General Route to Dissymmetric Heteroannular-Functionalized Ferrocenyl 1,2-Diphosphines: Selective Synthesis and Characterization of a New Class of Tri- and Tetrasubstituted Ferrocenyl Compounds

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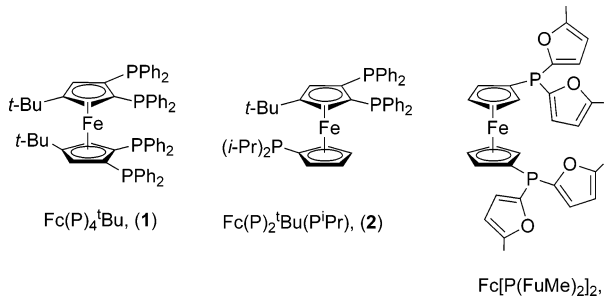
Several monosubstituted-cyclopentadienyl anions (**A**-Li) and [1,2-bis(diphenylphosphino)-4-*tert*-butylcyclopentadienyl]lithium (**B**-Li) react with $FeCl_2$ to afford a novel class of multidentate ferrocenylphosphines (**A**-Fe-**B**). The proposed synthetic method represents a unique means to produce achiral dissymmetric 1,1′,2-substituted ferrocenes (**A**-Fe-**B**) bearing a heteroannular 1′-substituent which is different from the homoannular 1- and 2-substituents. The selectivity for the two-step reaction favors formation of the desired dissymmetric product (**A**-Fe-**B**) rather than the concurrent formation of the symmetric di- and tetrasubstituted ferrocenes (**A**-Fe-**A** and **B**-Fe-**B**). Therefore, this method allows access to a great number of dissymmetric multidentate metalloligands, especially when one considers that functionalized-Cp salts continue to expand in terms of number and diversity. Herein, emphasis was placed upon the ^{1}H, ^{13}C, and ^{31}P NMR characterization of the metalloligands; several examples exhibit intriguing conformational properties and rare "through-space" phosphorus nuclear-spin couplings.

Introduction

The tertiary aryl- and alkylphosphines play a major role in modern metal-catalyzed organic reactions. For instance, most of the highly efficient catalytic procedures reported to date for C−C cross-coupling reactions are carried out in the presence of phosphine auxiliary ligands.[1] In addition to the classical mono- and bidentate phosphine ligands, we and others recently disclosed the high effectiveness of some *multi*dentate phosphines (tri- or tetraphosphines) in the palladium-catalyzed synthesis of fine chemicals.[2−4] C−C coupling that results from reaction of organo bromides or chlorides with various organometallic reagents has excellent synthetic scope. The ferrocenylphosphines depicted in Chart 1, 1,1′,2,2′-tetrakis(diphenylphosphino)-4,4′-di-*tert*-butylferrocene ($Fc(P)_4{}^tBu$; **1**), 1,2-bis(diphenylphosphino)-1′-(diisopropylphosphino)-4-*tert*-butylferrocene ($Fc(P)_2{}^tBu(P^iPr)$; **2**), and 1,1′-bis[bis(5-methyl-2-furyl)phosphino]ferrocene ($Fc[P(Fu^{Me})_2]_2$; **3**), have been successfully employed in coupling reactions such as the Suzuki−Miyaura (arylation), Heck (alkenyl arylation), Sonogashira−Hagihara (alkynyl arylation), and Tsuji-Trost type (allylation substitution with amine nucleophiles) reactions. Compound **1** has been used to stabilize palladium catalytic systems for Heck and Suzuki reactions at 0.01−0.0001% catalyst loadings.[2] Compound **2** has allowed palladium-catalyzed alkynylation at 0.1−0.0001% catalyst loading, in some cases under copper-free conditions.[3] Compound **3**, in combination with $[PdCl(allyl)]_2$, gives a base-free catalytic system for allylic amination of allyl acetates; the highest turnover frequencies (TOF, h^{-1}) reported to date resulted from these studies.[5,6]

Chart 1. Polyphosphine Catalytic Auxiliaries 1−3 Built on a Ferrocenyl Backbone



The intrinsic properties of these ligands, their stability toward air and moisture, allows them to be used under normal laboratory conditions (non-glovebox). Their stabilizing properties and their robustness under catalytic conditions (at low concentration in solution at temperatures >100 °C) prompted us to develop a synthetic route toward a more diverse structural class of 1′-substituted 1,2-ferrocenyldiphosphines. The present paper provides details of the results obtained when a variety of substituted-cyclopentadienyl anions were reacted with [1,2-bis(diphenylphosphino)-4-*tert*-butylcyclopentadienyl]lithium (t-$BuCp(PPh_2)_2Li$) and iron(II) salts. The characterization and notable features of the new dissymmetric 1′-substituted 1,2-ferrocenyldiphosphines are described thoroughly. The synthetic method is a unique means to producing multidentate ferrocenylphosphines bearing a heteroannular 1′-substituent different from the homoannular 1- and 2-substituents. Emphasis is placed upon the ^{1}H, ^{13}C, and

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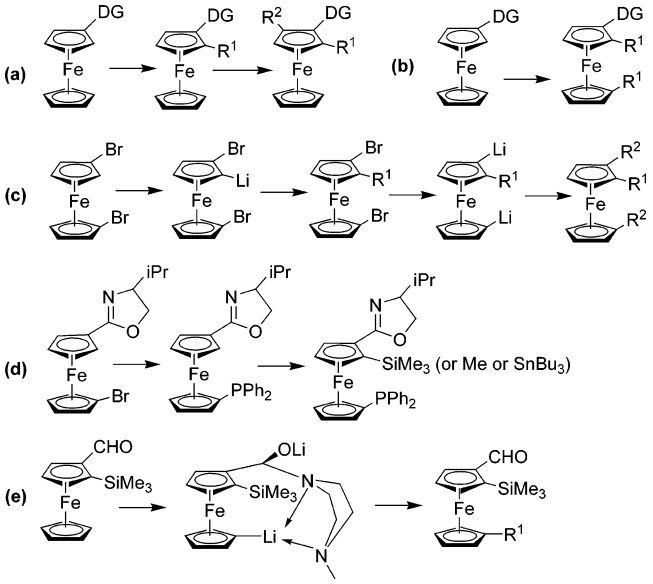
^{31}P NMR characterization of the formed metalloligands; several compounds exhibit intriguing phosphorus nuclear-spin coupling properties. A portion of this work has previously been published in communication form.[7]

