1-Indenyldialkylphosphines and Cyclopentadienyldialkylphosphines as Ligands for High-Activity Palladium-Catalyzed Cross-Coupling Reactions with Aryl Chlorides

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The reactions of three deprotonated indenes (1,2,3-trimethyl, 1,2,3,4,7-pentamethyl, and 1,2,3-trimethyl-4,7-dimethoxy) and the lithium salt of pentamethylcyclopentadiene (Cp*) with $ClPR_2$ (R = *i*Pr, Cy) resulted in the formation of six indenylphosphines and two cyclopentadienylphosphines, isolated as the respective phosphonium salts. The Pd−phosphine complexes, formed in the presence of Na_2PdCl_4, base, and coupling partners, were shown to be highly active Pd complexes for various aryl chloride cross-coupling reactions. Quantitative yields in the Suzuki coupling are possible with 0.05−0.1 mol % of catalyst. Aryl chlorides can be coupled in quantitative yields in the Sonogashira reaction using 1 mol % of catalyst complex, while the Buchwald−Hartwig reaction typically requires 0.5 mol % of catalyst. In addition to the standard substrates, ferrocenylamine was subjected to Buchwald−Hartwig aminations, resulting in ferrocenylarylamines in near-quantitative yield.

Introduction

Trialkylphosphines with bulky substituents are highly useful ligands for catalytically active palladium complexes in various cross-coupling reactions of the Suzuki,[1−11] Sonogashira,[12−22] Heck,[23−28] Buchwald−Hartwig amination[29−35] and ether formation,[36] Negishi,[37] Stille,[38−40] Hiyama,[41] Kumada,[42] α-arylation,[43,44] and carbonylation types.[45] In particular, *t*Bu_3P has been used for a wide range of different coupling reactions, due to the high catalytic activity of its Pd complexes and its commercial availability.[46] *t*Bu_3P combines the two features which are said to be essential for trialkylphosphines for cross-coupling

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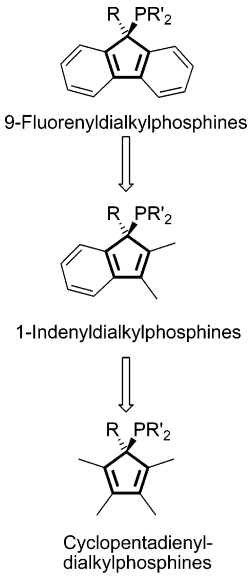
Chart 1. Relationship of Fluorenyl-, Indenyl-, and Cyclopentadienyldialkylphosphines

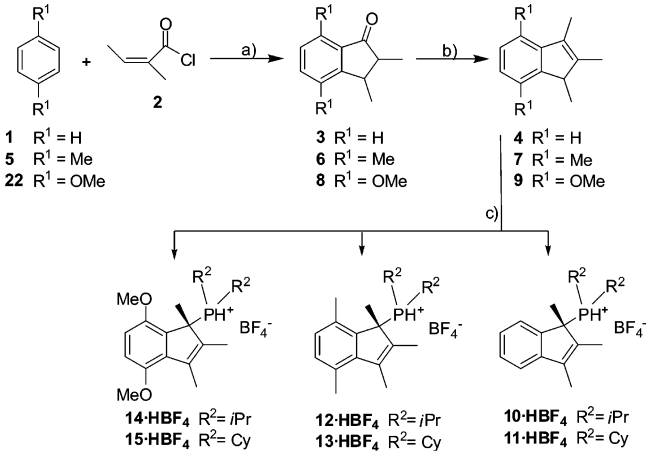


reactions: electron richness and steric bulk. We have recently reported a new class of 9-fluorenylphosphines[47] which combine the high catalytic activity of tBu$_3$P with the wide variability needed for the fine-tuning of the catalysts[48,49] or the introduction of phase tags[20,50−55] enabling biphasic catalysis[56] as well as catalyst recycling.[57,58]

Encouraged by the high catalytic activity and the facile synthesis of the fluorenyldialkylphosphines (isolated as the respective phosphonium salts), we wished to broaden this class of phosphines by variation of the fluorene lead structure. As visualized in Chart 1, the cyclopentadienyl ring embodies the core of the fluorenyl system. Replacement of the aromatic rings of fluorene by alkyl groups first leads to alkylated indenes and then to pentamethylcyclopentadiene (HCp*). All of these compounds are characterized by enhanced CH acidity of the central cyclopentadienyl ring, facilitating the selective formation of the respective carbanions. In this manner efficient C−C and C−P bond-forming reactions are possible. The respective phosphines stand a good chance to form a class of ligands with excellent properties in various Pd-mediated cross-coupling reactions.

Consequently, we wish to report here on the synthesis and characterization of various 1-indenyldialkylphosphonium and cyclopentadienyldialkylphosphonium salts and the application of the Pd complexes of the respective phosphines in Sonogashira, Suzuki, and Buchwald−Hartwig coupling reactions.

Scheme 1. Synthesis of Indenylphosphonium Salts[a]



[a] Reagents and conditions: (a) $AlCl_3$; (b) CH_3Li or CH_3MgI, H^+; (c) nBuLi, R_2PCl, Et_2O, −60 °C, HBF_4·Et_2O.

Results and Discussion

Synthesis of 1-Indenyldialkylphosphonium and Cyclopentadienyldialkylphosphonium Salts. Only a few cyclopentadienyl-[59−63] and indenyl-based trialkylphosphines[64−67] have been described in the literature, and none of them have been utilized in cross-coupling catalysis. In order to increase the steric bulk and to diversify the electronic nature of the such ligands, 1,2,3-trimethylindene (**4**), 1,2,3,4,7-pentamethylindene (**7**), and 4,7-dimethoxy-1,2,3-trimethylindene (**9**) were synthesized as backbones for phosphines. In general, the indenes were prepared via Friedel−Crafts acylation of the arene with tigloyl chloride (**2**) and subsequent ring closure, methylation, and acidic dehydration (Scheme 1). This synthetic strategy enables the easy modification of the 4,7-positions of indenes using the respective para-substituted arenes.

2,3-Dimethylindanone (**3**) was prepared according to the method of Rausch et al.[68] by reacting benzene (**1**) with $AlCl_3$ and tigloyl chloride (**2**) in benzene as a solvent in near-quantitative yield. When the same reaction protocol was utilized for the synthesis of 2,3,4,7-tetramethylindanone (**6**) with *p*-xylene (**5**) as reactant (and solvent), large amounts of isomerization products (32%) were formed due to a methyl shift of the aromatic methyl groups.[69,70] The separation of the two isomers was impractical on a multigram scale using rectification or column chromatography. It is noteworthy that even the improved synthesis of O'Hare et al.,[71,72] replacing the

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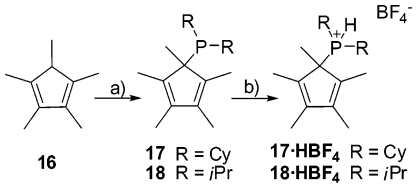
Scheme 2. Synthesis of Cyclopentadienylphosphonium Salts[a]



[a] Reagents and conditions: (a) *n*BuLi, R_2PCl, THF/Et_2O, −60 °C; (b) HBF_4·Et_2O.

undesirable CS_2 by dry CH_2Cl_2, could not completely suppress the isomerization (26% of the undesired isomer) in our hands. Consequently, for the synthesis of **6** we prefer CS_2, since the use of this solvent prevented the shift of methyl groups. ^{1}H NMR spectroscopy revealed that all indanones (**3**, **6**, **8**) were isolated as mixtures of the two cis/trans isomers in an approximate ratio of 3:1 for **3** and **6** and 4:1 for **8**. This poses no problem, since the cis/trans isomers react to give identical indenes. In order, to obtain the indenes **4**, **7**, and **9**, the respective indanones **3**, **6**, and **8** were reacted with MeLi or MeMgI to give the indanols, which were converted in situ into the desired indenes by acid-catalyzed elimination of water. As noted by O'Hare et al.,[72] the use of MeMgI as methylation agent gave better results than MeLi.

