# Conformational Control of Metallocene Backbone by Cyclopentadienyl Ring Substitution: A New Concept in Polyphosphane Ligands Evidenced by "Through-Space" Nuclear Spin-Spin Coupling. Application in Heteroaromatics Arylation by Direct C-H Activation

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The present study deals with the conformational control of the metallocene backbone within ferrocenyl polyphosphane ligands and their performance in the highly topical palladium-catalyzed heteroaromatics arylation by direct C-H activation. New substituted cyclopentadienyl rings were synthesized, which allowed the assembling of original tri- and diphosphanes. The bulky cyclopentadienyl lithium salts diphenylphosphino-3-(triphenyl)methylcyclopentadienyllithium (4) and 1,2-bis(diphenylphosphino)-4-(triphenyl)methylcyclopentadienyllithium (5) were prepared in excellent yield. The assembling of these new hindered cyclopentadienyl salts (Cp) with other Cp fragments was performed in order to prepare ferrocenyl ligands with controlled conformation. A comparison of conformations of 1,1',2-tris(diphenylphosphino)-3',4-di-tert-butylferrocene (3) and 1,1',2-tris(diphenylphosphino)-3'-(triphenyl)methyl-4*tert*-butylferrocene (6) allowed us to determine, for the first time, the conditions of an efficient control of the orientation of the phosphino substituents on the ferrocene backbone in the absence of an ansabridge. The characterization of these metallo-ligands, by multinuclear NMR in solution and by X-ray diffraction in the solid state, focused on nonbonded  $J_{PP}$  spin-spin couplings. These unusual couplings are especially useful for assessing the conformation of the ferrocene backbone in solution. The palladium complexes of the triphosphane ligand 6 and the diphosphane 1.1'-bis(diphenylphosphino)-3.3'-di(triphenvl)methylferrocene (7) were successfully used in the direct C-H activation of electron-rich heteroaromatics for coupling to demanding aryl bromides, whether electron rich and/or sterically congested. Products such as 2-butyl-5-(4-methoxyphenyl)furan (10), 2-butyl-5-o-tolylfuran (11), and thiophene analogues (12 and 13) were obtained in yields higher than 90%. The NMR examination of the reaction of  $[PdCl(\eta^3-C_3H_5)]_2$  with ligands 6 and 7 allowed us to determine the coordination chemistry of the precatalysts. The allylic palladium complexes 8 and 9 confirmed the unusual conformation present in 6. As a consequence, the selective and "genuinely" tridentate bonding of a triphosphane to one palladium center is reported. This seldom observed coordination mode is a direct consequence of the successful ferrocene backbone conformation control.

# Introduction

The "sandwich" arrangement of metallocenes, such as ferrocene and its derivatives, is an important structural motif in organometallic chemistry. The metallocenes have found applications in materials science and catalysis. Some attractive features of ferrocene derivatives such as planar chirality,<sup>1</sup> reversible redox properties,<sup>2</sup> high chemical stability, and a wide array of substitution patterns<sup>3</sup> have attracted intense interest both in academic research and in industry.<sup>4</sup> Recent ligand synthesis by Santelli, De Meijere, and our group have provided several examples of polyphosphane catalytic auxiliaries incorporating

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**Figure 1.** Ferrocenyl tetraphosphane 1 and triphosphane 2. 1 has a blocked conformation with pseudoeclipsed phosphorus atoms at internal positions for which  $J_{PP} = 60$  Hz (down); for 2 an unprecedented heteroannular  $J_{PC} = 5$  Hz was observed with the terminal methyl of *t*-Bu groups. The distances between NMR-active atoms and the lone-pair orientation are essential for the intensity of these spin-spin couplings and their mode of transmission.

three or four phosphorus atoms.<sup>5-9</sup> These compounds exhibit a high efficiency in stabilizing long-lived palladium-based catalysts under substantially low metal/ligand loading conditions (down to  $10^{-6}$  mol % of palladium and polyphosphane ligand).<sup>7</sup> For instance, the tetraphosphane metallo-ligand 1 (Figure 1) has been found to be active in Heck and Suzuki cross-coupling reactions with TONs up to 1 000 000. Under such conditions of low catalyst loadings, classical mono- and diphosphanes are ineffective.<sup>10</sup> In our case, the ferrocene backbone is used as a suitable robust platform for the introduction of three or four phosphorus atoms in very close spatial proximity.<sup>11–13</sup> One of our goals is to study the unfamiliar influence of postulated effects involving the multidentate nature of polyphosphane ligands. The use in metal catalysis of this kind of polydentate ligands, which include three or more donor atoms, might be very pertinent. Indeed, very often in catalytic reactions an excess of mono- or bidentate ligands with regard to the metal is employed.7,10 A direct application of the chemistry of such multidentate species is related to the development of more sustainable catalytic systems based on the *longevity* and the stabilization of active intermediary species. This stability would be attained via the enhancement of the coordination opportunities of the ligand to the metal center.7,12,13

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A close spatial proximity of the phosphorus donor atoms of 1 and its derivatives, imposed by the blocked conformation of the ferrocenyl backbone, has been evidenced.<sup>14-17</sup> The signals observed in the <sup>31</sup>P NMR spectrum of 1 and its derivatives revealed a collection of intense "through-space" J<sub>PP</sub> spin-spin coupling constants.<sup>14</sup> These  $^{TS}J_{PP}$  result from the overlap of the phosphorus lone-pairs having an appropriate orientation. Conversely, in the related triphosphane 2 (Figure 1),  $^{15,18}$  the conformational "cis-orientation" of the phosphorus atoms is lost, hypothetically because of the absence of the second tertiarybutyl group. As a consequence, no <sup>31</sup>P "through-space" spin coupling between the magnetically nonequivalent phosphorus atoms was observed for 2, as attested by the two 1:2 singlets observed in the solution NMR spectrum.<sup>19</sup> This discrepancy in the conformational features of closely related ferrocene derivatives raises important questions about the conditions required for a conformational control of metallocene backbones. We anticipated that a specific ligand design might force three substituents to adopt the same orientation within a metallocene backbone (not only phosphorus donors). This controlled orientation would in turn provoke their close spatial proximity, which could result in the emergence in chemical reactivity of cooperative effects between the substituents. This proximity and its associated effects can be a valuable feature in ferrocenyl polyphosphanes from both a fundamental and an applied point of view.10,13,14,19

