ORGANOMETALLICS

Article

pubs.acs.org/Organometallics

Converging and Diverging Synthetic Strategies to Tetradentate (*N,N′*)-Diaminomethyl,(*P,P′*)-Ferrocenyl Ligands: Influence of *tert*-Butyl Groups on Ferrocene Backbone Conformation

Fatima Allouch,[†,#] Nejib Dwadnia,[†,#] Nikolay V. Vologdin,[†] Yurii V. Svyaschenko,[†] Hélène Cattey,[†] Marie-José Penouilh,[†] Julien Roger,[†] Daoud Naoufal,[‡] Ridha Ben Salem,[§] Nadine Pirio,*[,†] and Jean-Cyrille Hierso*[,†,⊥]

[†]Institut de Chimie Moléculaire de l'Université de Bourgogne, ICMUB UMR 6302 CNRS, Université de Bourgogne Franche-Comté, 9 Avenue Alain Savary, 21078 Dijon, France

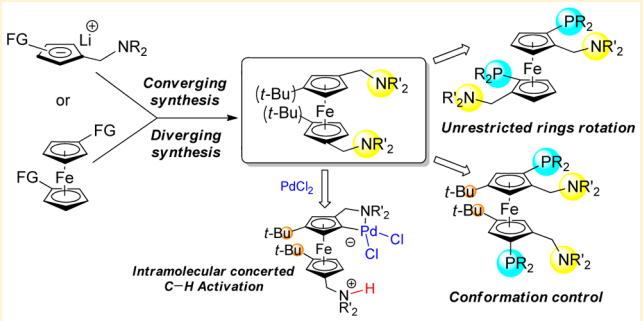
[‡]Laboratoire de Chimie de Coordination Inorganique et Organométallique, Faculté des Sciences, Université Libanaise, Beyrouth−Hadath, Lebanon

[§]Laboratoire de Chimie Organique Physique UR11ES74, Faculté des Sciences, Université de Sfax, 3038 Sfax, Tunisia

[⊥]Institut Universitaire de France (IUF), 103 Boulevard Saint-Michel, 75005 Paris, France

Supporting Information

ABSTRACT: Hexasubstituted hybrid tetradentate (*N,N′,P,P′*)-ferrocenes bearing phosphino and aminomethyl groups, plus hindering *tert*-butyl moieties, were synthesized by using two different strategies: a "diverging" synthesis involving successive functionalization of preformed di-*tert*-butylated ferrocene and a "converging" assembly of the species from appropriately substituted cyclopentadienyl rings. While the new cyclopentadienyl salts formed are of interest, their assembly with iron dichloride used as a "converging" way to produce tetradentate ferrocene ligands presented several drawbacks. Conversely, the synthesis of new *tert*-butylated (aminomethyl)ferrocene derivatives was found convenient to further form (*N,N′*)-aminomethyl,(*P,P′*)-*tert*-butylated-ferrocenyl diphosphines by N-directed *ortho*-metalation. The novel N_2-didentate and N_2P_2-tetradentate *tert*-butylated ferrocene compounds were all synthesized in good to high yields (48−96%) and tolerated aryl, alkyl, and heteroaryl phosphino groups as substituents on nitrogen and phosphorus atoms. They were characterized by X-ray diffraction and multinuclear NMR (^{1}H, ^{13}C, ^{31}P, ^{15}N). We observed the conformation control provided to *rac*-(*N,N′*)-diaminomethyl-(*P,P′*)-*tert*-butylated-ferrocenyldiphosphines with in particular the systematic near-eclipsed conformation of aminomethyl groups. This conformation is at the origin of the unexpected formation at RT of a zwitterionic cyclopalladate from an (aminomethyl)ferrocene derivative, arising from intramolecular Cp-proton transfer to the proximate free amino group by simple C−H activation reaction in the presence of palladium dichloride.



