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Congested Ferrocenyl Polyphosphanes Bearing Electron-Donating or Electron-Withdrawing Phosphanyl Groups: Assessment of Metallocene Conformation from NMR Spin Couplings and Use in Palladium-Catalyzed Chloroarenes Activation

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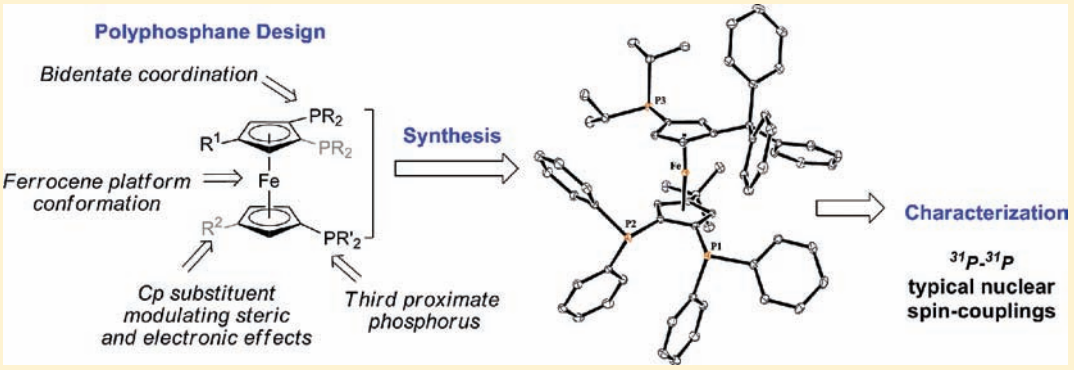
Supporting Information

ABSTRACT:



The synthesis of novel substituted cyclopentadienyl salts that incorporate both a congested branched alkyl group (*tert*-butyl, (triphenyl)methyl, or tri(4-*tert*-butyl)phenylmethyl) and a phosphanyl group is reported. The introduction of either electron-withdrawing or electron-donating substituents (furyl, *i*-propyl, cyclohexyl, *tert*-butyl) on P atoms was generally achieved in high yield. The modular synthesis of ferrocenyl polyphosphanes from an assembly of these cyclopentadienyl salts was investigated, leading to the formation of new triphosphanes (denoted as **9**−**12**) and diphosphanes (denoted as **14**−**16**). The resulting phosphanes are not sensitive to air or moisture, even when electron-rich substituents are present. This set of polyphosphanes displays varied conformational features, which are discussed in the light of their multinuclear NMR characterization in solution and of the X-ray solid state structure of the representative triphosphane 1,2-bis(diphenylphosphanyl)-1′-(di*iso*propylphosphanyl)-3′-(triphenyl)methyl-4-*tert*-butyl ferrocene, **11**. In particular, the existence of a range of significantly different nonbonded ("through-space", TS) spin−spin coupling constants between heteroannular P atoms, for the triphosphanes of this class, allowed their preferred conformation in solution to be appraised. The study evidences an unanticipated flexibility of the ferrocene platform, despite the presence of very congested *tert*-butyl and trityl groups. Herein, we show that, contrary to our first belief, the preferred conformation for the backbone of ferrocenyl polyphosphanes can not only depend on the hindrance of the groups decorating the cyclopentadienyl rings but is also a function of the substituents of the phosphanyl groups. The interest of these robust phosphanes as ligands was illustrated in palladium catalysis for the arylation of *n*-butyl furan with chloroarenes, using direct C−H activation of the heteroaromatic in the presence of low metal/ligand loadings (0.5−1.0 mol %). Thus, 4-chlorobenzonitrile, 4-chloronitrobenzene, 4-chloropropiophenone, and 4-(trifluoromethyl)chlorobenzene were efficiently coupled to *n*-butyl furan, using $Pd(OAc)_2$ associated to the new diphosphane ligands 1,1′-bis(di*iso*propylphosphanyl)-3,3′-di(triphenyl)methyl ferrocene (**15**) or 1,1′-bis(dicyclohexylphosphanyl)-3,3′-di(triphenyl)methylferrocene (**16**), which respectively hold the electron-rich −P*i*-Pr_2 and $-PCy_2$ groups.

INTRODUCTION

Ferrocene has emerged as an important motif in organometallic chemistry, because of its useful applications within materials science, electrochemistry, biomedical research, or ligand chemistry and homogeneous catalysis.[1] Tertiary phosphanes play also a major role in modern metal-catalyzed organic reactions, and many highly efficient catalytic procedures reported for C−C,

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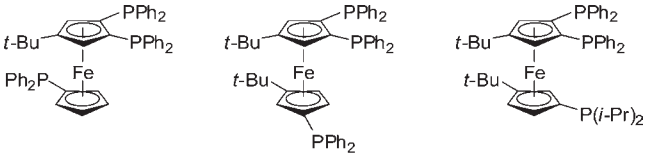


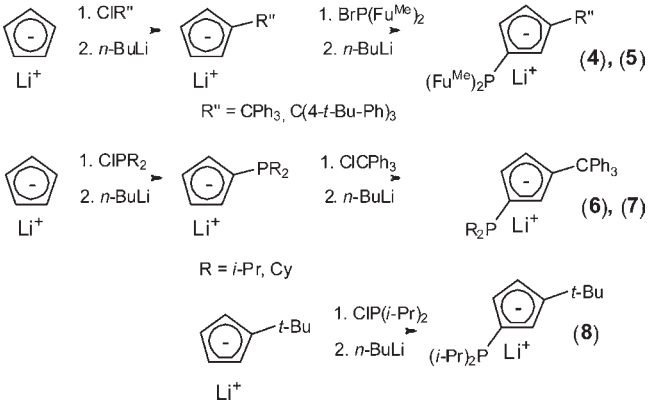
Figure 1. Polyphosphane catalytic auxiliaries **1**−**3** built on a ferrocenyl backbone.

C−N, or C−O bond formation by palladium-catalyzed cross-coupling reactions are carried out in the presence of phosphane auxiliary ligands.[2] In addition to monodentate and bidentate phosphane ligands, the high effectiveness of some polydentate phosphanes (triphosphanes or tetraphosphanes) in the palladium-catalyzed synthesis of fine chemicals has been recognized in the past decade.[2e−j] As a part of our program that is directed toward the development of air-stable efficient polydentate ligands for cross-coupling reactions,[3] we have showed that ferrocenyl phosphanes—and especially triphosphanes (Figure 1)—can be suitable ligands for C−H activation of heteroaromatic compounds.[4] The relevant properties of these phosphanes prompted us to enlarge the diversity of substituted ferrocenyl polyphosphanes *with a search for a controlled conformation of the ferrocene platform*, possibly because of congested branched alkyl substituents on the cyclopentadienyl rings (see **2** and **3** in Figure 1). We were also interested in the investigation of substantial changes in the electron-donating properties of P atoms and in the variation of the congested groups on cyclopentadienyl (Cp) rings. The synthesis of several new congested ferrocenyl diphosphane and triphosphane incorporating groups of the (triphenyl)methyl type (trityl) is reported. Tertiary phosphanes bearing electron-donor isopropyl and cyclohexyl groups were also introduced with the view to promote oxidative addition of haloarenes on metals. In addition, the synthesis of phosphanes bearing an electron-withdrawing furyl group was also achieved for the purpose of comparing ligand effects, and to possibly promote the reductive elimination step in metal-catalyzed processes. The analysis of the conformation adopted in solution by these new polyphosphanes was assessed from multinuclear NMR and from the X-ray structure of an original ferrocenyl triphosphane holding both a *tert*-butyl and a (triphenyl)methyl congested group on different cyclopentadienyl (Cp) rings. With the help of pertinent phosphorus nuclear-spin coupling analysis in solution, the preferred conformation for these metallocene was estimated, indicating an unanticipated flexibility of the phosphanes. These new ligands were tested in the direct arylation of *n*-butyl furan with chloroarenes to further substantiate their interest in palladium-catalyzed C−C cross-couplings and heteroarenes C−H activation.

RESULTS AND DISCUSSION

Cyclopentadienyl (Cp) Functionalized with Congested Groups and Electron-Rich or Electron-Poor Phosphanes. The functionalization of cyclopentadienyl (Cp) rings is fairly well-known and widely used.[5,6] Yet, only a limited number of metallocenic *poly*phosphanes of higher rank than *di*phosphanes are available for use in synthetic chemistry and homogeneous catalysis.[7−9] Regarding the general methods available to yield functionalized ferrocenes,[3c] some reactivity and selectivity problems may be encountered when a direct phosphanylation of the ferrocene backbone is employed to produce polyfunctionalized ferrocenes.[10,11] Thus, the formation of adequately substituted

Scheme 1. Synthetic Pathways to Cyclopentadienyl (Cp) Salts 4−8



cyclopentadienyl fragments and their assembly by reaction with an iron halide in a final step is also a pertinent pathway to yield polyfunctionalized ferrocenes. Following this way, ferrocenyl phosphanes incorporating two different Cp rings (dissymmetric ferrocenyl phosphanes) could be obtained and, sometimes, even preferentially formed than the expected symmetric species.[3c] Usually, the structural differences between the symmetric and dissymmetric ferrocenes formed allow their easy isolation by routine chromatography. Finally, the new Cp salts formed throughout this methodology may be used for the formation of other metallocene or hemimetallocene complexes (Group 4, lanthanides, etc.).[5,6] We have previously described the synthesis of a Cp lithium salt bearing a (diphenyl)phosphanyl group and the (triphenyl)methyl group starting from [Cp(trityl)Li].[3g] We further extended this work to the synthesis of Cp lithium salt variants **4**−**8** that are presented in Scheme 1.

These compounds were obtained in excellent yields, albeit following different synthetic pathways. The lithium salts **4** and **5**, featuring the electron-withdrawing furyl groups, were obtained in yields of >85% from the reaction of [Cp(trityl)Li] and [Cp(*t*-Bu-trityl)Li] (*t*-Bu-trityl = [tri(4-*tert*-butyl)phenyl)methyl]) with the appropriate bromophosphane ($BrP(Fu^{Me})_2$). Conversely, the attempts of functionalization with electron-rich phosphanyl groups of Cp lithium salts substituted by a trityl group failed. Presumably, a trityl group on the Cp ring diminishes the global nucleophilicity of the ring, in addition to the significant hindrance that it generates. As a consequence, chloro(dialkyl)phosphanes may have an electrophilic character that is too weak for the reaction to proceed easily. Thus, to synthesize lithium salts **6** and **7**, phosphanylation was first carried out on the nonsubstituted Cp ring, and the trityl group was introduced in a second step. The introduction of $-P(t\text{-Bu})_2$ fragments in place of $-P(i\text{-Pr})_2$ or $-PCy_2$ groups was determined to be particularly difficult. Lithium salts **6** and **7**, which incorporated electron-donating alkyl groups, were obtained in yields of >90% from the reaction of $[CpP(i\text{-Pr})_2Li]$ or $[CpPCy_2Li]$, with the chlorophosphane $ClCPh_3$. In contrast to the lack of reactivity found for [Cp(trityl)Li] and [Cp(*t*-Bu-trityl)Li] salts, we observed that, from [Cp(*t*-Bu)Li], it is nevertheless possible to obtain the lithium salt **8** $[Cp(t\text{-Bu})P(i\text{-Pr})_2Li]$ via successive reaction with $ClP(i\text{-Pr}_2)$ and *n*-BuLi, although a comparatively lower yield was obtained (77%). The difference in NMR chemical shifts observed for the P atoms in compounds **4**−**8**, ranging between 0.21 and −60 ppm.

