Zirconium Complexes Involving 2-Phosphorus-Substituted Indenyl Fragments

Denis N. Kazul'kin,[†] Alexey N. Ryabov,[†] Vyatcheslav V. Izmer,[†] Andrei V. Churakov,[‡] Irina P. Beletskaya,[†] Carol J. Burns,[§] and Alexander Z. Voskoboynikov*,[†]

Department of Chemistry, Moscow State University, Leninskie Gory, GSP-2, Moscow, 119992, Russian Federation, N. S. Kurnakov Institute of General and Inorganic Chemistry, 31 Leninsky Avenue, Moscow, 119991, Russian Federation, and Los Alamos National Laboratory, Chemical Division MS J515, Los Alamos, New Mexico 87545

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A series of 2-R_2P-substituted indenes, where R_2P = Ph_2P, Cy_2P, $^iPr_2P$, and ^{t}Bu(H)P, were obtained via Pd-catalyzed reactions of 2-bromo-1*H*-indene (or 1*H*-inden-2-yl trifluoromethane sulfonate) with R_2PH/Et_3N. Analogous indenes bearing Me_2P, ^{t}Bu(Cl)P, and $^tBu_2P$ substituents at position 2 were obtained through the reaction of 1*H*-inden-2-ylphosphonous dichloride with MeLi, ^{t}BuMgCl, and ^{t}BuMgCl/^{t}BuLi−CuCN, respectively. Diethyl 1*H*-inden-2-ylphosphonate, prepared via the Ni-catalyzed Arbuzov reaction of 2-bromo-1*H*-indene with $P(OEt)_3$, was found to be a convenient starting material for the synthesis of 2-H_2P-substituted indene. 1*H*-Inden-2-yl(phenyl)phosphine, prepared via the Pd-catalyzed arylation of 2-H_2P-substituted indene by PhI, turned out to react with 2-bromo-1*H*-indene in the presence of $Pd(PPh_3)_4$ and Et_3N to form di(1*H*-inden-2-yl)(phenyl)phosphine in almost quantitative yield. Analogously, di(1*H*-inden-2-yl)(*tert*-butyl)phosphine was prepared via catalytic reaction of $^tBuPH_2$ with 2 equiv of 2-bromo-1*H*-indene. Triethylamine-promoted condensation of indenes bearing P(H)^{t}Bu and P(Cl)^{t}Bu fragments gave a mixture of *cis*- and *trans*-bis-indenyldiphosphines. Zirconium complexes (2-R_2P-indenyl)$_2ZrCl_2$ (R_2P = Ph_2P, Me_2P, Cy_2P, $^iPr_2P$, $^tBu_2P$), as well as *ansa*-zirconocenes RP(2-indenyl)$_2ZrCl_2$ (R = Ph, ^{t}Bu), were obtained in good yields from $ZrCl_4(THF)_2$ and lithium salts of the respective 2-P-substituted indenes. *Ansa*-zirconocene (^tBuP)$_2$(2-indenyl)$_2ZrCl_2$ including a P_2R_2 bridge was synthesized in a similar manner and isolated as the pure *rac*-isomer.

Introduction

For the last two decades, the chemistry of group 4 metallocenes has exhibited a vigorous growth because of the outstanding catalytic properties of these compounds in olefin polymerization.[1] Zirconium complexes bearing more electron-rich cyclopentadienyl (indenyl, fluorenyl) ligands were shown to possess higher catalytic activity.[2] At the same time, well-designed metallocene precursors involving substituents and/or bridges in definite positions of cyclopentadienyl (indenyl, fluorenyl) fragments can result in highly stereospecific polymerization of propene and other α-olefins because of specific space blocking of the cationic zirconium center.[1,3,4] From these points of view, metallocenes including electron-rich organophosphorus(III) substituents in the cyclopentadienyl ring could be of particular importance. However, the synthesis of the respective indenyl ligands via the reaction of indenyllithium salts with organophosphorus(III) halides has some limitations. Only isomeric 1(3)-P-substituted indenes can be obtained in this manner,[5] while 2-alkyl(aryl)phosphino-substituted analogues are still inaccessible. Although analogous 2-aminoindenes can be readily obtained via simple condensation of indanone-2 with nucleophilic secondary amines (see, e.g., ref 6 and synthesis of the corresponding zirconocenes[7]), the respective indenylphosphines cannot be prepared in this manner. The only known pathway[8] to 2-P-substituted indenes, described by

* To whom correspondence should be addressed. E-mail: voskoboy@org.chem.msu.ru. Phone/fax: +7(095)939-4764.
[†] Moscow State University.
[‡] N. S. Kurnakov Institute of General and Inorganic Chemistry.
[§] Los Alamos National Laboratory.

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(8) Zirconium-mediated synthesis of the well-designed 2-Ph_2P-substituted indenes 2-(diphenylphosphino)-*N*-[(trimethylsilyl)methyl]-1*H*-inden-3-amine and *N*-(2,6-dimethylphenyl)-2-(diphenylphosphino)-1*H*-inden-3-amine is described in: Cadierno, V.; Zablocka, M.; Donnadieu, B.; Igau, A.; Majoral, J.-P.; Skowronska, A. *J. Am. Chem. Soc.* **1999**, *121*, 11086.

10.1021/om050236h CCC: $30.25
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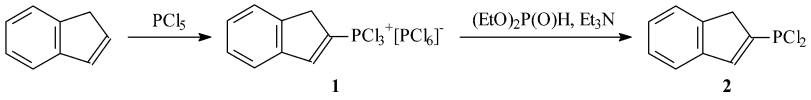
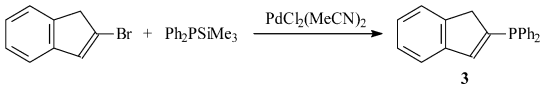
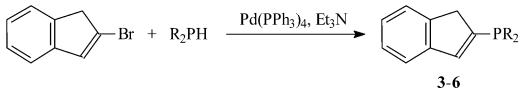
Scheme 1



Scheme 2



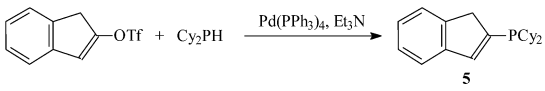
Scheme 3



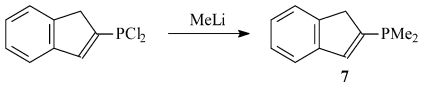
3-**6**

PR_2 = PPh_2 (**3**), P^iPr_2 (**4**), PCy_2 (**5**), P^tBu_2 (**6**)

Scheme 4



Scheme 5



Timokhin et al.,[9] is based on the reaction of indene with PCl_5 followed by reduction of trichloro(1*H*-inden-2-yl)-phosphonium hexachlorophosphate(1−) (**1**) by $(EtO)_2P(O)H$ in the presence of Et_3N (Scheme 1). This method results in pure 1*H*-inden-2-ylphosphonous dichloride, which then can be transferred into the desired 2-dialkyl(aryl)phosphino-substituted indenes using nucleophilic reagents, preferably with low basicity (see below) to exclude side metalation of the indenyl fragment.

This paper is aimed at the development of selective Pd-catalyzed and alternative routes to 2-alkyl(aryl)-phosphino-substituted indenes, as well as synthesis and characterization of zirconium complexes bearing these ligands.

Results and Discussion

Synthesis of 2-R_2P-Substituted Indenes (R = Alkyl, Aryl, H). For the synthesis of 2-R_2P-substituted indenes, we developed several synthetic procedures based on metal-catalyzed transformations of 2-bromo-1*H*-indene, as well as reaction of **2** with Grignard and organocopper reagents. Recently, Beletskaya and co-workers have shown that Pd-catalyzed coupling of vinyl bromides[10] with Ph_2PSiMe_3 results in the respective diphenylphosphinoethenes in good yield.[11] We have found that 2-bromo-1*H*-indene reacts with Ph_2PSiMe_3 in a manner similar to form 1*H*-inden-2-yl(diphenyl)-phosphine (**3**) in 89% yield (on the evidence of NMR spectroscopy) in the presence of 3 mol % of Pd(II) complex in benzene under reflux (Scheme 2). This colorless crystalline product was isolated in 65% yield after crystallization from ethanol.

It should be noted that an attempt to synthesize **3** using the Grignard reagent derived from 2-bromo-1*H*-indene failed.[12] On the evidence of NMR spectroscopy, this reaction with Ph_2PCl in ether at 0 °C gives **3** in as low as 6% yield along with ca. 70% of 1*H*-inden-3-yl-(diphenyl)phosphine. Taking into account this failure, we also applied an alternative catalytic approach to vinylphosphines requiring no preliminary synthesis of silylphosphine starting materials. Vinyl halides[11d,13] and triflates[13a,14] are known to react with Ph_2PH in the presence of Pd catalyst and base, such as trialkylamines or K_2CO_3, to form the respective cross-coupling products.[15] We found that this procedure can be applied for the synthesis of 2-R_2P-substituted indenes. Moreover, in this reaction besides Ph_2PH various dialkylphosphines can be used. In this way, the desired phosphinoindenes **3**−**5** were obtained in almost quantitative yields in the presence of 4 mol % of $Pd(PPh_3)_4$ and Et_3N in toluene under reflux (Scheme 3). However, on the evidence of ^{31}P NMR spectroscopy, sterically strained $^tBu_2PH$ gave di(*tert*-butyl)(1*H*-inden-2-yl)phosphine (**6**) in as low as 5% yield.

On the other hand, 1*H*-inden-2-yl trifluoromethanesulfonate was found to react readily with dicyclohexylphosphine to form indene **5** in almost quantitative yield (Scheme 4).

At the next stage of our research, we have found that, alternatively, 1*H*-inden-2-ylphosphonous dichloride (**2**) can be used to synthesize the desired 2-R_2P-substituted indenes. First, synthesis of **2** was improved; that is, trichlorosilane was used instead of $(EtO)_2P(O)H$ to reduce **1** (Scheme 1), so **2** was obtained in almost quantitative yield. Phosphine **2** was found to react readily with methyllithium in ether at −90 °C to give dimethyl(1*H*-inden-2-yl)phosphine (**7**) in almost quantitative yield also (Scheme 5).

Analogously, this starting material was successfully used to obtain **6**, which is practically unavailable via cross-coupling reaction of 2-bromoindene with $^tBu_2PH$ (see above). In this way, **2** and 1 equiv of ^{t}BuMgCl gave *tert*-butyl(1*H*-inden-2-yl)phosphinous chloride (**8**) and then the desired di(*tert*-butyl)(1*H*-inden-2-yl)phosphine applying the organocopper reagent (Scheme 6). The total

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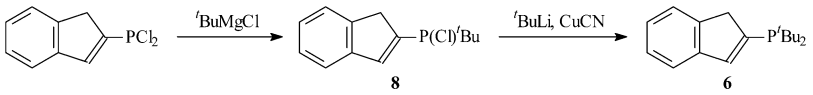
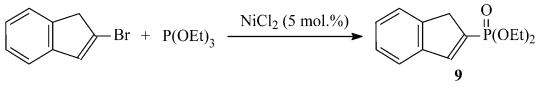
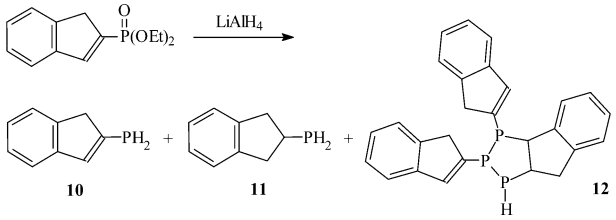
Scheme 6



Scheme 7



Scheme 8



yield of **6** from **2** was 27%. It should be noted that an alternative reaction of **2** with 2 equiv of Grignard or organolithium reagent resulted in very low yield of the desired products (**6** and **7**) because of side metalation of the indenyl fragment.

The other promising pathway to 2-R_2P-substituted indenes seems to be a $NiCl_2$-catalyzed Arbuzov reaction giving dialkyl vinylphosphonates from vinylbromides and trialkyl phosphites.[16] In this manner, we succeeded in the preparation of diethyl 1*H*-inden-2-ylphosphonate (**9**)[17] (Scheme 7), which was isolated in 75% yield as a yellowish oil.

Phosphonate **9** was reduced by an excess of $LiAlH_4$ in ether to give primary phosphine **10** (Scheme 8). The crude product distilled in vacuo was found to be a ca. 4:1 mixture of 1*H*-inden-2-ylphosphine (**10**) and 2,3-dihydro-1*H*-inden-2-ylphosphine (**11**). A careful fractional distillation of this mixture resulted in **10** of 93% purity, which was further used without additional purification. The overall yield of phosphines **10** and **11** was ca. 63%, so we decided to study other products of this reaction. One of them was isolated in 7% yield as a colorless crystalline solid using low-temperature crystallization from ether. This unusual compound **12** (Scheme 8), which was characterized by NMR spectroscopy and X-ray crystal structure analysis, includes a saturated P−P−P−C−C five-membered ring fused to a five-membered ring of indane. It should be noted that an alternative attempt to obtain **10**, of importance for *ansa*-metallocene synthesis (see below), via the reduction of **2** by $LiAlH_4$ failed.