Deprotonation of the indenes **4**, **7**, and **9** with *n*BuLi and quenching with Cy_2PCl or iPr_2PCl gave the respective 1-indenylphosphines in good yields, which were isolated as the respective phosphonium salts. The Cp*-based phosphines were prepared in good yields (Scheme 2) by reactions of LiCp* with various chlorophosphines (iPr_2PCl, Cy_2PCl) and converted in situ into the respective phosphonium salts for easier storage and handling.[21,73] The free phosphines can be liberated from the phosphonium salts in quantitative yields by treatment with Et_3N (see the Experimental Section). The Cp* group provides steric bulk as well as an electron-rich environment.

Pd Complexes of 1-Indenyldialkylphosphines and Cyclopentadienyldialkylphosphines in the Suzuki Reaction. We first tested Pd complexes of the 1-indenyldialkylphosphines **10**−**15** and the Cp*-derived dialkylphosphines Cp*P*i*Pr$_2$ (**17**) and Cp*PCy$_2$ (**18**) for their reactivity in the Suzuki coupling (Table 1). As a reference phosphine, the recently reported highly active EtFluPCy$_2$[47] (**21**) was incorporated in the screening experiments. The reaction of *p*-chloroacetophenone with *p*-tolylboronic acid using 0.125 mol % Na_2PdCl_4 and 0.25 mol % phosphonium salt with Cs_2CO_3 in dioxane at 80 °C was initially used to probe the performance of the various phosphines. In general, complexes formed with phosphines bearing two Cy groups showed significantly better results than those with two *i*Pr groups. The top performers among the phosphines examined, Cp*PCy$_2$ (**17**), 1,2,3,4,7-Me$_5$IndPCy$_2$ (**13**), and 1,2,3-Me$_3$-4,7-(MeO)$_2$IndPCy$_2$ (**15**), showed nearly twice the high activity of EtFluPCy$_2$ (**21**), the best phosphine of the recently reported fluorenylphosphine family. In addition, 4,7-disubstituted 1-indenylphosphines and the cyclopentadienylphosphines show a better performance than phosphines based on the unsubstituted indene. Because of its high activity and its easy synthetic access, Cp*PCy$_2$ (**17**) was used as the ligand for further investigations.

As found by screening a wide range of different activated and deactivated aryl chlorides, 0.05 mol % of catalyst is sufficient to reach full conversion over 20 h; sterically hindered (entry 8) and electron-rich substrates (entry 2) require 0.1 mol % of catalyst to reach full conversion.

Pd Complexes of 1-Indenyl- and Cyclopentadienylphosphines in the Buchwald−Hartwig Reaction. In the present work we also examined the conversion of aryl chlorides as cheap and readily available starting materials with various aromatic and aliphatic amines. When the conditions recently reported by Beller et al. were applied without further optimization,[74] the screening of several indenyldialkylphosphines and cyclopentadienyldialkylphosphines in the reactions of 4-chlorotoluene with 3,5-dimethylaniline and 2,4-dimethylaniline revealed 1,2,3,4,7-pentamethylindenyldicyclohexylphosphine (**13**) to be the most active ligand for palladium (Table 2, entries 1 and 2). Typical catalyst loadings of 0.5 mol % Pd were applied at 120 °C using NaO*t*Bu as the base in toluene to give quantitative conversion. Some deactivated substrates required 1 mol % Pd to reach full conversion.

Activated and deactivated aryl chlorides were reacted with the respective amines (aniline, morpholine, α-methylbenzylamine, dibutylamine) under the same conditions in quantitative yields, whereas full conversion of deactivated aryl chlorides was only possible with difficulties applying the previously reported fluorenyldialkylphosphines.[47]

In addition to anilines, we also tested the coupling reactions of organometallic amines such as ferrocenylamine in Pd-catalyzed amination reactions for the first time—to the best of our knowledge. The resulting N-arylated aminoferrocenes have been rarely reported[75−78] and were said to be elusive.[79] Simple N-arylated aminoferrocenes such as ferrocenylphenylamine have been prepared by the reaction of ferrocenyl bromide with the sodium salt of an amide in the presence of copper(I) bromide/pyridine.[75] A recent synthetic strategy developed by Knochel et al.[79] requires a toxic tin reagent (FcSnBu$_3$), which is converted to FcMgBr and reacted with an arylazotosylate to obtain the aminated ferrocenyl derivative in 58% yield in the last reaction step. Utilizing Pd-catalyzed C−N coupling, ferrocenylarylamines can be synthesized in 85% yield in a single reaction step by employing the respective aryl chloride and ferrocenylamine, which is readily available using the improved synthesis of van Leusen and Hessen.[80] The amination of 3-chlorobenzyl trifluoride or 4-chloroanisole as a deactivated aryl chloride with ferrocenylamine using 0.5 mol % Pd and phosphine **13** gave the respective N-arylated aminoferrocenes (Table 2, entries 11 and 12). The redox potentials of the two ferrocenes (Table 2, entries 11 and 12) were determined by cyclic voltammetry and found to vary significantly depending on the nature of the para substituent (R = OMe, $E_{1/2}$ = 0.142 V; R = CF_3, $E_{1/2}$ = 0.268 V).

Pd Complexes of 1-Indenyl- and Cyclopentadienylphosphines in the Sonogashira Reaction. We initially tested the complexes of Pd with the various 1-indenyl- and Cp*-dialkylphosphines for their activity in the Sonogashira cross-coupling of phenylacetylene and 4-chloroanisole, applying the conditions described previously by us[47] (Table 3, entry 1). The top six of the eight phosphines screened show similar catalytic activities;

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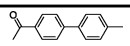
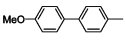
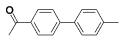
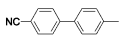
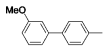
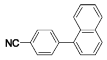
Table 1. Suzuki Reactions with Aryl Chlorides[a]

entry	aryl chloride	boronic acid	product	mol % catalyst / ligand	t (h)	conversion [c]
1				0.125 mol %/ **18**	15[d]	20 %
				0.125 mol %/ **17**	15[d]	60 %
				0.125 mol %/ **10**	15[d]	24 %
				0.125 mol %/ **11**	15[d]	36 %
				0.125 mol %/ **12**	15[d]	10 %
				0.125 mol %/ **13**	15[d]	51 %
				0.125 mol %/ **14**	15[d]	4 %
				0.125 mol %/ **15**	15[d]	49 %
				0.125 mol %/ **21**	15[d]	38 %
2				0.025 mol %/ **17**	20	11 %
				0.1 mol %/ **17**	20	≥ 99 %
3				0.025 mol %/ **17**	20	81 %
				0.05 mol %/ **17**	20	≥ 99 %
4				0.025 mol %/ **17**	20	85 %
				0.05 mol %/ **17**	20	≥ 99 %
5				0.025 mol %/ **17**	20	21 %
				0.1 mol %/ **17**	16	≥ 99 %
6				0.025 mol %/ **17**	20	63 %
				0.1 mol %/ **17**	16	≥ 99 %
7				0.1 mol %/ **17**	20	≥ 99 %
8				0.1 mol %/ **17**	16	≥ 99 %
9				0.05 mol %/ **17**	16	≥ 99 %

[a] Conditions: 1 mmol of aryl chloride, 1.5 mmol of boronic acid, 2.0 mmol of Cs_2CO_3, 5 mL of dioxane, 100 °C. The reaction conditions and the amount of catalyst have not been optimized. [b] Catalyst Na_2PdCl_4/ligand (1:2). [c] Average of two runs, determined by GC using hexadecane as internal standard. [d] Reaction was performed at 80 °C.

only **12** and **13**, which have methyl groups at the 4,7-positions of the indenyl ring, are less efficient. Interestingly, the same two phosphines did not behave conspicuously in Suzuki and amination reactions. A similar decrease in activity was also observed when Pd complexes of the related and recently reported fluorenyldialkylphosphines, bearing methyl moieties at the 1,8-positions, were used for Sonogashira reactions with aryl bromides.[47] With this in mind, it is quite surprising that phosphine ligands **14** and **15**, bearing a methoxy group instead of a methyl group at the 4,7-positions, show the highest catalytic activities within the range of the examined ligands. Steric effects within the phosphine ligand play a minor role in the Sonogashira reaction: phosphines bearing P*i*Pr_2 moieties at the phosphorus atom show activities comparable to those with a PCy_2 moiety. Because of its high activity, (4,7-dimethoxy-1,2,3-trimethylindenyl)dicyclohexylphosphine (**15**) was studied in more detail.