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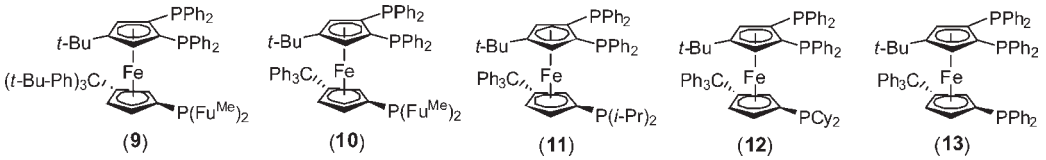

Figure 2. Triphosphanes **9**−**13** built on a ferrocenyl backbone.

70 ppm, attests the variety of steric and σ-electron-donating properties[12] of the phosphanyl groups in the lithium salts synthesized.

Synthesis and Characterization of Congested Ferrocenyl Triphosphanes. The Cp lithium salts **4**−**8** were engaged with $FeCl_2$ and [*t*-BuCp$(PPh_2)_2$Li] to form the dissymmetric triphosphanes **9**−**12** (see Figure 2). These compounds are worth comparing with the triphosphane **13** previously reported (Figure 2),[3g] especially regarding their structural and conformational features.

Table 1 gathers, for this set of triphosphanes, the P chemical shifts and their specific J_{PP} coupling constants in $CDCl_3$. We have established that constrained polyphosphanes may eventually show very intense nuclear spin−spin couplings between P nuclei, depending on their proximity in space and on a suitable orientation of their lone pairs.[13] These through-space (TS) couplings range from small values (i.e., 1−2 Hz) to very large values (sometimes >100 Hz).[14] They are frequently called "long-range" couplings, since the nuclei involved are generally separated by at least four covalent bonds. However, this term is misleading, since, with the exception of rare fully conjugated systems, spin−spin transmission does not occur through the many bonds that link the two remote interacting atoms. The coupling is actually a consequence of a *scalar* direct nuclear−nuclear nonbonded, electron-mediated interaction. This scalar nonbonded spin−spin coupling is directly observed between magnetically nonequivalent nuclei experiencing lone-pairs overlap, independent of any NMR pulse sequence.[13] Several relevant structural features are noticed for the electron-rich and electron-poor ferrocenyl triphosphanes **9**−**13**, from the comparison of their solution NMR data.

Except for compound **11**, three intense coupling constants between P_A, P_B, and P_M are detected, which lead to typical multiplet signals. The detectable coupling constants for the *heteroannular* P atoms pairs $J(P_AP_M)$ and $J(P_BP_M)$, which range between 6 Hz and 22 Hz, indicate nonbonded spin−spin nuclear coupling ($^{TS}J_{PP}$) operating via P lone-pair electrons rather than spin couplings through four covalent bonds. The existence of these spin couplings indicates the spatial proximity of the P atoms concerned and, therefore, is informative on the conformation of the metallocene backbone in solution. The similarity of $J(P_AP_M)$ and $J(P_BP_M)$ in **13** (11−12 Hz) had led us to propose, for this compound, a conformation in solution averaged around the one described in Figure 3a,[3g] in which the spatial distances between $P_A\cdots P_M$ and $P_B\cdots P_M$ would range within a similar value.

Thus, a similar time-averaged conformation is proposed for **9** and **10**, which hold the electron-withdrawing furyl moieties, with regard to their identical $J(P_AP_M)$ and $J(P_BP_M)$ of 17 and 23 Hz, respectively. As a result of the electronic properties of furyl groups, the pseudo-triplets corresponding to the resonance of the shielded P_M atoms in phosphanes **9** and **10** are observed at −69.3 and −68.9 ppm, respectively, as expected, at much higher field, compared to $-PPh_2$ groups (found between −17.0 and −25.0 ppm, depending on the atom environment). Consistently, deshielded P_M atoms with chemical shifts observed at −13.0 and −3.7 ppm are obtained with the more electron-donating cyclohexyl and isopropyl groups, respectively. Regarding the electron-rich triphosphanes **11** and **12**, based on the strong differences found for the through-space (TS) $J(P_AP_M)$ and $J(P_BP_M)$, the mutual distances between P atoms in solution are expected to be strongly dissimilar. Substantially different $J(P_AP_M)$ and $J(P_BP_M)$ were observed in each case with much weaker $J(P_BP_M)$ coupling constants found, compared to $J(P_AP_M)$. This suggests that the phosphorus P_M is in a closer proximity to P_A than to P_B (see Figure 3b), inducing a shorter $P_A\cdots P_M$ TS distance, and, thus, a more-efficient lone-pair overlap and a more-intense spin−spin nuclear coupling. An extreme situation is observed with phosphane **11**, for which no $J(P_BP_M)$ is detected, and a weaker $J(P_AP_M)$ coupling constant of 6 Hz is observed: this suggests a conformation that is in better agreement with Figure 3c.

Our first idea of a fully controlled rigid conformation of the ferrocene backbone by congested groups on Cp ring,[3g] which had been deduced from the structural features of compound **13** solely, is clearly not consistent with these results. From the different triphosphanes reported here, it is clearly observed that the conformational control of the ferrocene backbone is not systematically ensured by the introduction of congested trityl and *tert*-butyl groups on Cp rings, despite the strong hindrance that is created. Thus, several different metallocene conformations are obtained in solution, even when a strictly identical functionalized ferrocene platform is used. Herein, a ferrocene holding heteroannular trityl and *tert*-butyl groups constitutes the common backbone of triphosphanes **9**−**13**, yet their conformations, and the mutual positions of P atoms in solution, differ significantly. Thus, the nature of the substituents on the phosphanyl groups is also critical in establishing the preferred averaged conformation of these polyphosphanes.

X-ray structural characterization of a ferrocenyl polyphosphane incorporating a trityl group has never been reported until now, since we previously failed to generate suitable single crystals of compound **13**. However, proper single crystals of compound **11** were obtained and analyzed by X-ray diffraction (XRD) (see Figure 4, top). The solid-state structure determined is not in full agreement with the ^{31}P NMR observed in solution. The conformation found in the crystal (Figure 4, bottom) is different from that which is predictable in solution from $^{31}P^{31}P$ NMR spin couplings (see Figure 3c). The interaction evidenced in NMR between P_M and P_A ($J(P_AP_M)$ = 6 Hz) is not consistent with the solid-state conformation obtained due to the orientation of P lone pairs and the very long spatial distance between the nuclei ($dP_A\cdots P_M$ = 5.998 Å and $dP_B\cdots P_M$ = 7.180 Å). Nevertheless, the change from the conformation in Figure 3c to the conformation at the bottom of Figure 4 may be achieved by a counterclockwise rotation of 72° of the upper Cp ring. This rotation would not be hindered by the branched alkyl substituents on the Cp rings, since they would not cross each other.

An alternative is a slight rotation of the $C-P_M$ and $C-P_A$ bonds to allow overlapping of the P lone pairs of P_A and P_M,

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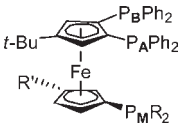
Table 1. ^{31}P NMR Data for Triphosphanes 9−13



	δ P_A		δ P_B		δ P_M				
triphosphane	(ppm)	signal	(ppm)	signal	(ppm)	signal	JP_AP_B (Hz)	JP_AP_M (Hz)	JP_BP_M (Hz)
(**9**)	−16.8	dd	−23.6	dd	−69.3	p-t	56	17	17
(**10**)	−19.3	dd	−24.3	dd	−68.9	p-t	72	23	23
(**11**)	−24.0	dd	−21.4	d	−3.7	d	59	6	*a*
(**12**)	−24.0	dd	−21.9	dd	−13.0	dd	63	22	6
(**13**)	−18.8	dd	−24.9	dd	−21.7	p-t	41	12	11

[a] Not detected (below 0.5 Hz).

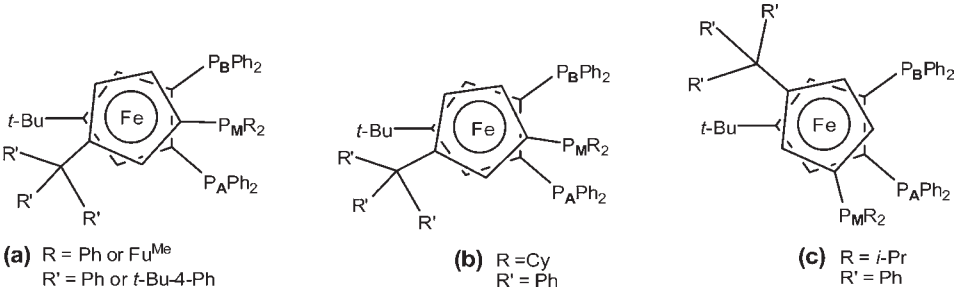


Figure 3. Time-averaged conformations in solution proposed for **9**, **10**, **13** (left), **12** (middle), and **11** (right) from ^{31}P^{31}P NMR spin−spin couplings.

which may lead to the small $^{TS}J_{PP}$ observed in solution. The rotational ability of the −P(*i*-Pr_2) group in **11** is also supported by a J_{PC} coupling constant of 5 Hz observed in ^{13}C NMR between the P-atom-bearing isopropyl groups and the methyl groups of *t*-Bu. Such rare J_{PC} coupling constants have been already observed in a parent compound and in other polyphosphanes.[2h,13c] They are explained as a TS (P,C) nuclear spin transmission between the P lone-pair electrons and the pairing electrons of the C−C bonds of the *t*-Bu methyl groups. The conformation displayed in the X-ray structure determined for **11** (Figure 4) is in good agreement with this interaction, evidenced in ^{13}C NMR, from an adequate orientation of P3 lone pair toward the *t*-Bu group.