Results and Discussion

Synthetic Strategy. An examination of the literature reveals that only a few ferrocenyl*poly*phosphine ligands of higher rank than *di*phosphines are available for use in synthetic chemistry and homogeneous catalysis.[8,9] Precise descriptions for the preparation and characterization of ferrocenyl*tri*phosphines are scarce. Additionally, while there have been numerous developments in the synthetic methodology of 1,2-substituted ferrocene derivatives,[10] the preparation of heteroannular 1,2,1′-trisubstituted ferrocenes, to our knowledge, is understudied. The elegant works by the groups of Balavoine et al. and Hou et al. for the synthesis of chiral polysubstituted ferrocenes[11,12] and by Butler et al. for the preparation of achiral or racemic analogues[13] represent recent important contributions in this area.[14,15]

The selectivity problems encountered when using the direct phosphorylation of the ferrocene backbone, in part, explains the limited development of ferrocenylpolyphosphine ligands. For example, the treatment of (diphenylphosphino)ferrocene with *n*-BuLi and $ClPPh_2$ typically yields four products at least: unreacted (diphenylphosphino)ferrocene (22%), 1,1′-bis(diphenylphosphino)ferrocene (dppf, 15%), 1,3,1′-tris(diphenylphosphino)ferrocene (51%), and 1,2,1′-tris(diphenylphosphino)-ferrocene (6%).[16] On the other hand, a number of efficient methods are available for the selective formation of 1,2-substituted ferrocenes via ortho-directing groups (chiral or nonchiral), such as—nonexhaustively—amine,[17] acetal,[18] oxazoline,[19] amide,[20] sulfoxide,[21] and phosphine oxide[22] groups. With these ferrocene derivatives as starting materials, a third substitution is possible (Scheme 1a). Some disadvantages are apparent, however, as noted previously by Togni and co-workers.[23] For example, in the subsequent reaction it appears difficult to selectively substitute the second Cp ring, since the "still active" ortho-directing effect leads to the formation of 1,2,3-trisubstituted ferrocenes.

Scheme 1. Strategies for the Synthesis of Trisubstituted Ferrocenes[a]



[a] DG = directing group.

Another strategy to obtain 1,1′,2-substituted ferrocenes is starting from 1-substituted ferrocenes with a directing group (DG), which allows the introduction of two groups in a one-pot procedure: the consequence is that the 1′,2-substitution leads to the formation of two equal heteroannular groups (R^1 in Scheme 1b).[23] The Butler method, based on the use of 1,1′-dibromoferrocene and its novel ortho-directed metalation effect,[13] does not increase "flexibility" in this particular problem, since the 1- and 1′-substituents remain equal (Scheme 1c). Some differently trisubstituted ferrocenes, called 1,1′-P,N-2-ferrocene ligands by the authors, were synthesized by Hou et al. starting from 1′-Br ferrocenyloxazoline (Scheme 1d);[12] a minor inconvenience of this method is that the 1′-Br ferrocenyloxazoline derivative results from a five-step reaction sequence starting with ferrocene (overall yield <20%).[12c] Finally, it is worth noting the methodology developed by Manoury and co-workers (Scheme 1e), using a 2-substituted ferrocenecarboxaldehyde, where an aminoalkoxide is formed as a temporary protecting group of the aldehyde function and as a temporary directing group for the 1′-ortho lithiation.[11] Nevertheless, to our knowledge, these last two synthetic strategies have not been applied to afford ferrocenyl*tri*phosphines, which are our primary targets.

Stimulated by preliminary results in our group,[24] we chose to develop the strategy previously employed to obtain ferrocenyl 1,1′- and 1,2-diphosphines, as well as 1,1′,2,2′-tetraphosphines.

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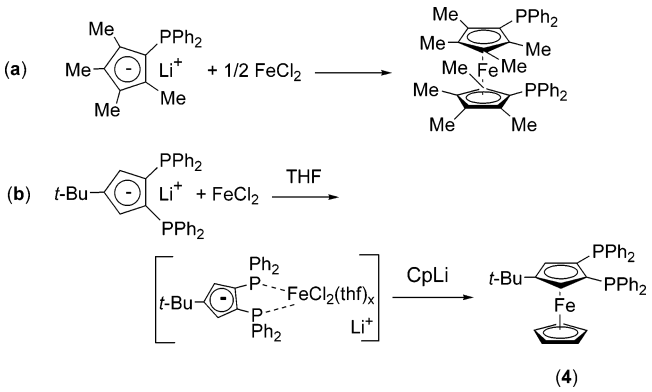
Scheme 2. Diphosphine Synthesis from Functionalized Cp Salts with (a) Identical and (b) Different Cp Rings



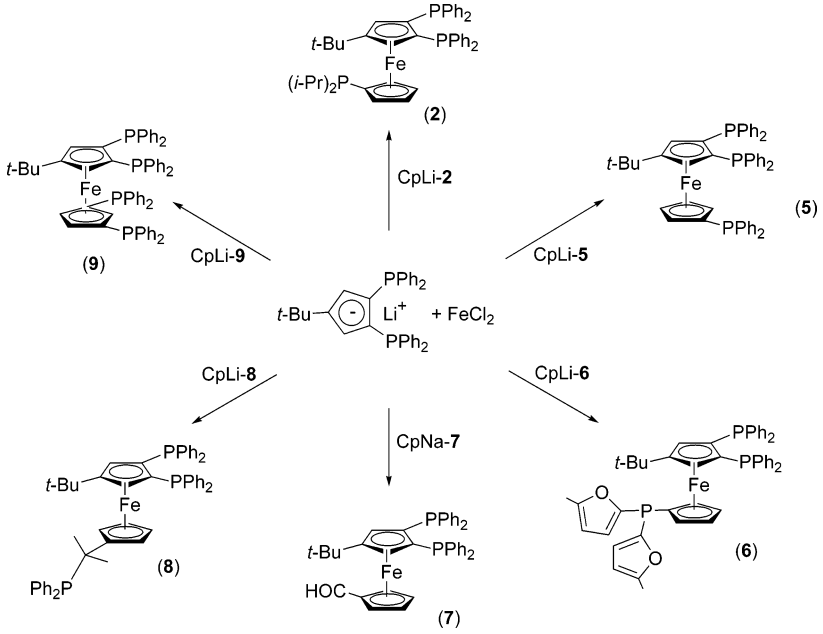
From the initial preparation of the adequately substituted cyclopentadienes and their transformation into the corresponding Cp alkali-metal salts, a variety of metallocenes are accessible through subsequent reaction with a convenient transition-metal chloride (see, for example, Scheme 2). This strategy is based on the well-known preparation of ferrocenes from fulvenes,[25] which can even be applied to form enantiopure ferrocenes from optically active Cp synthons.[23]