Sonogashira coupling of phenylacetylene with several aryl chlorides was tested (Table 2, entries 2−5). Excellent conversions of the reactants were observed for all substrates at 100−120 °C at 1 mol % of catalyst. More difficult acetylene substrates such as 1-hexyne were converted with activated as well as with deactivated aryl chlorides, giving conversions as high as 94%. Indenylphosphine- and cyclopentadienylphosphine-based palladium catalysts compare favorably with other catalytic systems described by us and by others for the conversion of aryl chlorides.[14,19,47,81−86]

There are several ligands of comparable (high) activity not different from those reported for other highly active phosphine ligands such as *t*Bu_3P and Ad_2PBn.[14] This indicates that the nature of the applied ligand is not limiting the catalytic activity of a Pd phosphine complex in the Sonogashira reaction with aryl chlorides. Further improvement of catalytic activity in Sonogashira reactions with aryl chlorides must go along with optimization of other factors such as reaction conditions and additives.

Summary and Conclusions

We were able to synthesize eight new 1-indenyldialkylphosphonium and cyclopentadienyldialkylphosphonium salts (alkyl = *i*Pr, Cy). The respective Pd complexes with the liberated phosphines are highly active for various cross-coupling reactions with aryl chlorides. Quantitative yields in Suzuki coupling screening for a wide range of different substrates were achieved with 0.05−0.1 mol % of catalyst. Aryl chlorides could be coupled in quantitative yields in the Sonogashira reaction using 1 mol % of catalyst and in the Buchwald−Hartwig reaction

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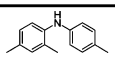
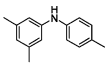
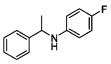
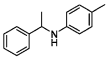
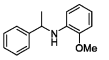
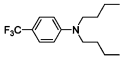
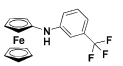
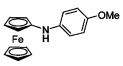
Table 2. Buchwald−Hartwig Amination[a] of Aryl Chlorides

entry	aryl chloride	amine	product	mol % catalyst / ligand	t (h)	conversion[b]
1				0.5 mol % / **18**	15	19 %
				0.5 mol % / **17**	15	40 %
				0.5 mol % / **10**	15	16 %
				0.5 mol % / **11**	15	16 %
				0.5 mol % / **12**	15	30 %
				0.5 mol % / **13**	15	63 %
				0.5 mol % / **14**	15	26 %
				0.5 mol % / **15**	15	43 %
				0.5 mol % / **21**	15	21 %
2				0.5 mol % / **17**	15	63 %
				0.5 mol % / **13**	15	54 %
				0.5 mol % / **15**	15	47 %
3				0.2 mol % / **13**	15	38 %
				0.5 mol % / **13**	20	≥ 99 %
4				0.5 mol % / **13**	15	51 %
				1.0 mol % / **13**	20	≥ 99 %
5				0.5 mol % / **13**	15	43 %
				1.0 mol % / **13**	20	95 %
6				0.5 mol % / **13**	15	≥ 99 %
7				0.5 mol % / **13**	15	≥ 99 %
8				0.5 mol % / **13**	15	≥ 99 %
9				0.5 mol % / **13**	20	≥ 99 %
10				0.5 mol % / **13**	20	16 %
11				0.5 mol % / **13**	20	85 %[c]
12				0.5 mol % / **13**	15	82 %[c]

[a] Conditions: 5 mL of toluene, 5 mmol of aryl chloride, 6 mmol of amine, 6 mmol of NaO*t*Bu, $Pd(OAc)_2$−ligand (phosphonium salt) (1:2), 120 °C. The reaction conditions have not been optimized. [b] Average of two runs, determined by GC using hexadecane as internal standard. [c] Isolated yield.

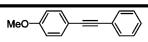
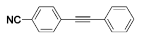
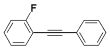
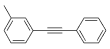
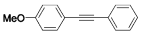
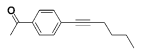
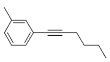
using 0.5 mol % of catalyst. Worthy of note is the successful implementation of ferrocenylamine in the Buchwald−Hartwig amination, resulting in ferrocenylarylamines in a single step in near-quantitative yield. In Sonogashira reactions the majority of the applied ligands showed activities comparable to reported activities of other highly active phosphine ligands such as tBu$_3$P and Ad$_2$PBn.[14] Further improvement of catalytic activity in Sonogashira reactions with aryl chlorides must go along with optimization of other factors such as reaction conditions and additives. Cp*PCy$_2$ (**17**) and 1,2,3,4,7-Me$_5$IndPCy$_2$ (**13**) are favorable ligands for amination reactions; Cp*PCy$_2$ (**17**) is favorable for Suzuki reactions involving aryl chlorides. Worthy of note is the facile synthesis of Cp*PCy$_2$ in a single step from commercially available precursors and the remarkable catalytic activity of the respective Pd complexes.

Experimental Section

All chemicals were purchased as reagent grade from commercial suppliers and used without furher purification, unless otherwise noted. Methyllithium (3.0 M in dimethoxyethane) was purchased from Sigma-Aldrich. THF was distilled over potassium and benzophenone under an argon atmosphere, diethyl ether was distilled over sodium/potassium alloy and benzophenone under an argon atmosphere, and toluene was distilled over sodium and benzophenone under an argon atmosphere. Dioxane was dried over CaH_2. Proton (^{1}H NMR), carbon (^{13}C NMR), and phosphorus (^{31}P NMR) nuclear magnetic resonance spectra were recorded on a Bruker DRX 500 spectrometer at 500, 125.75 and 202.46 MHz, respectively, or on a Bruker DRX 300 spectrometer at 300 and 75.07 MHz at 293 K. The chemical shifts are given in parts per million (ppm) on the delta scale (δ) and are referenced to tetramethylsilane (δ 0 ppm) for ^{1}H NMR and 65% aqueous H_3PO_4 (δ 0 ppm) for ^{31}P NMR. Abbreviations for NMR data: s = singlet; d = doublet; t = triplet; q = quartet; qi = quintet; dd = doublet of doublets; dt = doublet of triplets; dq = doublet of quartets; tt = triplet of triplets; m = multiplet. Mass spectra were recorded on a Finnigan MAT 95 magnetic sector spectrometer. Thin-layer chromatography (TLC) was performed using Fluka silica gel 60 F 254 (0.2 mm) on aluminum plates. Silica gel columns for chromatography were prepared with E. Merck silica gel 60 (0.063−0.20 mesh ASTM).

Cyclic voltammetry was carried out with an EG&G 263A-2 potentiostat. Cyclic voltammograms were recorded in dry CH_2Cl_2 under an argon atmosphere at ambient temperature. A three-electrode configuration was employed. The working electrode was a Pt disk (diameter 1 mm) sealed in soft glass with a Pt wire as counter electrode. The pseudo reference electrode was an Ag wire. Potentials were calibrated internally against the formal potential

Table 3. Sonogashira Reactions with Aryl Chlorides[a]

entry	aryl chloride	acetylene	product	mol % catalyst / ligand	t (h) / T (°C)	conversion [b]
1				1 mol %/ **18**	20 / 110	37 %
				1 mol %/ **17**	20 / 110	35 %
				1 mol %/ **10**	20 / 110	44 %
				1 mol %/ **11**	20 / 110	41 %
				1 mol %/ **12**	20 / 110	8 %
				1 mol %/ **13**	20 / 110	12 %
				1 mol %/ **14**	20 / 110	45 %
				1 mol %/ **15**	20 / 110	51 %
				1 mol %/ **21**	20 / 110	52 %
2				1 mol %/ **15**	15 / 100	95 %
3				1 mol %/ **15**	15 / 100	43 %
				1 mol %/ **15**	15 / 120	96 %
4				1 mol %/ **15**	15 / 120	91 %
5				1 mol %/ **15**	15 / 120	83 %
6				1 mol %/ **15**	15 / 120	94 %
7				1 mol %/ **15**	15 / 120	80 %

[a] Conditions: 1.5 mmol of aryl chloride, 2.1 mmol of acetylene, 3 mmol of Na_2CO_3, 5 mL of DMSO, catalyst 1 mol % (Na_2PdCl_4−ligand−CuI (4:8:3)). [b] Average of two runs.

of ferrocene (460 mV (CH_2Cl_2) vs Ag/AgCl).[87] NBu_4PF_6 (0.1 mol/L) was used as the supporting electrolyte.