J_{PP} and J_{PC} TS spin−spin couplings observed for the phosphanes **9**−**13** indicate an unforeseen flexibility of their backbone, despite the presence of *tert*-butyl and trityl congested groups. Another important element of the ferrocenylphosphane flexibility is indicated by the molecular structure of **11** with the dihedral angle of the two Cp ring planes. This angle would be normally expected to be close to zero with strictly parallel Cp ring planes; however, as visible from Ortep in Figure 4, a fairly open dihedral angle of 7.55(7)° is found. In the related ferrocenylphosphane bearing two *t*-Bu groups instead of one *t*-Bu and one trityl group,[4c] the corresponding dihedral angle was found to be 3.89(15)°.[15]

Synthesis and Characterization of Congested Electron-Rich Ferrocenyl Diphosphanes. Lithium salts **4**−**8** were employed to form the new electron-rich ferrocenyl diphosphanes **14**−**16** (see Figure 5) using our Cp assembly method. The diphosphane **17** has been previously determined to be an effective ligand to promote palladium-catalyzed direct coupling of furans and thiophenes with bromoarenes, but was useless for chloroarenes activation.[3g] Modified versions of **17**-bearing electron-enriched phosphanyl groups were synthesized as ferrocenylphosphanes **14**−**16**. This class of diphosphanes **14**−**17** usually forms mixtures of *rac* and *meso* diastereomers, since no asymmetric control is exerted during synthesis; eventually, upon purification, only the major diastereomer may be obtained, as has been the case for **17**.[16]

The P chemical shifts for **14**−**16** (Table 2, column 2) are found to be significantly deshielded, compared to **17**, because of the electron-donating properties of alkyl groups attached to the P nuclei. Similar to diphosphane **17**, **15** was obtained as a single diastereomer after workup, with a P signal shift at −2.4 ppm, and three signals for Cp protons at 3.99, 3.68, and 3.52 ppm. Phosphanes **14** and **16** were obtained showing two sets of signals, corresponding to the presence of two diastereomers. Compound **14** (*rac*+*meso*) is characterized by a major P signal at −0.2 ppm (85%) and a minor signal at −1.4 ppm. In agreement, two sets of three proton signals from Cp rings are found at 4.09, 3.96, and 3.93 ppm (major) and 4.01, 3.99, and 3.98 ppm (minor). Compound **16** (*rac*+*meso*) is characterized by a major P signal at −8.7 ppm (70%) and a minor signal at −10.7 ppm. Broad signals for protons of the cyclopentadienyl rings are observed at 3.84, 3.65, and 3.45 ppm.

In order to check the electron-donating ability of the novel polyphosphanes, we measured the ^{31}P−^{77}Se coupling constants for the diselenide derivatives of **14**−**17** (reported in Table 2). For comparison purposes, we also measured the $^{1}J_{P,Se}$ coupling constant for the diselenide derivative of the ferrocenyl diphosphane analogue 1,1′-bis[di(5-methyl-2-furyl)phosphanyl]ferrocene, $Fc[P(Fu^{Me})_2]_2$, incorporating furyl moieties. An increase in these coupling constants

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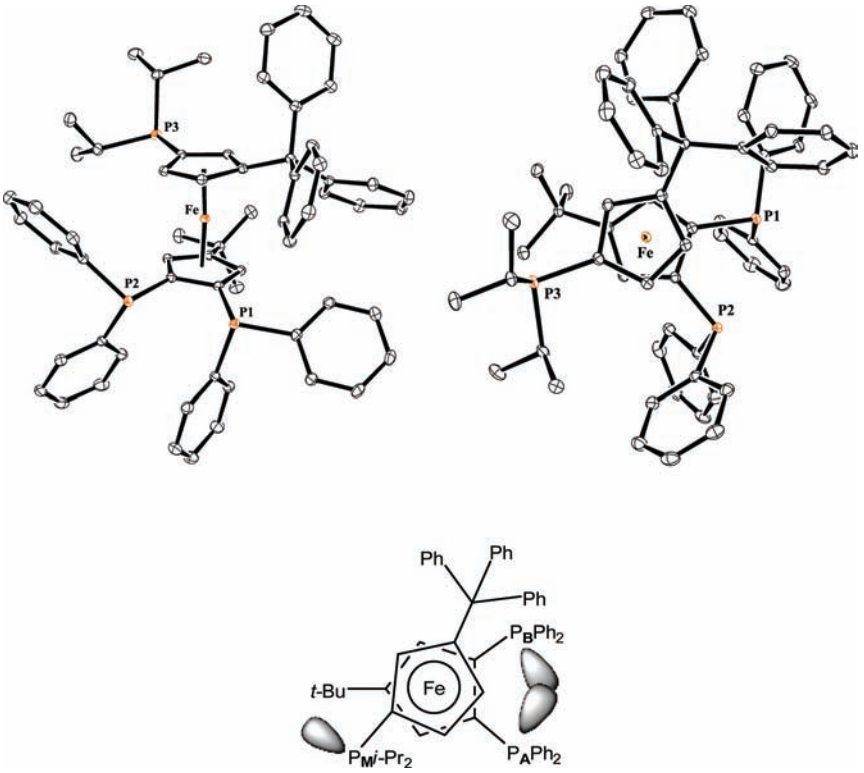

Figure 4. ORTEP views (top) and drawing (bottom) of the molecular structure determined in the solid state for **11** (H atoms are omitted for the sake of clarity, ellipsoids with 30% probability).

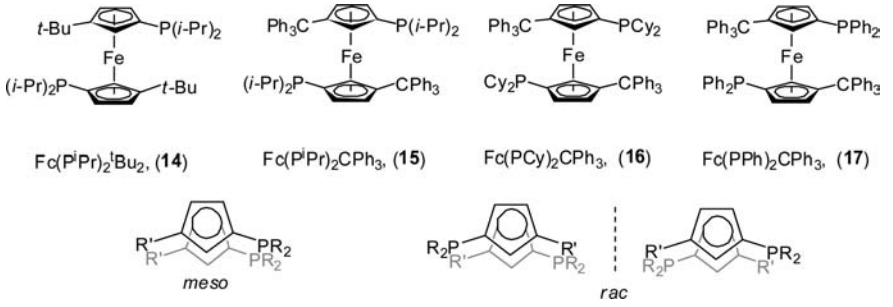

Figure 5. Diphosphanes **14**−**17** and their stereoisomeric properties (planar chirality).

indicates an increase in the *s* character of the P lone-pair orbital (i.e., an electron-withdrawing effect of the phosphane on the selenium (Se)).[12] As a benchmark, the $^1J_{P,Se}$ value for triphenylphosphine selenide (Se═PPh$_3$) and for 1,1′-bis[diphenylphosphanyl]ferrocene selenide have been reported to be 730 and 737 Hz, respectively.[12a,c] The $^1J_{P,Se}$ values determined from **14**, **15**, and **16** (710, 696, and 688 Hz, respectively), compared to $^1J_{P,Se}$ from **17** (741 Hz), confirmed the expected electron-donating properties of the phosphanes. Consistently, the electron-withdrawing properties induced at phosphorus by the presence of methylfuryl groups were supported by the $^1J_{P,Se}$ of 787 Hz found for Fc[Se═P(Fu^{Me})$_2$]$_2$, which is among the highest (P,Se) coupling constants reported to date for such types of tertiary phosphanes.[12]

Table 2. ^{31}P NMR Data for Diphosphanes 14−17 and Corresponding Phosphane Selenides

diphosphane	δ −PR$_2$ (ppm) *meso* and/or *rac*	δ −P(═Se)R$_2$ (ppm)	$^1J_{P,Se}$ (Hz)
(**14**)	−0.2 (85%) / −1.3 (15%)	58.9 / 58.5	710 / 712
(**15**)	−2.4	50.6	696
(**16**)	−8.7 (70%) / −10.7 (30%)	41.8[a]	688
(**17**)	−24.0	31.4	741
Fc[P(Fu^{Me})$_2$]$_2$[b]	−64.9	−8.1	787

[a] For the major isomer. [b] Data taken from refs 3a and 3b.

Arylation of Heteroaromatics with Chloroarenes via C−H Bond Activation. With this set of new diphosphanes and triphosphanes in hand, which are built by following the ligand design that we choose, we examined their influence in palladium catalysis in the activation of chloroarenes for arylation of heteroaromatics by direct C−H activation. Compared to arylation reactions using organometallic reagents (for example, boronic acids, or zinc or tin organometallics) the direct regioselective coupling of heteroaromatics with aryl halides via C−H bond activation/functionalization is an interesting synthetic

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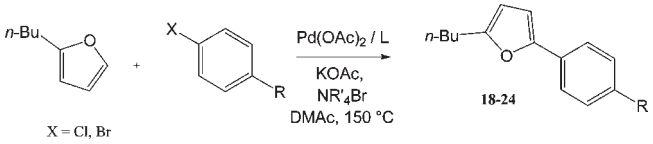
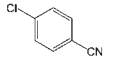
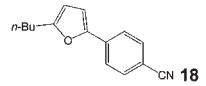
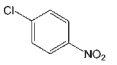
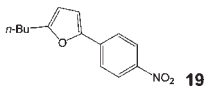
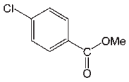
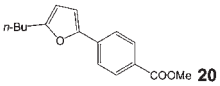
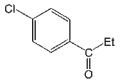
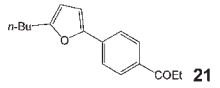
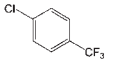
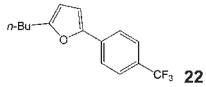
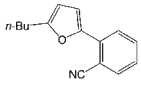
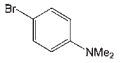
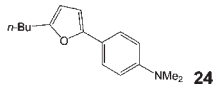
Table 3. Palladium-Catalyzed Direct 5-Arylation of *n*-Butylfuran with Ligands 15 or 16



Entry	Halide	Product	Ligand	Pd [mol%]	Yield [%][a]
1		 **18**	**14**	1	88
2			**15**	1	87
3			**16**	1	90
4			**17**	1	79
5			**dppf**	1	59
6		 **19**	**14**	1	69
7			**15**	1	90
8			**16**	1	80
9			**17**	1	64
10		 **20**	**15**	1	37
11		 **21**	**14**	1	82
12			**15**	1	90
13			**15**	0.5	73
14			**16**	0.5	94
15			**dppf**	1	24
16		 **22**	**16**	1	90
17		 **23**	**15**	1	34
18		 **24**	**14**	1	24
19			**15**	0.5	38
20			**15**	1	38
21			**16**	0.5	44

[a] $Pd(OAc)_2$, ligands **14**−**17** or dppf, aryl halide (1 mmol), 2-*n*-butylfuran (2 mmol), KOAc (2 mmol), Bu_4NBr (1 mmol), DMAc, 150 °C, 16 h, under argon.

strategy. Significant advantages are provided by this type of C−H activation, in terms of clean chemistry, with the formation of a halide salt as the main side-product and no stoichiometric metallic waste.[17,18]