INTRODUCTION

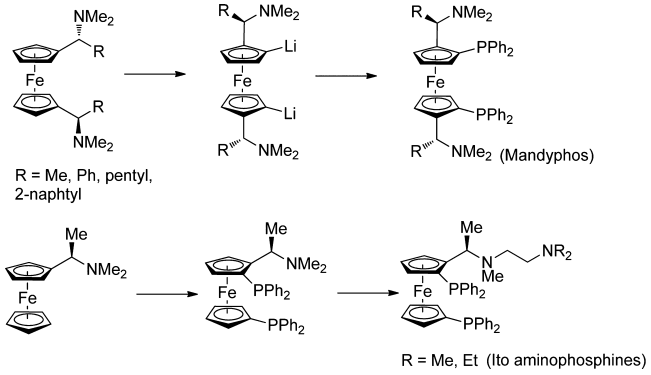
Functionalized ferrocene derivatives have a wide range of applications relating to homogeneous catalysis, electrochemistry, material sciences, and biomedical research.[1] Since the 1950s the synthesis of ferrocene derivatives incorporating atoms having bonding donor abilities such as phosphorus, sulfur, or nitrogen has attracted much attention.[2−4] Because of their unique geometric and electronic properties, robustness, and modular backbone, chiral hybrid didentate (P,N)-substituted ferrocenes have played a prominent role as ligands in asymmetric catalysis. Accordingly, numerous reviews have highlighted the synthetic routes to enantiopure ferrocene-based ligands.[5] Due to various synthetic complications, ferrocene derivatives that are iteratively functionalized with more than three different groups are much less developed.[5a,c,6] This is the case for *polydentate* hybrid (P,N)-functionalized ferrocenes, the term polydentate relating to species that bear at least three donor atoms. Only a very limited number of hybrid ferrocenyl tetradentate ligands have been developed, which are related to asymmetric catalysis[7−10] and heterocyclic chemistry.[11−14] A structural interest of polydentate ligands is their potential ability to form di- and polynuclear complexes that eventually promote metal nuclei cooperation.[15a] These can also provide catalytic systems with high-TON productivity through intramolecularly supported ligand cooperation.[15b−e] To this end, a strict control of the global ligand structures and/or conformations is needed.

Received: July 13, 2015
Published: October 2, 2015

DOI: 10.1021/acs.organomet.5b00601
Organometallics 2015, 34, 5015−5028

Concerning P_2N_2 tetradentate ligands Schwink and Knochel have first reported the formation of chiral diaminodiphosphinoferrocenes by double directed *ortho*-metalation of chiral methyldiaminoferrocenes (Scheme 1, top).[7]

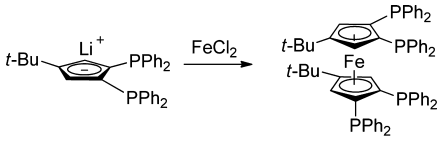
Scheme 1. Tetradentate P_2N_2 Ferrocene Derivatives



This work has led to the synthesis of the family of Mandyphos P_2N_2 chiral ligands used in asymmetric catalysis.[8b,16] The introduction of two phosphino groups into *N,N*-dimethyl-1-ferrocenylethylamine by *ortho*-lithiation, after Ugi's method, had been earlier reported by Hayashi and Kumada.[17] This method has been used by Ito et al. to produce compounds with rather original P_2N_2 frameworks on the ferrocenyl platform (Scheme 1, bottom).[9]

On the other hand, no synthetic works have been reported concerning the synthesis of polydentate hybrid (P,N)-functionalized ferrocene compounds through assembly of variously substituted cyclopentadienyl anions. We have initiated a program aimed at developing air-stable and moisture- and temperature-resistant polydentate auxiliaries for transition metal catalysis that seeks, in part, to address these limitations. This project originally focused on the synthesis of novel ferrocenyl-based polyphosphines (Scheme 2)[18] and met success in synthetic applications devoted to copper-[19] and palladium-catalyzed reactions of C−C and C−X cross-coupling (X = O, S, N).[20]

Scheme 2. Tetradentate P_4 *tert*-Butylated Ferrocenyl Phosphine Synthesized by a Converging Assembly Mode from Substituted Cyclopentadienyl Rings



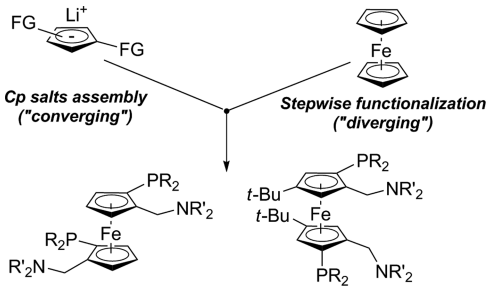
The robustness of the catalytic systems incorporating ligands based on the ferrocene platform allows for a low loading of palladium and led thus to remarkable catalytic turnover numbers. In order to selectively generate this new class of tetra- and triphosphines, we used a strategy based on the assembling of appropriately substituted cyclopentadienyl salts (Scheme 2). This converging synthetic route avoids many selectivity troubles encountered from successive direct metalation and phosphination of the ferrocene backbone.[21]

