (0.64 mmol); 88% of theory. ^1H NMR (THF-d_8, 600 MHz, δ in ppm): 5.76 (m, 2H, $H-C_5$), 5.54 (m, 2H, $H-C_3$), 2.49 (m, 4H, H_2-C_6), 2.25 (s, 6H, CH_3-C_2), 1.66 (m, 4H, H_2-C_7), 1.55 (m, 4H, H_2-C_8), 1.14 (s, 18H, $C(CH_3)_3$), 1.00 (t, 6H, H_3-C_9). ^{13}C NMR (THF-d_8, 151 MHz, δ in ppm): 136.4 (d, C_q, $J(P,C) = 14$ Hz), 118.3 (d, C_q, $J(P,C) =$ 14 Hz), 110.9 (d, C_3, $^3J(P,C) = 15$ Hz), 104.5, (d, C_5, $^2J(P,C) =$ 15 Hz), 90.4 (d, C_1, $^1J(P,C) = 98$ Hz), 33.4 ($C(CH_3)_3$), 32.4 ($C(CH_3)_3$), 25.3 (C_8), 25.2 (C_7) (as both signals are hidden under the THF-d_8-signal, the coupling constant cannot be determined), 21.9 (d, C_6, $^1J(P,C) = 57$ Hz), 16.6 (CH_3-C_2), 14.2 (C_9).

14. $Me_2P(2\text{-}Me\text{-}4\text{-}tBu\text{-}C_5H_2)_2BaN(SiMe_3)_2$ (8A). To a mixture of 0.307 g of **3A** (0.93 mmol) and 0.407 g of $Ba[N(SiMe_3)_2]_2$ (0.93 mmol) was added 20 mL of toluene. After stirring for 2 h at room temperature, solvent and amine were evaporated to give **8A** as a white solid. Yield: 5.24 g (0.8 mmol); 86% of theory. ^1H NMR (C_6D_6, 600 MHz, δ in ppm): 6.01 (br d, 2H, $H-C_3$, $^3J(P,H) = 5$ Hz), 5.75 (br d, 2H, $H-C_5$, $^2J(P,H) = 4$ Hz), 2.09 (s, 6H, CH_3-C_2), 1.42 (s, 18H, $C(CH_3)_3$) 1.24 (d, 6H, $P(CH_3)_2$, $^2J(P,H) = 13.4$ Hz), 0.30 (s, 18H, $Si(CH_3)_3$). ^{13}C NMR (C_6D_6, 151 MHz, δ in ppm): 141.6 (d, C_q, $J(P,C) = 14$ Hz), 122 (d, C_q, $J(P,C) = 13$ Hz), 114.4 (d, C_1, $^3J(P,C) = 14$ Hz) 106.4 (d, C_5, $^2J(P,C) = 15$ Hz), 95.4 (d, C_1, $^1J(P,C) = 95$ Hz), 31.96 ($C(CH_3)_3$), 32.9 ($C(CH_3)_3$), 15.6 (CH_3-C_2), 10.9 (d, $P(CH_3)_2$, $^1J(P,C) = 61$ Hz), 4.89 ($Si(CH_3)_3$). MALDI-MS: *m/e* 467 ($M^+ - N(SiMe_3)_2$, 54%), 330 ($M^+ - N(SiMe_3)_2 - Ba$, base peak, 100%).