Ligand-less palladium catalysts, and classical systems for C−H activation combining palladium and monophosphanes or diphosphanes ($Pd(OH)_2$−C*, $Pd(OAc)_2$, $Pd(PPh_3)_4$, $PdCl_2$−PCy_3, $Pd(OAc)_2/P(o\text{-tolyl})_3$, [$PdCl_2$(dppf)] (where dppf = bis(diphenylphosphanyl)ferrocene)) are not efficient for the activation of demanding bromoarenes and of chloroarenes for direct arylation of furans.[4a,17,18] This was confirmed by our preliminary screening experiments, and, in addition, we observed that triphosphanes **9** and **10** were not well-suited for direct arylation of heteroaromatics with aryl chlorides under our conditions (see Table 3). Their electron-poor character possibly disfavored one or several steps of the catalytic cycle, in particular, the oxidative addition of organic chlorides may be difficult, because of the low electronic density at P. We also observed that the catalytic performances of triphosphanes **11**−**13** in direct arylation of heteroaromatics with chloroarenes and hindered bromoarenes, if better than **9** and **10**, unfortunately did not match the performances previously obtained with related ferrocenyl triphosphanes.[4] Therefore, we focused our catalytic investigations on the diphosphanes **15** and **16**, which hold two electron-rich phosphanyl groups to promote the oxidative addition of chloroarenes, and for which the large bite angle that is associated to 1,1′-bidentate coordination may facilitate reductive elimination at palladium.[1a,11] A comparison with the $Pd(OAc)_2$/dppf (at 1 mol %) system was also conducted, and the results for the diphosphanes **14** and **17** were also checked, showing mainly that a catalyst loading below 1 mol % is not suited in their case. Table 3 summarizes the results obtained in the coupling of various chloroarenes with *n*-butylfuran. In the presence of the electron-deficient aryl chlorides (4-chlorobenzonitrile, 4-chloronitrobenzene, 4-chloropropiophenone, or 4-(trifluoromethyl)chlorobenzene) and 0.5−1.0 mol % $Pd(OAc)_2$, associated with 0.5−1.0 mol % of ligand **15** or **16**, the 5-arylation products **18**, **19**, **21**, and **22** were obtained in very high yields (entries 2, 3, 7, 8, 12, 13, 14, and 16), with the catalysts incorporating dppf (entries 5 and 15) being less efficient. On the other hand, the reaction toward the ester **20** was difficult (entry 10, 37% yield). In the presence of 2-chlorobenzonitrile, which is more congested, a modest yield of 34% in **23** was obtained, because of partial conversion of this aryl chloride (entry 17). An electron-rich aryl bromide, 4-bromo-*N*,*N*-dimethylaniline was also found to have a moderate reactivity in the presence of these catalysts, and **24** was obtained in yields of 38%−44% (entries 19, 20, and 21). Diphosphanes **14** and **17** may give satisfactory results, albeit at 1 mol % catalyst (entries 1, 4, 6, 9, 11, and 18). Therefore, this catalytic system tolerates substrates that incorporate useful functional groups such as nitriles, nitro, or keto

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groups, which can be manipulated for accessing more-sophisticated heterocyclic molecules.

The results obtained illustrate the potential of air-stable, moisture-insensitive electron-rich diphosphanes **15** and **16** in this specific arylation reaction. Assuming that these new phosphanes effectively promote oxidative addition, because of electron-enriched P donors, our study suggests that, to go further in the scope of these direct arylation reactions, and especially in using lower catalyst loadings, the oxidative addition of chloroarenes is probably not the single chemical step to facilitate. The design of ligands more specifically assisting the C−H activation of heteroarenes and arenes, which remains a catalytic step subject of much questioning,[19] might be of much interest. To extend the scope of this attractive reaction, our ongoing research is currently directed toward this goal.

■ CONCLUSION

Ferrocene-based diphosphane and triphosphane ligands for metal catalysis were synthesized from new cyclopentadienyl (Cp) salts substituted with both congested branched alkyl groups and phosphanyl groups, with the P atoms bearing either electron-donor isopropyl and cyclohexyl groups or electron-withdrawing furyl groups. The triphosphanes **9**−**13** formed present, in solution, a set of "through-space" (TS) spin−spin nuclear $^{31}P^{31}P$ couplings due to the proximity of the P atoms. The diversity of J_{PP} collected for compounds **9**−**13** (from 0 to 23 Hz) arises from their conformational differentiation and highlight the flexibility of their ferrocene backbone via Cp rings rotation. Thus, different conformations in solution are evidenced for these ferrocenyl triphosphanes, despite their identical ferrocene backbone, which incorporates very congested *tert*-butyl and (triphenyl)methyl groups. The X-ray structure determination of the triphosphane **11** also indicates that preferred conformations in the solid state and in solution can be different for the same species, since the long P···P distances obtained in the X-ray molecular structure are not consistent with the $^{TS}J_{PP}$ observed in solution. In addition, in the molecular structure of **11**, we observe that the ferrocene backbone can adapt itself to the congested environment by a significant deviation of parallelism of the Cp rings with a dihedral angle deviation above 7°. The cyclopentadienyl lithium salts **4**−**8** were also employed to form the electron-rich ferrocenyl diphosphanes **14**−**16** using the Cp assembly method. The effect of the diphosphane and triphosphane ligands was compared in the arylation of *n*-butyl furan, via C−H activation, with aryl chlorides catalyzed by palladium. To date, ligand-less palladium catalysts and classical systems for C−H activation combining palladium and monophosphanes or diphosphanes (such as $Pd(OH)_2$−C*, $Pd(OAc)_2$, $[Pd(PPh_3)_4]$, $PdCl_2$−PCy_3, $Pd(OAc)_2$/P(*o*-tolyl)$_3$, $[PdCl_2(ddpf)]$ are not efficient for the activation of demanding bromoarenes and of chloroarenes for direct arylation of furans. The results obtained demonstrate the higher performance of the electron-rich diphosphanes **15** and **16** in the arylation of substituted furans with functionalized electron-deficient aryl chlorides, such as 4-chlorobenzonitrile, 4-chloronitrobenzene, 4-chloropropiophenone, or 4-(trifluoromethyl)chlorobenzene.

■ EXPERIMENTAL SECTION

The reactions were carried out in oven-dried glassware (115 °C) under an argon atmosphere using Schlenk and vacuum-line techniques. For the synthesis and characterization of lithium salts and phosphanes, all of the solvents, including deuterated solvents used for NMR spectroscopy, were dried and distilled prior to use. $FeCl_2$ from a commercial source was used (Aldrich anhydrous beads, 99.9%, <100 ppm H_2O). All catalytic reactions were performed using analytical-grade DMAc that was not distilled prior to use. Potassium acetate (99%+) was used. Commercial aryl halides and 2-*n*-butylfuran were used without purification. Flash chromatography was performed on silica gel (230−400 mesh). ^{1}H NMR (300.13, 500.13, or 600.13 MHz), ^{31}P NMR (121.49, 202.46, or 242.93 MHz), and ^{13}C NMR (75.47, 125.77, or 150.92 MHz), including low-temperature, ^{13}C *J* modulation APT, ^{13}C-dept 135 NMR experiments were performed in our laboratories (on Bruker Model 300, 600 or DRX 500 equipment) in $CDCl_3$ at 293 K, unless stated otherwise. The exact mass was measured on a Bruker MicrOTOF Q system.

Synthesis of Cyclopentadienyl Lithium Salts. The starting halide reagents 1-[bis(4-*tert*-butylphenyl)(chloro)methyl]4-*tert*-butylbenzene (4-*t*-Bu-Ph)$_3$CCl[20] and bis(5-methyl-2-furyl)bromophosphane $BrP(Fu^{Me})_2$,[3b] and the lithium salts (triphenyl)methylcyclopentadienyl lithium [Ph_3CCpLi], (*tert*-butyl)cyclopentadienyl lithium [*t*-BuCpLi], 1-diphenylphosphanyl-3-*tert*-butylcyclopentadienyl lithium [1-PPh_2-3-*t*-Bu-CpLi], and 1,2-bis(diphenylphosphanyl)-4-*tert*-butylcyclopentadienyl lithium [1,2-$(PPh_2)_2$-3-*t*-BuCpLi], were synthesized following procedures described in the literature.[3g,c,21] The protocols for the synthesis of [P(*i*-Pr)$_2$CpLi] and [PCy_2CpLi] salts were modified from the literature.[2g,22,23]

Di-(5-methyl-2-furyl)phosphanyl-3-[(triphenyl)methyl]cyclopentadienyl Lithium (4). To a stirred suspension of [CPh_3CpLi] (3.19 g, 10.15 mmol) in 40 mL of toluene at −80 °C was added, dropwise, a solution of $BrP(Fu^{Me})_2$ (2.52 g, 9.23 mmol) in 10 mL of toluene. The reaction mixture was stirred for 2 h, which allowed the temperature to slowly rise up to 0 °C, and was then stirred for 18 h at room temperature. The solution was filtered over Celite, to remove the LiCl precipitate, which was washed with 15 mL of toluene. The filtrate was evaporated almost to dryness, and 50 mL of heptane was added to the residue. The resulting colorless solution was treated at −40 °C with *n*-BuLi (7.15 mL, 1.6 M in hexane, 11.44 mmol). The reaction mixture was stirred for 18 h at room temperature. The air-sensitive white precipitate formed was filtered, washed with heptane, and dried under vacuum to give 4.03 g of **4** (yield 86%).

^{1}H NMR (THF-d_8): δ 2.19 (s, 6H, CH_3 furyl), 5.85 (d, 2H, ^3J = 1 Hz, H-furyl), 5.94, 6.01, 6.15 (m, 1H each, H-Cp), 6.24 (d, 2H, ^3J = 1 Hz, H-furyl), 7.02−7.33 (m, 15H, Ph). ^{31}P{^{1}H} NMR (THF-d_8): δ −60.70 (s).

Di-(5-methyl-2-furyl)phosphanyl-3-[tri-(4-*tert*-butylphenyl)methyl]cyclopentadienyl Lithium (5). The precursor [tri(4-*tert*-butylphenyl)methyl]cyclopentadienyl lithium was first synthesized following this protocol. To a stirred suspension of Cp lithium (1.2 g, 15 mmol) in 20 mL of toluene at −20 °C was added, dropwise, a suspension of 1-[bis(4-*tert*-butylphenyl)(chloro)methyl]4-*tert*-butylbenzene (2.6 g, 5.8 mmol) in 30 mL of toluene. The mixture was stirred for 24 h at room temperature under argon. The solution was filtered over Celite, to remove the LiCl precipitate. The filtrate was evaporated almost to dryness, and 20 mL of hexane was added to the residue. The resulting colorless solution was treated with *n*-BuLi (9 mL, 1.6 M in hexane, 14.4 mmol) at −20 °C. The reaction mixture was stirred for 24 h at room temperature. The air-sensitive white precipitate formed was filtered, washed with hexane, and dried under vacuum to give 3.26 g of lithium salt [(4-*t*-Bu-Ph)$_3$CCpLi] (yield 83%).

^{1}H NMR (THF-d_8): δ 1.28 (s, 27H, *t*-Bu), 5.43 (t, 2H, *J* = 4 Hz, H-Cp), 5.62 (t, 2H, *J* = 4 Hz, H-Cp), 7.05−7.15 (m, 12H, Ph).