The molecular structure of **12** is shown in Figure 1. In this structure, bond angles about phosphorus atoms

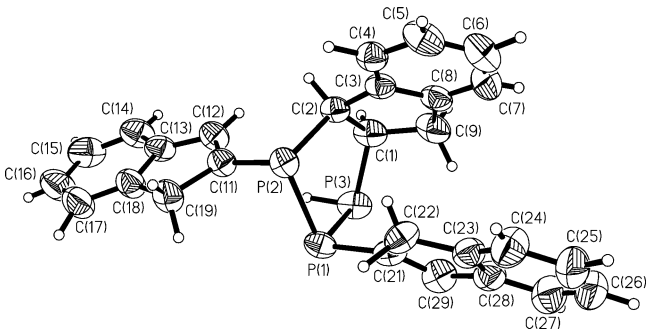
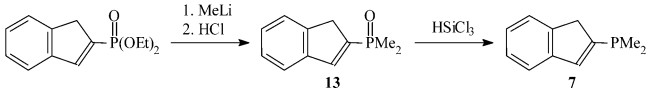


Figure 1. Crystal structure of **12**. Displacement ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) are P(1)−C(21) 1.819(5), P(1)−P(3) 2.205(2), P(1)−P(2) 2.211(2), P(2)−C(11) 1.805(4), P(2)−C(2) 1.879(4), P(3)−C(1) 1.864(4), P(3)−H(3) 1.30(3), C(1)−C(9) 1.537(8), C(1)−C(2) 1.568(6), C(1)−H(1) 0.96(4), C(2)−C(3) 1.497(6), C(2)−H(2) 1.04(4).

range within 87(2)−104.2(2)°. The P−P distances (2.205(2), 2.211(2) Å) are close to their ordinary value, 2.214 Å.[18] The P(2)−C(2) and P(3)−C(1) bond lengths (1.879(4) and 1.864(4) Å) are noticeably longer than P(1)−C(21) and P(2)−C(11) (1.819(5) and 1.805(4) Å) due to the different hybridization states of the carbon atoms involved (sp^3 and sp^2, respectively). All three inde(a)nyl fragments are planar within 0.05 Å.

Reaction of phosphonate **9** with 2 equiv of MeLi in ether followed by reduction by trichlorosilane gave dimethyl(1*H*-inden-2-yl)phosphine (**7**) in 29% total yield (Scheme 9). Thus, this synthetic pathway is inferior to

Scheme 9



the procedure using **2** and methylcuprate as starting materials (see above). The intermediate product, 1*H*-inden-2-yl(dimethyl)phosphine oxide (**13**), in the form of its HCl−H_2O solvate, was characterized by X-ray crystal structure analysis (Figure 2). The indenyl fragment of this compound is planar within 0.008 Å. The phosphorus atom lies on the indenyl plane (the sum of bond angles at carbon atom C(8) is 360.0°) and has a distorted tetrahedral configuration due to the formation by the hydroxyl group of a hydrogen bond with a solvate water molecule. In this hydrogen bond, the water molecule takes part as the acceptor, but it also forms

(15) (a) Herd, O.; Hessler, A.; Hingst, M.; Tepper, M.; Stelzer, O. *J. Organomet. Chem.* **1996**, *522*, 69. (b) Herd, O.; Hessler, A.; Hingst, M.; Machnitzki, P.; Tepper, M.; Stelzer, O. *Catal. Today* **1998**, *42*, 413. (c) Machnitzki, P.; Nickel, T.; Stelzer, O.; Landgrafe, C. *Eur. J. Inorg. Chem.* **1998**, 1029. (d) Hillhouse, J. H.; Depalo, M. WO Patent Application 0069866 for Cytec Technology Corp. (e) Hessler, A.; Kottsieper, K. W.; Schenk, S.; Tepper, M.; Stelzer, O. *Z. Naturforsch., B: Chem. Sci.* **2001**, *56*, 347. (f) Brauer, D. J.; Hingst, M.; Kottsieper, K. W.; Liek, Ch.; Nickel, T.; Tepper, M.; Stelzer, O.; Sheldrick, W. S. *J. Organomet. Chem.* **2002**, *645*, 14. (g) Hillhouse, J. H. WO Patent Application 0192276 for Cytec Technology Corp. (h) Hesser, A.; Stelzer, O. *J. Org. Chem.* **1997**, *62*, 2362. (i) Kumobayashi, H.; Miura, T.; Sayo, N.; Saito, T.; Zhang, X. *Synlett* **2001**, 1055. (k) Birdsall, D. J.; Hope, E. G.; Suart, A. M.; Chen, N.; Hu, Y.; Xiao, J. *Tetrahedron Lett.* **2001**, *42*, 8551. (l) Kraatz, H.-B.; Pletsch, A. *Tetrahydron: Asymmetry* **2000**, *11*, 1617, and references therein.

(16) (a) Tavs, P.; Weitkamp, H. *Tetrahedron* **1970**, *26*, 5529. (b) Honig, M. L.; Martin, D. M. *Phosphorus* **1974**, *4*, 63. (c) Tavs, P. *Chem. Ber.* **1970**, *103*, 2428. (d) Maier, L. *Phosphorus* **1973**, *3*, 19.

(17) Synthesis of this phosphonate can be also achieved by alcoholysis of trichloro(1*H*-inden-2-yl)phosphonium hexachlorophosphate-(1−) resulting from the reaction between indene and PCl_5 as described in: Pieroni, O. I.; Rodriguez, N. M.; Vuano, B. M.; Cabaleiro, M. C. *J. Chem. Res., Synop.* **1993**, 22.

(18) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.

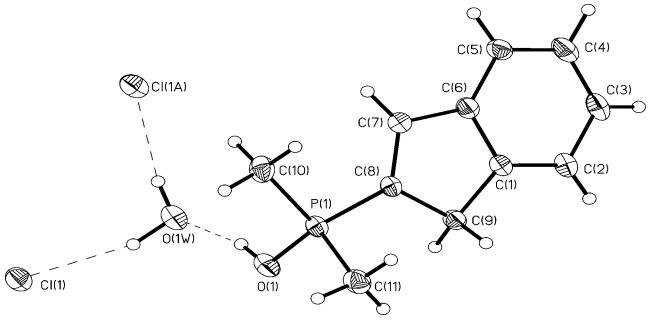
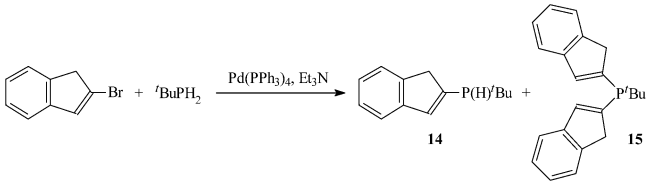


Figure 2. Crystal structure of **13**·HCl·H_2O (ellipsoids are drawn at the 50% probability level); hydrogen bonds are shown by dotted lines. Selected bond lengths (Å) are P(1)−O(1) 1.5439(12), P(1)−C(8) 1.7634(14), P(1)−C(11) 1.7775(16), P(1)−C(10) 1.7784(15), O(1)−H(1O) 0.90(4), C(1)−C(9) 1.5023(19), C(5)−C(6) 1.3969(19), C(6)−C(7) 1.4556(19), C(7)−C(8) 1.3523(19), C(8)−C(9) 1.5097(18).

Scheme 10



two hydrogen bonds with two chlorine anions as the donor.

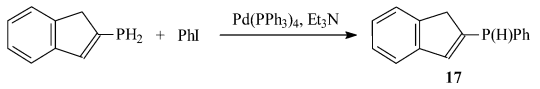
Thus, phosphonate **9** is a good starting material for obtaining primary indenylphosphine **10**, of importance for synthesizing further bridging indenyl ligands (see below).

Synthesis of Di(indenyl)phosphines. Actually, synthesis of alkyl- and aryldi(indenyl)phosphines can be achieved using metal-catalyzed reactions of 2 equiv of 2-bromo-1*H*-indene with primary phosphines. No examples of similar reactions with vinyl halides have been described so far. Moreover, the respective Pd-catalyzed reactions of primary phosphines with aryl halides proceed slowly and were only applied either for aryliodides[15a−f] or primary alkylphosphines.[15g]

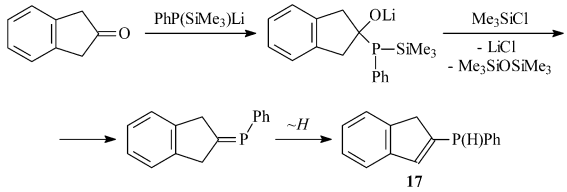
In this study, we found that ^{t}BuPH$_2$ reacts readily with 2-bromo-1*H*-indene in the presence of 5 mol % of Pd(PPh$_3$)$_4$ and Et$_3$N to form both mono- and disubstitution products in a ratio that depends strongly on the reagent ratio used (Scheme 10). On the evidence of ^{31}P NMR spectroscopy, *tert*-butyl(1*H*-inden-2-yl)phosphine (**14**) was formed in 79% yield for a 1 to 1.1 ratio of 2-bromo-1*H*-indene to the primary phosphine, whereas *tert*-butyl[di(1*H*-inden-2-yl)]phosphine (**15**) was formed in 21% yield in this case. The secondary phosphine **14** was isolated using fractional distillation in 31% yield only, probably because of its partial decomposition during the distillation. Alternatively, 2 equiv of 2-bromo-1*H*-indene and ^{t}BuPH$_2$ gave **15** in almost quantitative yield (^{31}P NMR). In this case, *tert*-butyl[di(1*H*-inden-2-yl)]phosphine was isolated in 85% yield in analytically pure form.

For the synthesis of the analogous compound involving a PPh fragment, i.e., di(1*H*-inden-2-yl)(phenyl)-phosphine (**16**), we used the alternative approach. The reason for this decision was that, unfortunately, primary aryl(vinyl) phosphines and the respective TMS derivatives, such as PhPH$_2$, phosphine **10**, PhP(H)SiMe$_3$, and

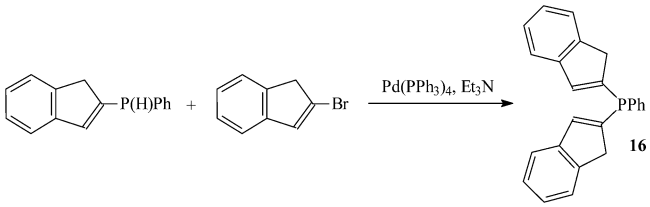
Scheme 11



Scheme 12



Scheme 13



PhP(SiMe$_3$)$_2$, turned out to not react with 2-bromo-1*H*-indene in the presence of Pd(PPh$_3$)$_4$, PdCl$_2$(MeCN)$_2$, or Ni(acac)$_2$.[19] On the other hand, we found that **10** is a good starting material for the synthesis of 1*H*-inden-2-yl(phenyl)phosphine (**17**). The arylation of **10** with PhI in the presence of 5 mol % of Pd(PPh$_3$)$_4$ and Et$_3$N gave **17** in 95% yield (Scheme 11).

To develop a less time-consuming procedure for synthesizing secondary phosphine **17**, we studied the reaction of indanone-2 with PhP(SiMe$_3$)Li. Von Becker et al. have shown that analogous reaction of lithium salts of trimethylsilylphosphines with ketones followed by treatment with Me$_3$SiCl gives thermodynamically unstable methylidenephosphines.[20] We found that the only phosphorus-containing product of the similar reaction of indanone-2 was secondary phosphine **17** (Scheme 12), which on the evidence of ^{31}P NMR spectroscopy was formed in as low as 10% yield, probably via rearrangement of unstable 1,3-dihydro-2*H*-inden-2-ylidene-(phenyl)phosphine. This low yield for the unoptimized procedure seems to result from slow addition of PhP-(SiMe$_3$)Li to indanone-2.

Next, the secondary phosphine **17** was found to react with 2-bromo-1*H*-indene in the presence of 5 mol % of Pd(PPh$_3$)$_4$ and Et$_3$N under reflux (Scheme 13). This Pd-catalyzed vinylation of the P−H bond of **17** gave the desired phosphine **16** in almost quantitative yield (^{31}P NMR). Analytically pure product was isolated in 58% yield after crystallization from ethanol.

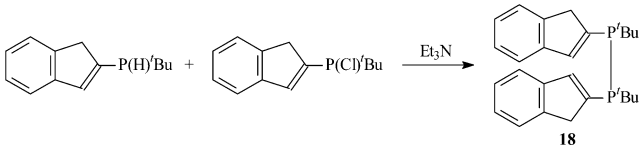
One more bis-indenyl ligand bearing a diphosphine fragment in position 2 that is of interest for *ansa*-metallocene synthesis was obtained using the well-known triethylamine-promoted condensation of P−H and P−Cl substrates.[21] In this way, diphosphine **18** was obtained in 51% yield from **8** and **14** (Scheme 14). On the evidence of NMR spectroscopy, this product consists

(19) A formation of traces of both **16** and **17** was detected by NMR spectroscopy in the case of PhPH$_2$ and PhP(H)SiMe$_3$.