To produce heteroannular 1′-functionalized ferrocenyl 1,2-diphosphines by assembling the Cp rings, the dissymmetry can be introduced via a two-step reaction (Scheme 2b). The first dissymmetric ferrocene (**4**) built on the [1,2-bis(diphenylphosphino)-4-*tert*-butylcyclopentadienyl]lithium synthon has been obtained in good yield (68%).[24c] This result was a priori surprising, since the preparation of ferrocene derivatives from two different Cp salts is generally regarded as leading to a quasi-statistic mixture containing all three possible combinations: two symmetric compounds and the dissymmetric species. We postulated that the two-step methodology used minimizes the quantities of symmetric species by stabilizing mono-Cp complexes of iron (see Scheme 2b).[7] Scheme 3 summarizes the various species (**2** and **5**−**9**) we attempted to form using this methodology from the corresponding Cp anions (CpLi-**2**, -**5**, -**6**, -**8**, and -**9** and CpNa-**7**) and [1,2-bis(diphenylphosphino)-4-*tert*-butylcyclopentadienyl]lithium.

In addition to the various ferrocenyltriphosphines obtained from the new synthons [(diisopropylphosphino)cyclopentadienyl]-lithium (CpLi-**2**) and [(bis(5-methyl-2-furyl)phosphino)cyclopentadienyl]lithium (CpLi-**6**) and from the known [(diphenylphosphino)cyclopentadienyl]lithium (CpLi-**5**),[26] we examined the results obtained from other functionalized-Cp salts with a view to increasing the synthetic potentiality of the method.

Syntheses and Characterization of the Triphosphines. From the phosphorylation and lithiation of CpLi, using first ClP-(*i*-Pr)$_2$ and then *n*-BuLi, CpLi-**2** was isolated in 94% yield. The metalloligand 1,2-bis(diphenylphosphino)-1′-(diisopropylphosphino)-4-*tert*-butylferrocene (Fc(P)$_2$^{t}Bu(P^{i}Pr); **2**) was then obtained in 60−70% yield (1.54 g) from the successive reaction of *t*-BuCp(PPh$_2$)$_2$Li and CpLi-**2** with FeCl$_2$. The X-ray diffraction structure and the ^{1}H, ^{13}C, and ^{31}P NMR spectroscopic studies in solution have been previously reported for **2**.[3,7] The NMR phosphorus signals detected at −0.93 ppm for P(*i*-Pr)$_2$ and −22.01 ppm for PPh$_2$ groups provide evidence for the electronic difference between the phosphorus atoms. The most remarkable feature of the compound is derived from the ^{13}C NMR spectroscopic data, for which a clear spin−spin nuclear coupling constant (J_{CP} = 5.5 Hz) between the three carbon atoms of the *t*-Bu group and the phosphorus atom bearing the isopropyl groups is detected (unambiguously demonstrated by selective phosphorus-decoupling NMR experiments; see Figure 1). As these atoms are not held by the same Cp ring, the "shortest" distance between the nucleus of interest is a five-bond distance (C−C−C−Fe−C−P) that should not lead to a detectable $^5J_{CP}$ spin−spin coupling interaction. Consistently, no other $^4J_{CP}$ or $^5J_{CP}$ coupling constants were observed. The conformation in solution can be compared to that observed in the solid state from single-crystal diffraction studies, since the molecular structure reveals the proximity in space of the coupled atoms (as pictured in Scheme 3). A short "through-space" distance of d(P···C) = 3.64 Å is favored by the staggered conformation (the Cp rings are staggered, with a twist angle calculated from the mean value of the dihedral angles Ci−CNT(1)−CNT(2)−Ci* = 30.4°). Thus, the lone pair of the phosphorus P(*i*-Pr)$_2$ is clearly pointing toward the carbon atoms of the *t*-Bu group and is most probably responsible for the transmission of the nuclear spin information. This type of nonbonded interaction, which

Scheme 3. Heteroannular 1′-Functionalized Ferrocenyl 1,2-diphosphines



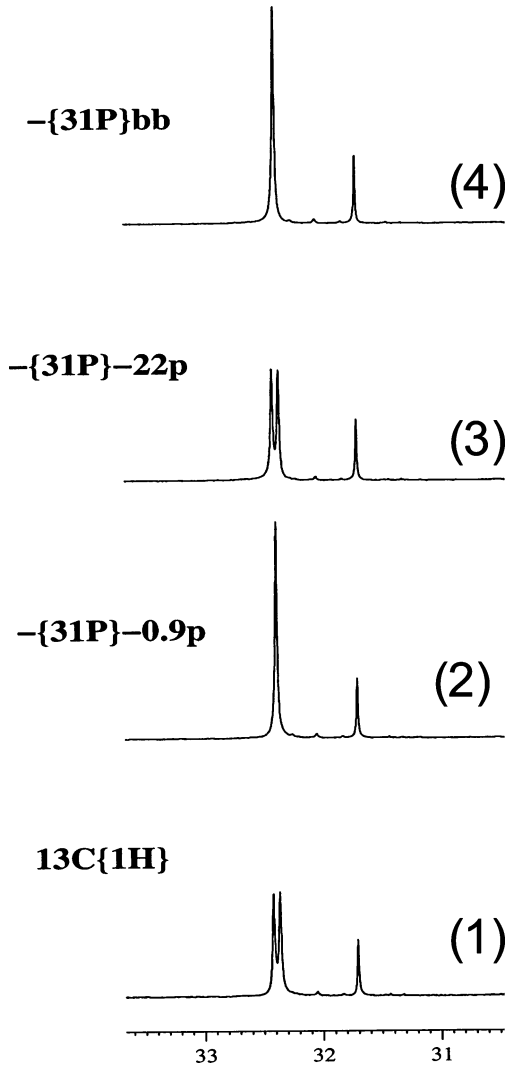
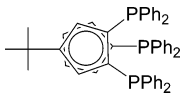


Figure 1. ^{13}C NMR spectra for **2** with selective phosphorus spin decoupling at *t*-Bu carbon chemical shifts: (1) δ 31.7 (s, 1C, *t*-Bu*C*CH$_3$), 32.4 (d, 3C, through-space $J_{CP} = 5.5$ Hz, t-BuC*C*H$_3$), no phosphorus decoupling; (2) same spectrum as (1), with P(*i*-Pr)$_2$ decoupling (at −0.9 ppm); (3) same spectrum as (1), with PPh$_2$ decoupling (at −22 ppm); (4) same spectrum as (1), with broad-band decoupling (bb).