GC experiments were run on a Clarus 500 GC instrument with autosampler and FID detector: column, Varian CP-Sil 8 CB (l = 15 m, d_i = 0.25 mm, d_F = 1.0 μm); N_2 flow (17 cm/s (split 1:50)); injector temperature, 270 °C; detector temperature, 350 °C; temperature program, isotherm 150 °C for 5 min, heating to 300 °C at a rate of 25 °C/min, isotherm for 15 min. HCp* was synthesized according to the Kohl and Jutzi procedure.[88] 2,3-Dimethyl-1-indanone (**3**) and 1,2,3-trimethylindene (**4**) were prepared according to the method of Rausch et al.[68] The ^{1}H NMR spectra were identical with those in the literature for **3**[89] and for **4**.[68]

2,3,4,7-Tetramethyl-1-indanone (6).[72] Under an argon atmosphere $AlCl_3$ (64 g, 0.48 mol) and CS_2 (250 mL) were placed in a 1 L three-necked round-bottomed flask fitted with a magnetic stirrer, addition funnel, thermometer, and reflux condenser. A mixture of tigloyl chloride (**2**; 42 g, 0.35 mol) and *p*-xylene (**5**; 42.8 mL, 0.35 mol) was added over a period of 1 h at −10 °C with vigorous stirring. The reaction mixture was stirred for 2 h at that temperature and then warmed to ambient temperature and stirred overnight. The brown reaction mixture was then refluxed for 3 h, cooled to ambient temperature, and poured carefully onto a mixture of concentrated HCl (300 mL) and ice (500 g). The CS_2 layer was separated in a separation funnel, and the aqueous layer was extracted with diethyl ether (3 × 100 mL). The combined organic layers were dried over magnesium sulfate and filtered, and the volatiles were removed in a rotary evaporator to give a red-brown liquid. This residue was rectified using a 35 cm Vigreux column to afford 2,3,4,7-tetramethyl-1-indanone (**6**; 34 g, 52%, 95−100 °C, 1.5−1.2 mbar) as a pale yellow liquid. **6** was found to be a mixture of the two isomers of 2,3,4,7-tetramethyl-1-indanone (the ratio of **6a** to **6b** was approximately 3:1). The ^{1}H NMR spectrum was identical with that in the literature.[71,72,90]

1,2,3,4,7-Pentamethylindene (7). In a 1 L three-necked round-bottomed flask fitted with a magnetic stirrer and a reflux condenser, 2,3,4,7-tetramethyl-1-indanone (**6**; 19.52 g, 0.1 mol) was dissolved in dry diethyl ether (300 mL) under an argon atmosphere. The mixture was cooled with an ice bath; methyllithium (45 mL, 3.0 M solution in dimethoxyethane, 0.135 mol) was added dropwise via a syringe. The mixture was refluxed for 3 h. The yellow reaction mixture was cooled to ambient temperature, and a mixture of concentrated HCl (20 mL) and H_2O (60 mL) was added via an addition funnel. The resulting mixture was transferred to a separation funnel and extracted with diethyl ether (3 × 200 mL). The combined organic layers were stirred overnight with 15 mL of concentrated HCl. After this time the reaction mixture was carefully adjusted to pH 7 with a saturated aqueous solution of Na_2CO_3. The reaction mixture was transferred into a separation funnel. The organic layer was washed with H_2O (3 × 100 mL), dried over $MgSO_4$, and filtered, and the volatiles were removed under reduced pressure to give a yellow liquid. This residue was purified via column chromatography (SiO_2, 25 × 9 cm; eluent cyclohexane) to afford 1,2,3,4,7-pentamethylindene (**7**; 8.35 g, 44%) as a yellow liquid followed by **6** (starting material; 9.60 g, 49%) (eluent cyclohexane−ethyl acetate (10:1)) as a yellow liquid. The NMR spectra were identical with those reported in the literature.[72]

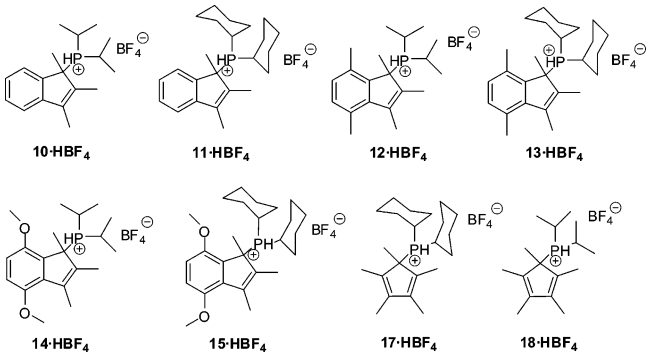
4,7-Dimethoxy-2,3-dimethyl-1-indanone (8). $AlCl_3$ (64 g, 0.48 mol) and CH_2Cl_2 (250 mL) (dried over $MgSO_4$) were placed under an argon atmosphere in a 500 mL three-necked round-bottomed flask fitted with a magnetic stirrer, addition funnel, inner thermometer, and reflux condenser. A mixture of tigloyl chloride (**2**; 42 g, 0.35 mol) and 1,4-dimethoxybenzene (**22**; 48.4 g, 0.35 mol, dissolved in 75 mL of CH_2Cl_2) was added over a period of 1 h at −10 °C with vigorous stirring. After 2 h of stirring at −2 to −5 °C, the mixture was warmed to ambient temperature and was

(87) Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877.
(88) Kohl, F. X.; Jutzi, P. *Organomet. Synth.* **1986**, *3*, 489.
(89) Sarrazin, J.; Tallec, A. *Tetrahedron Lett.* **1977**, *18*, 1579.
(90) Kaminsky, W.; Rabe, O.; Schauwienold, A.-M.; Schupfner, G. U.; Hanss, J.; Kopf, J. *J. Organomet. Chem.* **1995**, *497*, 181.

stirred overnight. The dark red mixture was then refluxed for 2 h; after it was cooled to ambient temperature, the reaction mixture was poured carefully onto a mixture of concentrated HCl (300 mL) and ice (500 g). Then the resulting yellow mixture was transferred to a separation funnel, the lower (CH_2Cl_2) layer was isolated, and the aqueous layer was extracted with diethyl ether (3 × 100 mL). The combined organic layers were dried over magnesium sulfate and filtered, and the volatiles were removed under reduced pressure to give a dark brown liquid. This residue was distilled using a 15 cm Vigreux column to give an orange-yellow light viscous liquid (110−115 °C, 0.8 mbar). The liquid was purified via column chromatography (SiO_2, 25 × 9 cm; eluent cyclohexane−ethyl acetate (1:1)) to afford 2,3-dimethyl-4,7-dimethoxy-1-indanone (**8**; 9.53 g, 12%), R_f = 0.35 (cyclohexane−ethyl acetate (5:1)) as a yellow solid. **8** was found to be a mixture of the two isomers of 4,7-dimethoxy-2,3-dimethyl-1-indanone (the ratio of **8a** to **8b** was approximately 4:1). ^{1}H NMR (500 MHz, $CDCl_3$): **8a**, δ 7.01 (d, ^3J = 8.0 Hz, 1H, arom), 6.74 (d, ^3J = 8.5 Hz, 1H, arom), 3.89 (s, 3H, O−C*H*$_3$), 3.84 (s, 3H, O−C*H*$_3$), 2.97 (qd, ^3J = 7.0 Hz, ^3J = 3.0 Hz, 1H, C*H* position 2), 2.22 (qd, ^3J = 7.5 Hz, ^3J = 3.0 Hz, 1H, C*H* position 3), 1.40 (d, ^3J = 7.0 Hz, 3H, CHC*H*$_3$), 1.26 (d, ^3J = 7.5 Hz, 3H, CHC*H*$_3$); **8b**, δ 6.99 (d, ^3J = 9.0 Hz, 1H, arom), 6.72 (d, ^3J = 7.5 Hz, 1H, arom), 3.89 (s, 3H, O−C*H*$_3$), 3.86 (s, 3H, O−C*H*$_3$), 3.53 (qi, ^3J = 7.5 Hz, 1H, C*H* position 2), 2.74 (qi, ^3J = 7.5 Hz, 1H, C*H* position 3), 1.20 (d, ^3J = 7.0 Hz, 3H, CHC*H*$_3$ position 2) 1.16 (d, ^3J = 7.0 Hz, 3H, CHC*H*$_3$ position 3). ^{13}C{^{1}H} NMR (125.77 MHz, $CDCl_3$): **8a**, δ 207.2, 151.8, 150.9, 148.2, 124.8, 117.5, 109.8, 56.0, 55.8, 51.6, 39.8, 19.5, 16.2; **8b**, δ 206.5, 151.5, 150.3, 149.3, 124.8, 116.9, 109.7, 56.0, 55.8, 47.1, 34.5, 16.1, 14.2. HRMS (*m*/*z*): calcd for $C_{13}H_{16}O_3$, 220.1099; found, 220.10909.