The synthesis of analogous tetradentate hybrid (P,N)-functionalized ferrocenes is very attractive because such hybrid ligands may potentially be suitable to accommodate coordination with both "soft" and "hard" transition metals and may give access to many diverse catalytic applications.[22] Following this perspective we investigated "converging" and "diverging" synthetic methods:[23] either from cyclopentadienyl salt assembly or from functionalization of preformed ferrocene backbones, respectively. We thus assessed the respective merit and interest of both strategies. A decisive structural and synthetic issue we addressed in the present study is the effect of the introduction of two hindering *tert*-butyl groups on Cp rings on the conformation of the ferrocene backbone. This feature distinguishes our targeted hybrid (P,N) species from the planar chiral Mandyphos. We demonstrate here that the *cisoid* position adopted by *t*-Bu hindering groups orientate the (P,N)-substituents on the ferrocene in the same direction and thus favor their spatial proximity. The synthesis of new *tert*-butylated (aminomethyl)ferrocene derivatives gave us the opportunity to establish synthetic conditions to form unprecedented hexasubstituted (*N,N′*)-aminomethyl,(*P,P′*)-*tert*-butylated-ferrocenyl diphosphines by N-directed *ortho*-metalation. Thus, novel P_2N_2 tetradentate ferrocene compounds are synthesized in good yields and tolerate various aryl, alkyl, and heteroaryl phosphino groups as substituents on nitrogen and phosphorus atoms. We report the unexpected formation of a zwitterionic cyclopalladate from intramolecular transfer of a Cp-proton to the proximate free amino group by simple C−H activation reaction in the presence of $PdCl_2$. This evidences one reactivity interest of the ferrocene-based species we formed with the introduction of *t*-Bu groups constraining the ferrocene backbone.

RESULTS AND DISCUSSION

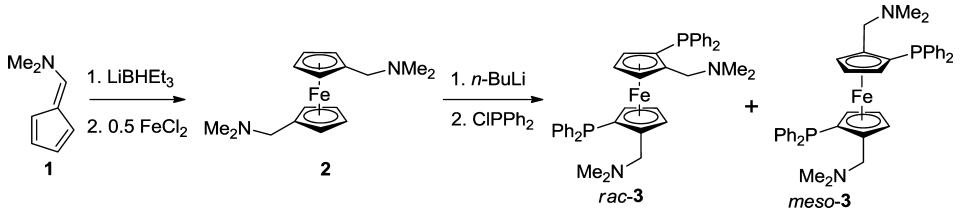
A steric control of the ferrocene backbone conformation has been previously evinced in ferrocenyl polyphosphines through introduction of a bulky *tert*-butyl group on each of the cyclopentadienyl rings (Scheme 2).[3a−e,20] This conformational control was supported in the solid state and in solution by X-ray and ^{31}P NMR studies, respectively. Such a particular conformation results in the same spatial orientation of the phosphino groups with a close proximity of the donor atoms and has been evidenced by the existence of strong nonbonded through-space (TS) spin−spin nuclear $^{TS}J_{PP'}$ couplings.[24−26] In the present work we targeted the synthesis of structurally related tetradentate (*N,N′*)-aminomethyl,(*P,P′*)-phosphino ferrocenes (Scheme 3), both with and without steric constraint from *tert*-butyl groups. We aimed also at providing a valuable modularity in the introduction of R and R′ groups on the phosphino and amino groups (R, R′ = aryl, heteroaryl, alkyl).

Scheme 3. Tetradentate (*N,N′*)-Aminomethyl,(*P,P′*)-Phosphino Ferrocenes Targeted *via* "Converging" and "Diverging" Synthetic Strategies



DOI: 10.1021/acs.organomet.5b00601
Organometallics 2015, 34, 5015−5028

Scheme 4. Synthesis of Compounds *rac*-3 and *meso*-3



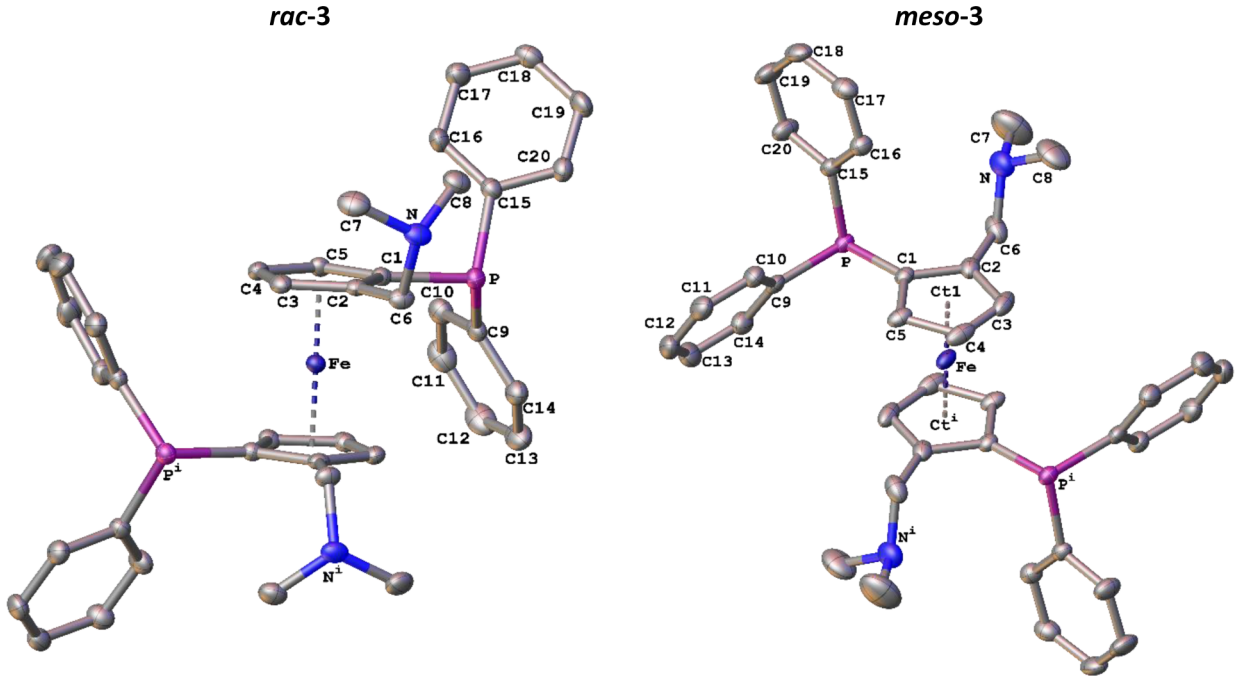
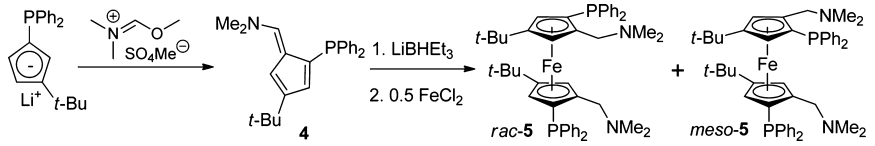