requires steric crowding, is very rare and was first experimentally detected in J_{FF} couplings[27] and recently for J_{PP} couplings in ferrocenylpolyphosphine metalloligands and their coordination complexes.[28]

From the successive reaction of *t*-BuCp(PPh$_2$)$_2$Li and CpLi-**5** with FeCl$_2$, 1,1′,2-tris(diphenylphosphino)-4-*tert*-butylferrocene (Fc(P)$_2$^{t}Bu(P); **5**) was obtained in high yield (2.60 g, 84%). The yield is lowered, partially due to the formation of about 10 mol % of dppf and ca. 3 mol % of the symmetric tetrakis-(diphenylphosphine)ferrocene compound. Surprisingly, the $^{31}P\{^1H\}$ NMR spectrum of **5** in CDCl$_3$ shows a triplet at −19.3 ppm and a doublet at −23.0 ppm, respectively assigned to the 1′-PPh$_2$ and 1,2-PPh$_2$ groups. The observed spin−spin coupling constant was found to be greater in C$_6$D$_6$ ($J_{PP} = 5.0$ Hz, a rather high value for a presumed through-bond $^4J_{PP}$) than in CDCl$_3$ ($J_{PP} = 2.8$ Hz). Hence, it should be attributed to the "through-space" spin coupling which is affected by Fc ring rotation and by the changes in the relative orientation of the phosphine groups, above all of the phosphorus lone pairs.[28] To facilitate via-space spin interaction of the phosphorus nucleus, the relative rotation of the Cp rings has to occur rapidly, though it is restricted to a certain degree through the conformation of higher symmetry (C_s) represented in Chart 2.

Chart 2. Molecular Conformation of Highest Symmetry for 5 (C_s)[a]



[a] A conformation close to this one would explain a "through-space" ^{31}P spin−spin coupling.

The ^1H NMR spectrum of **5** in CDCl$_3$ displays three multiplets from Cp H atoms (2H each) at 4.07, 4.17, and 4.20 ppm, assigned correspondingly to 3,5-, 2′,5′-, and 3′,4′-H. It is noteworthy that for the related compound 1,1′,2-tris(diphenylphosphino)ferrocene reported by Butler et al.[16] two singlet resonances are observed at −18.4 and −25.4 ppm in CDCl$_3$. The absence of multiplicity indicates that no phosphorus spin−spin coupling is observed. This highlights the crucial role of the *t*-Bu group in the conformation of **5** in solution.

The phosphorylation and lithiation of CpLi, using BrP(Fu^{Me})$_2$ and *n*-BuLi, give CpLi-**6** in excellent yield (90%). Following the methodology described above, the metalloligand Fc(P)$_2$-^{t}Bu(PFu^{Me}) (**6**) was obtained, as orange needles, in a disappointingly poor yield (3%, 160 mg) after workup procedures. In the various reactions conducted, the symmetric ferrocene species were obtained, together with a considerable amount of insoluble red solid material; clearly further optimization studies are required for the efficient synthesis of **6**. The ^{31}P NMR spectrum of **6** in CDCl$_3$ exhibits two singlets at −22.7 (1,2-*P*Ph$_2$) and −64.9 ppm (1′-*P*Fu^{Me}), confirming the expected electronic difference between the phosphorus nuclei. As observed in the case of **5**, the ^1H NMR spectrum of **6** in CDCl$_3$ displays three multiplets from the Cp H atoms (2H each) centered at 4.13, 4.10, and 4.18 ppm, respectively, assigned to 3,5-, 2′,5′-, or/and 3′,4′-H. The methyl substituents contained within the furyl groups are observed at 2.28 ppm. The furyl protons appear at 5.90 and 6.38 ppm.[29]

Other Functionalizations. With the view to evaluating access to other dissymmetric heteroannular-substituted ferrocenyl 1,2-diphosphines using the above strategy, various syntheses were carried out from known functionalized Cp synthons. We first obtained the new tetraphosphine 1,1′,2,3′-tetrakis(diphenylphosphino)-4-*tert*-butylferrocene (Fc(P)$_2$^{t}Bu(PP′); **9**). This kind of 1,2- plus 1′,3′-substitution is rare and extremely difficult to obtain in a controlled manner by starting from ferrocenes, whatever the method employed, since most of the approaches are based on ortho-directed substitutions.[30] The addition of [1,3-bis(diphenylphosphino)cyclopentadienyl]lithium (CpLi-**9**) to the

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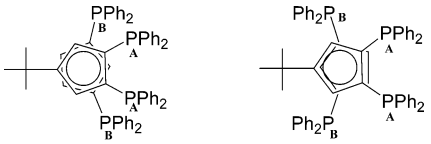
(29) The corresponding NMR spectrum is available as Supporting Information.

Chart 3. Symmetric Molecular Conformations S and T for 9



S T

mixture of $FeCl_2$ and *t*-BuCp$(PPh_2)_2$Li gave **9** in 45% yield (1.5 g) after workup procedures. Interestingly, the $^{31}P\{^1H\}$ NMR spectrum in $CDCl_3$ shows two broad singlets (visibly doublets)[29] at −19.6 and −23.9 ppm, suggesting the existence of $J_{P_AP_B} <$ 3 Hz between two groups of equivalent phosphorus atoms. The ^{31}P NMR experiments conducted at low temperature (243 and 213 K) did not simplify the spectrum. Consequently, from the two conformations of higher symmetry (displaying pairs (a P_A pair and a P_B pair) of *homoannular* chemically equivalent phosphorus) anticipated for **9** (S and T pictured in Chart 3), S should be the conformation allowing facile phosphorus spin−spin coupling "through-space". It appears reasonable to assume that, in solution, a rapid rotation of the Cp rings is restricted to a certain degree around the conformation S, since an unrestricted rotation probably would not facilitate the observation of through-space J_{PP} couplings between the heteroannular phosphorus atoms.

The ^1H NMR spectrum of **9** in $CDCl_3$ displays three multiplets from the Cp H atoms, two centered at 4.20 and 4.65 ppm (2H each) respectively assigned to 3,5- and 4′,5′-H, and one at 3.64 ppm (1H) for 2-H. The Experimental Section details a consistent attribution for the proposed structure, based on ^{13}C *J*-modulation and $^1H/^{13}C$, $^1H/^1H$ correlation spectroscopic studies (HMBC, HMQC).