4,7-Dimethoxy-1,2,3-trimethylindene (9). Diethyl ether (100 mL) and Mg turnings (0.96 g, 39 mmol) were placed in a 250 mL three-necked round-bottomed flask fitted with a magnetic stirrer and reflux condenser. Under an argon atmosphere a solution of CH_3I (2.66 mL, 43 mmol) in degassed and dried diethyl ether (50 mL) was added via an addition funnel. The resulting gray solution was stirred for 45 min before addition of dry light petroleum (bp 80−110 °C; 20 mL). The ether was then removed under reduced pressure to yield a gray suspension which was cooled with ice. A solution of 2,3-dimethyl-4,7-dimethoxy-1-indanone (**8**; 7 g, 32 mmol) in pentane (50 mL) was added dropwise over a period of 40 min; then the mixture was refluxed for 3 h. At this point the yellow reaction mixture was cooled to 0 °C and a mixture of HCl (10 mL) and H_2O (40 mL) was added via an addition funnel. The resulting solution was transferred into a separation funnel and extracted with diethyl ether (3 × 50 mL). The combined organic layers were washed with 0.25 M aqueous sodium thiosulfate (3 × 30 mL) and filtered into a round-bottomed flask. Concentrated HCl (15 mL) was added, and the mixture was stirred at ambient temperature overnight. Then pH 7 was adjusted by addition of a saturated aqueous solution of Na_2CO_3. The organic layer was washed with water (3 × 100 mL), dried over $MgSO_4$, and filtered, and the volatiles were removed in vacuo. The residual liquid was purified via column chromatography (SiO_2, 35 × 9 cm; initial eluent cyclohexane−ethyl acetate (50:1)) to afford two fractions: 1,2,3-trimethyl-4,7-dimethoxyindene (**9**; 4.63 g, 66%) as a yellow liquid with R_f = 0.42 (eluent cyclohexane−ethyl acetate (2:1)) and 4,7-dimethoxy-2,3-dimethyl-1-indanone (**8**; starting material) with R_f = 0.35 (cyclohexane−ethyl acetate (5:1)) as a pale yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.70 (d, ^3J = 8.5 Hz, 1H, arom), 6.56 (d, ^3J = 9 Hz, 1H, arom), 3.81 (s, 3H, O−C*H*$_3$), 3.78 (s, 3H, O−C*H*$_3$), 3.23 (q, ^3J = 7.5 Hz, 1H, C*H*), 2.17 (m, 3H, C*H*$_3$), 1.90 (m, 3H, C*H*$_3$), 1.28 (d, ^3J = 7.0 Hz, 3H, CHC*H*$_3$). ^{13}C{^{1}H} NMR (125.77 MHz, $CDCl_3$): δ 150.6, 149.1, 142.9, 137.2, 135.7, 131.1, 111.1, 107.5, 56.7, 56.0, 46.4, 14.7, 13.4, 12.0. HRMS (*m*/*z*): calcd for $C_{14}H_{18}O_2$, 218.1306; found, 218.13110.

Chart 2. Indenyl- and Cyclopentadienyldialkylphosphonium Salts



Diagrams of the indenyl− and Cp*−dialkylphosphonium salts are given in Chart 2.

(1,2,3-Tetramethylindenyl)diisopropylphosphonium Tetrafluoroborate (10·HBF$_4$). In a 250 mL Schlenk flask 1,2,3-trimethylindene (**4**; 5.14 g, 32.5 mmol) was dissolved in Et_2O (100 mL) under an argon atmosphere. The mixture was cooled to −60 °C (N_2/isopropyl alcohol), and *n*BuLi (12.38 mL, 2.5 M solution in hexane, 31 mmol) was added. The solution was stirred for 10 min at −60 °C and then for 3 h at ambient temperature. A white precipitate was formed. Then the mixture was cooled to −60 °C and *i*Pr$_2$PCl (4.1 mL, 25.8 mmol) was added. The mixture was warmed to room temperature and stirred for an additional 2 h, and the LiCl that formed was removed by filtration over a pad of Celite under Schlenk conditions. The resulting slightly yellowish filtrate was treated dropwise with HBF_4·Et_2O (4.42 mL, 32 mmol) to give a white precipitate, which was separated via filtration and dissolved in 10 mL of acetonitrile. After filtration the clear filtrate was dropped into Et_2O (900 mL, vigorously stirred). The white precipitate that formed was separated via suction filtration. Removal of the volatiles in vacuo afforded **10·HBF$_4$** as a white solid (8.53 g, 91%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.68 (d, ^3J = 8.0 Hz, 1H, arom), 7.49−7.46 (m, 1H, arom), 7.39−7.35 (m, 2H, arom), 6.44 (dt, ^1J(P) = 473 Hz, ^3J = 4.0 Hz, 1H, P−*H*), 2.74−2.65 (m, 1H, C*H*), 2.45−2.36 (m, 1H, C*H*), 2.16 (s, 3H, C*H*$_3$ position 3), 2.15 (d, ^3J = 3.5 Hz, 3H, C*H*$_3$ position 2), 1.81 (d, ^3J(P) = 17 Hz, 3H, C*H*$_3$ position 1), 1.44 (ddd, ^3J(P) = 96.0 Hz, ^3J = 18.5 Hz, ^3J = 7.5 Hz, 6H, C*H*$_3$), 1.13 (ddd, ^3J(P) = 91.0 Hz, ^3J = 18.0 Hz, J = 7.0 Hz, 6H, C*H*$_3$). ^{13}C{^{1}H} NMR (125.77 MHz, $CDCl_3$): δ 145.1 (d, J = 3.8 Hz), 141.6, 138.9 (d, J = 8.0 Hz), 137.7 (d, J = 3.8 Hz), 129.8, 126.7, 123.5 (d, J = 3.5 Hz), 120.2, 51.5 (d, J = 32.6 Hz), 21.1 (d, J = 6.7 Hz), 20.8 (d, J = 5.6 Hz), 20.0 (d, J = 2.6 Hz), 19.9, 19.1 (d, J = 2.1 Hz), 18.2 (d, J = 2.3 Hz), 17.7 (d, J = 2.3 Hz), 11.1, 10.8. ^{31}P{^{1}H} NMR (202.46 MHz, $CDCl_3$): δ 36.6. ^{31}P NMR (202.46 MHz, $CDCl_3$): δ 36.6 (d, J = 472.9 Hz).

(1,2,3-Trimethylindenyl)dicyclohexylphosphonium Tetrafluoroborate (11·HBF$_4$). In a 100 mL Schlenk 1,2,3-trimethylindene (**4**; 2.44 g, 15.4 mmol) was dissolved in Et_2O (50 mL) under an argon atmosphere. The mixture was cooled to −60 °C (N_2/isopropyl alcohol), and *n*BuLi (5.9 mL, 2.5 M solution in hexane, 14.7 mmol) was added. The solution was stirred for 10 min at −60 °C and then for 3 h at ambient temperature. A white precipitate was formed. Then the mixture was cooled to −60 °C and Cy_2PCl (2.7 mL, 12 mmol) was added. The mixture was warmed to room temperature and stirred for additional 2 h, and the LiCl that formed was removed by filtration over a pad of Celite under Schlenk conditions. The resulting slightly yellowish filtrate was treated dropwise with HBF_4·Et_2O (2 mL, 14.9 mmol) to give a white precipitate, which was separated via filtration and dissolved in 10 mL of acetonitrile. After filtration the clear filtrate was dropped into Et_2O (900 mL, vigorously stirred). The white precipitate that formed was separated via suction filtration. Removal of the volatiles in vacuo afforded