Figure 1. Molecular structures of compounds *rac*-**3** (left) and *meso*-**3** (right). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): *rac*-**3**, Fe−Ct = 1.6535(8); C1−P = 1.822(2); Ct−Fe−Ct^{i} = 179.05(5); C6−Ct−Ct^{i}−C6^{i} = 28.05(7); P−Ct−Ct^{i}−P^{i} = 169.82(3). Symmetry transformation: (i) 2−*x*, *y*, 0.5−*z*. *meso*-**3**, Fe−Ct = 1.6477(8); C1−P = 1.8168(15); Ct−Fe−Ct^{i} = 180; C6−Ct−Ct^{i}−C6^{i} = 180; P−Ct−Ct^{i}−P^{i} = 180. Symmetry transformation: (i) 1−*x*, −*y*, 1−*z*.

Scheme 5. Synthesis of Compounds *rac*-5 and *meso*-5



Following the synthetic route used for tetradentate polyphosphines synthesis,[24] we first synthesized specifically modified cyclopentadienyl salts for subsequent assembly of (P,N)-ferrocene derivatives.

Synthesis of Polyfunctionalized Ferrocenes from Assembly of Cyclopentadienyl Salts. The tetradentate (P,N)-ferrocene derivative **3** (Scheme 4) was synthesized from the cyclopentadienylidene-*N*,*N*-dimethylmethanamine, **1**. The synthesis of **3** was achieved as a 1:1 mixture of *meso* and *rac* stereoisomers, which were separated and independently crystallized for NMR and X-ray characterization (Figure 1). The lithiation of 1,1′-bis((*N*,*N*-dimethylamino)methyl)-ferrocene using *n*-BuLi followed by phosphination with $ClPPh_2$ had a limited efficiency with an overall yield of less than 60%.

^{31}P NMR of the crystals in $CDCl_3$ (298 K) indicated a chemical shift of −25.6 ppm for *rac*-**3** and −25.5 ppm for *meso*-**3**. Compound *rac*-**3** crystallizes in the centrosymmetric *C*2/*c* group. The Cp rings are in an almost eclipsed conformation, and the torsion angle C6−Ct−Ct^{i}−C6^{i} is equal to 28.05(7)°. The amino groups are in a *cisoid* position. Compound *meso*-**3** crystallizes in the space group $P\bar{1}$. In *meso*-**3** the Fe atom is an inversion center; thus the torsion angle C6−Ct−Ct^{i}−C6^{i} is equal to 180°. The Cp rings are in an almost staggered conformation, and in relation to the existence of a crystallographic inversion center, *meso*-**3** exhibits a *transoid* conformation for the amino groups. Consistently, the conformations adopted in the solid state by **3** are reminiscent of the conformations recently reported for parent compounds (aminomethyl)ferrocenes, bearing no phosphino group, for which various rotamers with *cisoid* and *transoid* arrangements have been found.[4a] An analogous synthetic approach was investigated for the synthesis of the *tert*-butyl-substituted

DOI: 10.1021/acs.organomet.5b00601
Organometallics 2015, 34, 5015−5028

compounds **5** (Scheme 5), cousin of the (P,N)-ferrocene derivatives **3**.