To a stirred suspension of [(4-*t*-Bu-Ph)$_3$CCpLi] (2.78 g, 5.76 mmol) in 30 mL of toluene at −80 °C was added, dropwise, a solution of $BrP(Fu^{Me})_2$ (1.57 g, 5.76 mmol) in 15 mL of toluene. The reaction mixture was stirred for 24 h at room temperature. The solution was filtered over Celite to remove the LiCl precipitate, which was washed

with 15 mL of toluene. The filtrate was treated with *n*-BuLi (4.3 mL, 1.6 M in hexane, 6.91 mmol) at −80 °C. The reaction mixture was stirred for 24 h at room temperature. The solution was evaporated almost to dryness, and 20 mL of heptane were added to the residue. The resulting mixture was filtered and the solid was washed with 15 mL of heptane and dried under vacuum to give 3.52 g of **5** (yield 90%).

^{1}H NMR (THF-d_8): δ 1.34 (s, 27H, *t*-Bu), 2.29, 2.21 (s, 1H each, CH_3 furyl), 5.48 (s, 1H, H-Cp), 5.90 (s, 2H, H-furyl), 6.09 (m, 2H, H-Cp), 6.31 (s, 2H, H-furyl), 7.05−7.15 (m, 12H, Ph). ^{31}P{^{1}H} NMR (THF-d_8): δ −60.60 (s).

Di-*iso*propylphosphanyl-3-[(triphenyl)methyl]cyclopentadienyl Lithium (6). The precursor [CpP(*i*-Pr)$_2$Li] was first synthesized following this protocol. To a stirred suspension of CpLi (3.17 g, 44.0 mmol) in 60 mL of toluene at −80 °C was added, dropwise, ClP(*i*-Pr)$_2$ (6.71 g, 44.0 mmol). The reaction mixture was stirred for 2 h, which allowed the temperature to slowly rise up to 0 °C, and was then stirred for 18 h at room temperature. Twenty milliliters (20 mL) of heptane were added to the mixture, and after 10 min, it was filtered over Celite to remove LiCl. The filtrate was evaporated almost to dryness and 30 mL of heptane were added to the residue. The resulting colorless solution was treated with *n*-BuLi (27.5 mL, 1.6 M in hexane, 44.0 mmol) at −40 °C. The reaction mixture was stirred for 18 h at room temperature. The air-sensitive white precipitate formed was filtered, washed with heptane, and dried under vacuum to give 7.99 g of [CpP(*i*-Pr)$_2$Li] (yield = 94%).

^{1}H NMR (THF-d_8): δ 0.92 (m, 12H, CH(CH_3)$_2$), 1.86 (m, 2H, CH(CH$_3$)$_2$), 5.85, 5.92 (m, 2H each, H-Cp). ^{31}P{^{1}H}(THF-d_8): δ −3.40 (s).

To a stirred suspension of [CpP(*i*-Pr)$_2$Li] (10.1 g, 53.1 mmol) in 50 mL of toluene at −80 °C was added, dropwise, a suspension of $ClCPh_3$ (14.5 g, 52.0 mmol) in 40 mL of toluene. The mixture was stirred overnight, which allowed the temperature to slowly rise to room temperature. The solution was filtered over Celite, to remove the LiCl precipitate, which was washed with 15 mL of toluene. The filtrate was evaporated almost to dryness, and 50 mL of heptane were added to the residue. The resulting reddish solution was treated with *n*-BuLi (36.5 mL, 1.6 M in hexane, 58.4 mmol) at −80 °C. The reaction mixture was stirred for 18 h at room temperature. The air-sensitive purple red powder that formed was filtered, washed with heptane, and dried under vacuum to give 21.1 g of **6** (yield = 92%).

^{1}H NMR (THF-d_8): δ 0.60−1.3 (m, 12H, CH(CH_3)$_2$), 1.90 (m, 2H, CH(CH$_3$)$_2$), 5.40−6.70 (m, 3H, *H*-Cp), 6.70−7.70 (m, 15H, Ph). ^{31}P{^{1}H} NMR (THF-d_8): δ −3.22 (s).

Dicyclohexylphosphanyl-3-[(triphenyl)methyl]cyclopentadienyl Lithium (7). The precursor dicyclohexylphosphanylcyclopentadienyl lithium was first synthesized following this protocol. To a stirred suspension of Cp lithium (0.64 g, 8.9 mmol) in 15 mL toluene at −80 °C was added, dropwise, $ClPCy_2$ (2.07 g, 8.88 mmol). The reaction mixture was stirred for 1 h, which allowed the temperature to slowly increase to 0 °C, and was then stirred for 18 h at room temperature. The mixture was filtered over Celite, to remove the LiCl precipitate, which was washed with 10 mL of toluene. The filtrate was evaporated almost to dryness and 20 mL of heptane were added to the residue. The resulting colorless solution was treated with *n*-BuLi (6.11 mL, 1.6 M in hexane, 9.77 mmol) at −40 °C. The reaction mixture was stirred for 18 h at room temperature. The air-sensitive white precipitate that formed was filtered, washed with heptane, and dried under vacuum to give 2.23 g of [CpPCy$_2$Li] (yield = 94%).

^{1}H NMR (THF-d_8): δ 0.80−2.00 (m, 22H, Cy), 5.83 (m, 2H, H-Cp), 5.89 (m, 2H, H-Cp). ^{31}P{^{1}H} NMR (THF-d_8): δ −12.28 (s).

To a stirred suspension of [CpPCy$_2$Li] (3.71 g, 13.83 mmol) in 40 mL of toluene at −80 °C was added, dropwise, a suspension of $ClCPh_3$ (3.64 g, 13.07 mmol) in 40 mL of toluene. The mixture was stirred overnight, which allowed the temperature to slowly increase to room temperature. The solution was filtered over Celite, to remove the LiCl precipitate, which was washed with 15 mL of toluene. The filtrate was evaporated almost to dryness, and 60 mL of heptane were added to the residue. The resulting reddish solution was treated with *n*-BuLi (9.50 mL, 1.6 M in hexane, 15.2 mmol) at −80 °C. The reaction mixture was stirred for 18 h at room temperature. The air-sensitive purple red precipitate that formed was filtered, washed with heptane, and dried under vacuum to give 7.04 g of **7** (yield = 96%).

^{1}H NMR (THF-d_8): δ 0.50−1.90 (m, 22H, Cy), 5.6−6.5 (m, 3H, H-Cp), 6.8−7.8 (m, 15H, Ph). ^{31}P{^{1}H} NMR (THF-d_8): δ −11.60 (s).

Di-*iso*propylphosphanyl-3-*tert*-butylcyclopentadienyl Lithium (8). To a stirred suspension of [*t*-BuCpLi] (4.11 g, 32.1 mmol) in 30 mL of toluene at −80 °C was added dropwise ClP(*i*-Pr)$_2$ (5.15 mL, 32.1 mmol). The mixture was stirred for 16 h overnight, which allowed the temperature to slowly increase to room temperature. The solution was filtered over Celite, to remove the LiCl formed, which was washed twice with 15 mL of toluene. The filtrate was concentrated to ∼15 mL and was treated with *n*-BuLi (27.5 mL, 1.6 M in hexane, 44.0 mmol) at −40 °C. The temperature was allowed to increase slowly to room temperature, and stirring was continued for 16 h. The filtrate was evaporated almost to dryness, and 15 mL of heptane was added to the residue. This mixture was vigorously stirred for 4 h, and the white solid formed was filtered, washed with 15 mL of heptane, and dried under vacuum to give 6.01 g of **8** (yield 77%).

^{1}H NMR (THF-d_8): δ 0.97−1.13 (m, 12H, CH(CH_3)$_2$), 1.21 (s, 9H, *t*-Bu), 1.97 (m, 2H, CH(CH$_3$)$_2$), 5.85, 5.94, 6.02 (m, 1H each, H-Cp). ^{31}P{^{1}H} NMR (THF-d_8): δ 0.21 (s).

Ferrocenyl Phosphanes Synthesis. *1,2-Bis(diphenylphosphanyl)-1′-di(5-methyl-2-furyl)phosphanyl-3′-tri(4-tert-butylphenyl) methyl-4-tert-butyl Ferrocene (**9**).* To a stirred suspension of $FeCl_2$ (0.51 g, 4.1 mmol) in 15 mL of THF was added, dropwise, by cannula, a solution of [*t*-BuCp-(PPh$_2$)$_2$Li] (1.98 g, 4.0 mmol) in 20 mL of THF at −40 °C. After the addition, the cooling bath was removed, which allowed the temperature to slowly increase to room temperature. After 1 h of stirring, a solution of [(*t*-BuPh)$_3$CCp(P(Fu^{Me})$_2$)Li] (2.4 g, 3.6 mmol) in 25 mL of THF at −10 °C was added to the reaction mixture. The mixture was refluxed for 24 h. After filtration of the brown-red suspension and evaporation of the filtrate, 4.3 g of an oily residue was obtained. Compound **9** was isolated in a pure form as an orange powder (1.5 g, 35% yield) from column chromatography on silica (toluene/heptane 7:3).

^{1}H NMR ($CDCl_3$): δ(ppm) = 0.67 (s, 9H, *t*-BuCp), 1.27 (s, 27H, (CH_3)$_3$CPh), 2.26, 2.07 (s, 3H each, CH_3-furyl), 4.12 (s broad, 2H, Cp), 4.17 (m, 2H, Cp), 4.24 (m, 1H, Cp), 5.80, 5.88, 6.32, 6.36 (m, 1H each, H-furyl), 6.85−7.45 (m, 32H, Ph). ^{31}P{^{1}H}($CDCl_3$): δ (ppm) = −16.8 (dd, 1P, $^3J_{PP}$ = 56 Hz, $^{TS}J_{PP}$ = 17 Hz, PPh$_2$), −23.6 (dd, 1P, $^3J_{PP}$ = 56 Hz, $^{TS}J_{PP}$ = 17 Hz, PPh$_2$), −69.3 (p-t, 1P, $^{TS}J_{PP}$ = 17 Hz, P(Fu^{Me})$_2$). ^{13}C NMR ($CDCl_3$): δ (ppm) = 156.4, 155.7 (s, 1C each, O*C*Me), 152.0 (d, 1C, $^1J_{PC}$ = 15 Hz, PCO), 149.4 (d, 1C, $^1J_{PC}$ = 22 Hz, PCO), 148.3 (s, 3C, *p*-Ph-trityl), 144.3 (s, 3C, *ipso*-Ph-trityl), 140.5 (d, 1C, $^1J_{PC}$ = 12 Hz, *ipso*-PhP), 138.8, (d, 1C, $^1J_{PC}$ = 15 Hz, *ipso*-PhP), 138.3 (d, 1C, $^1J_{PC}$ = 12 Hz, *ipso*-PhP), 137.7, (d, 1C, $^1J_{PC}$ = 12 Hz, *ipso*-PhP), 136.0 (d, J_{PC} = 20 Hz, Ph-P), 134.6 (d, J_{PC} = 5 Hz, Ph-P), 134.4 (d, J_{PC} = 4 Hz, Ph-P), 133.6 (d, J_{PC} = 20 Hz, Ph-P), 132.9 (d, J_{PC} = 20 Hz, Ph-P), 130.5 (s, 6C, *o*-Ph-trityl), 128.8 (s, Ph-P), 128.3 (d, J_{PC} = 9 Hz, Ph-P), 128.0 (s, Ph-P), 127.7 (d, J_{PC} = 6 Hz, Ph-P), 127.4 (d, J_{PC} = 6 Hz, Ph-P), 127.3 (d, J_{PC} = 8 Hz, Ph-P), 127.2 (s, Ph-P), 124.0 (s, 6C, *m*-Ph-trityl), 123.2 (d, 1C, $^2J_{PC}$ = 28 Hz, *C*H-furyl), 119.9 (d, 1C, $^2J_{PC}$ = 19 Hz, *C*H-furyl), 108.1 (s, 1C, 4-Fc), 106.7 (m, 2C, $^3J_{PC}$ = 5 Hz, *C*H-furyl), 104.2 (s, 1C, 3′-Fc), Cp quaternary C (1-Fc, 2-Fc, 1′-Fc) obscured, 75.0 (s, 1C, HC-Cp), 74.9 (m, 1C, HC-Cp), 73.2 (m, 1C, HC-Cp), 72.6 (m, HC-Cp), 72.5 (m, HC-Cp), 58.0 (s, 1C, *C*Ph$_3$), 34.3 (s, 3C, PhC-*t*-Bu), 31.4 (s, 9C, PhC-(CH_3)$_3$), 31.3 (s, 3C, CpC(CH_3)$_3$), 30.0 (s, 1C, Cp*C*-*t*-Bu) 14.0, 13.8 (s, 1C each, CH_3-furyl). $C_{79}H_{83}FeO_2P_3$ (1213.29). Exact mass [M+Na]$^+$: m/z = 1235.48379, simulated = 1235.48501, σ = 0.0427, err[ppm] = 0.8.