11·HBF$_4$ as a white solid (2.82 g, 53%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64 (d, ^3J = 7.5 Hz, 1H, arom), 7.48 (t, ^3J = 7.5 Hz, 1H, arom), 7.40−7.35 (m, 2H, arom), 6.36 (dt, ^1J(P) = 475 Hz, ^4J = 3.5 Hz, 1H, P−*H*), 2.34−2.26 (m, 1H, C*H*), 2.16 (d, ^4J(P) = 4.0 Hz, 3H, CH_3 position 2), 2.14 (s, 3H, CH_3 position 3), 2.09−1.14 (m, 21H, CH_2 and C*H*), 1.81 (d, ^3J(P) = 17.5 Hz, 3H, CH_3 position 1). ^{13}C{^{1}H} NMR (125.77 MHz, $CDCl_3$): δ 145.2 (d, J = 3.1 Hz), 141.8, 138.8 (d, J = 7.8 Hz), 137.8 (d, J = 2.9 Hz), 129.8, 126.7, 123.4, 120.0, 51.6 (d, J = 32.2 Hz), 31.0, 30.7 (d, J = 10.8 Hz), 30.5, 29.8 (d, J = 3.0 Hz), 29.0 (d, J = 3.5 Hz), 28.2 (d, J = 3.3 Hz), 28.1 (d, J = 3.1 Hz), 26.9 (d, J = 6.0 Hz), 26.8 (d, J = 5.8 Hz), 26.6, 26.5, 24.9 (d, J = 3.8 Hz), 19.6, 11.2, 10.7. ^{31}P{^{1}H} NMR (202.46 MHz, $CDCl_3$): δ 29.2. ^{31}P NMR (202.46 MHz, $CDCl_3$): δ 29.2 (d, J = 473.7 Hz).

(1,2,3,4,7-Pentamethylindenyl)diisopropylphosphonium Tetrafluoroborate (12·HBF$_4$). In a 100 mL Schlenk flask 1,2,3,4,7 pentamethylindene (**7**; 3.0 g, 16 mmol) was dissolved in Et_2O (50 mL) under an argon atmosphere. The mixture was cooled to −60 °C (N_2/isopropyl alcohol), and *n*BuLi (16.1 mL, 2.5 M solution in hexane, 15 mmol) was added. The solution was stirred for 10 min at −60 °C and then for 3 h at ambient temperature. A white precipitate was formed. The mixture was cooled to −60 °C, and *i*Pr$_2$PCl (2.0 mL, 12.8 mmol) was added. The mixture was warmed to room temperature and stirred for additional 2 h, and the LiCl that formed was removed by filtration over a pad of Celite under Schlenk conditions. The resulting slightly yellowish filtrate was treated dropwise with HBF_4·Et_2O (2.2 mL, 16 mmol) to give a white precipitate that was separated via filtration and dissolved in 10 mL of chloroform. After filtration the clear filtrate was dropped into Et_2O (900 mL, vigorously stirred). The white precipitate that formed was separated via suction filtration. Removal of the volatiles in vacuo afforded **12·HBF$_4$** as a white solid (4.23 g, 84%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.09 (d, ^3J = 8.0 Hz, 1H, arom), 6.97 (d, ^3J = 8.0 Hz, 1H, arom), 6.41 (dq, ^1J(P) = 468 Hz, ^3J = 5.3 Hz, 1H, P−*H*), 2.84−2.75 (m, 1H, C*H*), 2.59 (s, 3H, CH_3 benzylic), 2.58 (s, 3H, CH_3 benzylic), 2.31 (d, ^4J = 4.5 Hz, 3H, CH_3 position 2), 2.23−2.14 (m, 1H, C*H*), 2.13 (s, 3H, CH_3 position 3), 1.89 (d, ^3J(P) = 17 Hz, 3H, CH_3 position 1), 1.50 (ddd, ^3J(P) = 107 Hz, ^3J = 18.5 Hz, J = 7.0 Hz, 6H, CH_3), 1.12 (ddd, ^3J(P) = 96.5 Hz, ^3J = 18.5 Hz, J = 7.0 Hz, 6H, CH_3). ^{13}C{^{1}H} NMR (125.77 MHz, $CDCl_3$): δ 143.3, 141.4 (d, J = 9.2 Hz), 140.6, 136.2 (d, J = 6.3 Hz), 133.6, 132.2 (d, J = 2.1 Hz), 130.2, 130.0, 52.9 (d, J = 29.2 Hz), 22.1 (d, J = 3.6 Hz), 21.8, 20.7, 20.4 (d, J = 2.3 Hz), 20.2, 19.1 (d, J = 1.8 Hz), 18.9 (d, J = 1.9 Hz), 18.7 (d, J = 1.8 Hz), 18.1 (d, J = 3.1 Hz), 15.2, 12.3. ^{31}P{^{1}H} NMR (202.46 MHz, $CDCl_3$): δ 34.0. ^{31}P NMR (202.46 MHz, $CDCl_3$): δ 34.0 (d, J = 463 Hz).

(1,2,3,4,7-Pentamethylindenyl)dicyclohexylphosphonium Tetrafluoroborate (13·HBF$_4$). In a 100 mL Schlenk flask 1,2,3,4,7-pentamethylindene (**7**; 3.0 g, 16 mmol) was dissolved in Et_2O (50 mL) under an argon atmosphere. The mixture was cooled to −60 °C (N_2/isopropyl alcohol), and *n*BuLi (6.1 mL, 2.5 M solution in hexane, 15 mmol) was added. The solution was stirred for 10 min at −60 °C and then for 3 h at ambient temperature. A white precipitate was formed. Then the mixture was cooled to −60 °C and Cy_2PCl (2.8 mL, 12.7 mmol) was added. The mixture was warmed to room temperature and stirred for an additional 2 h at ambient temperature, and the LiCl that formed was removed by filtration over a pad of Celite under Schlenk conditions. The resulting slightly yellowish filtrate was treated dropwise with HBF_4·Et_2O (2.2 mL, 16 mmol) to give a white precipitate which was separated via filtration and dissolved in 10 mL of chloroform. After filtration the clear filtrate was dropped into Et_2O (700 mL, vigorously stirred). The white precipitate that formed was separated via suction filtration. Removal of the volatiles in vacuo afforded **13·HBF$_4$** as a white solid (4.12 g, 69%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.10 (d, ^3J = 8.0 Hz, 1H, arom), 6.97 (d, ^3J = 8.0 Hz, 1H, arom), 6.30 (dq, ^1J(P) = 470 Hz, J = 3.5 Hz, 1H, P−*H*), 2.58 (s, 3H, CH_3 benzylic), 2.58 (s, 3H, CH_3 benzylic), 2.46−2.39 (m, 1H, C*H*), 2.31 (d, ^4J(P) = 4.5 Hz, 3H, CH_3 position 2), 2.11 (s, 3H, CH_3 position 3), 1.89 (d, ^3J(P) = 16.5 Hz, 3H, CH_3 position 1), 1.86−0.93 (m, 21H, CH_2 and C*H*). ^{13}C{^{1}H} NMR (125.77 MHz, $CDCl_3$): δ 143.0, 140.9 (d, J = 9.3), 140.3, 136.0 (d, J = 4.9 Hz), 133.1, 131.9 (d, J = 4.0), 129.7, 129.6, 52.8 (d, J = 29.2 Hz), 31.5 (d, J = 7.2 Hz), 31.2, 29.6 (d, J = 3.5 Hz), 29.1 (d, J = 3.3 Hz), 28.2 (d, J = 3.5 Hz), 27.9 (d, J = 3.8 Hz), 27.0 (d, J = 11.9 Hz), 26.8, 26.7, 26.6 (d, J = 13.1), 25.0, 24.8, 20.2, 19.8, 18.1, 14.8, 11.9. ^{31}P NMR (202.46 MHz, $CDCl_3$): δ 25.5 (d, J = 472.3 Hz).