Dimethylaminomethylation of (diphenylphosphino)-3-*tert*-butylcyclopentadienyllithium was selectively achieved by using an iminium sulfate salt of Eschenmoser's salt type. A satisfactory 86% yield of **4** was obtained (Scheme 5). In the solid state compound **4** crystallizes in the space group $P\bar{1}$ (Figure 2). The three endo- and exocyclic conjugated

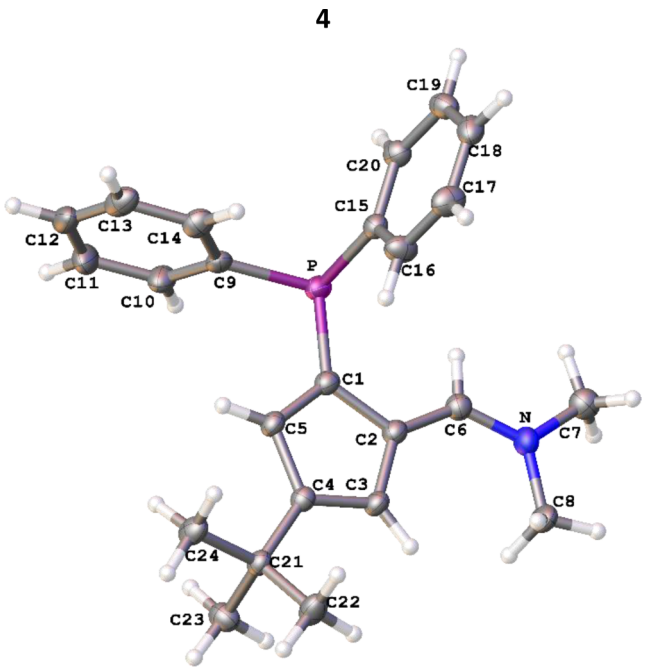


Figure 2. Molecular structure of compound **4**. Selected bond lengths (Å) and angles (deg): C1−P = 1.8084(16); C1−C2 = 1.459(2); C2−C3 = 1.450(2); C3−C4 = 1.375(2); C4−C5 = 1.445(2); C5−C1 = 1.374(2); C2−C6 = 1.382(2); C1−C2−C6−N = 178.95(16).

double bonds were clearly identified, together with a characteristic angle C1−C2−C6−N = 178.95(16)°. Aromatization of **4** was found difficult but can be achieved by reaction with $LiBHEt_3$ under specific conditions. THF had to be removed from the superhydride, that is suspended in dry toluene prior to use. The resulting lithiated Cp salt Li[**4**-H] was directly added to $FeCl_2$ to give **5** as a 2:1 mixture of *rac* and *meso* isomers isolated in low 39% overall yield.

Compound *rac*-**5** crystallizes in the space group *Pc* (Figure 3). Two independent enantiomers are presents in the asymmetric unit, and the crystal consists of a racemic mixture of two pairs of enantiomers. The cyclopentadienyl rings are in a slightly staggered conformation, and the torsion angles C11−Ct1−Ct2−C30 and C59−Ct3−Ct4−C78 are −23.9(3)° and 20.0(3)°, respectively.

Synthesis of Polyfunctionalized Ferrocenes from Aminomethyl-Substituted Ferrocenes. The assembly of substituted cyclopentadienyl salts with iron dichloride used as a "converging" way to produce species **5** and **3** presented several drawbacks. The synthesis of aminomethylcyclopentadienyl lithium salts from iminium sulfate is rather difficult to handle and lacks modularity concerning the substituents on the nitrogen atom (Me groups). In addition to low (or moderate) yields obtained in the assembly of the ferrocene, this route suffers from the absence of diastereoselectivity control. Thus, mixtures of *rac* and *meso* stereoisomers have to be separated. We thus envisioned that the synthesis of tetradentate (P,N)-ferrocene derivatives may be done in a comparatively "diverging" way through successive controlled functionalizations of the ferrocene backbone (Scheme 6).

A high diastereoselectivity is obtained in the formation of *rac*-1,1′-di-*tert*-butyl-3,3′-diformylferrocene from 1,1′-di-*tert*-butylferrocene reacted with *n*-BuLi in the presence of *N,N,N′,N′*-(tetramethyl)ethylenediamine (TMEDA).[27] Thus, following the retrosynthetic Scheme 6, tetradentate (P,N)-ferrocene derivatives may be obtained as pure *rac*-diastereomers from nitrogen-directed *ortho*-lithiation/phosphination steps. Such a synthetic route, which would lead to ferrocenes symmetrically decorated with six substituting groups, has never been reported, and we thus focused on its feasibility.

Aminomethyl-substituted ferrocenes can selectively be synthesized from reductive amination of 1,1′-diformylferrocene using primary and secondary alkylamines.[4a] This synthetic strategy was applied to 1,1′-di-*tert*-butyl-3,3′-diformylferrocene to form the *tert*-butylated aminomethylferrocenes **6**−**9** in excellent isolated yields around 90% (Scheme 7). $NaBH(OAc)_3$ is well suited to achieve the reduction of the electron-rich ferrocene iminium formed from 1,1′-di-*tert*-butyl-3,3′-diformylferrocene reacted with secondary amines.