Herein are presented our first investigations and results devoted to the conformational control in ferrocenyl triphosphane ligands. New substituted cyclopentadienyl rings, which allowed the assembling of original tri- and diphosphanes, were synthesized. Their characterization by multinuclear NMR in solution focused on nonbonded  $J_{\rm PP}$  spin couplings. These couplings are decisive indicators for assessing the conformation of the ferrocene backbone. The present study aims to discuss and detail the synthesis of polysubstituted metallocenes in which the conformation of the backbone is controlled in solution. This concept might find further applications in the rich chemistry of sandwich complexes. The coordination behavior of the ligands toward palladium confirms an unprecedented conformational control. The activities of palladium complexes of the new ligands were assessed in the highly topical palladium-catalyzed arylation of substituted heteroaromatics via C-H bond activation. Such a reaction, which involves C-C bond formation, does not result in the production of stoichiometric amounts of metallic waste and therefore contribute to a more sustainable chemistry.

### Background

The analysis of the structure of the tetraphosphane metalloligand **1** furthered our knowledge on the conformational control of ferrocenyl-based phosphanes. The specific *cis*-orientation of the four phosphorus atoms of the metallo-ligand **1**, as depicted in Figure 1, is a consequence of the *cisoid* conformation of the

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3 view from above

substituted cyclopentadienyl rings (Sb-Cp). A close spatial proximity of the donor atoms is imposed by the blocked conformation of the ferrocenyl backbone both in solution and in the solid state. The intensity of nuclear spin-spin J couplings between phosphorus atoms separated by at least four bonds was found to increase exponentially with the decrease of distances between the phosphorus atoms.<sup>14</sup> Consequently, NMR analysis on Pd(II)/1 precatalysts and electrochemistry studies on analogous Pd(II)/Pd(0) species have revealed the involvement of at least three phosphorus atoms in the coordination of palladium.<sup>10,13</sup> We additionally reported the synthesis and properties of triphosphane  $2^{15,18}$  for which, conversely, the phosphorus "orientation" was lost (Figure 1), hypothetically because of the absence of the second tertiary-butyl group. As a consequence, no "through-space" coupling between the magnetically nonequivalent phosphorus atoms was observed for 2 by solution <sup>31</sup>P NMR.

The most usual way of exerting a conformational control on metallocene backbones consists in bridging the cyclopentadienyl rings.<sup>20</sup> The resulting ansa-metallocenes display a number of interesting properties often related to their rigidity. This kind of conformation control by short interannular bridge bonding clearly obviates any rotational flexibility.<sup>21</sup> Additionally, as demonstrated in some elegant syntheses,<sup>22</sup> the introduction of an interannular bridge in polysubstituted metallocenes together with their ring functionalization may require several steps, some potentially critical in terms of selectivity. To the best of our knowledge, while a wide array of substitution patterns have been applied in the preparation of substituted ferrocenes, including 1,1'- and 1,2-disubstituted, 1,1',2-trisubstituted, and 1,1',2,2'tetrasubstituted ferrocenes, the specific issue of gaining control over a given conformation by means of the Cp substituents was not addressed. This might in part be due to the dominant development and applications of chiral diphosphanes, for which the involvement of a third or fourth donor atom in their reaction chemistry was seldom envisaged. Nevertheless, the catalytic performances of ferrocenyl polyphosphanes make them worthwhile ligands, and the improvement of their design with the control of their conformation in mind appeared to us a pertinent issue.

# **Results and Discussion**

Different strategies were envisaged in order to prepare ferrocenyl triphosphanes in which the orientation of the substituents would ensure a close spatial proximity of the phosphorus atoms as observed in the tetraphosphane 1 and contrary to the case of triphosphane 2.

Conformation Control by tert-Butyl Groups. Like 1, the triphosphane ligand 3 was designed by incorporating two *t*-Bu groups (one on each of the Sb-Cp rings), with the view to lead to the desired conformation with three nearby phosphorus atoms pointing in the same direction. 3 was obtained by reacting alkali metal salts of adequately substituted cyclopentadienyl rings with iron dichloride, following the method previously described for producing dissymmetric ferrocenyl polyphosphanes (Scheme 1).<sup>16</sup> The characterization of the new ligand revealed the failure of this strategy since, as depicted in Figure 2, the X-ray structure analysis reveals, in the solid state, a large spatial separation (>5.0 Å) between the third phosphorus atom and the 1,2-P chelating pair (P1...P2 = 5.1098(2) Å, P1...P3 = 6.6591(2) Å). In solution the <sup>31</sup>P NMR consistently confirmed the absence of spatial proximity between the heteroannular phosphorus nuclei. For the chelating pair of phosphorus atoms an AB quartet centered at -25.2 ppm is observed ( $J_{AB} = 98$  Hz), while a singlet at -20.7 ppm is attributed to the third one.<sup>23</sup> The absence of a coupling constant between AB and X resonances clearly indicates the absence of a significant lone-pair overlap interaction. The AB quartet is indicative of the slight difference of environment between the two homoannular phosphorus atoms, as illustrated in Scheme 1 (view from above). In the solid state, an almost eclipsed conformation of the Sb-Cp rings is observed for 3, which allows in fact a clear lessening of the steric hindrance between the five substituents on the Sb-Cp rings.

The comparison of the preferred geometry observed in 2 and 3 (views from above in Figure 1 and Scheme 1) in the solid state as well as in solution shows that the orientation of a third phosphorus cannot be the result of only steric hindrance between *two* tertiary-butyl groups. While 2 possess one *t*-Bu and 3 has two *t*-Bu groups, their third phosphorus atoms display a comparable orientation, away from the chelating pair. This prevents *de facto* an easy cooperative coordination effect of the three phosphorus nucleus in 3. Most probably the steric hindrance of the phenyl groups attached to the phosphorus atoms plays also a significant role in imposing the final conformation in 2 and 3.

We subsequently envisioned that more bulky substituents than *tert*-butyl groups might perturb the eclipsed conformation of the *Sb*-Cp rings in ferrocenyl triphosphanes. Consequently, it would be possible to reach a hindered conformation in which three phosphorus atoms get a *cis*-conformation and come in closer spatial proximity and eventually interact.