(20) von Becker, G.; Uhl, W.; Wessely, H. J. *Z. Anorg. Allg. Chem.* **1981**, *479*, 41.

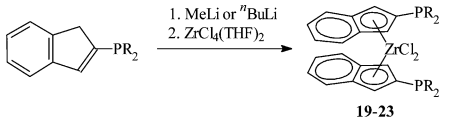
(21) (a) Kuchen, W.; Buchwald, H. *Chem. Ber.* **1958**, *91*, 2871. (b) *Inorganic reactions and methods*; Zuckerman, J. J., Ed.; VCH: New York, 1988; Vol. 7, p 17; and references therein.

Scheme 14



18

Scheme 15



19-23

PR_2 = PPh_2 (**19**), PMe_2 (**20**), P^iPr_2 (**21**), PCy_2 (**22**), P^tBu_2 (**23**)

of two isomers, i.e., *d*-/*l*- and *meso*-1,2-di-*tert*-butyl-1,2-di(1*H*-inden-2-yl)diphosphines. This seems to result from the known hindered inversion at phosphorus in phosphines.[22]

Synthesis and Molecular Structures of Zirconocenes. Zirconocenes **19**−**23** bearing 2-R_2P-substituted indenyl ligands were obtained using the exchange reaction between $ZrCl_4(THF)_2$ and the respective lithium-indenyls in ether (Scheme 15). Complexes **19** and **22** were precipitated from saturated toluene solutions on addition of hexanes and isolated in 58 and 47% yields, respectively. Crystals of zirconocene **21** were obtained in 43% yield from ether solution at −30 °C. Analogously, zirconocenes **20** and **23** bearing PMe_2 and P^tBu_2 fragments were isolated in 61 and 64% yields using low-temperature crystallization from toluene−hexanes and toluene, respectively.

Zirconium complex **22** bearing Cy_2P substituents was characterized by X-ray crystal structure analysis (Figure 3). The zirconium atom of this molecule has a distorted pseudotetrahedral coordination, with the distances to the centers of the cyclopentadienyl rings being 2.234(1) and 2.243(1) Å, respectively. The angle Cp_1−Zr(1)−Cp_2 is 132.0(1)°. The Zr−Cl bond lengths (2.4132(7) and 2.4178(7) Å) are close to their ordinary value.[23] The phosphorus atoms are trigonal-pyramidal with stereochemically active lone pairs. The indenyl fragments are planar within 0.026 Å. The angle between the indenyl planes is 55.5°, and the angle Cp_1−Zr(1)−Cp_2 is 132.0°. The five-membered cycles of the indenyl fragments are disposed in the staggered conformation with respect to each other. The phosphorus atoms lie on the indenyl planes (the sums of the bond angles at carbon atoms C(1) and C(10) are 359.5° and 360.0°, respectively), which indicates the absence of geometric strains in ligands. The cyclohexyl substituents have the chair conformation. The molecule **22** has the intrinsic symmetry C_2 (a 2-fold axis passes through the Zr(1) atom and the middle of the Cl(1)···Cl(2) length), which is not realized in the crystal (space group $P\bar{1}$).

Zirconocene **24**, involving Cp* and indenyl bearing a 2-Cy_2P fragment, was synthesized from Cp^*ZrCl_3 and lithium salt of **5** in toluene as shown below (Scheme 16). This complex was isolated in 67% yield as a yellowish

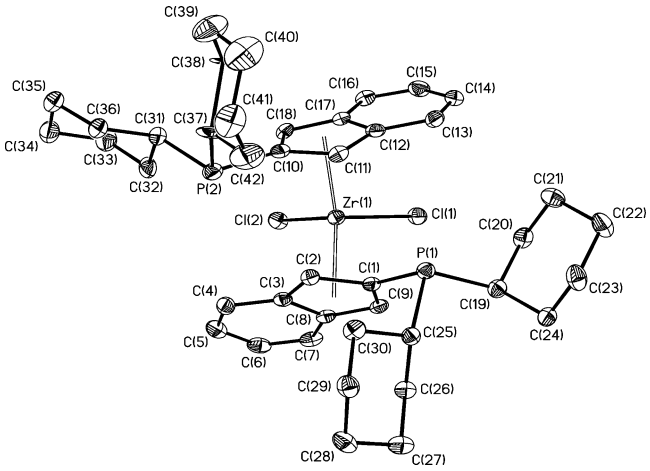
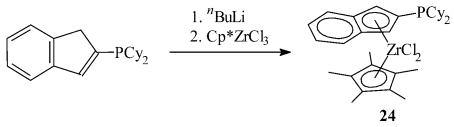


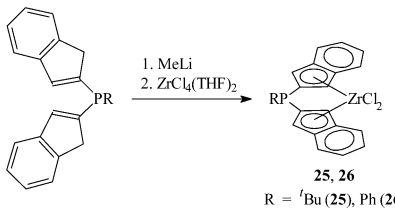
Figure 3. Crystal structure of **22**. Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) are Zr(1)−Cl(1) 2.4132(7), Zr(1)−Cl(2) 2.4178(7), Zr(1)−C(1) 2.518(2), Zr(1)−C(2) 2.455(2), Zr(1)−C(3) 2.562(2), Zr(1)−C(8) 2.610(2), Zr(1)−C(9) 2.554(2), Zr(1)−C(10) 2.543(2), Zr(1)−C(11) 2.472(3), Zr(1)−C(12) 2.578(2), Zr(1)−C(17) 2.594(2), Zr(1)−C(18) 2.560(2), P(1)−C(1) 1.838(2), P(1)−C(19) 1.873(3), P(1)−C(25) 1.866(2), P(2)−C(10) 1.836(3), P(2)−C(31) 1.862(3), P(2)−C(37) 1.86(2), P(2)−C(37′) 1.900(17).

Scheme 16



24

Scheme 17



25, **26**

R = ^{t}Bu (**25**), Ph (**26**)

crystalline solid through low-temperature crystallization from toluene.

Ansa-zirconocenes **25** and **26** of C_s symmetry including RP bridges in position 2 of indenyls[24] were prepared from $ZrCl_4(THF)_2$ and dilithium salts of **15** and **16**, respectively (Scheme 17). The complexes were isolated in analytically pure form in 56 and 36% yields by low-temperature crystallization from toluene and toluene−hexanes, respectively.

Ansa-zirconocene **25**, including a ^{t}BuP bridge, was characterized by X-ray crystal structure analysis (Figure 4). The zirconium atom has a distorted pseudotetrahedral coordination, with the distances to the centers of the cyclopentadienyl rings being 2.225(1) and 2.219(1) Å, respectively. The Zr−Cl bond lengths (2.414(1) and 2.429(1) Å) are close to their ordinary value.[23] The phosphorus atom is trigonal-pyramidal with a stereochemically active lone pair. The indenyl fragments are planar within 0.021 and 0.024 Å, respectively. The angle between the indenyl planes is 70.7°,

(22) Inversion at phosphourus is slow, as shown in: (a) Baechler, R. D.; Mislow, K. *J. Am. Chem. Soc.* **1970**, *92*, 3090. (b) Rauk, A.; Allen, L. C.; Mislow, K. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 400.

(23) Cambridge Crystallographic Data Base. Cambridge, release 2003.

(24) *Ansa*-zirconocenes with RP bridges and cationic *ansa*-complexes with R_2P bridges were described in the following papers.[5,7,25]

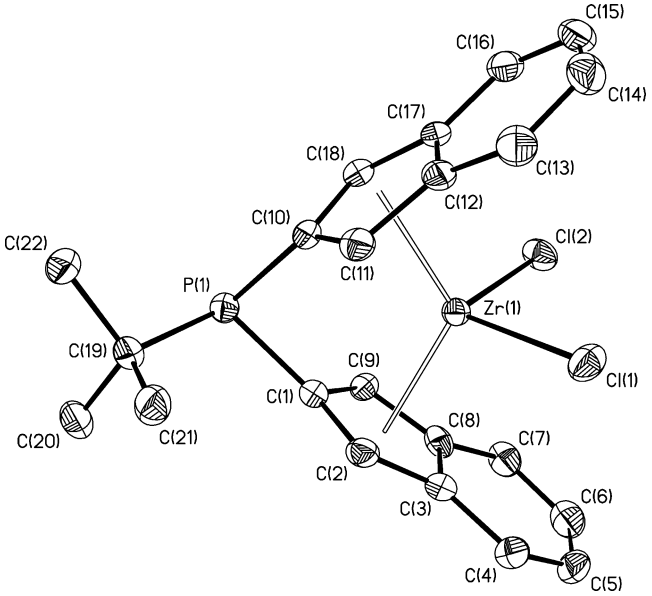
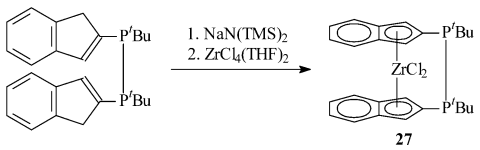


Figure 4. Crystal structure of **25**. Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) are Zr(1)−Cl(1) 2.4140(11), Zr(1)−Cl(2) 2.4293(11), Zr(1)−C(1) 2.461(4), Zr(1)−C(2) 2.458(4), Zr(1)−C(3) 2.623(4), Zr(1)−C(8) 2.623(4), Zr(1)−C(9) 2.496(3), Zr(1)−C(10) 2.458(4), Zr(1)−C(11) 2.447(4), Zr(1)−C(12) 2.620(4), Zr(1)−C(17) 2.625(3), Zr(1)−C(18) 2.492(4), P(1)−C(1) 1.838(4), P(1)−C(10) 1.834(4), P(1)−C(19) 1.864(4).

Scheme 18



27

and the Cp_1−Zr(1)−Cp_2 angle is 122.7°. Unlike molecule **22**, the five-membered cycles of the indenyl fragments are disposed in the eclipsed conformation with respect to each other. The phosphorus atoms are not located in the indenyl planes (the sums of the bond angles at carbon atoms C(1) and C(10) are 356.7° and 356.5°, respectively) due to geometric strain in the ligand (the bond angle C(1)−P(1)−C(10) is 90.3(2)°). Molecule **25** has the intrinsic symmetry C_s (a mirror plane passes through the Zr(1), Cl(1), Cl(2), P(1), C(19), and C(21) atoms), which is not realized in the crystal (space group $P2_1/c$).

Finally, ansa-zirconocene **27** including a P(tBu)P(tBu) bridge was synthesized from disodium salt of **18** and $ZrCl_4(THF)_2$ in ether and isolated in 52% yield by low-temperature crystallization from toluene (Scheme 18). In this case, $NaN(TMS)_2$ instead of nucleophilic lithium alkyls was used to metalate **18** to exclude possible nucleophilic cleavage of the P−P bond.[26] Interestingly, the isolated complex is pure *rac*-isomer with *anti* configuration of ^{t}Bu groups, as confirmed by NMR spectroscopy and X-ray crystal structure analysis (Figure 5).[27] Since the inversion of phosphorus in this compound should not occur,[22] the interconversion of *meso*- and *rac*-isomers cannot take place. The isolation of pure *rac*-isomer seems to be accounted for by lower solubility of this isomer as compared to the *meso*-isomer. It should also be taken into account that the *meso*-isomer is less stable due to unfavorable steric repulsion of ^{t}Bu groups.

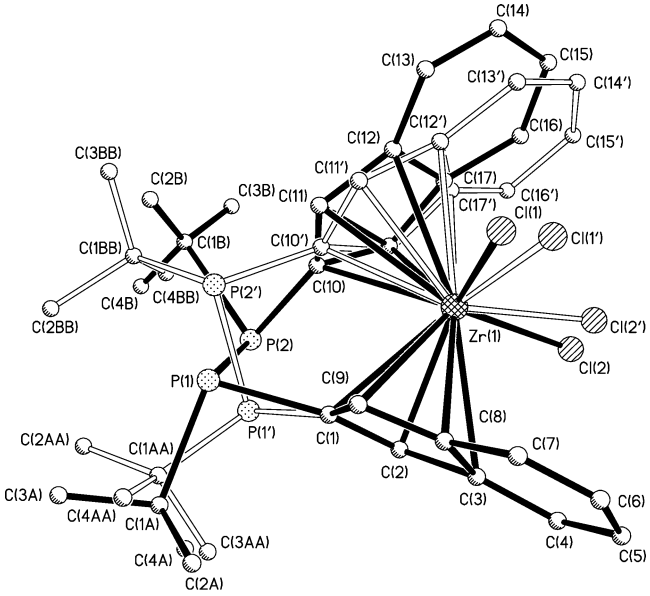


Figure 5. PLUTO view of **27**. Hydrogen atoms are omitted for clarity.