X-ray structures for **7**−**9** are illustrated in Figure 4 and confirmed, together with multinuclear NMR (Table 1), the high diastereoselectivity of the synthetic method (100% *rac*). The molecular structure showed both different conformations for the ferrocene backbone and different mutual arrangements of amino groups. Compounds **7** and **8**, which crystallize in the $P2_12_12_1$, and $P\bar{1}$ groups, respectively, have an eclipsed conformation for their Cp rings with torsion angles C11−Ct1−Ct2−C20 and C11−Ct1−Ct2−C21 respectively equal to 66.54(12)° and 146.87(7)°. The Cp rings of compound **9** ($C2/c$ space group) are in a staggered conformation with a torsion angle C6−Ct−Ct^{i}−C6^{i} equal to 50.95(5)°. In compounds **7** and **9**, the amino groups are in a *cisoid* arrangement, with N1−Ct1−Ct2−N2 dihedral angles equal to 56.54(9)° and 54.05(4)°, respectively. The same torsion angle for **8**, equal to 137.25(4)°, is closer to a *transoid* mutual arrangement of the amino groups. In comparison to the non-*tert*-butylated analogues we have recently reported,[4a] no rotamer displaying a *transoid* arrangement for amino groups that would be closer to 180° was obtained, clearly because of the difficulties in positioning the hindered *tert*-butyl groups in eclipsed positions.

The ^{1}H NMR spectra showed resonances for the *tert*-butylated alkyl amines **6**−**9**, which are fairly similar (Table 1), while in the ^{13}C and ^{15}N nuclei NMR spectra the resonances associated with the cyclic amines in **7** and **8** are distinct from those of alkyl amines in **9**. ^{1}H NMR spectra of **6**−**9** showed for methylene groups typical diastereotopic AB proton signals with geminal coupling constants $^{2}J_{HH}$ around 13 Hz.

Slight modification of the protocol in the stoichiometry amine/aldehyde (= 3:1) allowed us to use *n*-butylamine with 1,1′-di-*tert*-butyl-3,3′-diformylferrocene to generate the *tert*-butylated ferrocenylimines **10** and secondary (aminomethyl)-ferrocene **11** (Scheme 8).

Compound **10** was characterized in the ^{1}H NMR by a *HC*=N proton at 8.02 ppm and in the ^{13}C NMR by the corresponding signal at 160.3 ppm. The ^{15}N NMR shift of the ferrocenylimines was found at a rather low field (−58.1 ppm). We believe this to be the first report of ^{15}N NMR data from such a ferrocenylimine. The reduction of imine **10** is