Preliminary experiments were conducted to prepare the compounds **7** and **8**, these two trisubstituted ferrocene derivatives being potentially interesting. The diphosphine **7**, bearing a reactive aldehyde function at the "lower" Cp ring,[23] might provide access to 1′-substituted ferrocene derivatives, in addition to the triphosphines, or could allow anchoring of the 1,2-bis(diphenylphosphino)-4-*tert*-butylferrocenyl moiety to a surface or to a suitable polymer or dendritic core. In the case of **8**, the idea was to give to the resulting triphosphine a more flexible arm through use of a methylene spacer and to observe the effect induced on the stability of the ligand through the removal of a phosphorus from the Cp aromaticity (*flexibility* and *stability*;[31] these two concepts are important in relation to catalysis).

The dissymmetric ferrocene derivatives **7** and **8** were obtained in satisfying quantities (700 mg and 1 g, respectively) but in insufficient yields (20% and 15% of pure recrystallized material). For both of these compounds, less than 1 mol % of the symmetric ferrocene derivatives was detected in the crude product by NMR spectroscopy; therefore, the decomposition (or oligomerization) of the monosubstituted-Cp synthons, under the standardized conditions employed, is possible. From the successive reaction of *t*-BuCp$(PPh_2)_2$Li and a THF solution of (formylcyclopentadienyl)sodium (CpNa-**7**)[32] with $FeCl_2$, 1,2-bis(diphenylphosphino)-1′-formyl-4-*tert*-butylferrocene (Fc(P)$_2$-^{t}Bu(CHO); **7**) is obtained in pure form as brick red spangles after recrystallization from heptane and then from ethanol. The ^{31}P NMR spectrum of **7** exhibits a singlet at −24.4 ppm. The ^1H NMR spectrum shows three multiplets for the Cp H atoms (2H each) at 4.21 (3,5-H), 4.42 (2′,5′-H), and 4.64 (3′,4′-H).[29] The peak corresponding to the formyl group is found at 8.47 ppm.

Following the method described by Brasse et al., the synthon [(1-methyl-1-(diphenylphosphino)ethyl)cyclopentadienyl]-lithium[33] (CpLi-**8**) was prepared from $HPPh_2$, *n*-BuLi, and 6,6-dimethylfulvene. Without isolation, CpLi-**8** was directly added as a THF solution to a *t*-BuCp$(PPh_2)_2$Li/$FeCl_2$ mixture to give the metalloligand Fc(P)$_2$^{t}Bu(Me$_2$CP) (**8**). The pure product was obtained after column chromatography (SiO_2, 4:1 v/v toluene−hexane) and then recrystallized from hot methanol. The ^{31}P NMR spectrum of **8** exhibits two singlets at 29.4 and −24.0 ppm (Cp*P*Ph_2),[29] consistent with the reported data from the literature concerning the chemical shift of the −(*P*Ph_2)C(Me)$_2$ moiety (about 30 ppm).[33,34] The ^1H NMR spectrum shows a doublet for the methyl groups centered at 0.81 ppm ($^3J_{PH}$ = 14.4 Hz) and three multiplets (2 H each) centered at 3.64, 3.82, and 4.11 ppm for the Cp H atoms.[29]

Conclusion

A methodology for the preparation of dissymmetric achiral trisubstituted ferrocenes from two different Cp salts has been described; the process is efficient and is complete in two simple steps. The yields of ferrocene derivatives vary from poor (3%) to high (84%), depending on the functionalized Cp synthons. To check the generality of the preparative method, the syntheses have been carried out following similar conditions; clearly, some reactions will require further optimization studies. Nevertheless, in almost all cases, the selectivity was in favor of the formation of the dissymmetric 1,1′,2-substituted ferrocene, against the concurrent formation of the symmetric di- and tetrasubstituted ferrocenes. Therefore, this method opens up the way to an important eclectic array of multidentate metalloligands, particularly considering the ever-expanding availability of Cp salts.[35] The newly prepared ferrocenylphosphines display, especially at the phosphorus atoms, very different electronic, steric, and conformational properties. Further work will aim at taking advantage of these structural properties in homogeneous and heterogeneous catalysis, as well as in materials science.

Experimental Section

The reactions were carried out in oven-dried (115 °C) glassware under an argon atmosphere using Schlenk and vacuum-line techniques. $FeCl_2$ from a commercial source was used (Aldrich anhydrous beads, 99.9%, H_2O <100 ppm). The solvents were distilled over appropriate drying and deoxygenating agents prior to use. ^1H (300.13 and 500.13 MHz), ^{31}P (121.49 and 202.46 MHz), and ^{13}C NMR (75.47 and 125.77 MHz), including low-temperature, ^{13}C *J*-modulation APT, COSY $^1H-^1H$, HMQC, and HMBC NMR experiments, were performed in our laboratory (on Bruker 300 and DRX 500 instruments), in $CDCl_3$ at 293 K unless otherwise stated. Elemental analyses were performed by the analytical service of the

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LSEO of the "Université de Bourgogne" (Eager 200). Mass spectra were recorded on a Kratos Concept IS instrument.

Synthesis of Cyclopentadienyl Salts. The known cyclopentadienyl salts *t*-BuCp(PPh_2)$_2$Li,[2,24c] CpLi-**5**,[26] CpLi-**8**,[33] CpLi-**9**[24c] and NaCp-**7**[32] were synthesized according to literature reports.

(a) [(Diisopropylphosphino)cyclopentadienyl]lithium (CpLi-2). To a stirred suspension of CpLi (2.07 g, 28.7 mmol) in 25 mL of toluene was added dropwise a solution of ClP(*i*-Pr)$_2$ (3.95 g, 25.9 mmol) in 10 mL of toluene at −80 °C. The reaction mixture was stirred for 2 h, with the temperature slowly raised up to 0 °C. A 20 mL portion of hexane was then added to the mixture, and after 10 min it was filtered over Celite. The filtrate was evaporated almost to dryness, and 40 mL of hexane was added to the residue. The resulting colorless solution was treated with *n*-BuLi (17 mL, 1.6 M in hexane, 27.2 mmol) at 0 °C. As no precipitate appeared, the reaction mixture was evaporated to dryness and then triturated with hexane (60 mL) to provide a air-sensitive white precipitate of CpLi-**2** that was filtered off, washed with hexane, and dried under vacuum (4.59 g, 94% yield). ^{1}H NMR (THF-d_8): δ 0.92 (m, 12H, CH_3), 1.86 (m, 2H, C*H*(CH_3)$_2$), 5.83 (m, 2H, Cp H), 5.89 (m, 2H, Cp H). ^{31}P{^{1}H} NMR (THF-d_8): δ −3.7 ppm.