The structure of compound **27** was confirmed by X-ray diffraction studies. In the structure of **27**, chlorine atoms, one of the indenyl ligands, and the bridging ^{t}Bu−P−P−^{t}Bu moiety were found to be disordered over two positions with approximately equal occupancies (Figure 5). This is related to rotation of the indenyl ligand as well as chlorine atoms with respect to the zirconium atom so that the chlorine atoms are rotated by ca. 20°, while disordered indenyl fragments are rotated by ca. 7° in the aromatic plane and inclined at 10°. This leads to disordering of the P(^{t}Bu)−P(^{t}Bu) fragments. It might be suggested that such disorder is caused by the sterical effects. In general, the structure of **27** is typical for *ansa*-bisindenyl complexes. However, the low precision of determined parameters prevents the detailed discussion of its geometry.

Preliminary polymerization results[29] show a relatively low ethylene polymerization activity for **19** and **21**/MAO (Table 1) to give high molecular weight polyethylene, particularly, in the case of the last catalytic system

(25) (a) Leyser, N.; Schmidt, K.; Brintzinger, H.-H. *Organometallics* **1998**, *17*, 2155. (b) Shin, J. H.; Hascall, T.; Parkin, G. *Organometallics* **1999**, *18*, 6. (c) Hap, M.; Gilles, T.; Kruck, T.; Tebbe, K.-F. *Z. Naturforsch., B* **1999**, *54*, 482. (d) Shin, J. H.; Bridgewater, B. M.; Parkin, G. *Organometallics* **2000**, *19*, 5155.

(26) Maier, L. In *Organic Phosphorous Compounds*; Kosolapoff, G. M., Maier, L., Eds.; Wiley: New York, 1972−1974; Vol. 1, Chapter 2.

(27) Detailed description of structure of **27** as well as the respective experimental details will be published elsewhere.

(28) Olefin polymerization in the presence of "open" and *ansa*-zirconocenes bearing phosphorus-substituted cyclopentadienyl ligands was described in: (a) Gobley, O.; Meunier, P.; Gautheron, B.; Gallucci, J. C.; Erker, G.; Dahlmann, M.; Schloss, J. D.; Paquette, L. A. *Organometallics* **1998**, *17*, 4897. (b) Alt, H. G.; Jung, M. *J. Organomet. Chem.* **1998**, *568*, 127. (c) Schaverien, C. J.; Ernst, R.; Terlouw, W.; Schut, P.; Sudmeijer, O.; Budzelaar, P. H. M. *J. Mol. Catal. A* **1998**, *128*, 245. (d) Shin, J. H.; Hascall, T.; Parkin, G. *Organometallics* **1999**, *18*, 6. (e) Antinolo, A.; Fernandez-Galan, R.; Orive, I.; Otero, A.; Prashar, S. *Eur. J. Inorg. Chem.* **2002**, 2470.

(29) (a) MacDowell, D. W. H.; Lindley, W. A. *J. Org. Chem.* **1982**, *47*, 705. (b) McEwen, I.; Rönnqvist, M.; Ahlberg, P. *J. Am. Chem. Soc.* **1993**, *115*, 3989. (c) Halterman, R. L.; Fahey, D. R.; Bailly, E. F.; Dockter, D. W.; Stenzel, O.; Shipman, J. L.; Khan, M. A.; Dechert, S.; Schumann, H. *Organometallics* **2000**, *19*, 5464.

Table 1. Ethylene Polymerization (PE) and Ethylene/Octane-1 Copolymerization (PEO) Results for 19, 21, and 25

metallocene	run type[a]	activity, g/mmol h·atm	M_w	M_n	PDI	comonomer wt %	mp, °C
19	PE	600	532,000	239,000	2.23		
21	PE	540	1,374,000	484,000	2.84		
25	PE	64,050	6,130	4,260	1.44		130
25	PEO[b]	76,300	6,030	4,160	1.45	6.1	97

[a] 0.02 μmol of zirconocene, 9.98 μmol of MAO ([Zr]/[Al] = 1/500), 3.97 mL of toluene, 80 °C, 5 atm of ethylene. [b] 638 μmol of octene-1.

based on the metallocene bearing 2-diisopropylphosphinoindenyl ligands. On the other hand, the catalyst **25**/MAO involving *ansa*-zirconocene with a P^{t}Bu bridge (Table 1) exhibits very high activity in ethylene polymerization and ethylene/octene-1 copolymerization producing low molecular weight polymers.

In conclusion, we elaborated straightforward methods, including Pd-catalyzed pathways, to synthesize dialkyl/aryl/inden-2-yl- and alkyl/aryl/diinden-2-ylphosphines, as well as 1,2-di-*tert*-butyl-1,2-di(1*H*-inden-2-yl)-diphosphane, of importance for developing new families of olefin polymerization catalysts. Preliminary studies showed that the zirconocenes obtained are active catalysts of ethylene polymerization and ethylene/octane-1 copolymerization.

Experimental Section

All manipulations were performed either in an atmosphere of thoroughly purified argon using the standard Schlenk technique or in a controlled atmosphere glovebox (VAC). Tetrahydrofuran and ether for synthesis were purified by distillation over $LiAlH_4$ and kept over sodium benzophenone ketyl or Na/K alloy. Hydrocarbon solvents (including benzene-d_6 for NMR measurements) were distilled and stored over CaH_2 or Na/K alloy. Methylene chloride-d_2 was distilled and stored over CaH_2. Chloroform-d was distilled over P_4O_{10} and stored over molecular sheves (3 Å). Iodobenzene (Acros), indene, tech. (Acros), Ph_2PH (Strem), $PhPH_2$ (Strem), Cy_2PH (Strem), triethyl phosphite (Acros), $LiAlH_4$ (Aldrich), CuCN (Merck), PCl_5 (Merck), $HSiCl_3$ (Aldrich), triethylamine (Acros), $NaN(TMS)_2$ (Aldrich), ^{n}BuLi in hexanes (Chemetall), MeLi in ether (Aldrich), ^{t}BuLi in pentane (Acros), and ^{t}BuMgCl in ether (Aldrich) were used as obtained. Triethylamine (Acros) was dried with CaH_2, then was distilled from sodium. 2-Bromo-1*H*-indene,[29] 1*H*-inden-2-yl trifluoromethanesulfonate,[30] $PdCl_2(MeCN)_2$,[31] $Pd(PPh_3)_4$,[32] $ZrCl_4(THF)_2$,[33] ^{i}Pr$_2$PH,[34] ^{t}Bu$_2$PH,[34] ^{t}BuPH$_2$,[35] and Ph_2PSiMe_3[36] were prepared according to the published methods. Celite 403 (Fluka) was dried in a vacuum for 20 h at 200 °C. ^{1}H, ^{13}C, and ^{31}P spectra were recorded with Varian VXR-400 or Bruker DPX-300 spectrometers for 1−10% solutions in deuterated solvents. Chemical shifts for ^{1}H and ^{13}C were measured relative to TMS. In ^{1}H NMR spectra, the assignment was made on the evidence of double resonance and NOE experiments. Chemical shifts for ^{31}P were measured relative to H_3PO_4. C, H microanalyses were done using a CHN-O-Rapid analyzer (Heracus).

Trichloro(1*H*-inden-2-yl)phosphonium Hexachlorophosphate(1−) (1). To a suspension of 154 g (0.74 mol) of PCl_5 in 200 mL of toluene was added a solution of 48.2 mL (43.0 g, 0.37 mol) of indene (tech., 90%) in 30 mL of toluene under vigorous stirring (mechanical stirrer) for 30 min at 0 °C. The resulting mixture was stirred for 10 h at ambient temperature. Then, the precipitate was filtered off (G3), washed with 3 × 50 mL of hexanes, and dried in a vacuum. Yield: 165 g (90%) of a white solid, which was further used without additional purification.

1*H*-Inden-2-ylphosphonous Dichloride (2). To a suspension of 4.96 g (10 mmol) of **1** in 50 mL of toluene was added 2.22 mL (2.98 g, 22 mmol) of $HSiCl_3$ at ambient temperature. This mixture was refluxed for 6 h to form a clear yellow solution. Volatile components were distilled off at 50 °C, and the yellow oil formed was dried in a vacuum at this temperature. The crystalline material formed was pure **2**. Yield: 2.17 g (99%). Anal. Calcd for $C_9H_7Cl_2P$: C, 49.81; H, 3.25. Found: C, 49.67; H, 3.18. ^{1}H NMR (C_6D_6): δ 7.14−7.17 (m, 4H, 4,5,6,7-H), 6.92 (dt, J = 8.1 Hz, J = 1.7 Hz, 1H, 3-H), 3.61 (d, J = 1.7 Hz, 2H, 1,1′-H). ^{13}C{^{1}H} NMR (C_6D_6): δ 147.2 (d, J = 54.9 Hz), 145.9 (d, J = 2.8 Hz), 144.1 (d, J = 54.9 Hz), 142.2 (d, J = 12.2 Hz), 127.8, 127.0, 124.3, 123.2, 37.9. ^{31}P{^{1}H} NMR (C_6D_6): δ 151.4.

1*H*-Inden-2-yl(diphenyl)phosphine (3). Method A. To 5.18 g (0.026 mol) of 2-bromo-1*H*-indene and 1.02 g (0.88 mmol) of $Pd(PPh_3)_4$ in 20 mL of toluene were added 4.2 mL (3.05 g, 0.030 mol) of Et_3N and then 4.93 g (0.027 mol) of Ph_2PH. This mixture was refluxed for 17 h, cooled to room temperature, and passed through a short column with silica gel using 350 mL of toluene as eluent. The resulting solution was evaporated to dryness. The crude product was crystallized from ethanol. Yield: 6.20 g (76%) of white crystals of **3**. Anal. Calcd for $C_{21}H_{17}P$: C, 83.98; H, 5.71. Found: C, 83.90; H, 5.63. ^{1}H NMR ($CDCl_3$): δ 7.30−7.47 (m, 13H, 4,5,7-H in indenyl and PPh_2), 7.24 (m, 1H, 6-H in indenyl), 7.15 (dt, J = 7.3 Hz, J = 1.2 Hz, 1H, 3-H in indenyl), 3.43 (m, 2H, 1,1′-H in indenyl). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 146.1 (d, J = 6.1 Hz), 145.2 (d, J = 12.2 Hz), 144.6 (d, J = 7.6 Hz), 140.6 (d, J = 16.8 Hz), 136.8 (d, J = 9.2 Hz), 133.6 (d, J = 19.8 Hz), 128.7 (d, J = 27.5 Hz), 128.5, 126.5, 125.1, 123.6, 121.0, 42.0 (d, J = 13.7 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 0.3.

Method B. To a mixture of 5.18 g (26.0 mmol) of 2-bromo-1*H*-indene and 0.20 g (0.78 mmol) of $Pd(MeCN)_2Cl_2$ in 20 mL of toluene was added 7.23 g (28.0 mmol) of Ph_2PSiMe_3 at ambient temperature. This mixture was refluxed for 20 h and then cooled to ambient temperature and evaporated to dryness in a vacuum. The residue was recrystallized from hot ethanol. Yield: 5.07 g (65%) of colorless crystalline product. Anal. Found: C, 83.72; H, 5.59.

1*H*-Inden-2-yl(diisopropyl)phosphine (4). Following the procedure described for the synthesis of **1** (method A) from Ph_2PH, 15.81 g (0.081 mol) of 2-bromo-1*H*-indene, 9.54 g (0.081 mol) of ^{i}Pr$_2$PH, 13.9 mL (10.09 g, 0.100 mol) of Et_3N, and 2.95 g (2.55 mmol) of $Pd(PPh_3)_4$ in 60 mL of toluene gave the title compound. The crude product was distilled in a vacuum (104−106 °C/2 mmHg). Yield: 14.8 g (80%) of colorless oil of **4**. Anal. Calcd for $C_{15}H_{21}P$: C, 77.55; H, 9.11. Found: C, 77.68; H, 9.18. ^{1}H NMR (C_6D_6): δ 7.35 (m, 1H, 7-H in indenyl), 7.31 (m, 1H, 4-H in indenyl), 7.22 (m, 1H, 5-H in indenyl), 7.17 (m, 1H, 6-H in indenyl), 7.15 (dt, J = 7.3 Hz, J = 1.2 Hz, 3-H in indenyl), 3.35 (m, 2H, 1,1′-H in indenyl), 1.89 (d-sept, J = 7.0 Hz, J = 2.3 Hz, 2H, CHMe$_2$), 1.10 (dd, J = 14.7 Hz, J = 7.0 Hz, 6H, CHMe_2), 0.97 (dd, J = 11.7 Hz, J = 7.0 Hz, 6H,

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CH*Me*$_2$*). ^{13}C{^{1}H} NMR (C_6D_6): δ 146.1 (d, J = 3.1 Hz), 145.0 (d, J = 10.7 Hz), 144.7 (d, J = 24.4 Hz), 142.4 (d, J = 25.9 Hz), 126.7, 125.2, 123.8, 121.2, 42.8 (d, J = 4.6 Hz), 23.8 (d, J = 12.2 Hz), 20.4 (d, J = 18.3 Hz), 20.0 (d, J = 10.7 Hz). ^{31}P-{^{1}H} NMR (C_6D_6): δ 14.9.