**Conformation Control by a Trityl Group.** Knowing the role of *tert*-butyl groups in defining the conformation of **1**, **2**, and **3**, we explored whether a more hindered substituent might induce a different effect on the conformation of triphosphane ligands. To reach this goal, the (triphenyl)methyl group (trityl) was chosen due to its easy access via ClCPh<sub>3</sub>. The lithium salts diphenylphosphino-3-(triphenyl)methylcyclopentadienylli-

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<sup>(21)</sup> Bridges containing three or more atoms are generally less rigid and offer less stereochemical control, and they have received much less attention; see ref 20.

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<sup>(23)</sup> A copy of the NMR spectrum is available in the Supporting Information.



**Figure 2.** Plot of metallo-ligand **3** (30% probability). Hydrogen atoms are omitted for clarity. Selected bond distances (Å): Fe-Ct(1) = 1.6677(7), Fe-Ct(2) = 1.6590(7). Selected internuclear distances (Å):  $P_1 \cdots P_2 = 5.1098(2)$ ,  $P_1 \cdots P_3 = 6.6591(2)$ ,  $P_2 \cdots P_3 = 3.4507(3)$ . Selected torsion angles (deg): P1-Ct(1)-Ct(2)-P2 = -80.75(4), P1-Ct(1)-Ct(2)-P3 = -149.68(4).

Scheme 2. Synthesis of Trityl-Substituted Cyclopentadienyl Rings 4 and 5



thium (4) and 1,2-bis(diphenylphosphino)-4-(triphenyl)methylcyclopentadienyllithium (5) were obtained from [( $Ph_3C$ )-CpLi] in 80% and 50% yield, respectively (Scheme 2). Unfortunately, the second phosphorylation of the Cp ring appears sluggish under our conditions, probably because of the bulkiness of the Cp substituents.

The NMR characterization of the lithium salts **4** and **5** in THF indicates proton shifts between 5.5 and 6.0 ppm and phosphorus shifts at -19.4 ppm. The cyclopentadienyl fragment **4** was successfully used for assembling both dissymmetric and symmetric new ferrocenyl phosphane ligands, following the general methods previously reported.<sup>16</sup> Curiously, the various attempts to build ferrocenyl polyphosphanes from the fragment **5** were unsuccessful or suffered from a significant lack of selectivity. The triphosphane **6** and the diphosphane **7** were conversely obtained with fairly good yield of pure product ( $\geq 55\%$ , Scheme 3).

The solution multinuclear NMR spectrum of **6** is very informative.<sup>23</sup> From <sup>31</sup>P NMR measurements a set of multiplets in agreement with the existence of an intense interaction between the three phosphorus atoms was observed (Figure 3).

The analysis of the spectrum can be done at first order (ABC spin system). The signals corresponding to the phosphorus of the chelating pair, 1-P and 2-P, are centered at -18.8 and -24.9 ppm. They appear as a doublet of doublets, due to a strong but classical coupling constant,  ${}^{3}J_{PP} = 41$  Hz, but also due to more intriguing coupling constants with the phosphorus atom 1'-P, of the other cyclopentadienyl ring. The signal for the third phosphorus is a pseudotriplet due to the  $J_{PP} = 11$  and 12 Hz with 1-P and 2-P. It is now recognized that this kind of intense spin—spin coupling (herein  ${}^{4}J_{PP} > 10$  Hz) between heteroannular phosphorus atoms operates "through-space" ( ${}^{TS}J_{PP}$ ) and results from a close spatial proximity of the spin-active nucleus.<sup>14</sup>

the trityl group controls the global conformation of the ferrocene backbone and consequently orients the third phosphorus atom toward the chelating pair of phosphorus atoms. The trityl group is certainly positioned far away enough from the homoannular  $-PPh_2$  groups. This conformational constraint was not observed for analogous ligands such as **2** and **3**. In the absence of an X-ray structure for **6**, but based on related semiquantitative relationships,<sup>14,17</sup> the proximity of phosphorus atoms (1-P, 1'-P) and (1'-P, 2-P) can be predicted as less than 4.3 Å. The proposed conformation for the triphosphane **6** is depicted in Figure 4. A complete attribution was achieved by means of <sup>13</sup>C and <sup>1</sup>H with <sup>31</sup>P broadband decoupling and selective irradiation NMR (HMBC <sup>1</sup>H/<sup>13</sup>C{<sup>31</sup>P}, HSQC <sup>1</sup>H/<sup>13</sup>C{<sup>31</sup>P}).<sup>23</sup>

The proposed conformation should have substantial consequences in the coordination to metals of **6**; this hypothesis is confirmed by the studies conducted with the palladium precursor utilized in the catalytic applications and described below.

The diphosphane **7** displays a more classical <sup>31</sup>P NMR spectrum with one singlet detected at -20.50 ppm. In the <sup>1</sup>H



Figure 3. <sup>31</sup>P NMR spectrum of metallo-ligand 6 in toluene- $d_8$ .





Scheme 3. Synthesis of Triphosphane 6 (racemic) and Diphosphane 7 from Trityl-Substituted Cyclopentadienyl Rings



NMR spectrum, three signals are observed for the protons of the cyclopentadienyl rings at 3.45, 3.92, and 4.05 ppm. The <sup>13</sup>C NMR spectrum displays typical quaternary signals from a trityl group attached to Cp (C[CPh<sub>3</sub>] at 58.32 ppm and C-C[CPh<sub>3</sub>] at 103.38 ppm). Thus, multinuclear NMR experiments at room temperature indicate a symmetrical structure for the ligand. Compound **7** is stable in the solid state but undergoes phosphorus oxidation in solution if no precaution is taken (inert atmosphere and deoxygenated solvent): a signal attributed to **P**=O at a chemical shift of 26.83 ppm is observed, and the signals for Cp protons appeared slightly shifted to higher field. This behavior is rather uncommon for ferrocenic triarylphosphanes of this family and might be a sign of electron enrichment of the phosphorus atoms.