*1,2-Bis(diphenylphosphanyl)-1′-di(5-methyl-2-furyl)phosphanyl-3′-(triphenyl)methyl-4-tert-butyl Ferrocene (**10**).* To a stirred suspension

of $FeCl_2$ (0.30 g, 2.3 mmol) in 10 mL of THF was added, dropwise, by cannula, a solution of [*t*-BuCp(PPh_2)$_2$Li] (1.15 g, 2.3 mmol) in 20 mL of THF at −40 °C. After the addition, the cooling bath was removed, which allowed the temperature to slowly increase to room temperature. After 1 h of stirring, a solution of [$Ph_3CCp(P(Fu^{Me})_2)Li$] (1.13 g, 2.3 mmol) in 20 mL of THF at −10 °C was added to the reaction mixture. The mixture was refluxed for 24 h. After filtration and evaporation of the filtrate, a brown-red oil (1.92 g) was obtained, and 0.79 g of **10** was isolated as an orange powder (33% yield) from column chromatography on silica (toluene/heptane 7:3).

^{1}H NMR ($CDCl_3$): δ(ppm) = 0.68 (s, 9H, *t*-BuCp), 2.27, 2.07 (s, 3H each, C*H*$_3$-furyl), 4.19 (s broad, 3H, Cp), 4.14 (s, 1H, Cp), 4.05 (s, 1H, Cp), 5.78, 5.89 (s large, 1H each, H-furyl), 6.33, 6.36 (m, 1H each, H-furyl), 6.83−7.41 (m, 35H, Ph). ^{31}P{1H}($CDCl_3$): δ (ppm) = −19.3 (dd, 1P, $^3J_{PP}$ = 72 Hz, $^{TS}J_{PP}$ = 23 Hz, 1-PPh_2), −24.3 (dd, 1P, $^3J_{PP}$ = 72 Hz, $^{TS}J_{PP}$ = 23 Hz, 2-PPh_2), −68.9 (p-t, 1P, $^{TS}J_{PP}$ = 23 Hz, 1′-P(Fu^{Me})$_2$). ^{13}C NMR ($CDCl_3$): δ (ppm) = 155.5, 154.9 (s, 1C each, OC*M*e), 150.8 (d, 1C, $^1J_{PC}$ = 15 Hz, P*C*O), 148.2 (d, 1C, $^1J_{PC}$ = 22 Hz, P*C*O), 146.1 (s, 3C, *ipso*-Ph-trityl), 139.0 (d, 1C, $^1J_{PC}$ = 11 Hz, *ipso*-Ph), 137.4 (d, 1C, $^1J_{PC}$ = 14 Hz, *ipso*-Ph), 137.0 (d, 1C, $^1J_{PC}$ = 11 Hz, *ipso*-Ph), 136.6 (d, 1C, $^1J_{PC}$ = 10 Hz, *ipso*-Ph), 134.9 (d, J_{PC} = 24 Hz, Ph-P), 133.1 (d, J_{PC} = 20 Hz, Ph-P), 133.0 (d, J_{PC} = 20 Hz, Ph-P), 132.0 (d, J_{PC} = 20 Hz, Ph-P), 129.9 (s, 6C, *o*-Ph-trityl), 127.8 (s, Ph-P), 127.3 (d, J_{PC} = 9 Hz, Ph-P), 127.0 (s, Ph-P), 126.9 (m, Ph-P), 126.4 (m, Ph-P), 126.2 (s, 6C, *m*-Ph-trityl), 125.0 (s, 3C, *p*-Ph-trityl), 122.1 (d, 1C, $^2J_{PC}$ = 28 Hz, *C*H-furyl), 119.2 (d, 1C, $^2J_{PC}$ = 20 Hz, *C*H-furyl), 107.0 (s, 1C, 4-Fc), 105.7 (d, 2C, $^3J_{PC}$ = 8 Hz, *C*H-furyl), 102.6 (s, 1C, 3′-Fc), 79.5 (m, 2C, 1,2-Fc), Cp quaternary C (1′-Fc) obscured, 75.0 (m, 1C, HC-Cp), 74.4 (s, 1C, HC-Cp), 73.4 (s, 1C, HC-Cp), 72.0 (s, 1C, HC-Cp), 71.7 (m, 1C, HC-Cp), 58.2 (s, 1C, CPh_3), 30.2 (s, 3C, C(CH_3)$_3$), 29.1 (s, 1C, *C*(CH_3)$_3$), 13.0, 12.7 (s, 1C each, CH_3-furyl). $C_{67}H_{59}FeO_2P_3$ (1044.95). Exact mass [M+Na]$^+$: *m*/*z* = 1067.29636, simulated = 1067.29714, σ = 0.039, err[ppm] = 0.6.

*1,2-Bis(diphenylphosphanyl)-1′-(diisopropylphosphanyl)-3′-(triphenyl)methyl-4-tert-butyl Ferrocene (**11**).* To a stirred suspension of $FeCl_2$ (0.30 g, 2.4 mmol) in 15 mL of THF at −40 °C was added, dropwise, by cannula, a solution of 1,2-bis(diphenylphosphanyl)-4-*tert*-butylcyclopentadienyl lithium (1.16 g, 2.3 mmol) in 20 mL of THF. The reaction mixture was allowed to slowly warm to room temperature and was stirred for 2 h. The reaction mixture was then cooled to −40 °C, and a solution of 1-di*iso*propylphosphanyl-3-(triphenyl)methylcyclopentadienyl lithium **6** (1.00 g, 2.3 mmol) in 20 mL of THF was added. After the addition, the reaction mixture was allowed to slowly warm to room temperature, and then it was stirred for 18 h overnight. The THF solvent was removed, the residue was dissolved in 50 mL of toluene, and the resulting solution was refluxed for 18 h. The brown solution was then filtered through silica to yield a mixture of ferrocenyl phosphanes. This mixture was purified by column chromatography (alumina gel, column height = 30 cm, column diameter = 5.5 cm), using a 2:1 toluene/heptane mixture to separate, as the first fraction, the symmetric ferrocenyl tetraphosphane (0.63 g), then a 1:1 toluene/heptane solution was used to separate 0.27 g of the dissymmetric triphosphane 1,2-bis(diphenylphosphanyl)-1′-(di*iso*propylphosphanyl)-3′-(triphenyl)methyl-4-*tert*-butylferrocene **11** (12% yield).

^{1}H NMR ($CDCl_3$): δ(ppm) = 0.65 (dd, 3H, $^3J_{PH,}$ $^3J_{HH}$ = 13 and 8 Hz, CH_3-*i*-Pr), 0.79 (dd, 3H, $^3J_{PH,}$ $^3J_{HH}$ = 13 and 8 Hz, CH_3-*i*-Pr), 0.86 (m, 6H, CH_3-*i*-Pr), 1.15 (s, 9H, ^{t}Bu), 1.53 (m, 2H, J_{HH} = 5 and 2.5 Hz, CH), 3.76, 4.01, 4.16, 4.23, 4.54 (s, 1H each, *H*-Cp), 6.73−7.55 (m, 35H, *H*-Ph). ^{31}P{^{1}H}($CDCl_3$): δ (ppm) = −3.7 (d, $^{TS}J_{PP}$ = 6 Hz, 1′-$PiPr_2$), −21.4 (d, $^3J_{PP}$ = 59 Hz, 1-PPh_2), −24.0 (dd, $^3J_{PP}$ = 59 Hz, $^{TS}J_{PP}$ = 6 Hz, 2-PPh_2). ^{13}C NMR ($CDCl_3$): δ (ppm) = 146.31 (s, 3C, *ipso*-Ph-trityl), 138.9 (d, 1C, $^1J_{PC}$ = 10 Hz, *ipso*-Ph), 137.6 (m, 3C, *ipso*-Ph), 135.0 (d, J_{PC} = 24 Hz, Ph-P), 133.6 (d, J_{PC} = 21 Hz, Ph-P), 132.8 (d, J_{PC} = 21 Hz, Ph-P), 131.8 (d, J_{PC} = 21 Hz, Ph-P), 129.8 (s, 6C, *o*-Ph-trityl), 127.8 (s, Ph-P), 127.2 (s, Ph-P), 127.1 (d, J_{PC} = 8 Hz, Ph-P), 126.9 (d, J_{PC} = 8 Hz, Ph-P), 126.8 (s, Ph-P), 126.3 (m, Ph-P), 126.1 (s, 6C, *m*-Ph-trityl), 124.9 (s, 3C, *p*-Ph-trityl), 106.5 (s, 1C, 4-Fc), 102.6 (s, 1C, 3′-Fc), 82.3 (dd, 1C, J_{PC} = 26 and 14 Hz, 1-or 2-Fc), 80.3 (d, 1C, J_{PC} = 23 Hz, 1′-Fc), 77.3 (p-t, 1C, 2 J_{PC} = 14 Hz, 1- or 2-Fc), 74.9, 74.8, 71.6, 70.7, 69.8 (s, 1C each, *C*H-Cp), 58.2 (s, 1C, CPh_3), 30.8 (d, 3C, $^{TS}J_{PC}$ = 5 Hz, CH_3-*t*-Bu), 30.1 (s, 1C, *C*(CH_3)$_3$-*t*-Bu), 23.1 (d, 1C, $^1J_{PC}$ = 18 Hz, *C*H-*i*-Pr), 22.1 (d, 1C, $^1J_{PC}$ = 16 Hz, *C*H-*i*-Pr), 20.8 (d, 1C, $^2J_{PC}$ = 21 Hz, CH_3-*i*-Pr), 19.6 (d, 1C, $^2J_{PC}$ = 14 Hz, CH_3-*i*-Pr), 19.4 (d, 1C, $^2J_{PC}$ = 14 Hz, CH_3-*i*-Pr), 18.8 (d, 1C, $^2J_{PC}$ = 6 Hz, CH_3-*i*-Pr). $C_{63}H_{63}FeP_3$ (968.94). Exact mass [*M*+Na]$^+$: *m*/*z* = 991.34134, simulated = 991.33859, σ = 0.5952, err[ppm] = −2.7.