Dicyclohexyl(1*H*-inden-2-yl)phosphine (5). Method A. Following the procedure described for the synthesis of **1** (method A) from Ph_2PH, 13.02 g (0.067 mol) of 2-bromo-1*H*-indene, 12.84 g (0.065 mol) of Cy_2PH, 10.3 mL (7.48 g, 0.074 mol) of Et_3N, and 1.55 g (1.34 mmol) of $Pd(PPh_3)_4$ in 50 mL of toluene gave the title compound. The crude product was crystallized from ethanol. Yield: 15.33 g (76%) of yellowish crystals of **5**. Anal. Calcd for $C_{21}H_{29}P$: C, 80.73; H, 9.36. Found: C, 80.41; H, 9.45. ^{1}H NMR (C_6D_6): δ 7.33 (m, 1H, 7-H in indenyl), 7.28 (m, 1H, 4-H in indenyl), 7.15−7.23 (m, 2H, 5,6-H in indenyl), 7.12 (dt, J = 7.3 Hz, J = 1.2 Hz, 1H, 3-H in indenyl), 3.38 (m, 2H, 1,1′-H in indenyl), 1.02−1.98 (m, 20H, PCy_2). ^{13}C{^{1}H} NMR (C_6D_6): δ 146.2, 145.2 (d, J = 10.7 Hz), 144.7 (d, J = 24.4 Hz), 142.8 (d, J = 29.0 Hz), 126.8, 125.2, 123.8, 121.2, 42.9 (d, J = 3.1 Hz), 33.8 (d, J = 11.8 Hz), 30.9 (d, J = 15.3 Hz), 30.4 (d, J = 9.2 Hz), 27.5 (d, J = 12.0 Hz), 27.4 (d, J = 7.6 Hz). ^{31}P{^{1}H} NMR (C_6D_6): δ 5.7.

Method B. Compound **5** was prepared also via Pd-catalyzed phosphination of 1*H*-inden-2-yl trifluoromethanesulfonate. Following the procedure described for the synthesis of **3** from Ph_2PH, 6.60 g (0.025 mol) of 1*H*-inden-2-yl trifluoromethanesulfonate, 4.98 g (0.025 mol) of Cy_2PH, 3.9 mL (2.82 g, 0.027 mol) of Et_3N, and 0.72 g (0.62 mmol) of $Pd(PPh_3)_4$ in 50 mL of toluene gave the title compound. Yield: 7.81 g (82%) of **5**. Anal. Found: C, 80.63; H, 9.31.

Diethyl 1*H*-Inden-2-ylphosphonate (9). To 91.0 g (0.467 mol) of 2-bromo-1*H*-indene and 3.02 g (0.023 mol) of $NiCl_2$ in a 250 mL flask equipped with a distillation head was added 85.0 mL (82.4 g, 0.496 mol) of $(EtO)_3P$. This black mixture was heated in an oil bath at 185−190 °C for 3 h. During this procedure, argon gas was bubbled through the mixture to eliminate ethyl bromide formed (actually, its mixture with the starting triethyl phosphite). The crude product was distilled in a vacuum (171−175 °C/1 mmHg). Yield: 102.4 g (87%) of a colorless oil of **9**. Anal. Calcd for $C_{13}H_{17}O_3P$: C, 61.90; H, 6.79. Found: C, 62.03; H, 6.82. ^{1}H NMR ($CD\tilde{N}l_3$): δ 7.63 (m, 1H, 3-H), 7.51 (m, 2H, 4,7-H), 7.32 (m, 2H, 5,6-H), 4.07−4.23 (m, 4H, OCH_2Me), 3.65 (m, 2H 1,1′-H in indenyl), 1.35 (t, J = 7.0 Hz, 6H, Me). ^{31}P{^{1}H} NMR ($CD\tilde{N}l_3$): δ 31.2.

1*H*-Inden-2-yl(dimethyl)phosphine Oxide (13). To a solution of 12.6 g (50 mmol) of **9** in 100 mL of diethyl ether was added dropwise 81.5 mL of 1.84 M MeLi (150 mmol) in ether under vigorous stirring for 2 h at −30 °C. The resulting mixture was stirred overnight at ambient temperature; then, 20 mL of 10% HCl was added. The resulting mixture was additionally stirred for 1 h. The ether layer was separated, dried over anhydrous Na_2SO_4, and evaporated to dryness. The yellow-brown oil obtained was recrystallized from chloroform. Yield: 3.70 g (30%) of the title compound as a mono solvate with H_2O and HCl. Anal. Calcd for $C_{11}H_{13}OP$: C, 68.74; H, 6.82. Found: C, 68.98; H, 6.90. ^{1}H NMR ($CD\tilde{N}l_3$): δ 7.44−7.53 (m, 3H, 3,5,7-H), 7.24−7.36 (m, 2H, 4,6-H), 3.63 (m, 2H, 1,1′-H in indenyl), 2.30 (br s, 3H, H_2O and HCl), 1.70 (d, J = 13.0 Hz, 6H, Me). ^{13}C{^{1}H} NMR: δ 145.0 (d, J = 7.6 Hz), 142.9 (d, J = 16.8 Hz), 141.9 (d, J = 10.7 Hz), 140.6 (d, J = 103.8 Hz), 127.0, 126.9, 124.0, 122.6, 30.5 (d, J = 12.2 Hz), 17.7 (d, J = 73.2 Hz). ^{31}P{^{1}H} NMR ($CD\tilde{N}l_3$): δ 44.5.

1*H*-Inden-2-yl(dimethyl)phosphine (7). Method A. To a solution of 3.40 g (13.8 mmol) of **13**·H_2O·HCl in 100 mL of CH_2Cl_2 was added at 0 °C 5.61 g (4.18 mL, 41.4 mmol) of $HSiCl_3$. The reaction mixture was stirred for 24 h at room temperature and then evaporated to dryness. The crude product was purified by flash chromatography on silica gel 60 (*d* 30 mm, l 50 mm; eluent: benzene). Yield: 2.33 g (96%). Anal. Calcd for $C_{11}H_{13}P$: C, 74.98; H, 7.44. Found: C, 75.22; H, 7.51. ^{1}H NMR ($CDCl_3$): δ 7.38 (m, 1H, 7-H), 7.29 (m, 1H, 4-H), 7.21 (m, 1H, 5-H), 7.10 (m, 1H, 6-H), 6.86 (m, 1H, 3-H), 3.41 (m, 2H, 1,1′-H in indenyl), 1.24 (d, 6H, J = 2.3 Hz, Me). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 150.7 (d, J = 15.3 Hz), 145.0 (d, J = 4.6 Hz), 144.8 (d, J = 6.1 Hz), 134.5 (d, J = 14.3 Hz), 126.2, 124.3, 123.3, 120.2, 40.3 (d, J = 12.2 Hz), 29.5, 13.4 (d, J = 12.2 Hz). ^{31}P{^{1}H} NMR ($CD\tilde{N}l_3$): δ −56.0.

Method B. To a solution of 2.17 g (10 mmol) of **2** in 60 mL of diethyl ether−hexanes (1:1, vol) was added dropwise 10.9 mL of 1.84 M MeLi (20 mmol) in ether under vigorous stirring for 2 h at −90 °C. The reaction mixture was slowly warmed to ambient temperature, stirred overnight, and then filtered though a glass frit (G4). The precipitate was additionally washed with 10 mL of ether. The combined extract was evaporated to dryness, and the residue was dried in a vacuum. Yield: 1.76 g (99%) of colorless crystalline solid. Anal. Found: C, 75.19; H, 7.50.

***tert*-Butyl(1*H*-inden-2-yl)phosphinous Chloride (8).** To a solution of 1.09 g (5.0 mmol) of **2** in 40 mL of diethyl ether−hexanes (1:1, vol) was added dropwise 4.7 mL of 1.06 M ^{t}BuMgCl in ether under vigorous stirring for 2 h at −90 °C. The resulting mixture was slowly warmed to ambient temperature, stirred overnight, and filtered through a glass frit (G3). The precipitate was additionally washed with 3 × 15 mL of ether. The combined filtrate was evaporated to dryness, and the residue was dried in a vacuum. Yield: 1.19 g (99%) of colorless solid. Anal. Calcd for $C_{13}H_{16}ClP$: C, 65.41; H, 6.76. Found: C, 65.62; H, 7.85. ^{1}H NMR (C_6D_6): δ 7.15−7.34 (m, 5H, 3,4,5,6,7-H), 3.43−3.68 (m, 1,1′-H in indenyl), 1.11 (d, J = 14.0 Hz, 9H, ^{t}Bu). ^{13}C{^{1}H} NMR (C_6D_6): δ 146.1, 144.5 (d, J = 45.8 Hz), 144.1 (d, J = 10.7 Hz), 142.9 (d, J = 35.1 Hz), 126.9, 126.2, 124.0, 121.9, 42.6 (d, J = 6.1 Hz), 34.8 (d, J = 29.0 Hz), 25.8 (d, J = 18.3 Hz). ^{31}P{^{1}H} NMR (C_6D_6): δ 104.5.

Di(*tert*-butyl)(1*H*-inden-2-yl)phosphine (6). To 40 mL of THF were added 12.4 mL of 1.70 M ^{t}BuLi (21 mmol) in pentane and then 1.88 g (21 mmol) of CuCN. The resulting mixture was warmed under vigorous stirring for 30 min to −70 °C. Then, 5.00 g (21 mmol) of **8** in 40 mL of THF was added in one portion. The mixture was slowly (ca. 5 h) warmed to ambient temperature, stirred for 24 h, and then evaporated to dryness. The product was extracted with 3 × 50 mL of toluene. The combined toluene extract was filtered through a glass frit (G4) and evaporated to dryness. High-vacuum sublimation (0.01 mmHg, 150−190 °C) gave 1.49 g (27%) of **6**. Anal. Calcd for $C_{17}H_{25}P$: C, 78.42; H, 9.68. Found: C, 78.23; H, 9.56. ^{1}H NMR (C_6D_6): δ 7.44 (m, 1H, 7-H), 7.39 (m, 1H, 4-H), 7.22−7.35 (m, 2H, 5,6-H), 6.12 (dt, J = 7.3 Hz, J = 1.5 Hz, 1H, 3-H), 3.66 (m, 2H, 1,1′-H in indenyl), 1.27 (d, J = 1.5 Hz, 18H, ^{t}Bu). ^{13}C{^{1}H} NMR (C_6D_6): δ 146.3 (d, J = 2.3 Hz), 145.5 (d, J = 32.9 Hz), 144.5 (d, J = 12.0 Hz), 127.0 (d, J = 7.5 Hz), 126.7, 125.6, 123.7, 121.4, 44.7 (d, J = 3.8 Hz), 32.5 (d, J = 18.7 Hz), 27.5 (d, J = 14.2 Hz). ^{31}P{^{1}H} NMR (C_6D_6): δ 22.8 (br s).

1*H*-Inden-2-ylphosphine (10) and Compound 12. To a suspension of 13.3 g (0.350 mol) of $LiAlH_4$ in 200 mL of ether was added dropwise over 2 h a solution of 58.7 g (0.233 mol) of **9** in 140 mL of ether. The resulting mixture was refluxed for 2 h and then cooled to room temperature, and 50 mL of water was added dropwise to decompose an excess of metal hydrides. The ether solution was separated, and the residue was diluted with 2 × 200 mL of ether. The combined extract was evaporated to ca. 100 mL. A white solid that precipitated at −30 °C was separated, washed with 10 mL of cold ether, and dried in a vacuum. Yield: 2.39 g (7%) of compound **12**. The yellow solution was evaporated, and the obtained oil was distilled in a vacuum (108−110 °C/8 mmHg). Yield: 21.90 g of a ca. 4 to 1 mixture of **10** (51%) and **11** (12%). Additional careful fractional distillation of this mixture gave 14.52 g of **10** of 93% purity (^{31}P NMR). Compound **10**. Anal. Calcd for C_9H_9P: C, 72.97; H, 6.12. Found: C, 72.85; H, 6.20. ^{1}H NMR (C_6D_6): δ 7.15−7.27 (m, 3H, 5,6,7-H), 7.06−7.12 (m, 1H, 3-H), 6.83−6.87 (m, 1H, 4-H), 3.56 (m, J_{P-H} = 199.6 Hz, 2H, PH_2),

3.05 (m, 2H, 1,1′-H). ^{13}C NMR (C_6D_6): δ 146.2, 145.3 (d, J = 9.2 Hz), 142.0 (d, J = 26.0 Hz), 134.8 (d, J = 13.7 Hz), 126.6, 125.2, 123.5, 120.8, 46.7. ^{31}P NMR (C_6D_6): δ −131.6 (dt, J_{P-H} = 199.6 Hz, J_{P-H} = 7.8 Hz). Compound **11**. ^{31}P NMR (C_6D_6): δ −102.6 (m, J_{P-H}= 189.5 Hz, J_{P-H} = 11.7 Hz, J_{P-H} = 9.8 Hz). Compound **12**. Anal. Calcd for $C_{27}H_{23}P_3$: C, 73.64; H, 5.26. Found: C, 73.56; H, 5.20. For ^{1}H NMR spectrum (in CD_2Cl_2) see the Supporting Information. ^{31}P{^{1}H} NMR ($CD_2\tilde{N}l_2$): δ 36.2 (d, J_{P-P} = 270.9 Hz), −26.0 (dd, J_{P-P} = 235.9 Hz, J_{P-P} = 270.9 Hz), −40.3 (d, J_{P-P} = 235.9 Hz). ^{31}P NMR ($CD_2\tilde{N}l_2$): δ 36.2 (d, J_{P-P} = 270.9 Hz), −26.0 (ddd, J_{P-P} = 270.9 Hz, J_{P-P} = 235.9 Hz, J_{P-H} = 16.9 Hz), −40.3 (dddt, J_{P-P} = 235.9 Hz, J_{P-H} = 208.9 Hz, J_{P-H} = 19.0 Hz, J_{P-H} = 12.4 Hz).