(4,7-Dimethoxy-1,2,3-trimethylindenyl)diisopropylphosphonium Tetrafluoroborate (14·HBF$_4$). In a 100 mL Schlenk flask 4,7-dimethoxy-1,2,3-trimethylindene (**9**; 1.7 g, 7.79 mmol) was dissolved in Et_2O (50 mL) under an argon atmosphere. The mixture was cooled to −60 °C (N_2/isopropyl alcohol), and *n*BuLi (3.0 mL, 2.5 M solution in hexane, 7.43 mmol) was added. The solution was stirred for 10 min at −60 °C and then for 3 h at ambient temperature. A white precipitate was formed. Then the mixture was cooled to −60 °C and *i*Pr$_2$PCl (1.0 mL, 6.24 mmol) was added. The mixture was warmed to room temperature and stirred for an additional 2 h at ambient temperature, and the LiCl that formed was removed by filtration over a pad of Celite under Schlenk conditions. The resulting slightly yellowish filtrate was treated dropwise with HBF_4·Et_2O (1 mL, 7.72 mmol) to give a white precipitate, which was separated via filtration and dissolved in 10 mL of chloroform. After filtration the clear filtrate was dropped into Et_2O (700 mL, vigorously stirred). The white precipitate that formed was separated via suction filtration. Removal of the volatiles in vacuo afforded **14·HBF$_4$** as a white solid (1.73 g, 66%). ^{1}H NMR (500 MHz, CD_3CN): δ 7.13 (dd, ^3J = 9.0 Hz, J = 1.5 Hz, 1H, arom), 6.99 (d, ^3J = 9.0 Hz, 1H, arom), 6.39 (dq, ^1J(P) = 465.5 Hz, ^3J = 3.0 Hz, 1H, P−*H*), 3.99 (s, 3H, O−CH_3), 3.87 (s, 3H, O−CH_3), 3.10−3.00 (m, 1H, C*H*), 2.62−2.51 (m, 1H, C*H*), 2.30 (dd, ^4J(P) = 5.0 Hz, J = 1.0 Hz, 3H, CH_3 position 2), 2.13 (s, 3H, CH_3 position 3), 1.86 (d, ^3J(P) =16.5 Hz, 3H, CH_3 position 1), 1.45 (ddd, ^3J(P) = 100 Hz, ^3J = 19 Hz, ^3J = 7.0 Hz, 6H, CH_3), 1.18 (ddd, ^3J(P) = 72.5 Hz, ^3J = 17.5 Hz, ^3J = 7 Hz, 6H, CH_3). ^{13}C{^{1}H} NMR (125.77 MHz, CD_3CN): δ 150.8 (d, J = 2.1 Hz), 150.4, 139.7 (d, J = 9.0 Hz), 137.6 (d, J = 3.4 Hz), 134.7 (d, J = 3.5 Hz), 130.5, 115.0, 110.5, 56.6, 56.1, 52.4 (d, J = 31.8 Hz), 23.4 (d, J = 35.8 Hz), 21.3 (d, J = 39.5 Hz), 19.9 (d, J = 2.64 Hz), 19.5 (d, J = 1.9 Hz), 19.0 (d, J = 2.9 Hz), 18.3 (d, J = 2.0 Hz), 17.7 (d, J = 2.3 Hz), 13.8, 10.8. ^{31}P NMR (202.46 MHz, CD_3CN): δ 33.1 (d, J = 464.8).

(4,7-Dimethoxy-1,2,3-trimethylindenyl)dicyclohexylphosphonium Tetrafluoroborate (15·HBF$_4$). In a 100 mL Schlenk flask 4,7-dimethoxy-1,2,3-trimethylindene (**9**; 1.7 g, 7.79 mmol) was dissolved in Et_2O (50 mL) under an argon atmosphere. The mixture was cooled to −60 °C (N_2/isopropyl alcohol), and *n*BuLi (3.0 mL, 2.5 M solution in hexane, 7.43 mmol) was added. A white precipitate was formed. The solution was stirred for 10 min at −60 °C and for 3 h at ambient temperature. Then the mixture was cooled to −60 °C and Cy_2PCl (1.3 mL, 6.19 mmol) was added. The mixture was warmed to room temperature and then for an additional 2 h at ambient temperature and the LiCl that formed was removed by filtration over a pad of Celite under Schlenk conditions. The resulting slightly yellowish filtrate was treated dropwise with HBF_4·Et_2O (1 mL, 7.79 mmol) to give a white precipitate, which was separated via filtration and dissolved in 10 mL of chloroform. After filtration the clear filtrate was dropped into Et_2O (700 mL, vigorously stirred). The white precipitate that formed was separated via suction filtration. Removal of the volatiles in vacuo afforded **15·HBF$_4$** as a white solid (1.72 g, 55%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.93 (dd, ^3J = 9.0 Hz, J = 1.5 Hz, 1H, arom), 6.77 (d, ^3J = 9.0 Hz, 1H, arom), 6.24 (ddd, ^1J(P) = 472.5, ^3J = 5.5 Hz, J

= 2.5 Hz, 1H, P−*H*), 3.92 (s, 3H, O−CH_3), 3.84 (s, 3H, O−CH_3), 2.60−2.49 (m, 1H, C*H*), 2.28 (dd, ^4J(P) = 4.0 Hz, J = 1.0 Hz, 3H, CH_3 position 2), 2.18−2.11 (m, 1H, C*H*), 2.06 (s, 3H, CH_3 position 3), 1.76 (d, ^3J(P) =16.5 Hz, 3H, CH_3 position 1), 2.04−1.01 (m, 20H, CH_2). $^{13}C\{^1H\}$ NMR (125.77 MHz, $CDCl_3$): δ 149.7 (d, J = 1.9 Hz), 149.5, 138.9 (d, J = 7.0), 136.9 (d, J = 3.0 Hz), 134.2 (d, J = 2.8), 129.7, 113.8, 109.1, 56.3, 55.7, 51.6 (d, J = 32.2 Hz), 32.3, 32.0, 30.6, 30.3, 29.3(d, J = 3.3 Hz), 29.2 (d, J = 5.3 Hz), 28.2 (d, J = 3.3 Hz), 27.7 (d, J = 3.1 Hz), 27.0 (d, J = 13.1 Hz), 26.9 (d, J = 14.2 Hz), 25.1, 24.9, 17.8, 13.6, 10.7. $^{31}P\{^1H\}$ NMR (202.46 MHz, $CDCl_3$): δ 25.4. ^{31}P NMR (202.46 MHz, $CDCl_3$): δ 25.4 (d, J = 471.1 Hz).

Cp*PCy$_2$·HBF$_4$ (17·HBF$_4$). In a 250 mL Schlenk flask pentamethylcyclopentadiene (HCp* (**16**);[88] 2.9 g, 21.3 mmol) was dissolved in diethyl ether (100 mL) and treated with *n*BuLi (8.1 mL, 2.5 M in hexane, 20.3 mmol) at −60 °C. The mixture was stirred for 4 h at ambient temperature, to give a thick white suspension. THF (absolute, 100 mL) was added, and the suspension was quenched with Cy_2PCl (3.93 g, 16.9 mmol) at −60 °C. The reaction mixture was stirred at ambient temperature overnight and filtered over a small pad of Celite. The clear, colorless filtrate was then quenched with HBF_4·Et_2O (2.7 mL, 19.9 mmol), which led to precipitation of the phosphonium salt as a white solid about 3 min after the addition of the acid. The solid was separated via suction filtration and washed with Et_2O, and the volatiles were removed in vacuo to afford **17·HBF$_4$** as a white solid (3.7 g, 52%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.06 (dt, ^1J(PH) = 470 Hz, ^3J = 4 Hz, 1 H, P*H*), 2.15−2.07 (m, 2 H, C*H*), 2.03−1.99 (m, 2 H, CH_2), 1.98 (s, 6 H, CH_3), 1.89 (d, ^4J(PH) = 3.5 Hz, 6 H, CH_3), 1.89−1.85 (m, 6 H, CH_2), 1.73−1.56 (m, 6 H, CH_2), 1.51 (d, ^3J(PH) = 17.5 Hz, 3 H, CH_3), 1.32−1.25 (m, 6 H, CH_2). $^{13}C\{^1H\}$ NMR (125.75 MHz, $CDCl_3$): δ 142.7 (d, J(P−C) = 6.8 Hz), 134.8, 55.1 (d, J(P−C) = 28.3 Hz), 30.3, 30.0, 29.6 (d, J(P−C) = 3.5 Hz), 28.5 (d, J(P−C) = 3.4 Hz), 26.9 (d, J(P−C) = 11.9 Hz), 26.7 (d, J(P−C) = 13.6 Hz), 25.0, 17.3 (d, J(P−C) = 3.3 Hz), 11.4 (d, J(P−C) = 22.1 Hz). ^{31}P NMR (202.45 MHz, $CDCl_3$): δ 26.7 (d, J(P−H) = 471.5 Hz).