(b) [(Bis(5-methyl-2-furyl)phosphino)cyclopentadienyl]lithium (CpLi-6). To a stirred suspension of CpLi (6.03 g, 83.7 mmol) in 120 mL of toluene was added dropwise a solution of bis(5-methyl-2-furyl)bromophosphine (BrP(Fu^{Me})$_2$; 15.3 g, 79.7 mmol) in 40 mL of toluene at −80 °C. The reaction mixture was stirred for 1 h, with the temperature to slowly raised to 20 °C, and then was stirred for 1 h at room temperature. The mixture was filtered over Celite. The precipitate of LiBr was washed with toluene (10 mL). The filtrate was evaporated almost to dryness, and 100 mL of hexane was added to the residue. The resulting colorless solution was treated with *n*-BuLi (50 mL, 1.6 M in hexane, 80 mmol) at 0 °C. The reaction mixture was stirred for 10 min at 0 °C. The air-sensitive white precipitate of CpLi-**6** that formed was filtered, washed with hexane, and dried under vacuum (13.08 g, 90% yield). ^{1}H NMR (THF-d_8): δ 2.25 (m, 6H, CH_3), 5.89 (m, 4H, Cp), 6.18 (m, 2H, furyl), 6.27 (m, 2H, furyl). ^{31}P{^{1}H} NMR (THF-d_8): δ −63.9 ppm.

Synthesis of Substituted Ferrocenes. The syntheses of compounds **1**−**4** have been reported elsewhere.[2,3,5−7,24c]

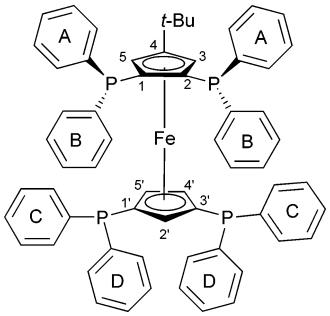
(a) 1,1′,2-Tris(diphenylphosphino)-4-*tert*-butylferrocene (5). To a stirred suspension of $FeCl_2$ (0.53 g, 4.2 mmol) in 15 mL of THF was added dropwise at −40 °C a solution of *t*-BuCp(PPh_2)$_2$Li (2.18 g, 4.4 mmol) in 25 mL of THF. After it was stirred for 2 h at room temperature, the reaction mixture was treated at −40 °C with a THF solution (10 mL) of CpLi-**5** (1.00 g, 3.9 mmol). The solvent was then evaporated under vacuum, and the residue was refluxed in 50 mL of toluene for 3 h. The reaction mixture was cooled and filtered under air. The crude product was subjected to column chromatography (SiO_2, 4:1 toluene−hexane) to provide first 0.15 g (3 mol %) of **1**, 0.10 g (10 mol %) of 1,1′-bis(diphenylphosphino)ferrocene, and 2.60 g of **5** (yield 84%). Anal. Calcd for $C_{50}H_{45}FeP_3$ (794.7): C, 75.57; H, 5.71. Found: C, 75.59; H, 5.68. MS (EI): *m*/*z* (%) 794 (24) $[M]^+$, 717 (<1) $[M - Ph]^+$, 609 (2) $[M - PPh_2]^+$, 554 (100) $[M - PPh_2 - C_4H_8]^+$, 477 (9) $[M - PPh_2 - C_4H_8 - Ph]^+$. ^{1}H NMR: δ 1.03 (s, 9H, *t*-Bu), 4.07 (dd, J_{PH} = 3.3 Hz, $^3J_{HH}$ = 1.8 Hz, 2H, 2′,5′-Cp), 4.17 (dd, $^3J_{HH} \approx J_{PH}$ = 1.8 Hz, 2H, 3′,4′-Cp), 4.20 (dd, 2 $J_{PH} \approx$ 1.5 Hz, 2H, 3,5-Cp), 6.91−7.12 (m, 10H, Ph, 1,2-PPh_2), 7.13−7.26 (m, 10H, Ph, 1′-PPh_2), 7.33 (m, 6H, *m*,*p*-Ph 1,2-PPh_2), 7.64 (m, 4H, *o*-Ph 1,2-PPh_2). The J_{PH} values observed could be either "through-bond" (homoannular) or "through-space" (heteroannular) couplings. ^{13}C{^{1}H} NMR: δ 30.5 (s, *C*(CH_3)$_3$), 31.3 (d, J_{PC} = 1.5 Hz, C(*C*H$_3$)$_3$), 71.4 (m, 3, 5-Fc), 72.0 (m, 3′,4′-Fc), 74.4 (d, J_{PC} = 11.0 Hz, 2′,5′-Fc), 80.2 (d, J_{PC} = 12.5 Hz, 1′-Fc), 81.9 (m, 1,2-Fc), 106.8 (s, 4-Fc), 127.4 (t, $^2J_{PC} \approx$ 3.5 Hz, *m*-Ph), 127.5 (s, *p*-Ph), 128.0 (d, J_{PC} = 7.2 Hz, *m*-Ph), 128.1 (t, $^2J_{PC} \approx$ 8.8 Hz, *m*-Ph), 128.3 (s, *p*-Ph), 128.8 (s, *p*-Ph), 132.9 (t, $^2J_{PC} \approx$ 10.3 Hz, *o*-Ph), 133.8 (d, J_{PC} = 21.0 Hz, *o*-Ph), 135.1 (dt, $^2J_{PC} \approx$ 10.9 Hz, $J_{P'C}$ = 1.5 Hz, *o*-Ph), 137.6 (t, $^2J_{PC} \approx$ 2.9 Hz, *ipso*-Ph), 138.8 (t, $^2J_{PC} \approx$ 4.7 Hz, *ipso*-Ph), 139.5 (d, J_{PC} = 14.8 Hz, *ipso*-Ph). ^{31}P{^{1}H} NMR: δ −22.7 (d, ^{TS}J = 2.8 Hz, 1,2-PPh_2), −19.3 (t, ^{TS}J = 2.8 Hz, 1′-PPh_2). ^{31}P{^{1}H} NMR (C_6D_6): δ −21.9 (d, ^{TS}J = 5.0 Hz, 1,2-PPh_2), −20.0 (t, ^{TS}J = 5.0 Hz, 1′-PPh_2).