***tert*-Butyl(1*H*-inden-2-yl)phosphine (14).** To 9.61 g (0.049 mol) of 2-bromo-1*H*-indene and 1.13 g (0.98 mmol) of $Pd(PPh_3)_4$ in 25 mL of toluene were added 7.5 mL (5.45 g, 0.054 mol) of Et_3N and 4.88 g (0.054 mol) of ^{t}BuPH$_2$. This mixture was refluxed for 14 h, cooled to room temperature, and filtered through a glass frit (G3) to separate from the compound **15**. The filtrate was evaporated to dryness. The crude product was distilled in a vacuum (108−110 °C/3 mmHg). Yield: 3.07 g (31%) of crystalline solid of **14**. Anal. Calcd for $C_{13}H_{17}P$: C, 76.45; H, 8.39. Found: C, 76.32; H, 8.33. ^{1}H NMR ($CDCl_3$): δ 7.42 (m, 1H, 7-H), 7.36 (m, 1H, 4-H), 7.25 (m, 1H, 5-H), 7.16 (m, 1H, 6-H), 7.06 (m, 1H, 3-H), 3.86 (br s, 1H, PH), 3.56 (m, 2H, 1,1′-H in indenyl), 1.18 (d, 9H, J = 12.9 Hz, ^{t}Bu). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 145.9 (d, J = 3.3 Hz), 145.1 (d, J = 6.1 Hz), 141.4 (d, J = 19.8 Hz), 140.7 (d, J = 16.8 Hz), 126.4, 124.8, 123.3, 120.6, 45.8 (d, J = 7.6 Hz), 30.2 (d, J = 13.7 Hz), 29.4 (d, J = 7.6 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −28.7 (d, J = 207.4 Hz).

***tert*-Butyl[di(1*H*-inden-2-yl)]phosphine (15).** To 15.61 g (0.080 mol) of 2-bromo-1*H*-indene and 1.38 g (1.19 mmol) of $Pd(PPh_3)_4$ in 60 mL of toluene were added 22.3 mL (16.19 g, 0.160 mol) of Et_3N and 3.60 g (0.040 mol) of ^{t}BuPH$_2$. This mixture was refluxed for 24 h, cooled to room temperature, and passed through a short column with silica gel using 200 mL of toluene as eluent. The filtrate was evaporated to dryness to give an oil, which after treatment with 150 mL of hot ethanol gave a gray precipitate. This precipitate was separated (G3), washed with 3 × 5 mL of cold ethanol, and dried in a vacuum. Yield: 10.83 g (85%) of **15**. Anal. Calcd for $C_{22}H_{23}P$: C, 82.99; H, 7.28. Found: C, 82.71; H, 7.38. ^{1}H NMR (C_6D_6): δ 7.26 (m, 2H, 7-H), 7.23 (m, 2H, 5-H), 7.13−7.19 (m, 4H, 3,6-H), 7.11 (m, 2H, 4-H), 3.42 (s, 4Í, 1,1′-H in indenyl), 1.14 (d, J = 12.6 Hz, 9H, ^{t}Bu). ^{13}C{^{1}H} NMR (C_6D_6): δ 148.0 (d, J = 4.6 Hz), 144.9 (d, J = 9.2 Hz), 144.6 (d, J = 22.9 Hz), 141.8 (d, J = 24.4 Hz), 126.8, 125.3, 123.8, 121.2, 43.9 (d, J = 9.2 Hz), 31.0 (d, J = 12.2 Hz), 29.0 (d, J = 13.7 Hz). ^{31}P{^{1}H} NMR (C_6D_6): δ −6.4.

1*H*-Inden-2-yl(phenyl)phosphine (17). To 7.40 g (0.050 mol) of **10** and 2.88 g (2.49 mmol) of $Pd(PPh_3)_4$ in 20 mL of toluene were added 7.7 mL (5.59 g, 0.055 mol) of Et_3N and then 5.6 mL (10.21 g, 0.050 mol) of iodobenzene. This mixture was refluxed for 8 h, cooled to room temperature, and passed through a short column with silica gel using 30 mL of toluene as eluent. The resulting solution was evaporated to dryness. The crude product was distilled in a vacuum (120−121 °C/2 mm). Yield: 5.71 g (51%) of a colorless oil of **17**. Anal. Calcd for $C_{15}H_{13}P$: C, 80.34; H, 5.84. Found: C, 80.22; H, 5.90. ^{1}H NMR (C_6D_6): δ 7.08−7.68 (m, 10H, 3,4,5,6,7-H in indenyl and C_6H_5), 5.13 (d, J = 216.3 Hz, 1H, PH), 3.24 (m, 2H, 1,1′-H in indenyl). ^{13}C{^{1}H} NMR (C_6D_6): δ 146.4 (d, J = 3.1 Hz), 145.2 (d, J = 9.2 Hz), 141.7 (d, J = 15.3 Hz), 141.4 (d, J = 24.4 Hz), 134.0 (d, J = 16.8 Hz), 128.8 (d, J = 6.1 Hz), 128.6 (d, J = 6.1 Hz), 128.5, 126.7, 125.4, 123.8, 121.2, 43.7 (d, J = 4.6 Hz). ^{31}P-{^{1}H} NMR (C_6D_6): δ −43.1 (d, J = 211.3 Hz).

Di(1*H*-inden-2-yl)(phenyl)phosphine (16). To 4.00 g (0.021 mol) of 2-bromo-1*H*-indene and 0.46 g (0.40 mmol) of $Pd(PPh_3)_4$ in 20 mL of toluene were added 3.2 mL (2.32 g, 0.023 mol) of Et_3N and then 4.52 g (0.020 mol) of **17**. This mixture was refluxed for 13 h, cooled to room temperature, and passed through a short column with silica gel using 150 mL of toluene as eluent. The resulting solution was evaporated to dryness. The crude product was crystallized from ethanol. Yield: 1.63 g (28%) of white crystals of **16**. Anal. Calcd for $C_{24}H_{19}P$: C, 85.19; H, 5.66. Found: C, 85.01; H, 5.58. ^{1}H NMR ($CD\tilde{N}l_3$): δ 7.53 (m, 4H, 2,6-H in C_6H_5), 7.38 (m, 2H, 7-H in indenyl), 7.35 (m, 6H, 3,4,5-H in C_6H_5), 7.33 (m, 2H, 4-H in indenyl), 7.16 (m, 2H, 5-H in indenyl), 7.24 (m, 2H, 6-H in indenyl), 7.01 (m, 2Í, 3-H in indenyl), 3.47 (m, 4Í, 1,1′-H in indenyl). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 145.9 (d, J = 3.1 Hz), 144.6 (d, J = 7.6 Hz), 140.3 (d, J = 18.3 Hz), 136.5 (d, J = 4.6 Hz), 133.7, (d, J = 19.8 Hz), 129.1, 128.9 (d, J = 6.1 Hz), 126.6 (d, J = 6.1 Hz), 126.5, 125.1, 123.6, 121.0, 42.1 (ä, J = 13.7 Hz). ^{31}P{^{1}H} NMR (C_6D_6): δ −29.7.

A Mixture of *d*-/*l*- and *meso*-1,2-Di-*tert*-butyl-1,2-di(1*H*-inden-2-yl)diphosphanes (18). To a solution of 335 mg (1.74 mmol) of **14** in 3 mL of diethyl ether were added 0.49 mL (356 mg, 3.52 mmol) of triethylamine and 415 mg (1.74 mmol) of **8** at −78 °C. The reaction mixture was slowly warmed to ambient temperature under vigorous stirring. This mixture was additionally stirred for 5 h at room temperature and 100 h at 40 °C and then evaporated to dryness. The residue was dissolved in 50 mL of toluene. This solution in a glovebox was passed through a short column with silica gel 60 (*d* 20 mm, l 70 mm). This column was additionally washed with 250 mL of toluene. The combined extract was evaporated to dryness to give a white solid. Yield: 357 mg (51%) as a mixture of *d*-/*l*-(trans-) and *meso*-(*cis*-)isomers in a ratio ca. 3 to 2. Anal. Calcd for $C_{26}H_{32}P_2$: C, 76.83; H, 7.93. Found: C, 76.99; H, 8.01. *d*-/*l*-**18**. ^{1}H NMR (C_6D_6): δ 7.27 (m, 2H, 3-H in indenyl), 7.19 (m, 2H, 7-H in indenyl), 7.09 (m, 2H, 5-H in indenyl), 6.89 (m, 2H, 6-H in indenyl), 6.76 (m, 2H, 4-H in indenyl), 3.12 (d, J = 22.6 Hz, 2H, 1-H in indenyl), 2.65 (d, J = 22.6 Hz, 2H, 1′-H in indenyl), 1.27 (t, J = 6.9 Hz, 18H, ^{t}Bu). ^{13}C NMR (C_6D_6): δ 148.8, 146.6, 144.7 (t, J = 18.7 Hz), 144.3, 126.5, 125.4, 123.6, 121.2, 43.4, 29.8 (t, J = 11.5 Hz), 25.7. ^{31}P{^{1}H} NMR (C_6D_6): δ −13.1. *meso*-**18**. ^{1}H NMR (C_6D_6): δ 7.48 (m, 2H, 3-H in indenyl), 7.24 (m, 2H, 7-H in indenyl), 7.07 (m, 2H, 5-H in indenyl), 7.04 (m, 2H, 6-H in indenyl), 7.01 (m, 2H, 4-H in indenyl), 3.80 (d, J = 22.9 Hz, 2H, 1-H in indenyl), 3.55 (d, J = 22.9 Hz, 2H, 1′-H in indenyl), 0.97 (t, J = 6.4 Hz, 18H, ^{t}Bu). ^{13}C{^{1}H} NMR (C_6D_6): δ 148.5, 146.7, 145.5 (t, J = 18.4 Hz), 144.0, 126.8, 125.8, 124.0, 121.5, 44.3, 30.1 (t, J = 9.3 Hz), 26.0. ^{31}P{^{1}H} NMR (C_6D_6): δ −19.5.

Complex 19. To a solution of 5.12 g (17.0 mmol) of **3** in 100 mL of ether was added 9.3 mL (17.0 mmol) of 1.83 M MeLi in ether at −90 °C. This mixture was stirred for 4 h at ambient temperature; then, 3.13 g (8.3 mmol) of $ZrCl_4(THF)_2$ was added at −90 °C. The mixture was stirred for 24 h at room temperature and then filtered through glass frit (G4). The precipitate was washed with 300 mL of hot toluene. To this toluene extract was added 300 mL of hexanes. The precipitate formed was separated by filtration (G3), washed with 3 × 20 mL of hexanes, and dried in a vacuum. Yield: 3.75 g (58%) of a yellow crystalline solid of **19**. Anal. Calcd for $C_{42}H_{32}Cl_2P_2Zr$: C, 66.31; H, 4.24. Found: C, 66.17; H, 4.18. ^{1}H NMR (CD_2Cl_2): δ 7.43−7.48 (dd, J = 6.4 Hz, J = 3.1 Hz, 4H, 5,6-H in indenyl), 7.26−7.37 (m, 20H, C_6H_5), 7.07−7.13 (dd, J = 6.4 Hz, J = 3.1 Hz, 4H, 4,7-H in indenyl), 6.21 (s, 4H, 1,3-H in indenyl). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 138.6 (d, J = 4.6 Hz), 138.5 (d, J = 4.6 Hz), 136.1 (d, J = 7.7 Hz), 136.0 (d, J = 10.7 Hz), 135.9 (d, J = 10.7 Hz), 135.8 (d, J = 7.7 Hz), 130.9, 130.1 (d, J = 3.0 Hz), 130.0 (d, J = 3.0 Hz), 129.8 (d, J = 1.5 Hz), 127.9, 126.4, 112.3 (d, J = 6.1 Hz), 112.2 (d, J = 6.1 Hz). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −16.4.