15. $[Me_2P(2\text{-}Me\text{-}4\text{-}tBu\text{-}C_5H_2)_2]_2Ba$ (9A). To a mixture of 0.69 g of **3A** (2,1 mmol) and 0.47 g of $Ba[N(SiMe_3)_2]_2$ (1.02 mmol) was added 20 mL of toluene. The reaction mixture was stirred for 2 h at room temperature, evaporated to dryness, and heated to 70 °C in vacuo until the amine was completely removed. In this manner, **9A** was obtained as a white solid. Yield: 0.74 g (0.93 mmol); 91% of theory. ^1H NMR (C_6D_6, 600 MHz, δ in ppm): 6.14, 5.87 (2m, 4H each, $H-C_3$ and $H-C_5$), 2.32 (s, 12H, CH_3-C_2), 1.57 (s, 36H, $C(CH_3)_3$), 1.35 (d, 12H, $P(CH_3)_2$, $^2J(P,H) = 13.2$ Hz). ^{13}C NMR (C_6D_6, 151 MHz, δ in ppm): 140.15 (d, C_q, $J(P,C) = 14$ Hz), 121.7 (C_q), 115.4 (d, C_3, $^3J(P,C) = 14$ Hz), 106.6 (d, C_5, $^2J(P,C) = 15$ Hz), 91.4 (d, C_1, $^1J(P,C) = 90$ Hz), 33.4 ($C(CH_3)_3$), 32.4 ($C(CH_3)_3$), 17.1 (CH_3-C_2), 13.3 (d, $P(CH_3)_2$, $^1J(P,C) = 61$ Hz). EI-MS/70 eV/$T = 220$ °C: *m/e* 796 (M^+, 10%), 467 ($M^+ - C_{22}H_{34}P$, base peak, 100%).

16. $Me_2P(2\text{-}Me\text{-}4\text{-}tBu\text{-}C_5H_2)_2Ba^+I^-$ (10A). To a mixture of 0.44 g of **2A** (0.96 mmol) and 0.44 g of $Ba[N(SiMe_3)_2]_2$ (0.96

Table 3. Crystallographic Data[a] for Compounds 7A and 11A

	7A[b]	**11A**[c]
formula	$C_{22}H_{34}KP$	$C_{66}H_{94}BBaO_5P$
fw	368.6	1146.53
cryst dimens (mm)	0.1 × 0.1 × 0.2	0.6 × 0.6 × 0.6
color, habit	brown needle	colorless
cryst syst	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$
a (Å)	9.672(2)	13.371(6)
b (Å)	21.990(5)	13.414(6)
c (Å)	10.707(3)	17.764(7)
α (deg)		83.57(2)
β (deg)	109.060(10)	9.73(3)
γ (deg)		76.50(4)
volume (Å^3)	2152.4(9)	3077.8(23)
density$_{calc}$ (g/cm^3)	1.137	1.237
Z	4	2
abs coeff (mm^{-1})	0.318	0.718
T (K)	153	233
weighting scheme	$w^{-1} = \sigma^2(F) + 0.00060F^2$	$w^{-1} = \sigma^2(F_o^2) + (0.0694P)^2 + 2.1613P$[d]
scan mode	$\omega/2\theta$	adaptive ω-scans
scan range (ω)	$1.1 + 0.35 \tan\theta$	2.0
θ range (deg)	$4.0 < 2\theta < 54.0$	$2.05 < \theta < 27.00$
no. of collected reflns	3178	13 938
no. of indep reflns	2976	13 350
no. of obsd reflns	1439	10 071
observation criterion	$F > 5.0\sigma(F)$	$F > 2\sigma(I)$
solution	direct	direct
refinement	SHELXTL PLUS	SHELXL-93
no. of params	217	662
R_F (%)	6.52	5.30
R_{wF} (%)	7.00 (F)	12.51 (F^2)
residual density (e Å^{-3})	0.46	0.616

[a] Crystals were obtained by crystallization from a THF/pentane mixture at room temperature. [b] Measurement conditions: Enraf-Nonius CAD4 diffractometer, Mo Kα radiation (0.7107 Å), and graphite monochromator. [c] Measurement conditions: Siemens P4 diffractometer, Mo Kα radiation (0.7107 Å), and graphite monochromator. [d] $P = (F_o^2 + 2F_c^2)/3$.