**Coordination Chemistry of 6 and 7 to Palladium.** Due to its inherent stability and solubility, as well as easiness of reduction to Pd(0), the dimeric complex of palladium [PdCl- $(\eta^3$ -C<sub>3</sub>H<sub>5</sub>)]<sub>2</sub> is a convenient source of Pd(II) in various catalytic cross-coupling reactions.<sup>10,18,24</sup> It was used in the present study as a palladium source for the catalytic arylation of heteroaromatics, and it was also employed to determine the coordination behavior of complexes **6** and **7** toward palladium. The complexes **8** and **9**, depicted in Scheme 4, were quantitatively obtained in NMR tubes from stoichiometric mixtures of [PdCl( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)]<sub>2</sub>/2L (L = **6** or **7**) in CD<sub>2</sub>Cl<sub>2</sub> at room temperature (<sup>31</sup>P NMR in Figures 5 and 6).

The <sup>31</sup>P NMR spectrum, recorded 5 min after the addition of a solution of palladium allyl dimer to a solution of **6** in  $CD_2Cl_2$ ,





shows the immediate and quantitative coordination of the three phosphorus donors to the metal center (Figure 5). The three multiplets around -20 ppm are replaced by three broad signals downfield shifted to -9.1, 24.0, and 29.8 ppm. These chemical shifts indicate the bonding of all the phosphorus donors to the metal center and show also that the chelating pair is certainly more tightly bonded than the third heteroannular phosphorus atom (signal at -9.1 ppm). The broadness of the signals suggests a possible fluxional character of this bonding; however variable-temperature measurement between -5 and 45 °C did not produce a significant modification of the spectrum. This "true" tridentate coordination (triligation) is unprecedented in the



**Figure 5.** <sup>31</sup>P NMR spectrum of palladium complex **8** in  $CD_2Cl_2$  at 318 K (10 min after Pd/2L addition).

<sup>(24)</sup> Hierso, J.-C.; Fihri, A.; Amardeil, R.; Meunier, P.; Doucet, H.; Santelli, M. *Tetrahedron* **2005**, *61*, 9759.



Figure 6. Temperature dependence of the  ${}^{31}P$  NMR spectrum of palladium complex 9 in CD<sub>2</sub>Cl<sub>2</sub>.

coordination chemistry of ferrocenyl triphosphanes (such as **2**, for which only the chelating pair has been found to coordinate palladium).<sup>25</sup> The corresponding <sup>1</sup>H NMR spectrum recorded in CD<sub>2</sub>Cl<sub>2</sub> confirms the structure proposed for **8** (and the formation of only one species), with a clear shift of the five resonances attributed to cyclopentadienyl protons from 3.93, 4.25, 4.28, 4.33, and 4.37 ppm to 3.51, 4.03, 4.67, 4.77, and 4.85 ppm, respectively.<sup>23</sup> The characteristic multiplet of allylic-CH is also shifted from 5.51 to 5.88 ppm.

The coordination of ligand 7 to palladium was found to be fast with a complete disappearance of the signal at -20.50ppm.<sup>23</sup> Upon coordination, two signals of a nearby chemical shift are observed at 298 K: 21.06 and 21.51 ppm (middle spectrum in Figure 6). The variable-temperature experiments confirmed that the signals are due to the formation of a single dissymmetric species for which only one <sup>31</sup>P NMR signal is found at higher temperature (rapid exchange at 318 K, top spectrum in Figure 6). At 278 K, the exchange between the anisochronous phosphorus is slower and a typical AB pattern is found for compound 9 (centered at 21.2 ppm,  $J_{AB} = 46$  Hz). The formulation proposed in Scheme 4 for 9 was confirmed by <sup>1</sup>H NMR analysis, the shift of the three resonances attributed to cyclopentadienyl protons (from 3.45, 3.92, and 4.05 ppm in CD<sub>2</sub>Cl<sub>2</sub> to 3.80, 4.39, and 4.56 ppm) being clearly observed. The characteristic signals of allylic protons are also shifted

(25) Boudon, J.; Hierso, J.-C. Unpublished results.

downfield from 3.05, 4.11, and 5.51 ppm to 3.60, 4.22, and 5.83 ppm, respectively. These modified ferrocenyl phosphane ligands and their complexes were tested in cross-coupling reactions between aryl halides and heterocyclic compounds, in order to evaluate their potential in palladium-catalyzed C–H activation.

Direct C-H Activation in Heteroaromatics Arylation Catalyzed by 8 and 9. The pallado-catalyzed formation of aryl/ heteroaryl coupling products via direct C-H activation is a relatively recently reported reaction.<sup>26</sup> This synthetic strategy is attractive in terms of green chemistry and atom economy when compared to alternative coupling methods that involve organometallic heteroaryl or aryl reagents, the metallic groups being either ZnX,<sup>27</sup> SnR<sub>3</sub>,<sup>28</sup> or B(OR)<sub>2</sub>.<sup>29</sup> Such coupling reactions lead to the subsequent formation of metallic waste in stoichiometric amounts. Table 1 summarized the catalytic coupling reactions that have been explored. The selection of demanding substrates, such as the electron-rich bromoanisole or congested 2-bromotoluene and 2-bromo-m-xylene, was made on purpose since it was recently shown that the influence of the ligand is decisive in these cases.<sup>26f-h</sup> Conversely, with less challenging substrates such as electron-deficient aryl bromides ligand-free couplings are achievable. Ligands 6 and 7 associated with 0.5 mol % of  $[PdCl(\eta^3-C_3H_5)]_2$  were found to give very efficient catalysts for the coupling between 2-n-butylfuran or 2-n-butylthiophene and 4-bromoanisole or 2-bromotoluene. Both ligands gave target products 10-13 in good yields (70 to 100%) and high selectivity (Table 1, entries 5, 6, 8, 9, and 12-15). For such reactions, other previously reported catalytic systems,<sup>26</sup> such as Pd(PPh<sub>3</sub>)<sub>4</sub>, Pd(OH)<sub>2</sub>/C, PdCl<sub>2</sub>/2PCy<sub>3</sub>, or Pd(OAc)<sub>2</sub>, gave very low to moderate yields (Table 1, entries 1-4 and 7). The coupling of 2-n-propylthiazole with highly congested 2-bromo*m*-xylene gave 14 with moderate conversion and yields (Table 1, entries 11 and 16). Nevertheless, it should be noted that the ligand-free Pd(OAc)<sub>2</sub> catalyst did not produce 14 from this very challenging aryl bromide (Table 1, entry 10).