Cp*P*i*Pr$_2$·HBF$_4$ (18·HBF$_4$). In a 250 mL Schlenk flask pentamethylcyclopentadiene (HCp* (**16**); 2.79 g, 20.5 mmol) was dissolved in diethyl ether (absolutely, 175 mL) and treated with *n*BuLi (7.8 mL of a 2.5 M solution in hexane, 19.5 mmol) at −60 °C. The mixture was stirred for 4 h at ambient temperature (magnetic stirrer), resulting in a thick white suspension. THF (absolute, 50 mL) was added, followed by *i*Pr_2PCl (2.48 g, 16.25 mmol) at −60 °C. The reaction mixture was stirred at ambient temperature overnight and filtered over a small pad of Celite. The clear, colorless filtrate was quenched with HBF_4·Et_2O (2.76 mL, 20.3 mmol), which led to precipitation of the phosphonium salt as a white solid. The solid was separated via suction filtration and washed with Et_2O, and the volatiles were removed in vacuo to afford **18·HBF$_4$** as a white solid (5.2 g, 94%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.21 (dt, ^1J(PH) = 468.5 Hz, ^3J = 4.5 Hz, 1 H, P*H*), 2.52−2.43 (m, 2 H, C*H*), 2.00 (s, 6 H, CH_3), 1.89 (d, ^4J(PH) = 3.0 Hz, 6 H, CH_3), 1.51 (d, ^3J(PH) = 17.5 Hz, 3 H, CH_3), 1.47 (dd, ^3J(PH) = 18.5 Hz, ^3J = 7.0 Hz, 6 H, CH_3), 1.38 (dd, ^3J(PH) = 18 Hz, ^3J = 7.5 Hz, 6 H, CH_3). $^{13}C\{^1H\}$ NMR (125.75 MHz, $CDCl_3$): δ 143.2 (d, J(P−C) = 6.7 Hz), 135.0, 55.2 (d, J(P−C) = 29.2 Hz), 20.8 (d, J(P−C) = 38.4 Hz), 20.1 (d, J(P−C) = 2.5 Hz), 18.8 (d, J(P−C) = 3.3 Hz), 18.1 (d, J(P−C) = 3.4 Hz), 11.8 (d, J(P−C) = 39.4 Hz). $^{31}P\{^1H\}$ NMR (202.45 MHz, $CDCl_3$): δ 34.9. ^{31}P NMR (202.45 MHz, $CDCl_3$): δ 34.9 (d, J(P−H) = 469.3 Hz).

General Procedure for the Synthesis of Phosphines from the Respective Phosphonium Salts. The phosphonium salt was first dissolved in the minimum amount of CH_2Cl_2, and then Et_3N (10 equiv per phosphonium group) was added. After the mixture was stirred for 30 min, twice the volume of Et_2O was added to quantitatively precipitate the Et_3NH^+ salt. Following the filtration of the precipitates, the volatiles were evaporated from the filtrate. The remaining material is pure phosphine, typically formed in quantitative yields.

General Procedures for the Cross-Coupling Reactions. All cross-coupling reactions are carried out under an argon atmosphere in deaerated solvents (*freeze and thaw*).

Suzuki Reaction of Aryl Chlorides (in Dioxane). (a) Preparation of the Catalyst Stock Solution. Na_2PdCl_4 (0.05 mmol), phosphonium salt (0.1 mmol), and Cs_2CO_3 (0.2 mmol) were placed in a Schlenk tube. Dioxane (5.0 mL) was added, and the mixture was stirred at 45 °C for 2 h until the solution turned off-white. This stock solution had a concentration of 0.01 M in [Pd].

(b) Cross-Coupling Reaction. To the aryl chloride (1 mmol) were added boronic acid (1.5 mmol), Cs_2CO_3 (2 mmol), dioxane (5 mL), and the catalyst stock solution. The reaction mixture was stirred at 100 °C in an aluminum block. After it was cooled to room temperature, the reaction mixture was diluted with ether (15 mL) and washed with water (10 mL) and the organic phase was dried over $MgSO_4$, filtered, and concentrated in vacuo. The product was isolated by column chromatography (silica, cyclohexane−ethyl acetate (100:2)). Alternatively, the yield was determined via gas chromatography with hexadecane or diethylene glycol di-*n*-butyl ether as an internal standard.

Sonogashira Reaction of Aryl Chlorides (in dmso). Dry dmso (5 mL, crown cap), aryl chloride (1.5 mmol), acetylene (2.1 mmol), and Na_2CO_3 (3 mmol) were placed in a Schlenk tube. Then the catalyst was added in the given concentration, Na_2PdCl_4−ligand (phosphonium salt)−CuI (4:8:3), under argon. The reaction mixture was stirred at 100−120 °C in an aluminum block for 12−20 h. After it was cooled to room temperature, the reaction mixture was diluted with ether (15 mL) and washed with water (10 mL) and the organic phase was dried over $MgSO_4$, filtered, and concentrated in vacuo. The product was isolated by column chromatography (silica, cyclohexane−ethyl acetate (100:2)). Alternatively, the yield was determined via gas chromatography with hexadecane or diethylene glycol di-*n*-butyl ether as an internal standard.

Buchwald−Hartwig Amination of Aryl Chlorides (in Toluene). Dry toluene (5 mL), aryl chloride (5 mmol), amine (6 mmol) and NaO*t*Bu (6 mmol) were placed in a Schlenk tube. Next the catalyst was added in the given concentration, followed by Na_2PdCl_4/ligand (phosphonium salt) (1:2). The reaction mixture was stirred at 120 °C in an aluminum block. After it was cooled to room temperature, the reaction mixture was diluted with ether (15 mL) and washed with water (10 mL) and the organic phase was dried over $MgSO_4$, filtered, and concentrated in vacuo. The product was isolated by column chromatography (silica, cyclohexane−ethyl acetate (90:10)). Alternatively, the yield was determined via GC with hexadecane or diethylene glycol di-*n*-butyl ether as an internal standard.

***N*-Ferrocenyl-4-methoxyaniline (19).** ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.89 (d, ^3J = 9.0 Hz, 2 H, C*H*, ar), 6.81 (d, ^3J = 9.0 Hz, 2 H, C*H*, ar), 4.61 (s (br), 1 H, N*H*), 4.16 (s, 7 H, Fc), 3.99 (s, 2 H, Fc), 3.77 (s, 3 H, CH_3). $^{13}C\{^1H\}$ NMR (125.77 MHz, $CDCl_3$): δ 153.3, 139.5, 117.2, 114.6, 102.8, 68.7, 64.1, 60.4, 55.7. CV: $E_{1/2}$ = 0.142 V; ΔE = 76 mV. HRMS (*m*/*z*): calcd for $C_{17}H_{17}NOFe$, 307.0659, found, 307.06654.

***N*-Ferrocenyl-3-(trifluoromethyl)aniline (20).** ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27−7.24 (m, 2 H, ar), 7.01 (d, ^3J = 7.5 Hz, 1 H, C*H*, ar), 6.95 (dd, ^3J = 8.0 Hz, J = 2.0 Hz, 1 H, C*H*, ar), 5.10 (s (br), 1 H, N*H*), 4.23 (t, ^3J = 2.0 Hz, 2 H, Fc), 4.20 (s, 5 H, Fc), 4.07 (t, ^3J = 1.5 Hz, 2 H, Fc). $^{13}C\{^1H\}$ NMR (125.77 MHz, $CDCl_3$): δ 146.5, 131.4 (q, ^2J = 31.2 Hz, *C*−CF_3, ar), 129.5, 125.8 (q, ^1J = 273.3 Hz, *C*F_3), 117.4, 114.8 (q, ^3J = 4.8 Hz), 110.6 (q, ^3J = 4.1 Hz), 98.7, 69.0, 64.9, 62.4. CV: $E_{1/2}$ = 0.268 V; ΔE = 72 mV). HRMS (*m*/*z*): calcd for $C_{17}H_{14}NF_3Fe$, 345.0427; found, 345.04401.

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Note Added after ASAP Publication. In the version of this paper published on the Web on April 11, 2007, the two boldface paragraph heads in the right-hand column of the third page were incorrect. The version that now appears is correct.

Note Added in Proof. After submission of the manuscript a copper catalyzed amination of ferrocenyl iodide was reported: Özçubukçu, S.; Schmitt, E.; Leifert, A.; Bolm, C. *Synth.* **2007**, 389.

Supporting Information Available: Figures giving NMR spectra of the new products and cyclic voltammograms of the ferrocenes. This material is available free of charge via the Internet at http://pubs.acs.org.

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