mmol) was added 15 mL of toluene. The mixture was stirred for 1 h at room temperature and then evaporated to dryness. The product was washed several times with THF and pentane and then evaporated to dryness over a period of 2 days at 70 °C; this procedure gave **10A** as a white solid. Yield: 0.176 g (0.297 mmol); 31% of theory. ^{1}H NMR (CDCl$_3$, 600 MHz, δ in ppm): **(***rac1***)** 6.03 (m, 2H, H−C$_3$), 5.94 (m, 2H, H−C$_5$), 2.32 (s, 6H, CH_3−C$_2$), 2.22 (d, 6H, P(CH_3)$_2$, ^2J(P,H) = 13.4 Hz), 1.28 (s, 18H, C(CH_3)$_3$); (*rac2*) 5.9 (m, 2H, H−C$_3$), 5.85 (m, 2H, H−C$_5$), 2.43 (s, 6H, CH_3−C$_2$), 2.20 (d, 6H, P(CH_3)$_2$, ^2J(P,H) = 13.4 Hz), 1.24 (s, 18H, C(CH_3)$_3$). ^{13}C NMR (CDCl$_3$, 151 MHz, δ in ppm): (*rac1*) 141.8 (d, C_q, J(P,C) = 15 Hz), 122.6 (d, C_q, J(P,C) = 13 Hz), 115.4 (d, C_3, ^3J(P,C) = 12 Hz), 106.4 (C_5), 93.5 (d, C_1, ^1J(P,C) = 96 Hz), 32.8 (C(CH$_3$)$_3$), 31.88 (C(CH$_3$)$_3$), 15.98 (CH$_3$−C$_2$), 11.8 (d, P(CH$_3$)$_2$, ^1J(P,C) = 61 Hz); (*rac2*) 143.2 (d, C_q, J(P,C) = 14 Hz), 124.2 (d, C_q, J(P,C) = 13 Hz), 113.8 (d, C_3, ^3J(P,C) = 14 Hz), 106.11 (C_5), 93.5 (C_1 hidden by C_1 of *rac1*), 32.7 (C(CH$_3$)$_3$), 30.1 (C(CH$_3$)$_3$), 17 (CH$_3$−C$_2$), 11.8 (P(CH$_3$)$_2$ hidden by P(CH$_3$)$_2$ of *rac1*). Anal. Calcd for $C_{22}H_{34}$-BaIP: C, 44.51; H, 5.77. Found: C, 44.13; H, 6.63.

17. ***n*****Bu$_2$P(2-Me-4-*t*Bu-C$_5$H$_2$)$_2$Ba$^+$ I$^-$ (10B).** To a mixture of 0.466 g of **2B** (0.866 mmol) and 0.395 g of Ba[N(SiMe$_3$)$_2$]$_2$ (0.866 mmol) was added 15 mL of toluene. The resulting dark yellow solution was stirred over a period of 2 h at room temperature and evaporated to dryness, to give **10B** as a white solid. Yield: 0.55 g (0.817 mmol); 94.3% of theory. The ^{1}H NMR spectrum shows two racemic barocene isomers. ^{1}H NMR (C$_6$D$_6$, 600 MHz, δ in ppm): (*rac1*) 6.42 (m, 2H, H−C$_3$), 6.09 (m, 2H, H−C$_5$), 2.37 (s, 6H, CH_3−C$_2$), 2.09 (m, 4H, H_2−C$_6$), 1.66 (s, 18H, C(CH_3)$_3$), 1.35 (m, 4H, H_2−C$_7$), 1.09 (m, 4H, H_2−C$_8$), 0.66 (t, 6H, H_3−C$_9$); (*rac2*) 6.29 (m, 2H, H−C$_3$), 6.04 (m, 2H, H−C$_5$), 2.60 (s, 6H, CH_3−C$_2$), 2.24 (m, 4H, H_2−C$_6$), 1.57 (s, 18H, C(CH_3)$_3$), 1.3 (m, 4H, H_2−C$_7$), 1.17 (m, 4H, H_2−C$_8$), 0.71 (t, 6H, H_3−C$_9$). ^{13}C NMR (C$_6$D$_6$, 151 MHz, δ in ppm): (*rac1*) 142.1 (d, C_q, J(P,C) = 13 Hz), 122.6 (d, C_q, J(P,C) = 13 Hz), 115.6; 107.1 (d, C_3 and C_5, J(P,C) = 14 and 13 Hz), 91.6 (d, C_1, ^1J(P,C) = 92 Hz), 33.37 (C(CH$_3$)$_3$), 24.16 (C_7), 24.16 (C_8), 20.04 (C_6) 16.1 (CH$_3$−C$_2$), 13.6 (C$_9$); (*rac2*) 143.6 (d, C_q, J(P,C) = 14 Hz), 124.7 (d, C_q, J(P,C) = 11 Hz), 114.1; 106.5 (d, C_3 and C_5, J(P,C) = 14 and 14 Hz), 91.9 (d, C_1, ^1J(P,C) = 92 Hz), 33.19 (C(CH$_3$)$_3$), 23.58 (C_7), 24.05 (C_8), 21.38 (C_6), 17.66 (CH$_3$−C$_2$), 13.6 (C_9) (hidden by C_9 of *rac1*). Anal. Calcd for $C_{28}H_{46}$-BaIP: C, 49.6; H, 6.84. Found: C, 49.85; H, 6.95.