The catalytic systems based on the ferrocenyl phosphane ligands **6** and **7** efficiently complement the few systems reported to date for direct C–H activation of heteroaromatics.<sup>26</sup> According to these preliminary results, they are of particular interest for the coupling of electron-rich heteroaromatics to demanding aromatic substrates. In particular, their robustness to temperature in solution as well as to air and moisture in the solid state make these compounds of rather easy and convenient use. Under our conditions, however, only a slight difference in activity (in favor of the diphosphane **6**) is observed. Therefore, in the absence of kinetic data on the Pd<sup>0</sup> intermediaries of the catalytic cycle,<sup>13</sup>

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Table 1. Heteroaromatics Arylation from Various Pd/L Systems



<sup>*a*</sup> Conditions: [PdCl( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)]<sub>2</sub> 0.005 mmol, L = **6** or **7** 0.01 mmol, heteroaryl 2 mmol, aryl bromide 1 mmol, KOAc 2 mmol, DMAc, 150 °C, 20 h. GC yields and yields in parentheses are isolated. The following systems have been employed for heteroaryl/aryl halide couplings:<sup>26</sup> 1 mol % with AcONa in DMF 110 °C. <sup>*b*</sup> 1 mol % with AcOK in DMAc, 150 °C. <sup>*c*</sup> 1 mol % with KOAc/Bu<sub>4</sub>NBr in DMF 110 °C. <sup>*d*</sup> 1 mol % Pd(OAc)<sub>2</sub> as catalyst.

the relationship between their activity and their very different coordination modes toward palladium (as evidenced with the  $Pd^{II}$  complexes 8 and 9) remains to be clarified.

#### Summary

The design of ligands is of paramount importance for the development of metal catalysis, in keeping with an ever more sustainable approach of chemistry. The present work shows for the first time that a conformational control of the metallocenes backbone is possible in solution by substituting the cyclopentadienyl ring with a very hindered substituent, such as the (triphenyl)methyl group. For instance, the ferrocenyl ligand 6 in the absence of any *ansa*-bridge between its Cp rings displays a cis-orientation of its three phosphorus donors. This unprecedented conformation leads to the bonding of the three phosphorus atoms to the same metal center in palladium complexes. This was demonstrated in solution by the presence of intense "through-space"  $J_{pp}$  couplings between phosphorus atoms separated by at least four bonds and confirmed by studies concerning palladium coordination. The nuclear spin-spin couplings of proximate phosphorus atoms are key indicators for assessing the conformation of the ferrocene backbone. The activity of the new ligands was tested with success in the palladium-catalyzed arylation of substituted electron-rich aromatic heterocycles via C-H bond activation. Demanding substrates such as electron-rich and/or hindered aryl bromides were quantitatively coupled to thiophenes and furans. This kind of C-C bond forming, which does not result in stoichiometric metallic waste production, is in conformity with the necessary expansion of a more sustainable chemistry. The heteroaromatic/ aromatic products are potential building blocks in the synthesis of natural and biologically active compounds. Ongoing studies are dedicated to a better comprehension of the relationship between the structure and catalytic potential of the designed polyphosphanes.

### **Experimental Section**

The reactions were carried out in oven-dried glassware (115 °C) under an argon atmosphere using Schlenk and vacuum-line techniques. Solvents, including deuterated solvents used for NMR spectroscopy, were dried and distilled prior to use. FeCl<sub>2</sub> from a commercial source was used (Aldrich anhydrous beads, 99.9%, H<sub>2</sub>O < 100 ppm). <sup>1</sup>H (300.13, 500.13, or 600.13 MHz), <sup>31</sup>P (121.49, 202.46, or 242.93 MHz), and <sup>13</sup>C NMR (75.47, 125.77, or 150.92 MHz), including low-temperature, <sup>13</sup>C J modulation APT, COSY <sup>1</sup>H–<sup>1</sup>H, HMQC, and HMBC NMR experiments were performed in our laboratories (on Bruker 300, 600, or DRX 500), in CDCl<sub>3</sub> at 293 K unless otherwise stated. Elemental analyses and mass spectra were performed by the analytical service of the CSM of the "Université de Bourgogne".

1,1',2-Tris(diphenylphosphino)-3',4-di-tert-butylferrocene (3). To a suspension of FeCl<sub>2</sub> (500 mg, 3.93 mmol) in 50 mL of THF was added at -40 °C a solution of diphenylphosphino-3-tertbutylcyclopentadienyllithium (1.08 g, 3.45 mmol) in 15 mL of THF. The reaction mixture was allowed to slowly rise to room temperature and was stirred for 2 h. The reaction mixture was then cooled to -40 °C, and a solution of 1,2-bis(diphenylphosphino)-4-tertbutylcyclopentadienyllithium (1.71 g, 3.45 mmol) in 15 mL of THF was added. After addition, the reaction mixture was allowed to slowly rise to room temperature and was stirred for 2 h. THF was removed, the residue was dissolved in 100 mL of toluene, and the resulting solution was refluxed for 15 h. The brown solution was then filtrated through silica to yield 2 g of a mixture of ferrocenylphosphanes 3 and 1. This mixture was difficult to purify, and several preparative chromatography steps using hexane with 5% of ethyl acetate as eluent were necessary to finally separate 550 mg (20%) of **3**. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 0.71, 0.93 (s, 9H each, t-Bu), 3.63, 4.30, 4.32, 4.40, 4.62 (s, 1H each, H-Cp), 6.60-7.80 ppm (m, 30H, *H*-Ph).  ${}^{31}P{}^{1}H{}$  (CDCl<sub>3</sub>):  $\delta$  (ppm) -20.65 (s, 1'-P), -25.00 (AB q,  $J_{AB} = 98$  Hz, 1,2-P). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 127.0-143.0 (m, 36 C, C<sub>6</sub>H<sub>5</sub>), 107.4 (s, 1C, 4-Fc), 107.0 (s, 1C, 3'-Fc), 82.0 (d, 1C, 1-Fc,  ${}^{1}J_{CP} = 20$  Hz), 80.1(d, 1C, 2-Fc,  ${}^{1}J_{CP} =$ 15 Hz), 76.8 (d, 1C, 1'-Fc,  ${}^{1}J_{CP} = 13.5$  Hz), 76.0 (dd, 1C, 3-Fc,  ${}^{2}J_{CP} = 28$  Hz,  ${}^{3}J_{CP} = 4.5$  Hz), 72.5 (s, 1C, 5'-Fc), 70.9 (s, 1C, 4'-Fc), 70.35 (dd, 1C, 5-Fc,  ${}^{2}J_{CP}$  4.5 Hz,  ${}^{3}J_{CP} \le 1$  Hz), 68.5 (d, 1C, 2'-Fc, <sup>2</sup>J<sub>CP</sub> 4.5 Hz), 31.9, 31.7 (s, 3C each, C(CH<sub>3</sub>)<sub>3</sub>), 30.4, 30.0 (s, 1C each, C(CH<sub>3</sub>)<sub>3</sub>). C<sub>54</sub>H<sub>53</sub>FeP<sub>3</sub> (850.76): calcd C 76.2, H 6.28; found C 75.80, H 6.82. Exact mass: m/z 850.268 (M+), simulated 850.271, (σ) 0.043.