Complex 20. To a solution of 7.05 g (40 mmol) of **7** in 100 mL of diethyl ether was added dropwise 21.8 mL of 1.84 M (40 mmol) MeLi in ether under vigorous stirring at −90 °C. The reaction mixture was slowly warmed to ambient temperature and stirred for 4 h. To this solution cooled to −90 °C

was added 7.55 g (20 mmol) of $ZrCl_4(THF)_2$. The resulting mixture was stirred for 12 h at ambient temperature and evaporated to dryness, and 50 mL of toluene was added. This suspension was stirred for 12 h and then filtered through a glass frit (G4). The precipitate was additionally washed by 3 × 100 mL of hot toluene. The combined extracts were evaporated to ca. 100 mL, and 150 mL of hexanes was added. Crystals that precipitated from this solution at −30 °C were collected, washed with 20 mL of cold toluene and 3 × 20 mL of hexanes, and dried in a vacuum. Yield: 12.5 g (61%). Anal. Calcd for $C_{22}H_{24}Cl_2P_2Zr$: C, 51.56; H, 4.72. Found: C, 51.42; H, 4.64. ^{1}H NMR (CD_2Cl_2): δ 7.45−7.51 (dd, J = 6.4 Hz, J = 3.1 Hz, 4H, 5,6-H), 7.12−7.18 (dd, J = 6.4 Hz, J = 3.1 Hz, 4H, 4,7-H), 6.44 (s, 4H, 1,3-H in indenyl), 1.25 (d, J = 1.8 Hz, 6H, Me), 1.24 (d, J = 1.8 Hz, 6H, Me*). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 130.5, 130.0, 127.6, 126.3, 110.4 (d, J = 6.1 Hz), 110.3 (d, J = 6.1 Hz), 16.1 (d, J = 3.8 Hz), 16.0 (d, J = 3.8 Hz). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −48.8.

Complex 21. To a solution of 5.02 g (21.6 mmol) of **4** in 70 mL of ether was added 10.8 mL (21.6 mmol) of 2.00 M MeLi in ether at −90 °C. This mixture was stirred for 4 h at ambient temperature; then, 4.02 g (10.6 mmol) of $ZrCl_4(THF)_2$ was added at −90 °C. This mixture was stirred for 18 h at room temperature and then evaporated to dryness. The residue was washed with 100 mL of ether. The resulting yellow solution was filtered (G4) and evaporated to ca. 2/3 of its initial volume. Crystallization of this solution at −30 °C gave orange crystals of **21**, which were separated, washed with 5 mL of cold ether, and dried in a vacuum. Yield: 2.91 g (43%). Anal. Calcd for $C_{30}H_{40}Cl_2P_2Zr$: C, 57.68; H, 6.45. Found: C, 57.83; H, 6.52. ^{1}H NMR (CD_2Cl_2): δ 7.46−7.52 (dd, J = 6.4 Hz, J = 3.1 Hz, 4H, 5,6-H), 7.13−7.19 (dd, J = 6.4 Hz, J = 3.1 Hz, 4H, 4,7 H), 6.46 (s, 4H, 1,3-H in indenyl), 2.05 (d-sept, 4H, J = 6.9 Hz, J = 1.5 Hz, C*H*Me$_2$), 1.18 (dd, J = 13.4 Hz, J = 7.0 Hz, 12H, CH*Me*$_2$), 0.98 (dd, J = 12.8 Hz, J = 6.9 Hz, 12H, CH*Me*$_2$*). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 135.5, 135.2, 129.9, 128.0, 126.4, 112.2 (d, J = 7.6 Hz), 112.1 (d, J = 7.6 Hz), 25.9, 25.7, 21.9 (d, J = 13.6 Hz), 21.5 (d, J = 15.3 Hz). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 4.6.

Complex 22. To a solution of 4.14 g (13.0 mmol) of **5** in 70 mL of ether was added 5.3 mL (13.0 mmol) of 2.50 M ^{n}BuLi in hexanes at −90 °C. This mixture was stirred for 5 h at ambient temperature; then, 2.41 g (6.4 mmol) of $ZrCl_4(THF)_2$ was added at −90 °C. The mixture was stirred for 48 h at room temperature and then filtered through a glass frit (G4). The precipitate was washed with 200 mL of hot toluene. The toluene extract was evaporated to 1/2 of its initial volume; then, 100 mL of hexanes was added. The precipitate formed was separated by filtration (G3), washed with 15 mL of hexanes, and dried in a vacuum. Yield: 2.41 g (47%) of a yellow crystalline solid of **22**. Anal. Calcd for $C_{42}H_{56}Cl_2P_2Zr$: C, 64.26; H, 7.19. Found: C, 64.45; H, 7.26. ^{1}H NMR (C_6D_6): δ 7.48−7.54 (dd, J = 6.5 Hz, J = 3.1 Hz, 4H, 5,6-H in indenyl), 6.95−7.02 (dd, J = 6.5 Hz, J = 3.1 Hz, 4H, 4,7-H in indenyl), 6.83 (s, 4H, 1,3-H in indenyl), 1.00−2.11 (m, 44H, Ñó). ^{13}C{^{1}H} NMR (C_6D_6): δ 136.3, 128.7, 126.9, 125.1, 111.1 (d, J = 8.2 Hz), 111.0 (d, J = 8.2 Hz), 34.7, 34.5, 31.5 (d, J = 13.7 Hz), 30.8 (d, J = 12.2 Hz), 27.6 (d, J = 11.7 Hz), 27.5 (d, J = 11.7 Hz), 26.7. ^{31}P{^{1}H} NMR (C_6D_6): δ 12.8.

Complex 23. To a solution of 850 mg (3.26 mmol) of **23** in 35 mL of diethyl ether was added dropwise 1.30 mL of 2.5 M (3.25 mmol) of ^{n}BuLi in hexanes under vigorous stirring at −30 °C. The resulting mixture was slowly warmed to ambient temperature and stirred for 3 h. To this solution cooled to −30 °C was added 615 mg (1.63 mmol) of $ZrCl_4(THF)_2$. The mixture was stirred for 24 h at room temperature and then evaporated to dryness. The product was extracted with 30 mL of toluene. This toluene solution was filtered through a glass frit (G4). Crystals precipitated at −30 °C from the filtrate were collected, washed with 10 mL of cold toluene and 3 × 30 mL of hexanes, and dried in a vacuum. Yield: 712 mg (64%). Anal. Calcd for $C_{34}H_{48}Cl_2P_2Zr$: C, 59.98; H, 7.11. Found: C, 60.19; H, 7.20. ^{1}H NMR (C_6D_6): δ 7.53−7.59 (dd, J = 6.5 Hz, J = 3.0 Hz, 4H, 5,6-H in indenyl), 7.135 (s, 2H, 1/3-H in indenyl), 7.130 (s, 2H, 3/1-H in indenyl), 7.06−7.11 (dd, J = 6.5 Hz, J = 3.0 Hz, 4H, 4,7-H in indenyl), 1.30 (d, J = 11.2 Hz, 36H, ^{t}Bu). ^{31}P{^{1}H} NMR (C_6D_6): δ 34.6.

Complex 24. To a solution of 1.50 g (4.80 mmol) of **5** in 35 mL of toluene was added 1.92 mL of 2.5 M (4.80 mmol) of ^{n}BuLi in hexanes at ambient temperature. This mixture was stirred for 12 h at this temperature; then, 1.60 g (4.80 mmol) of Cp*$ZrCl_3$ was added. The resulting mixture was stirred for 12 h at ambient temperature and 12 h at 90 °C and then filtered through Celite 403. The filtrate was evaporated to ca. 20 mL. Crystals precipitated at −30 °C were collected, washed with 3 × 20 mL of hexanes, and dried in a vacuum. Yield: 2.01 g (67%). Anal. Calcd for $C_{31}H_{43}Cl_2PZr$: C, 61.16; H, 7.12. Found: C, 60.92; H, 7.04. ^{1}H NMR (CD_2Cl_2): δ 7.58−7.64 (dd, J = 6.5 Hz, J = 3.0 Hz, 2H, 5,6-H in indenyl), 7.28−7.34 (dd, J = 6.5 Hz, J = 3.0 Hz, 2H, 4,7-H in indenyl), 6.79 (s, 2H, 1,3-H in indenyl), 2.21 (s, 15H, C_5Me_5), 2.29−2.41, 1.84−2.08, and 1.33−1.67 (m, 22H, Ñó). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 135.7, 129.5, 126.3, 125.2, 124.3, 109.0 (d, J = 9.2 Hz), 34.4 (d, J = 15.3 Hz), 34.7 (d, J = 18.3 Hz), 31.5 (d, J = 9.2 Hz), 28.2 (d, J = 12.2 Hz), 28.0 (d, J = 9.2 Hz), 27.0, 13.2. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −8.9.

Complex 25. To a solution of 4.66 g (14.6 mmol) of **15** in 130 mL of ether was added 16.0 mL (29.2 mmol) of 1.83 M MeLi in ether at −90 °C. This mixture was stirred for 3 h at ambient temperature, and then, 5.37 g (14.2 mmol) of $ZrCl_4(THF)_2$ was added at −90 °C. The mixture was stirred for 48 h at room temperature and then filtered through glass frit (G4). The precipitate was washed with 5 × 100 mL of hot toluene. The combined extract was evaporated to 2/3 of its initial volume. Crystallization of the solution at −30 °C gave yellow crystals of **25**. Yield: 3.81 g (56%). Anal. Calcd for $C_{22}H_{21}Cl_2PZr$: C, 55.22; H, 4.42. Found: C, 55.47; H, 4.49. ^{1}H NMR (CD_2Cl_2): δ 7.57 (dq, J = 8.5 Hz, J = 1.0 Hz, 2H, 4/7-Í in indenyl), 7.42 (dq, J = 8.5 Hz, J = 1.0 Hz, 2H, 7/4-Í in indenyl), 7.24 (ddd, J = 8.5 Hz, J = 6.5 Hz, J = 1.2 Hz, 2Í, 5/6-H in indenyl), 7.17 (ddd, J = 8.5 Hz, J = 6.5 Hz, J = 1.2 Hz, 2Í, 5/6-H in indenyl), 6.62 (dt, J = 2.6 Hz, J = 1.0 Hz, 2Í, 1/3-H in indenyl), 6.36 (ddd, J = 5.6 Hz, J = 2.6 Hz, J = 1.0 Hz, 2Í, 3/1-H in indenyl), 1.58 (d, J = 14.7 Hz, 9H, ^{t}Bu). ^{13}C-{^{1}H} NMR (CD_2Cl_2): δ 130.5 (d, J = 7.9 Hz), 129.7 (d, J = 17.2 Hz), 128.7, 127.7, 126.4, 126.1, 114.7 (d, J = 42.7 Hz), 110.9 (d, J = 33.6 Hz), 103.5 (d, J = 7.6 Hz), 33.2 (d, J = 15.3 Hz), 30.7 (d, J = 16.8 Hz). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −12.0.

Complex 26. To a solution of 1.48 g (4.37 mmol) of **16** in 50 mL of ether was added 4.8 mL (8.75 mmol) of 1.84 M MeLi in ether at −90 °C. This mixture was stirred for 12 h at ambient temperature; then, 1.65 g (4.37 mmol) of $ZrCl_4(THF)_2$ was added at −90 °C. The mixture was stirred for 24 h at room temperature and then evaporated to dryness. To the residue was added 50 mL of toluene, and this mixture was stirred additionally for 12 h. The orange slurry formed was filtered through a glass frit (G4). The precipitate was washed with 50 mL of hot toluene. To the combined toluene extract was added 60 mL of hexanes. Crystallization of this solution at −30 °C gave orange crystals of **26**. Yield: 0.79 g (36%). Anal. Calcd for $C_{24}H_{17}Cl_2PZr$: C, 57.83; H, 3.44. Found: C, 58.11; H, 3.56. ^{1}H NMR (C_6D_6): δ 7.53 (dq, J = 8.5 Hz, J = 1.0 Hz, 2H, 4/7-Í in indenyl), 7.41−7.47 (m, 2H, 2,6-H in C_6H_5), 7.26 (dq, J = 8.5 Hz, J = 1.0 Hz, 2H, 7/4-Í in indenyl), 6.98−7.20 (m, 3H, 3,4,5-H in C_6H_5), 6.96 (ddd, J = 8.5 Hz, J = 6.7 Hz, J = 1.2 Hz, 2Í, 5/6-H in indenyl), 6.87 (ddd, J = 8.5 Hz, J = 6.7 Hz, J = 1.2 Hz, 2Í, 5/6-H in indenyl), 6.21 (ddd, J = 4.4 Hz, J = 2.6 Hz, J = 0.9 Hz, 2Í, 1/3-H in indenyl), 5.97 (m, 2Í, 3/1-H in indenyl). ^{13}C{^{1}H} NMR (C_6D_6): δ 134.5, 134.1, 134.0, 131.2 (d, J = 13.7 Hz), 129.2 (d, J = 4.1 Hz), 127.3, 126.8, 126.5, 125.1, 125.0, 109.7 (d, J = 38.2 Hz), 107.2 (d, J = 27.5 Hz), 101.4 (d, J = 7.6 Hz). ^{31}P{^{1}H} NMR (C_6D_6): δ −30.4.