18. Me$_2$P(2-Me-4-*t*Bu-C$_5$H$_2$)$_2$Ba$^+$BPh$_4^-$ (11A). To a mixture of 0.57 g of **4A** (0.88 mmol) and 0.4 g of Ba[N(SiMe$_3$)$_2$]$_2$ (0.88 mmol) was added 15 mL of toluene. The reaction mixture was stirred over a period of 15 h at room temperature. The white solid was washed three times with toluene and evaporated to dryness. Yield: 0.213 g (9.16 mmol); 36% of theory. **11A** was crystallized from THF/pentane to give colorless crystals which were suitable for crystal structure analysis. **11A** crystallized as a THF adduct with three solvent molecules and two additional THF molecules in each unit cell. ^{1}H NMR (THF-d_8, 600 MHz, δ in ppm): 7.29 (br d, 8H, o-H−phenyl), 6.87 (br t, 8H, m-H−phenyl), 6.72 (br t, 4H, p-H−phenyl), 5.9 (m, 2H, H−C$_5$), 5.85 (m, 2H, H−C$_3$), 2.3 (s, 6H, CH_3−C$_2$), 2.21 (d, 6H, P(CH_3)$_2$, ^2J(P,H) = 13.7 Hz), 1.2 (s, 18H, C(CH_3)$_3$). ^{13}C NMR (THF-d_8, 151 MHz, δ in ppm): 165.2 (q, C_q−B, J(P,C) = 49 Hz), 141.2 (C_q), 123.3 (d, C$_q$, J(P,C) = 13 Hz), 137 (o-C_{Ph}), 125.9 (m-C_{Ph}), 121.8 (p-C_{Ph}), 114.7 (m, C_4), 106.6 (d, C_2, ^2J(P,C) = 16 Hz), 94 (C_1, the coupling constant cannot be determined), 32.9 (C(CH$_3$)$_3$), 32.6 (C(CH$_3$)$_3$), 16.3 (CH$_3$−C$_2$), 11.5 (d, P(CH$_3$)$_2$, ^1J(P,C) = 54 Hz). Anal. Calcd for $C_{46}H_{54}$BaBP: C, 70.29; H, 6.92. Found: C, 70.11; H, 7.32.

19. Crystal Structures. For the crystal structure determinations, crystallization of **7A** and **11A** was induced by covering THF solutions with a pentane layer. Experimental procedures and parameters for the collection of diffraction data and the solution and refinement of the crystal structures are summarized in Table 3. Both structures were solved by direct methods and refined using SHELXTL PLUS (**7A**) and SHELXL-93 (**11A**) programs. Hydrogen atom positions were calculated and refined with fixed isotropic U using riding model techniques. The disorder of the C(9)−*t*Bu group in **7A** was resolved and refined isotropically with equal, unrestrained occupation factors. The disorder of THF molecules in **11A** was not resolved.

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Supporting Information Available: ^{1}H NMR spectra of **3A**, **7A**, **8B**, and **9A**; mass spectra of **8A** and **9A**; and tables of crystal data collection parameters, atom coordinates and U values, bond distances and angles, isotropic parameters and thermal ellipsoid plots for compounds **7A** and **11A** (28 pages). Ordering information is given on any current masthead page. This information is also available upon request from Fachinformationzentrum Karlsruhe, Eggenstein-Leopoldshafen, D-76344, upon quotation of the depository number CSD-59452, the names of the authors, and the journal reference for this article.

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