DOI: 10.1021/acs.organomet.5b00601
Organometallics 2015, 34, 5015−5028

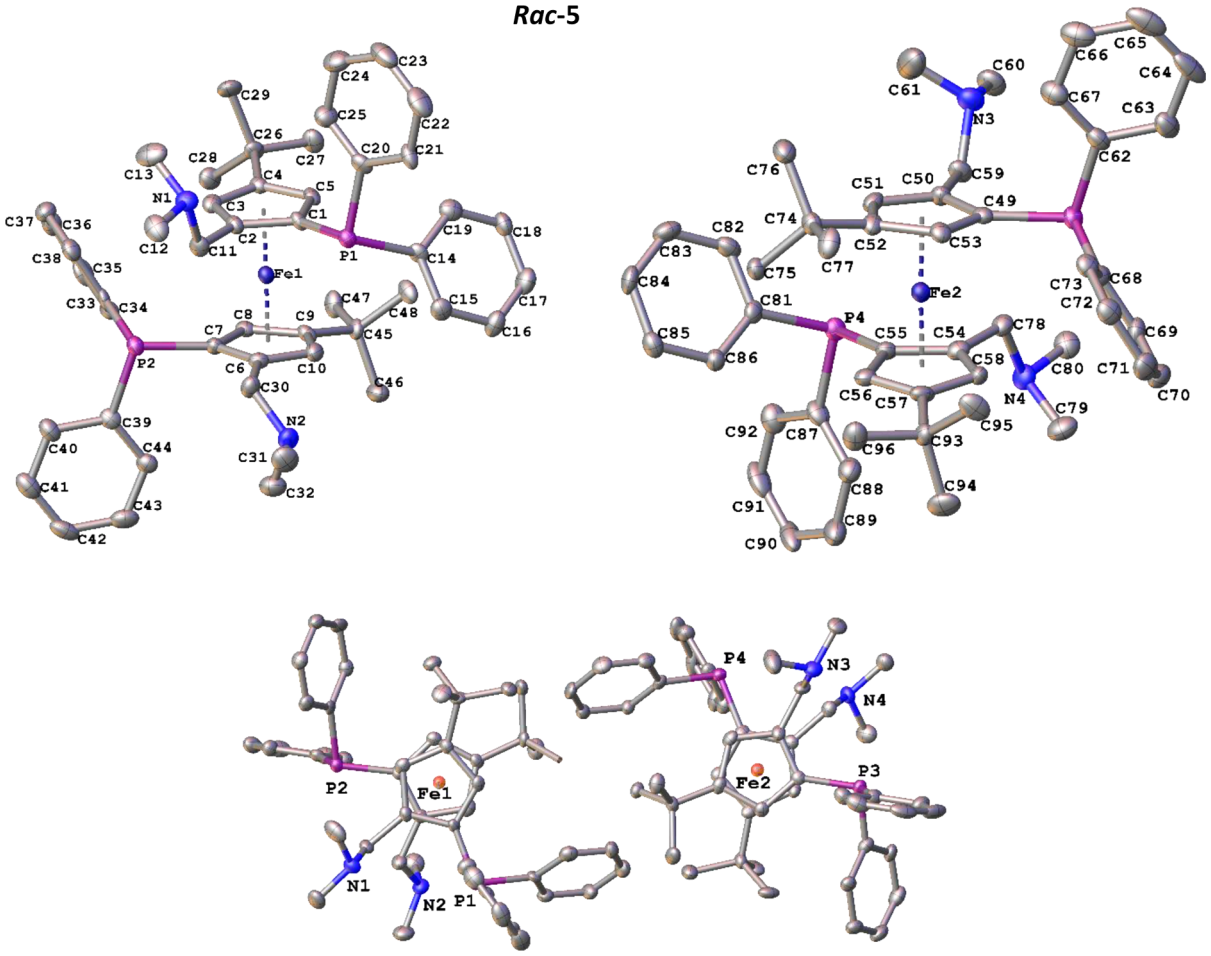
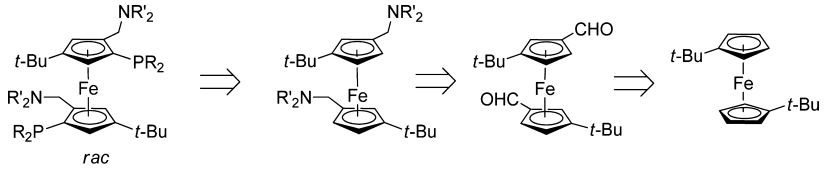
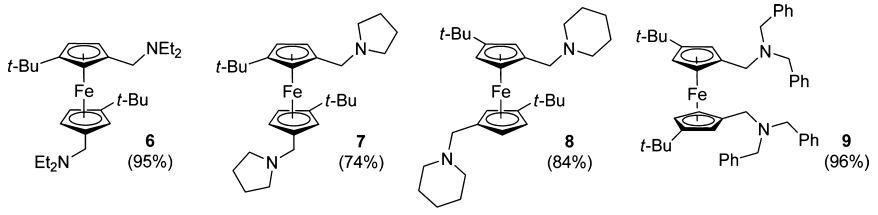


Figure 3. Molecular structures of the two independent molecules present in the asymmetric unit of compound *rac*-**5** (hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): left, Fe1−Ct1 = 1.674(4); Fe1−Ct2 = 1.670(4); C1−P1 = 1.808(9); C7−P2 = 1.828(9); Ct1−Fe1−Ct2 = 178.08(19); C11−Ct1−Ct2−C30 = −23.9(3); P1−Ct1−Ct2−P2 = 119.51(11); right, Fe2−Ct3 = 1.669(4); Fe2−Ct4 = 1.670(4); C49−P3 = 1.817(9); C55−P4 = 1.824(9); Ct3−Fe2−Ct4 = 177.6(2); C59−Ct3−Ct4−C78 = 20.0(3); P3−Ct3−Ct4−P4 = −122.87(12).

Scheme 6. *tert*-Butylated (*N*,*N*′)-Aminomethyl-(*P*,*P*′)-Ferrocenyldiphosphine Retrosynthesis



Scheme 7. Compounds 6−9 Formed from Reductive Amination (Isolated Yields, %)



quantitative and the secondary amine **11** was characterized in the ^{1}H NMR by its *H*−N at 1.23 ppm and in the ^{15}N NMR by a signal at −332.0 ppm. Such secondary amines are valuable compounds since, notably, amido complexes are in principle accessible by simple deprotonation.[28]

The synthesis of these (aminomethyl)ferrocene derivatives gave us the opportunity to establish synthetic conditions to (*N*,*N*′)-aminomethyl,(*P*,*P*′)-*tert*-butylated-ferrocenyl diphosphines by N-directed *ortho*-metalation. Thus, compounds **12**−**15** were synthesized in moderate to good yield (48−78%) from **6** and **7** by introducing aryl-, alkyl-, and heteroarylphosphino groups (Scheme 9).