*1,2-Bis(diphenylphosphanyl)-1′-(dicyclohexylphosphanyl)-3′-(triphenyl)methyl-4-tert-butyl Ferrocene (**12**).* To a stirred suspension of $FeCl_2$ (0.57 g, 4.6 mmol) in 20 mL of THF at −40 °C was added, dropwise, by cannula, a solution of 1,2-bis(diphenylphosphanyl)-4-*tert*-butylcyclopentadienyl lithium (2.21 g, 4.5 mmol) in 25 mL of THF. The reaction mixture was allowed to slowly warm to room temperature and was stirred for 2 h. The reaction mixture was then cooled to −40 °C and a solution of 1-dicyclohexylphosphanyl-3-(triphenyl)methylcyclopentadienyllithium **7** (2.26 g, 4.4 mmol) in 25 mL of THF was added. After the addition, the reaction mixture was allowed to slowly warm to room temperature, and then it was stirred for 1 h. The THF solvent was removed, the residue was dissolved in 50 mL of toluene, and the resulting solution was refluxed for 24 h. The brown solution was then filtered through silica to yield a mixture of ferrocenyl phosphanes. This mixture was purified by column chromatography (alumina gel, column height = 30 cm, column diameter = 5.5 cm), using a 2:1 toluene/heptane mixture to separate, as the first fraction, the symmetric ferrocenyl tetraphosphane (3.35 g); then, as the last fraction, 1.21 g of phosphane **12** was obtained (26%).

^{1}H NMR ($CDCl_3$): δ (ppm) = 0.95 (s, 9H, ^{t}Bu), 1.09−1.29 (m, 11H, H-Cy), 1.43−1.95 (m, 11H, H-Cy), 3.71, 3.98, 4.12, 4.14, 4.32 (s, 1H each, *H*-Cp), 6.69−7.55 ppm (m, 35H, *H*-Ph). ^{31}P{^{1}H}($CDCl_3$): δ (ppm) = −13.0 (dd, $^{TS}J_{PP}$ = 22 and 6.0 Hz, 1′-PCy_2), −21.9 (dd, $^3J_{PP}$ = 63 Hz, $^{TS}J_{PP}$ = 6 Hz, 1-PPh_2), −24.0 (dd, $^3J_{PP}$ = 63 Hz, $^{TS}J_{PP}$ = 22 Hz, 2-PPh_2). ^{13}C NMR ($CDCl_3$): δ (ppm) = 146.3 (s, 3C, *ipso*-Ph-trityl), 139.2 (d, 1C, $^1J_{PC}$ = 11 Hz, *ipso*-Ph), 137.8 (m, 1C, *ipso*-Ph), 137.5 (m, 1C, *ipso*-Ph), 137.3 (m, 1C, *ipso*-Ph), 135.2 (d, J_{PC} = 23 Hz, Ph-P), 133.9 (d, J_{PC} = 21 Hz, Ph-P), 132.4 (d, J_{PC} = 20 Hz, Ph-P), 132.2 (d, J_{PC} = 21 Hz, Ph-P), 129.7 (s, 6C, *o*-Ph-trityl), 127.5 (s, Ph-P), 127.4 (s, Ph-P), 126.9 (m, Ph-P), 126.5 (s, Ph-P), 126.4 (m, Ph-P), 126.0 (s, 6C, *m*-Ph-trityl), 125.0 (s, 3C, *p*-Ph-trityl), 106.94 (s, 1C, 4-Fc), 102.32 (s, 1C, 3′-Fc), 80.1(dd, 1C, J_{PC} = 20 and 14 Hz, 1-Fc), 79.5 (d, 1C, J_{PC} = 25 Hz, 1′-Fc), 79.1 (d, 1C, J_{PC} = 15 Hz, 2-Fc), 73.6 (s, 1C, *CH*-Cp), 73.3 (s, 1C, *CH*-Cp), 72.9 (m, 1C, *CH*-Cp), 72.6 (s, 1C, *CH*-Cp), 72.3 (m, 1C, *CH*-Cp), 58.2 (s, 1C, CPh_3), 34.2, 32.7 (d, 1C each, $^1J_{PC}$ = 15 Hz, *C*H-Cy), 30.49 (s, 3C, CH_3-*t*-Bu), 30.1 (d, 1C, J_{PC} = 15 Hz, CH_2−Cy), 29.7 (s, 1C, *C*(CH_3)$_3$-*t*-Bu), 28.8 (d, 1C, J_{PC} = 9 Hz, CH_2−Cy), 28.7 (d, 1C, J_{PC} = 8 Hz, CH_2−Cy), 26.5 (m, 5C, CH_2−Cy), 25.7 (s, 1C, CH_2−Cy), 25.3 (s, 1C, CH_2−Cy). $C_{69}H_{71}FeP_3$ (1049.07). Exact mass [*M*+H]$^+$: *m*/*z* = 1049.418, simulated = 1049.419, σ = 0.5939, err[ppm] = 1.1. Despite repeated work-up procedures, and a good exact-mass analysis, additional peaks are observed in the ^{31}P NMR spectrum, possibly due to conformers of **12** being present in trace amounts (<10%).

*1,1′-Bis(diisopropylphosphanyl)-3,3′-di-tert-butyl Ferrocene (**14**).* To a stirred suspension of $FeCl_2$ (0.60 g, 4.7 mmol) in 15 mL of THF at −80 °C was added a solution of di*iso*propylphosphanyl-3-*tert*-butylcyclopentadienyl lithium **8** (2.30 g, 9.4 mmol) in 20 mL of THF. The reaction mixture was allowed to slowly warm to room temperature, and then it was stirred for 2 h. The THF solvent was removed, the residue was dissolved in 20 mL of toluene, and the resulting solution was refluxed for 3 h. The brown solution was then filtered through silica to give an orange oil. This crude product was purified by column chro-

matography (alumina gel, column height = 30 cm, column diameter = 5.5 cm), using first a 3:2 (toluene/heptane) mixture and then a 1:1 (toluene/heptane) mixture to give 1.05 g of diphosphane **14** (yield = 42%).

H NMR ($CDCl_3$, *rac+meso*): δ(ppm) = 0.65 (p-t, 6H, $^3J_{PH}$, $^3J_{HH}$ = 10 Hz, *i*-Pr−CH_3, minor isomer), 0.98 (dd, 6H, $^3J_{PH}$, $^3J_{HH}$ = 15 and 5 Hz, *i*-Pr−CH_3, minor isomer), 1.16 (dd, 6H, $^3J_{PH}$, $^3J_{HH}$ = 15 and 10 Hz, *i*-Pr−CH_3, major isomer), 1.22 (s, 18H, *t*-Bu, major isomer 85%), 1.23 (s, 18H, *t*-Bu, minor isomer 15%), 1.40 (dd, 6H, $^3J_{PH}$, $^3J_{HH}$ = 18 and 8 Hz, *i*-Pr−CH_3, major isomer), 1.71 (hept, 2H, $^3J_{HH}$ = 5 Hz, *i*-Pr−C*H*), 2.16 (hept, 2H, $^3J_{HH}$ = 5 Hz, *i*-Pr−C*H*), 3.93, 3.96, 4.09 (m, 2H each, *H*-Cp, major isomer), 3.99 (m, *H*-Cp, minor isomer). $^{31}P\{^1H\}$($CDCl_3$): δ (ppm) = −0.2 (s, 2P-*i*-Pr_2, major isomer 85%), −1.4 (s, 2P-*i*-Pr_2, minor isomer 15%). ^{13}C NMR ($CDCl_3$): δ (ppm) = 104.0 (s, 2C, Cp*C*-*t*-Bu, minor isomer 85%), 103.9 (s, 2C, Cp*C*-*t*-Bu, major isomer 85%), 76.4 (d, 2C, $^1J_{PC}$ = 20 Hz, Cp*C*-P*i*-Pr_2), 72.2 (d, 2C, J_{PC} = 24 Hz, Cp-*C*H, major isomer), 70.9 (d, 2C, J_{PC} = 23 Hz, Cp-CH, minor isomer), 69.1 (s, 2C, Cp-CH, minor isomer), 69.0 (s, 2C, Cp-CH, major isomer), 68.0 (s, 2C, Cp-CH, minor isomer), 67.3 (s, 2C, Cp-CH, major isomer), 32.1 (s, 6C, *t*-Bu-$(CH_3)_3$, minor isomer), 31.9 (d, 6C, $^{TS}J_{PC}$ = 3 Hz, *t*-Bu-$(CH_3)_3$, major isomer), 30.7 (s, 2C, $C(CH_3)_3$, major isomer), 29.7 (s, 2C, $C(CH_3)_3$, minor isomer), 24.4 (d, 2C, $^1J_{PC}$ = 16 Hz, *C*H-*i*-Pr), 22.7 (d, 2C, $^1J_{PC}$ = 19 Hz, *C*H-*i*-Pr), 22.8, 22.7 (m, 2C each, *C*H-*i*-Pr, minor isomer), 22.6 (d, 2C, $^1J_{PC}$ = 11 Hz, *C*H_3-*i*-Pr), 20.8 (d, 2C, $^1J_{PC}$ = 20 Hz, *C*H_3-*i*-Pr), 19.7 (d, 2C, $^1J_{PC}$ = 9 Hz, *C*H_3-*i*-Pr), 18.2 (d, 2C, $^1J_{PC}$ = 5 Hz, *C*H_3-*i*-Pr), 22.2, 20.7, 19.8, 18.1 (m, 2C each, *C*H_3-*i*-Pr, minor isomer). $C_{30}H_{52}FeP_2$ (530.53). Exact mass $[M+H]^+$: m/z = 531.29661, simulated = 531.29664, σ = 0.1495, err[ppm] = 0.1.

*1,1′-Bis(diisopropylphosphanyl)-3,3′-di(triphenyl)methyl Ferrocene (**15**).* To a stirred suspension of $FeCl_2$ (0.74 g, 5.8 mmol) in 20 mL of THF at −80 °C was added a solution of di*iso*propylphosphanyl-3-(triphenyl)methylcyclopentadienyl lithium (**6**) (5.02 g, 11.7 mmol) in 25 mL of THF. The reaction mixture was allowed to slowly warm to room temperature, and then it was stirred for 2 h. The THF solvent was removed, the residue was dissolved in 30 mL of toluene, and the resulting solution was refluxed for 3 h. The brown solution was then filtered through silica to give an orange oil. This crude product was purified by column chromatography (silica gel, column height = 30 cm, column diameter = 5.5 cm), using, first, a 2:1 heptane/acetone mixture and then methanol (MeOH) to obtain 0.54 g of diphosphane **15** (10%).