X-ray Analysis of 3. Intensity data were collected on a Nonius Kappa CCD at 115 K. The structures were solved by direct methods  $(SIR92)^{30}$  and refined with full-matrix least-squares methods based on  $F^2$  (SHELXL-97)<sup>31</sup> with the aid of the WINGX program.<sup>32</sup> All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in their calculated positions and refined with a riding model. Crystallographic data are reported in Supporting Information.

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Diphenylphosphino-3-(triphenyl)methylcyclopentadienyllithium (4). A 15 g (53.8 mmol) amount of degassed trityl chloride were dissolved in 35 mL of tetrahydrofuran.<sup>33</sup> This solution was added by cannula at -20 °C to a suspension of 4.1 g (56.9 mmol) of cyclopentadienyllithium in 15 mL of THF. The reaction mixture was stirred 10 min at low temperature and then heated at reflux for 3 h. After solvent evaporation, the residue was triturated with 100 mL of 40% aqueous EtOH for 20 min. The solvent was removed by decantation, and the residue was dissolved in 60 mL of toluene. The resulting solution was dried on MgSO<sub>4</sub> and filtered through silica. After evaporation of the toluene, the oily residue was crystallized from a mixture of *n*-octane/toluene (3:1) kept one night at 5 °C in a refrigerator. The product was filtrated on a glass filter, washed with 30 mL of cold ether, and dried to give 10 g of pale vellow crystals (vield 60%). To a suspension of 10 g (32.42 mmol) of this diene in 60 mL of hexane was added dropwise 21 mL of n-BuLi (1.6 M, 33.60 mmol) at -20 °C. The temperature was slowly raised to room temperature, and stirring was continued overnight. During this time the initially almost colorless suspension turned pink. The resulting mixture was filtrated, and the solid was washed with 30 mL of hexane (or toluene/hexane for further purification) and dried under vacuum to yield 10 g of [(Ph<sub>3</sub>C)CpLi] (yield 98%). <sup>1</sup>H NMR (THF- $d_8$ ):  $\delta$  (ppm) 5.40, 5.60 (t, J = 2.8Hz, 2H each, H-Cp), 6.70-7.40 (m, 15H, H-Ph).

To a stirred suspension of [(Ph<sub>3</sub>C)CpLi] (10 g, 31.81 mmol) in 60 mL of toluene was added dropwise a solution of Ph2PCl (6 mL, 33.45 mmol) in 20 mL of toluene at -80 °C. The mixture was stirred overnight, allowing the temperature to slowly rise to room temperature. The solution was filtrated over Celite, to remove the LiCl precipitate, which was washed two times with 15 mL of toluene. The filtrate was reduced to approximately 30 mL. The concentrated solution was treated with 22 mL of n-BuLi (1.6 M, 35.20 mmol) at -20 °C and then evaporated almost to dryness; 60 mL of hexane was added to the residue, and this mixture was vigorously stirred overnight. The resulting suspension was filtrated, and the desired product was recovered as a white solid and washed two times with 30 mL of hexane before drying under vacuum. The lithium salt 4 was obtained pure in 80% yield (12.70 g). <sup>1</sup>H NMR (THF-*d*<sub>8</sub>): δ (ppm) 5.45, 5.65, 5.95 (m, 1H, *H*-Cp), 6.80–7.40 (m, 25H, *H*-Ph). <sup>31</sup>P NMR (THF- $d_8$ ):  $\delta$  (ppm) –19.35 ppm.

**1,2-Bis(diphenylphosphino)-4-(triphenyl)methylcyclopentadienyllithium (5).** To a stirred solution of **4** (5 g, 10.03 mmol) in a mixture of 30 mL of toluene and 15 mL of THF was added dropwise Ph<sub>2</sub>PCl (2.3 mL, 13.04 mmol) at room temperature. The mixture was stirred for 48 h under argon and evaporated almost to dryness. The residue was triturated with toluene (45 mL), the resulting solution was filtrated over Celite, the precipitate of LiCl was washed with toluene (two times 10 mL), and the filtrate was reduced to 20 mL. This solution was treated with 9 mL of *n*-BuLi (1.6 M, 14.00 mmol) at -20 °C and evaporated almost to dryness. After addition of 30 mL of hexane and vigorous stirring for 8 h a pink precipitate was formed. It was filtered off, washed with hexane, and dried under vacuum to yield 3.6 g of **5** (52%). <sup>1</sup>H NMR (THF*d*<sub>8</sub>):  $\delta$  (ppm) 5.57 (s, 2H, *H*-Cp), 6.80–7.40 (m, 35H, *H*-Ph). <sup>31</sup>P NMR (THF-*d*<sub>8</sub>):  $\delta$  (ppm) –19.40 ppm.