(b) 1,2-Bis(diphenylphosphino)-1′-[bis(5-methyl-2-furyl)phosphino]-4-*tert*-butylferrocene (6). To a stirred suspension of $FeCl_2$ (0.88 g, 6.9 mmol) in 25 mL of THF was added dropwise at −40 °C a solution of *t*-BuCp(PPh_2)$_2$Li (3.64 g, 7.3 mmol) in 40 mL of THF. After it was stirred for 2 h at room temperature, the reaction mixture was treated at −40 °C with a 25 mL THF solution of CpLi-**6** (1.23 g, 6.7 mmol). The reaction mixture was then stirred for 1 h at room temperature, and the solvent was evaporated under vacuum. The residue was refluxed in 80 mL of toluene for 5 h. The mixture was cooled and filtered under air over a paper filter. A red solid material insoluble in toluene as well as in other organic solvents and water was obtained in considerable quantity. The crude product was subjected to column chromatography (SiO_2, 5:1 toluene−hexane) to yield first 0.92 g of **1** (24 mol %), 0.26 g (14 mol %) of 1,1′-bis[bis(5-methyl-2-furyl)phosphino]ferrocene, and finally 0.16 g of **6** (3% yield). Anal. Calcd for $C_{48}H_{45}FeO_2P_3$ (802.7): C, 71.83; H, 5.65. Found: C, 71.69; H, 5.59. ^{1}H NMR: δ 1.13 (s, 9H, *t*-Bu), 2.27 (s, 6H, CH_3), 4.10 (dd, $J_{HH} \approx J_{PH}$ = 1.8 Hz, 2H, 3′,4′-Fc (or 2′,5′-Fc)), 4.13 (m, 2H, 3,5-Fc), 4.18 (dd, J_{PH} = 3.3 Hz, $^3J_{HH}$ = 1.8 Hz, 2H, 2′,5′-Fc (or 3′,4′-Fc)), 5.91 (m, 2H, 3-H furyl), 6.37 (m, 2H, 4-H furyl), 6.90−7.09 (m, 10H, Ph), 7.35 (m, 6H, *m*,*p*-Ph), 7.62 (m, 4H, *o*-Ph). ^{31}P{^{1}H} NMR: δ −64.9 (s, P[Fu^{Me}]$_2$), −22.7 (s, 1,2-PPh_2).

(c) 1,2-Bis(diphenylphosphino)-1′-formyl-4-*tert*-butylferrocene (7). To a stirred suspension of $FeCl_2$ (0.67 g, 5.3 mmol) in 10 mL of THF was added dropwise, at −40 °C, a solution of *t*-BuCp(PPh_2)$_2$Li (2.72 g, 5.5 mmol) in 25 mL of THF. After it was stirred for 2 h at room temperature, the reaction mixture was treated at −40 °C with a 10 mL THF solution of (formylcyclopentadienyl)-sodium prepared without isolation from CpNa and HCO_2Et[32] (0.64 g, 5.5 mmol). The reaction mixture was stirred overnight at room temperature and evaporated under vacuum, and the residue was refluxed in 60 mL of cyclohexane for 30 min. The reaction mixture was then cooled and filtered under air over a paper filter. The crude product was submitted to recrystallization first from heptane and then from ethanol to give 0.69 g (20% yield) of **7** as brick-red spangles. Anal. Calcd for $C_{39}H_{36}FeOP_2$ (638.5): C, 73.36; H, 5.68. Found: C, 73.32; H, 5.66. MS (EI): *m*/*z* (%) 638 (100) $[M]^+$, 623 (22) $[M - CH_3]^+$, 610 (33) $[M - CO]^+$, 595 (18) $[M - CO - CH_3]^+$. ^{1}H NMR: δ 1.18 (s, 9H, *t*-Bu), 4.21 (m, 2H, 3,5-Fc), 4.42 (m, 2H, 2′,5′-Fc), 4.64 (m, 2H, 3′,4′-Fc), 6.9−7.1 (m, 10H, Ph), 7.38 (m, 6H, *m*,*p*-Ph), 7.64 (m, 4H, *o*-Ph). ^{13}C{^{1}H} NMR: 30.8 (s, *C*(CH_3)$_3$), 31.2 (s, C(*C*H$_3$)$_3$), 71.6, 71.8 (s, 1C each, Fc *C*H), 75.2 (m, 1C, Fc *C*H), 80.4 (s, 1′-Fc), 83.6 (dd, J_{PC} = 9.8 Hz, $J_{P'C}$ = 8.8 Hz, 1,2-Fc), 127.7 (t, J_{PC} = 3.5 Hz, *m*-Ph), 127.9 (s, *p*-Ph), 128.4 (t, J_{PC} = 4.3 Hz, *m*-Ph), 129.5 (s, *p*-Ph), 132.7 (t, J_{PC} = 10.2 Hz, *o*-Ph), 135.0 (t, J_{PC} = 10.9 Hz, *o*-Ph), 136.9 (t, J_{PC} = 2.6 Hz, *ipso*-Ph), 137.9 (t, J_{PC} = 4.5 Hz, *ipso*-Ph), 193.7 (s, *C*HO). ^{31}P-{^{1}H} NMR: δ −24.4 (s).

(d) 1,2-Bis(diphenylphosphino)-1′-[1-methyl-1-(diphenylphosphino)ethyl]-4-*tert*-butylferrocene (8). According to the method of Brasse et al.,[33] to a stirred solution of Ph_2PH (2 mL, 11.5 mmol) in Et_2O (20 mL) at −80 °C was added first *n*-BuLi (7.3 mL, 1.6 M in hexane, 11.7 mmol) and then after 20 min a solution of 6,6-dimethylfulvene (1.18 g, 11.1 mmol) in THF (10 mL) at −40 °C. The reaction mixture was stirred for 1 h at room temperature and the solution of CpLi-**8** used for the following synthesis. To a stirred suspension of $FeCl_2$ (1.20 g, 9.5 mmol) in 30 mL of THF was added dropwise at −40 °C a solution of *t*-BuCp(PPh_2)$_2$Li (5.00 g, 10.1 mmol) in 20 mL of THF. After it was stirred for 2 h at room

Chart 4. Conformational View Consistent with NMR Data and Phenyl Assignments[a]



[a] The phenyl types are A (exo), B (endo), and C.