^1H NMR ($CDCl_3$): δ (ppm) = 0.87−1.11 (m, 24H, *i*-Pr−CH_3), 1.51 (m, 2H, C*H*), 2.03 (m, 2H, *i*-Pr−C*H*), 3.52, 3.68, 3.99 (m, 2H each, *H*-Cp), 7.09−7.27 (m, 30H, Ph-trityl). $^{31}P\{^1H\}$($CDCl_3$): δ (ppm) = −2.4 (s, 2P-*i*-Pr_2). ^{13}C NMR ($CDCl_3$): δ (ppm) = 146.5 (s, 6C, *ipso*-Ph-trityl), 129.5 (s, 12C, *o*-Ph-trityl), 126.2 (s, 12C, *m*-Ph-trityl), 125.1 (s, 6C, *p*-Ph-trityl), 100.2 (s, 2C, 3,3′-Fc), 80.1 (m, 2C, 1,1′-Fc), 73.8, 73.4, 72.8 (m, 2C, Cp-*C*H), 58.0 (s, 2C, *C*Ph_3), 22.8 (m, 2C, *C*H-*i*-Pr), 22.7 (m, 2C, CH-*i*-Pr), 21.0 (d, 2C, $^2J_{PC}$ = 24 Hz, CH_3-*i*-Pr), 20.6 (d, 2C, $^2J_{PC}$ = 18 Hz, CH_3-*i*-Pr), 19.7 (m, 2C, CH_3-*i*-Pr), 19.0 (m, 2C, CH_3-*i*-Pr). $C_{60}H_{64}FeP_2$ (902.94). Exact mass $[M+H]^+$: m/z = 903.38899, simulated = 903.39069, σ = 0.0232, err[ppm] = 1.7.

*1,1′-Bis(dicyclohexylphosphanyl)-3,3′-di(triphenyl)methyl Ferrocene (**16**).* To a stirred suspension of $FeCl_2$ (0.44 g, 3.5 mmol) in 20 mL of THF at −80 °C was added a solution of dicyclohexylphosphanyl-3-(triphenyl)methylcyclopentadienyl lithium (**7**) (2.73 g, 5.4 mmol) in 25 mL of THF. The reaction mixture was allowed to slowly warm to room temperature, and then it was stirred for 1 h. The THF solvent was removed, the residue was dissolved in 20 mL of toluene, and the resulting solution was refluxed for 24 h. The brown solution was then filtered through silica to yield an orange oil. This crude product was purified by column chromatography (alumina gel, column height = 30 cm, column diameter = 5.5 cm), using a 2:1 toluene/heptane mixture, to give 0.185 g of diphosphane **16** (5%).

^1H NMR ($CDCl_3$, *rac+ meso*): δ(ppm) = 1.10−1.33 (m, 22 H, *H*-Cy), 1.48−1.72 (m, 22 H, *H*-Cy), 3.45, 3.64, 3.84 (m, 2H each, *H*-Cp), 7.13−7.27 (m, 30 H, Ph); the signals for the minor isomer are obscured. $^{31}P\{^1H\}$($CDCl_3$): δ (ppm) = −8.7 (s, 2PCy_2, major isomer 70%), −10.7 (s, 2PCy_2, minor isomer 30%). ^{13}C NMR ($CDCl_3$): δ (ppm) = 146.8 (s, 6C, *ipso*-Ph-trityl, major isomer 70%), 146.4 (s, 6C, *ipso*-Ph-trityl, minor isomer 30%), 130.0 (s, 12C, *o*-Ph-trityl, minor isomer), 129.5 (s, 12C, *o*-Ph-trityl, major isomer), 126.2 (s, 12C, *m*-Ph-trityl, major isomer), 126.1 (s, 12C, *m*-Ph-trityl, minor isomer), 125.1 (s, 6C, *p*-Ph-trityl, major isomer), 125.0 (s, 6C, *p*-Ph-trityl, minor isomer), 99.5 (s, 2C, 3,3′-Fc), 79.5 (m, 2C, 1,1′-Fc), 74.7 (m, 2C, Cp-*C*H), 72.6 (m, 4C, Cp-*C*H), 58.4 (s, 2C, *C*Ph_3, minor isomer), 58.0 (s, 2C, *C*Ph_3, major isomer), 33.8, 33.7, 31.1, 29.2 (m, 1C each, *C*H-Cy, *rac+meso*), 29.6−25.2 (m, 20C, *C*H_2−Cy, *rac+meso*). $C_{72}H_{80}FeP_2$ (1063.20). Exact mass $[M+H]^+$: m/z = 1063.51861, simulated = 1063.51596, σ = 0.135, err[ppm] = −2.5.

Synthesis of Phosphorus Selenides for $^1J_{P=Se}$ Measurement. The diphosphanes **14**−**17** or 1,1′-bis[di(5-methyl-2-furyl)phosphanyl]-ferrocene $Fc[P(Fu^{Me})_2]_2$[3a,b] (0.028 mmol, <30 mg) were dissolved in 3 mL of toluene, and selenium powder was added (4.4 mg, 0.056 mmol). The mixture was stirred at room temperature overnight. The solution was filtered over Celite to remove the selenium in excess and was directly analyzed by ^{31}P NMR.

General Procedure for Catalytic Experiments. In a typical experiment, the aryl halide (1.00 mmol), heteroaromatic derivative (2.00 mmol), KOAc (2.00 mmol), and Bu_4NBr (1.00 mmol) were introduced in a Schlenk tube that was equipped with a magnetic stirring bar. The $Pd(OAc)_2$/ligand **15** or **16** catalyst (ratio 1:1) and DMAc (5 mL) were added, and the Schlenk tube was purged several times with argon. The Schlenk tube was placed in a preheated oil bath at 150 °C, and reactants were subjected to stirring for 16 h. The reaction mixture then was analyzed by gas chromatography to determine the conversion of the aryl halide. The solvent was removed by heating of the reaction vessel under vacuum, and the residue was charged directly onto a silica gel column. The products were eluted, using an appropriate ratio of diethyl ether and pentane.

2-*n*-Butyl-5-(4-cyanophenyl)furan (18).[24] The combination of 4-chlorobenzonitrile (0.138 g, 1 mmol), 2-*n*-butylfuran (0.248 g, 2 mmol), AcOK (0.196 g, 2 mmol), Bu_4NBr (0.322 g, 1.00 mmol), $Pd(OAc)_2$ (2.24 mg, 0.01 mmol), and ligand **16** (10.1 mg, 0.01 mmol) affords **18** in 90% yield (0.202 g). Anal. Calcd for $C_{15}H_{15}NO$: C, 79.97; H, 6.71. Found: C, 80.06; H, 6.67.

2-*n*-Butyl-5-(4-nitrophenyl)furan (19).[24] The combination of 4-bromonitrobenzene (0.158 g, 1 mmol), 2-*n*-butylfuran (0.248 g, 2 mmol), AcOK (0.196 g, 2 mmol), Bu_4NBr (0.322 g, 1.00 mmol), $Pd(OAc)_2$ (2.24 mg, 0.01 mmol), and ligand **15** (9.03 mg, 0.01 mmol) affords **19** in 90% yield (0.221 g). Anal. Calcd for $C_{14}H_{15}NO_3$: C, 68.56; H, 6.16. Found: C, 68.70; H, 6.07.

Methyl 4-(5-butylfuran-2-yl)-benzoate (20).[25] The combination of methyl 4-chlorobenzoate (0.171 g, 1 mmol) 2-*n*-butylfuran (0.248 g, 2 mmol), AcOK (0.196 g, 2 mmol), Bu_4NBr (0.322 g, 1.00 mmol), $Pd(OAc)_2$ (2.24 mg, 0.01 mmol), and ligand **15** (9.03 mg, 0.01 mmol) affords **20** in 37% yield (0.095 g). Anal. Calcd for $C_{16}H_{18}O_3$: C, 74.39; H, 7.02. Found: C, 74.45; H, 7.18.

2-*n*-Butyl-5-(4-propionylphenyl)furan (21).[4b] The combination of 4-chloropropiophenone (0.169 g, 1 mmol), 2-*n*-butylfuran (0.248 g, 2 mmol), AcOK (0.196 g, 2 mmol), Bu_4NBr (0.322 g, 1.00 mmol), $Pd(OAc)_2$ (1.12 mg, 0.005 mmol), and ligand **16** (5.03 mg, 0.005 mmol) affords **21** in 94% yield (0.240 g). Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.71, H, 7.98.

2-*n*-Butyl-5-(4-trifluoromethylphenyl)furan (22).[25] The combination of 4-(trifluoromethyl)chlorobenzene (0.181 g, 1 mmol), 2-*n*-butylfuran (0.248 g, 2 mmol), AcOK (0.196 g, 2 mmol), Bu_4NBr (0.322 g, 1.00 mmol), $Pd(OAc)_2$ (2.24 mg, 0.01 mmol), and ligand **16** (10.1 mg, 0.01 mmol) affords **22** in 90% yield (0.241 g). Anal. Calcd for $C_{15}H_{15}F_3O$: C, 67.16; H, 5.64. Found: C, 66.99; H, 5.67.

2-(5-*n*-Butylfuran-2-yl)benzonitrile (23).[24] The combination of 2-chlorobenzonitrile (0.138 g, 1 mmol), 2-*n*-butylfuran (0.248 g, 2 mmol), AcOK (0.196 g, 2 mmol), Bu_4NBr (0.322 g, 1.00 mmol), $Pd(OAc)_2$ (2.24 mg, 0.01 mmol), and ligand **15** (9.03 mg, 0.01 mmol) affords **23** in 34% yield (0.077 g). Anal. Calcd for $C_{15}H_{15}NO$: C, 79.97; H, 6.71. Found: C, 79.69; H 6.96.

2-*n*-Butyl-5-(4-*N*,*N*-dimethylaminophenyl)-furan (24).[26] The combination of 4-bromo-*N*,*N*-dimethylaniline (0.200 g, 1 mmol), 2-*n*-butylfuran (0.248 g, 2 mmol), AcOK (0.196 g, 2 mmol), Bu_4NBr (0.322 g, 1.00 mmol), $Pd(OAc)_2$ (1.12 mg, 0.005 mmol), and ligand **16** (5.03 mg, 0.005 mmol) affords **24** in 44% yield (0.107 g). Anal. Calcd for $C_{16}H_{21}NO$: C, 78.97; H, 8.70. Found C, 78.95; H, 8.72.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. ^1H, ^{13}C, and ^{31}P NMR spectrum for polyphosphanes **9**−**12** and **14**−**16**, and X-ray data for **11**, with the corresponding CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ■ DEDICATION

This paper is dedicated to Dr. Christian Bruneau on the occasion of his 60th birthday.

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