**1,1',2-Tris(diphenylphosphino)-3'-(triphenyl)methyl-4**-*tert*-**bu-tylferrocene (6).** To a stirred suspension of 0.26 g of FeCl<sub>2</sub> (2.05 mmol) in 10 mL of THF was added dropwise by cannula a solution of  $[(t-Bu)Cp(PPh_2)_2Li]$  (1.0 g, 2.01 mmol) in 20 mL of THF at -40 °C. After addition the cooling bath was removed, allowing the temperature to slowly rise to room temperature. After 1 h stirring, a solution of  $[(Ph_3C)Cp(PPh_2)Li]$  (2.00 mmol, 1.0 g) in 20 mL of THF was added at -10 °C to the reaction mixture. The mixture was then evaporated to dryness, and 45 mL of toluene was added to the residue and refluxed for 24 h. After filtration of the

brown-red mixture and evaporation of the filtrate, 1.14 g of pure product was isolated in 55% yield from column chromatography on silica (eluent toluene/hexane, 1:2). The attribution of the nucleus (except for Ph groups) was done from NMR experiments (spectra available as Supporting Information or upon request to the authors): <sup>13</sup>C and <sup>1</sup>H with <sup>31</sup>P broadband decoupling and selective irradiation, HMBC <sup>1</sup>H/<sup>13</sup>C{<sup>31</sup>P}, HSQC <sup>1</sup>H/<sup>13</sup>C{<sup>31</sup>P}, HMBC <sup>1</sup>H/<sup>31</sup>P, COSY 45{<sup>31</sup>P}. <sup>1</sup>H NMR (toluene-d<sub>8</sub>): δ 0.77 (s, 9H, t-Bu), 3.94 (s, 1H, 2'-Cp), 4.28 (s, 1H, 4'-Cp), 4.29 (s, 1H, 3-Cp), 4.32 (s, 1H, 5'-Cp), 4.35 (s, 1H, 5-Cp), 6.70–7.39 (m, 45H, Ph). <sup>13</sup>C{<sup>1</sup>H} NMR: δ 30.22 (s, 1C, C(CH<sub>3</sub>)<sub>3</sub>), 31.24 (s, 3C, C(CH<sub>3</sub>)<sub>3</sub>), 59.24 (s, 1C, CPh<sub>3</sub>), 73.21 (dd, 1C,  ${}^{2}J_{PC} = 16.4$ ,  ${}^{3}J_{PC} = 2.5$  Hz, 3-Fc), 73.28 (s, 1C, 4'-Fc), 75.06 (s, 1C, 2'-Fc), 75.08 (s, 1C, 5'-Fc), 75.86 (dd, 1C,  ${}^{2}J_{PC} =$ 15.1,  ${}^{3}J_{PC} = 5.0$  Hz, 5-Fc), 79.90 (d, 1C,  ${}^{1}J_{PC} = 13.8$  Hz, 1'-Fc), 80.65 (dd, 1C,  ${}^{1}J_{PC} = 23.9$ ,  ${}^{2}J_{PC} = 18.2$  Hz, 2-Fc), 81.61 (dd, 1C,  ${}^{1}J_{PC} = 11.3$ ,  ${}^{2}J_{PC} = 17.6$  Hz, 1-Fc), 103.72 (s, 1C, 3'-Fc), 108.65 (d, 1C,  ${}^{3}J_{PC} \approx 3.8$  Hz, 4-Fc), 126.14 (s, Ph), 127.26–128.28 (m, CPh<sub>3</sub>), 128.73 (s, Ph), 128.93 (s, Ph), 130.78 (s, Ph), 133.03 (d, Ph), 133.07 (d,  $J_{PC} = 7.2$  Hz, Ph), 134.13 (d, Ph), 134.18 (dd, Ph), 135.17 (d, Ph), 136.22 (dd), 137.53 (dd,  $J_{PC} = 12.5$ . and 1.2 Hz, 1C, *ipso*-PhP), 138.07 (d,  $J_{PC} \approx 13.8$  Hz, 1C, *ipso*-Ph), 138.42 (dd, 1C,  $J_{PC} \approx 2.9$  Hz, *ipso*-PhP), 138.66 (d, 1C,  $J_{PC} = 15.0$  Hz, *ipso*-PhP), 140.41 (d, 1C,  $J_{PC} = 12.6$  Hz, *ipso*-PhP), 141.46 (d, 1C,  $J_{PC}$ = 17.6 Hz, *ipso*-PhP).  ${}^{31}P{}^{1}H{}$  NMR:  $\delta -24.9$  (dd,  ${}^{3}J_{PP} = 41.0$ Hz,  $^{TS}J_{PP} = 11.0$  Hz, 2-PPh<sub>2</sub>), -21.7 (p-t,  $^{TS}J_{PP} = 11.0$  and 12.0 Hz, 1'-PPh<sub>2</sub>), -18.8 (dd,  ${}^{3}J_{PP} = 41$  Hz,  ${}^{TS}J_{PP} = 12.0$  Hz, 1-PPh<sub>2</sub>). C<sub>69</sub>H<sub>59</sub>FeP<sub>3</sub> (1036.97): calcd C 79.92, H 5.73; found C 79.87, H 5.66. Exact mass: m/z 1036.313 (M+), simulated 1036.318, ( $\sigma$ ) 0.059.

1,1'-Bis(diphenylphosphino)-3,3'-di(triphenyl)methylferrocene (7). To a stirred suspension of 0.2 g of FeCl<sub>2</sub> (1.58 mmol) in 10 mL of THF was added dropwise by cannula a solution of 4 (0.8 g, 1.6 mmol) in 20 mL of THF at -10 °C. After THF addition the cooling bath was removed, and 45 mL of toluene was added. Reflux was carried out until completion of the reaction as followed by <sup>31</sup>P NMR. 7 was isolated pure by column chromatography using a mixture of toluene/hexane (1:1) (1.09 g, 65% yield). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$ 3.45 (s, 2H, Cp), 3.92 (s, 2H, Cp), 4.05 (s, 2H, Cp), 6.88-7.75 (m, 50H, Ph). <sup>13</sup>C{<sup>1</sup>H} NMR: 125.77 MHz: δ 58.32 (s, 2C, CPh<sub>3</sub>), 72.74, 74.50, 79.01 (w, 2C each), 86.71 (w, 2C, 1-1'-Fc); due to coupling to phosphorus, cyclopentadienyl CH and quaternary signals were of weak intensity except for 103.38 (s, 2C, 3,3'-Fc), 125.30 (s, Ph), 126.25 (s, Ph), 127.05 (m, Ph), 127.92 (s, Ph), 129.85 (s, Ph), 131.71 (d, Ph), 133.09 (d, Ph), 146.18 (s, *ipso*-Ph). <sup>31</sup>P{<sup>1</sup>H} NMR:  $\delta -20.50$  (s, PPh2). C<sub>72</sub>H<sub>56</sub>FeP<sub>2</sub> (1039.03): calcd C 83.23, H 5.43; found C 83.09, H 5.28. Exact mass: m/z 1039.325 (M+), simulated 1038.320, ( $\sigma$ ) 0.198.