temperature, the reaction mixture was treated at −40 °C with the above-prepared solution of CpLi-**8**. The reaction mixture was evaporated under vacuum, and the residue was refluxed in 100 mL of toluene for 20 h. The reaction mixture was cooled and filtered under air over a paper filter. The crude product was subjected to column chromatography (SiO_2, 4:1 v/v toluene−hexane) to provide 1.0 g (15% yield) of the desired product **8** after recrystallization from hot methanol. An important red fraction does not migrate on the column. The product in solution is more air-sensitive than its congeners; consequently, the chromatography fractions should be rapidly handled. Anal. Calcd for $C_{53}H_{51}FeP_3$ (836.8): C, 76.08; H, 6.14. Found: C, 76.05; H, 6.14. ^{1}H NMR: δ 0.81 (d, $^3J_{PH}$ = 14.4 Hz, 6H, CH_3), 1.17 (s, 9H, *t*-Bu), 3.64 (m, 2H, 2′,5′-Fc (or 3′,4′-Fc)), 3.82 (m, 2H, 3′,4′-Fc (or 2′,5′-Fc)), 4.11 (m, 2H, 3,5-Fc), 6.75−6.97 (m, 10H, Ph), 7.05−7.32 (m, 16H, Ph), 7.54 (m, 4H, *o*-Ph). ^{13}C{^{1}H} NMR: 27.4 (d, $^2J_{PC}$ = 18.6 Hz, C(CH$_3$)$_2$PPh$_2$), 31.2 (s, C(CH$_3$)$_3$), 32.5 (s, C(CH$_3$)$_3$), 35.2 (d, $^1J_{PC}$ = 19.8 Hz, C(CH$_3$)$_2$-PPh$_2$), 68.8 (m, 3′,4′-Fc (or 2′,5′-Fc)), 69.8 (d, $^3J_{PC}$ = 4.5 Hz, 2′,5′-Fc (or 3′,4′-Fc)), 71.0 (s, 3,5-Fc), 80.7 (m, 1,2-Fc), 102.2 (d, $^2J_{PC}$ = 6.0 Hz, 1′-Fc), 107.3 (s, 4-Fc), 127.9 (s, *p*-Ph), 127.9 (t, *m*-Ph), 128.0 (d, $^3J_{PC}$ = 7.2 Hz, *m*-Ph), 128.7 (t, J_{PC} = 4.4 Hz, *m*-Ph), 129.1 (s, *p*-Ph), 129.5 (s, *p*-Ph), 133.1 (t, J_{PC} = 10.3 Hz, *o*-Ph), 135.4 (d, J_{PC} = 20.4 Hz, *o*-Ph), 135.9 (t, J_{PC} = 11.6 Hz, *o*-Ph), 136.3 (d, J_{PC} = 20.3 Hz, *ipso*-Ph), 138.0 (m, *ipso*-Ph), 139.5 (m, *ipso*-Ph). ^{31}P{^{1}H} NMR: δ 29.4 (s, CMe$_2$PPh$_2$), −24.0 (s, 1,2-PPh$_2$).

(e) 1,1′,2,3′-Tetrakis(diphenylphosphino)-4-*tert*-butylferrocene (9). To a stirred suspension of $FeCl_2$ (0.46 g, 3.7 mmol) in 12 mL of THF was added dropwise at −40 °C a solution of *t*-BuCp(PPh$_2$)$_2$-Li (1.86 g, 3.7 mmol) in 20 mL of THF. After it was stirred for 2 h at room temperature, the reaction mixture was treated at −40 °C with a 20 mL THF solution of CpLi-**9** (1.60 g, 3.6 mmol). The solvent was evaporated, and the residue was refluxed in 40 mL of toluene for 3 h. The reaction mixture was cooled and filtered in air over a paper filter. The crude product was subjected to column chromatography (SiO_2, 4:1 v/v hexane−dioxane) to yield 1.50 g (45%) of 1,1′,2,3′-tetrakis(diphenylphosphino)-4-*tert*-butylferrocene (**9**). Anal. Calcd for $C_{62}H_{54}FeP_4$ (978.9): C, 76.00; H, 5.56. Found: C, 76.06; H, 5.60. MS (EI): *m*/*z* (%) 978 (100) $[M]^+$, 901 (10) $[M - Ph]^+$, 794 (75) $[M - PPh_2]^+$. For compound **9**, a complete NMR attribution has been done with the help of 2D correlation spectroscopy; the chemical shifts are attributed by the numbering given in Chart 4. ^{1}H NMR: δ 0.70 (s, 9H, *t*-Bu), 3.64 (m, 1H, 2′-Fc), 4.20 (m, 2H, 3,5-Fc), 4.65 (m, 2H, 4′,5′-Fc), 6.86−7.06 (m, 10H, A-Ph), 7.10−7.32 (m, 26H, C-, D-Ph, *m*,*p*-B-Ph), 7.59 (m, 4H, *o*-B-Ph). ^{13}C{^{1}H} NMR: δ 30.5 (s, C(CH$_3$)$_3$), 31.8 (m, C(CH$_3$)$_3$), 73.7 (d, J_{PC} = 3.8 Hz, 3,5-Fc), 75.2 (s, 2′-Fc), 78.6 (m, 4′,5′-Fc), 82.0 (d, J_{PC} = 14.3 Hz, 1′,3′-Fc), 82.7 (dd (pseudo-t), $^2J_{PC}$ ≈ 8.3 Hz, 1,2-Fc), 108.6 (s, 4-Fc), 127.9 (dd (pseudo-t), $^2J_{PC}$ ≈ 4.5 Hz, *m*-A-Ph), 128.0 (s, *p*-Ph), 128.3−128.5 (m, Ph), 128.8 (ddd (p-sext), $^2J_{PC}$ = 4.5 Hz, $J_{P'C}$ ≈ 0.8 Hz, *m*-B-Ph), 129.4 (s, *p*-Ph), 133.0 (d, J_{PC} = 19.6 Hz, *o*-C-Ph (or *o*-D-Ph)), 133.5 (dd (pseudo-t), $^2J_{PC}$ ≈ 10.6 Hz, *o*-A-Ph), 135.6 (d, J_{PC} = 23.4 Hz, *o*-D-Ph (or *o*-C-Ph)), 136.0 (ddd (p-sext), $^2J_{PC}$ ≈ 10.6 Hz, $J_{P'C}$ = 2.3 Hz, *o*-B-Ph), 137.6 (m, *ipso*-B-Ph (or *ipso*-A-Ph)), 138.7 (d, J_{PC} = 14.3 Hz, *ipso*-C-Ph (or *ipso*-D-Ph)), 139.3 (m, *ipso*-A-Ph (or *ipso*-B-Ph)), 141.8 (d, J_{PC} = 15.9 Hz, *ipso*-D-Ph (or *ipso*-C-Ph)). ^{31}P-{^{1}H} NMR: δ −19.6 (d, $^{TS}J_{PP}$ ≈ 2.2 Hz, 1′,3′-PPh$_2$), −23.9 (d, $^{TS}J_{PP}$ ≈ 2.2 Hz, 1,2-PPh$_2$).

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Supporting Information Available: Figures giving ^{1}H NMR spectra of **6**−**8** and ^{31}P NMR spectra of **8** and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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