Table 2. Crystallographic Data for 12, 13, 22, 25, and 27

	12	**13**·(HCl)·(H_2O)	**22**	**25**	**27**
empirical formula	$C_{27}H_{23}P_3$	$C_{11}H_{16}ClO_2P$	$C_{42}H_{56}Cl_2P_2Zr$	$C_{22}H_{21}Cl_2PZr$	$C_{26}H_{30}Cl_2P_2Zr$
fw	440.36	246.66	784.93	478.48	566.56
temperature (K)	295(2)	110(2)	120(2)	120(2)	120(2)
cryst size (mm)	0.50 × 0.50 × 0.20	0.85 × 0.78 × 0.09	0.40 × 0.25 × 0.15	0.50 × 0.25 × 0.10	0.45 × 0.30 × 0.20
cryst syst	orthorhombic	monoclinic	triclinic	monoclinic	orthorhombic
space group	$Pna2_1$	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P2_12_12_1$
a, Å	29.717(10)	13.044(2)	10.8977(11)	8.5662(16)	10.1403(18)
b, Å	11.720(3)	10.5451(16)	10.9949(15)	20.264(4)	11.598(2)
c (Å)	6.498(2)	9.0834(14)	16.459(2)	11.765(2)	21.762(4)
α (deg)	90	90	78.178(4)	90	90
β (deg)	90	102.569(3)	79.980(4)	102.098(4)	90
γ (deg)	90	90	76.357(4)	90	90
V (Å^3)	2263.1(12)	1219.5(3)	1859.3(4)	1997.0(7)	2559.5(8)
Z	4	4	2	4	4
d_c (Mg m^{-3})	1.292	1.343	1.402	1.591	1.470
F(000)	920	520	824	968	1160
μ (mm^{-1})	0.275	0.423	0.555	0.902	0.776
θ range (deg)	2.21 to 25.00	2.51 to 32.32	1.93 to 30.03	2.01 to 30.03	2.22 to 26.03
index range	$-4 \le h \le 36$ $-14 \le k \le 2$ $-1 \le l \le 8$	$-19 \le h \le 19$ $-15 \le k \le 15$ $-11 \le l \le 13$	$-15 \le h \le 15$ $-15 \le k \le 15$ $-23 \le l \le 23$	$-12 \le h \le 11$ $-27 \le k \le 28$ $-16 \le l \le 16$	$-12 \le h \le 12$ $-14 \le k \le 13$ $-26 \le l \le 26$
no. of rflns collected	3557	12 641	22 427	23 173	18 501
no. of unique rflns	2553 [R_{int} = 0.0180]	4078 [R_{int} = 0.0217]	10760 [R_{int} = 0.0302]	5804 [R_{int} = 0.0374]	5003 [R_{int} = 0.0538]
no. of rflns with $I > 2\sigma(I)$	1670	3307	7379	4060	3717
R_1; wR_2 ($I > 2\sigma(I)$)	0.0366; 0.0850	0.0504; 0.1293	0.0468; 0.0921	0.0573; 0.1292	0.0702; 0.1692
R_1; wR_2 (all data)	0.0829; 0.1009	0.0607; 0.1397	0.0686; 0.0982	0.0824; 0.1430	0.0937; 0.1855
no. of data/restraints/params	2553/1/363	4078/0/200	10 760/0/658	5804/1/235	5003/42/452
GOF on F^2	1.067	1.073	1.028	0.887	1.012
max shift/error	0.000	0.001	0.001	0.001	0.212
largest diff peak/hole (e Å^{-3})	0.281/−0.333	1.595/−0.324	1.056/−0.733	2.091/−0.614	0.778/−0.855
abs corr T_{max}; T_{min}	0.824; 0.635	0.928; 0.571	0.939; 0.856	0.802; 0.621	0.702; 0.862

Complex 27. To a solution of 713 mg (1.75 mmol) of **18** in 15 mL of toluene was added a solution of 642 mg (3.50 mmol) of NaN(TMS)$_2$ in 10 mL of toluene at ambient temperature. This mixture was stirred for 24 h. The white precipitate formed was filtered off (G3), washed with 3 × 30 mL of hexanes, and dried in a vacuum. To a suspension of this sodium salt in 25 mL of diethyl ether was added 660 mg (1.75 mmol) of $ZrCl_4$-(THF)$_2$. The resulting mixture was stirred for 48 h at ambient temperature and then evaporated to dryness. The crude product was extracted with 30 mL of toluene. The toluene solution was filtered through a glass frit (G4), and the filtrate was evaporated to ca. 10 mL. Crystals precipitated at −30 °C were collected, washed with 3 × 30 mL of hexanes, and dried in a vacuum. Yield: 520 mg (52%) of pure *rac*-complex (*trans*-^{t}BuPPBu^t). Anal. Calcd for $C_{26}H_{30}Cl_2P_2Zr$: C, 55.12; H, 5.34. Found: C, 55.28; H, 5.38. ^{1}H NMR (CD_2Cl_2): δ 7.52 (m, 2H, 4/7-Í in indenyl), 7.42 (m, 2H, 7/4-Í in indenyl), 7.20 (m, 2Í, 5/6-H in indenyl), 7.12 (m, 2Í, 5/6-H in indenyl), 6.85 (m, 2Í, 1/3-H in indenyl), 6.62 (m, 2Í, 3/1-H in indenyl), 1.19 (t, J = 6.9 Hz, 18H, ^{t}Bu). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 134.8, 130.9 (t, J = 5.8 Hz), 128.3, 127.9, 127.6 (t, J = 11.5 Hz), 127.0, 126.3, 116.8 (t, J = 20.7 Hz), 106.5 (t, J = 4.6 Hz), 32.8 (t, J = 4.6 Hz), 31.1 (t, J = 9.2 Hz). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −7.3.

X-ray Structural Determinations of 12, 13, 22, 25, and 27. Intensity measurements for **12** were carried out on an Enraf-Nonius CAD4 diffractometer (Table 2). The structure was solved by direct methods[37] and refined by full matrix least-squares on F^2 with anisotropic thermal parameters for all non-hydrogen atoms.[38] Atom H(3) was found from difference Fourier synthesis; other hydrogens were placed in calculated positions. All H atoms were refined isotropically. Data for **13**, **22**, **25**, and **27** were collected on a Bruker SMART 1000 CCD diffractometer and corrected for Lorentz and polarization effects and for absorption.[39] The structures were determined by direct methods and by full matrix least-squares refinement with anisotropic thermal parameters for non-hydrogen atoms. The crystal **13** contains a solvate water molecule. One of the four cyclohexyl substituents in **22** was disordered over two sites with equal occupancies. The hydrogen atoms in **13** were objectively localized in the difference Fourier map and refined isotropically. The hydrogen atoms in **25** were placed in calculated positions and refined using a riding model with fixed thermal parameters. The hydrogen atoms in **22** were objectively localized in the difference Fourier map and refined isotropically except for the hydrogen atoms of disordered cyclohexyl substituent, which were placed in calculated positions and refined using a riding model with fixed thermal parameters. In the structure of **27**, chlorine atoms, one of the indenyl ligands, and the bridging ^{t}Bu−P−P−^{t}Bu moiety were found to be disordered over two positions with approximately equal occupancies. In **27**, all non-hydrogen atoms (except some methyl carbons) were refined with anisotropic thermal parameters; all hydrogen atoms were placed in calculated positions and refined using a riding model. All calculations for **13**, **22**, **25**, and **27** were carried out by use of the SHELXTL (PC Version 5.10) program.[40]

Crystallographic data for the structures **12**, **13**, **22**, **25**, and **27** have been deposited with the Cambridge Crystallographic Data Center, CCDC nos. 271236−271240, respectively, and may be obtained free of charge from the Director CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

Olefin Polymerization Studies. Transition metal compound (TMC) solutions (0.2 mmol/L) were typically prepared

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(40) Sheldrick, G. M. *SHELXTL*, V5.10. Bruker AXS Inc.: Madison, WI, 1997.

using toluene. Solvents, polymerization grade toluene, and hexanes were supplied by ExxonMobil Chemical Co. and thoroughly dried and degassed prior to use. 1-Octene (98%, Aldrich) was dried by stirring over NaK overnight followed by filtration through basic alumina (Brockman Basic 1, Aldrich). Polymerization grade ethylene was used and further purified by passing it through a series of columns: 500 cm^3 Oxyclear cylinder from Labclear (Oakland, CA) followed by a 500 cm^3 column packed with dried 3 Å molecular sieves (Aldrich), and a 500 cm^3 column packed with dried 5 Å molecular sieves (Aldrich). MAO (methylalumoxane, 10 wt % in toluene) was purchased from Albemarle and was used as a 1 wt % in toluene solution. Micromoles of MAO reported in the Experimental Section are based on the micromoles of aluminum in MAO. The formula weight of MAO is 58.0 g/mol. Polymerizations were conducted in an inert atmosphere (N_2) drybox using autoclaves equipped with an external heater for temperature control, glass inserts (internal volume of reactor = 23.5 mL), septum inlets, and a regulated supply of nitrogen and ethylene and equipped with disposable PEEK mechanical stirrers (800 rpm). The autoclaves were prepared by purging with dry nitrogen at 110 or 115 °C for 5 h and then at 25 °C for 5 h. The reactor was purged with ethylene. Toluene, 1-octene, and MAO were added via syringe at room temperature and atmospheric pressure. The reactor was then brought to process temperature (80 °C) and charged with ethylene to process pressure (75 psig = 517.1 kPa) while stirring at 800 rpm. The TMC (0.02 μmol) was added via syringe with the reactor at process conditions. Amounts of reagents not specified above are given in Table 1. Ethylene was allowed to enter (through the use of computer-controlled solenoid valves) the autoclaves during polymerization to maintain reactor gauge pressure (± 2 psig). Reactor temperature was monitored and typically maintained within ±1 °C. Polymerizations were halted by addition of approximately 50 psid O_2/Ar (5 mol % O_2) gas mixture to the autoclaves for approximately 30 s. The polymerizations were quenched after a predetermined cumulative amount of ethylene had been added or for a maximum of 20 min polymerization time. The reactors were cooled and vented. The polymer was isolated after the solvent was removed in vacuo.

For analytical testing, polymer sample solutions were prepared by dissolving polymer in 1,2,4-trichlorobenzene (TCB, 99+% purity, Aldrich) containing 2,6-di-*tert*-butyl-4-methylphenol (BHT, 99%, Aldrich) at 160 °C in a shaker oven for approximately 3 h. The typical concentration of polymer in solution is between 0.4 and 0.9 mg/mL with a BHT concentration of 1.25 mg BHT/mL of TCB. Samples are cooled to 135 °C for testing. Molecular weights (weight average molecular weight (M_w) and number average molecular weight (M_n)) and molecular weight distribution (MWD = M_w/M_n), which is also sometimes referred to as the polydispersity (PDI) of the polymer, were measured by gel permeation chromatography using a Symyx Technologies GPC equipped with evaporative light scattering detector and calibrated using polystyrene standards. Samples were run in TCB (135 °C sample temperatures, 160 °C oven/columns) using three Polymer Laboratories PLgel 10 μm Mixed-B 300 × 7.5 mm columns in series. Thermal analysis was measured on a Symyx Technologies SAMMS (sensory array modular measurement system) instrument that measures polymer melt temperatures via the 3 ω technique. Samples for infrared analysis were subsequently analyzed on a Brucker Equinox 55 FTIR spectrometer equipped with Pikes MappIR specular reflectance sample accessory. For ethylene-1-octene copolymers, the wt % copolymer is determined via measurement of the methyl deformation band at ~1375 cm^{-1}. The peak height of this band is normalized by the combination and overtone band at ~4321 cm^{-1}, which corrects for path length differences. The normalized peak height is correlated to individual calibration curves from ^{1}H NMR data to predict the wt % copolymer content within a concentration range of ~2 to 35 wt % for octane-1. Typically, R^2 correlations of 0.98 or greater are achieved.

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Supporting Information Available: Tables of crystal data, data collection, structure solution and refinement parameters, atomic coordinates, anisotropic thermal parameters, and bond lengths and angles for **12**, **13**, **22**, **25**, and **27**. ^{1}H-{^{13}C} and ^{31}P{^{1}H} NMR spectra of compound **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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