Reaction of the Palladium Allyl Chloride Dimer with 2 equiv of Ligands 6 and 7. A solution of the allyl dimer [PdCl- $(\eta^3-C_3H_5)$ ]<sub>2</sub> in 0.3 mL of CD<sub>2</sub>Cl<sub>2</sub> (3.5 mg, 0.97 × 10<sup>-5</sup> mole) was added to a solution of 6 or 7 (20 mg, 1.93 × 10<sup>-5</sup> mole) in 0.3 mL of CD<sub>2</sub>Cl<sub>2</sub> under an argon atmosphere at room temperature. The resulting orange-red solution was immediately monitored by NMR (600 MHz) at variable temperature between 268 and 318 K. With the view to check the stability of the formed species, measurements were conducted for several hours (2–6 h) and the solutions were also checked after reflux in the NMR solvent.

**Preparation of the Pd/L Catalysts.** An oven-dried Schlenk tube equipped with a magnetic stirring bar, under argon atmosphere, was charged with  $[Pd(\eta^3-C_3H_5)Cl]_2$  (18.3 mg, 0.05 mmol) and **6** or **7** (104 mg, 0.1 mmol). Then 5 mL of anhydrous DMAc was added, and the solution was stirred at room temperature for 20 min. The appropriate amount of catalyst solution was transferred to the catalytic experiments.

**Catalytic Experiments.** In a typical experiment, the aryl bromide (1 mmol), heteroaryl derivative (2 mmol), and KOAc (2 mmol) were introduced in an oven-dried Schlenk tube, equipped with a

<sup>(33)</sup> Hoch, M.; Duch, A.; Rehder, D. Inorg. Chem. 1986, 25, 2907.

magnetic stirring bar. The palladium catalyst solution (1 mol %) and DMAc (4 mL) were added, and the Schlenk tube was purged five times with argon. The mixture in the Schlenk tube was stirred for 20 h at 150 °C. Then, the reaction mixture was analyzed by gas chromatography to determine the conversion of the aryl bromide. 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-Butyl-5-(4-methoxyphenyl)furan (10).**<sup>26g</sup> The reaction of 4-bromoanisole (0.187 g, 1 mmol), 2-*n*-butylfuran (0.248 g, 2 mmol), and KOAc (0.196 g, 2 mmol) with the palladium complex (0.01 mmol) using ligand **6** affords the corresponding product **10** in 81% (0.187 g) isolated yield.

**2-Butyl-5-***o***-tolylfuran (11).** The reaction of 2-bromotoluene (0.171 g, 1 mmol), 2-*n*-butylfuran (0.248 g, 2 mmol), and KOAc (0.196 g, 2 mmol) with the palladium complex (0.01 mmol) using ligand 7 affords the corresponding product **11** in 90% (0.193 g) isolated yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 0.98 (t, J = 7.4 Hz, 3H), 1.41 (sext., J = 7.4 Hz, 2H), 1.70 (quint., J = 7.4 Hz, 2H), 2.51 (s, 3H), 2.72 (t, J = 7.4 Hz, 2H), 6.11 (d, J = 3.2 Hz, 1H), 6.46 (d, J = 3.2 Hz, 1H), 7.20–7.40 (m, 3H), 7.71 (d, J = 7.9 Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 13.9, 22.0, 22.3, 27.8, 30.3, 106.6, 109.3, 125.9, 126.5, 126.8, 130.6, 131.1, 134.1, 151.7, 155.9. C<sub>15</sub>H<sub>18</sub>O (214.30): calcd C 84.07, H 8.47; found C 84.01, H 8.60.

**2-Butyl-5-(4-methoxyphenyl)thiophene (12).**<sup>26f</sup> The reaction of 4-bromoanisole (0.187 g, 1 mmol), 2-*n*-butylthiophene (0.280 g, 2 mmol), and KOAc (0.196 g, 2 mmol) with the palladium complex (0.01 mmol) using ligand **6** affords the corresponding product **12** in 90% (0.222 g) isolated yield.

**2-Butyl-5**-(*o*-tolyl)thiophene (13).<sup>26h</sup> The reaction of 2-bromotoluene (0.171 g, 1 mmol), 2-*n*-butylthiophene (0.280 g, 2 mmol), and KOAc (0.196 g, 2 mmol) with the palladium complex (0.01 mmol) using ligand **6** affords the corresponding product **13** in 74% (0.170 g) isolated yield.

**5-(2,6-Dimethylphenyl)-2-propylthiazole (14).** The reaction of 2-bromo-*m*-xylene (0.185 g, 1 mmol), 2-*n*-propylthioazole (0.254 g, 2 mmol), and KOAc (0.196 g, 2 mmol) with the palladium complex (0.01 mmol) using ligand **6** affords the corresponding product **14** in 32% (0.074 g) isolated yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 1.05 (t, J = 7.4 Hz, 3H), 1.89 (sext, J = 7.4 Hz, 2H), 2.46 (s, 6H), 3.02 (t, J = 7.4 Hz, 2H), 7.05–7.25 (m, 3H), 7.36 (s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 13.7, 20.9, 23.3, 35.5, 127.4, 128.5, 130.4, 134.3, 138.6, 140.4, 171.8. C<sub>14</sub>H<sub>17</sub>NS (231.36): calcd C 72.68, H 7.41; found C 72.60, H 7.61.

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**Supporting Information Available:** Crystal structure data for **3** as a CIF file, NMR spectra corresponding to ref 23, and exact mass ES analysis of **3**, **6**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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