A lithiation/phosphination sequence was successfully achieved with both electron-rich and electron-poor halophos-

DOI: 10.1021/acs.organomet.5b00601
Organometallics 2015, 34, 5015−5028

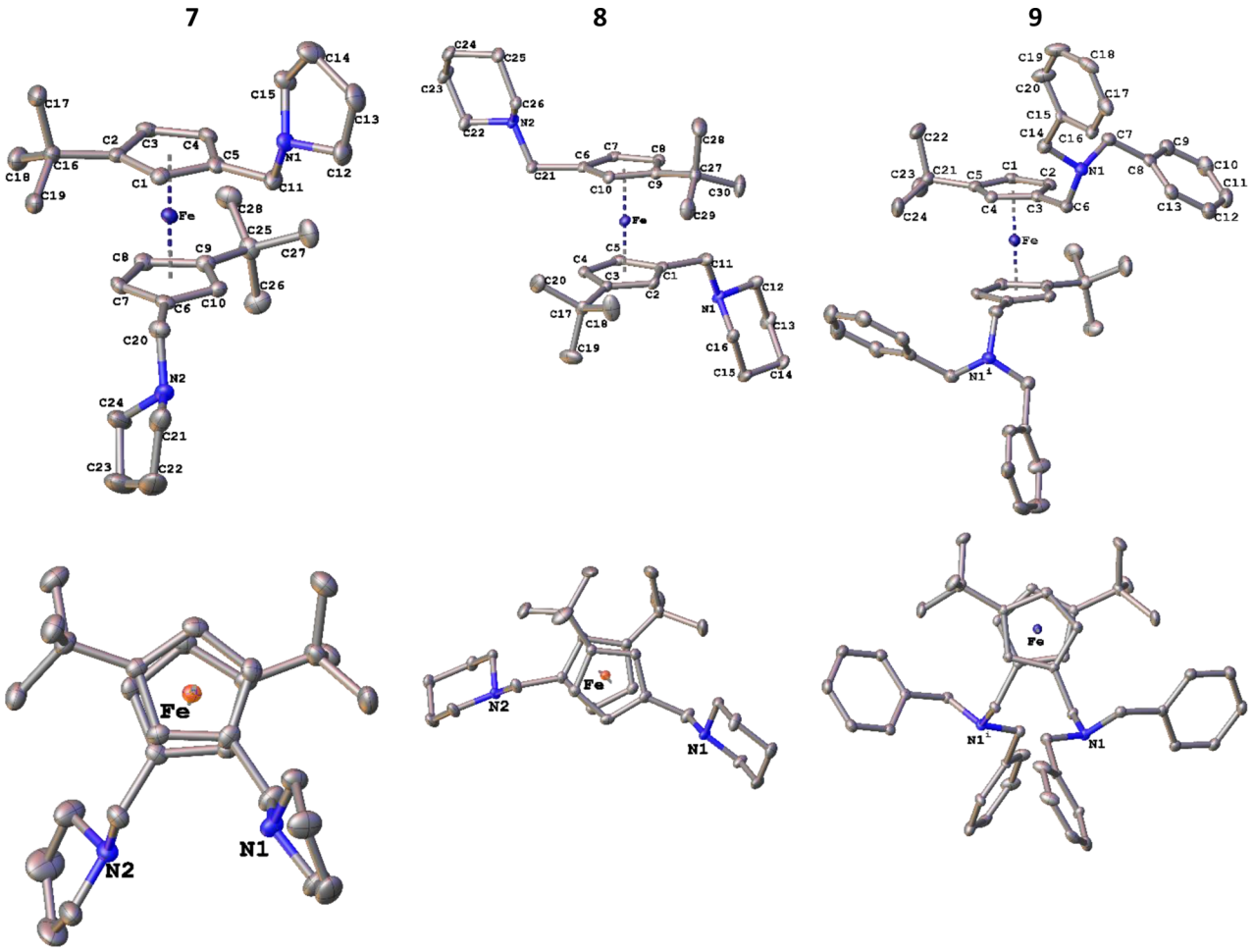


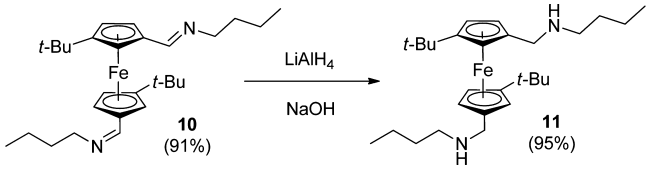
Figure 4. Molecular structures of compounds **7**, **8**, and **9** (hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): **7**, Fe−Ct1 = 1.6488(17); Fe−Ct2 = 1.6502(16); Ct1−Fe−Ct2 = 177.49(8); C11−Ct1−Ct2−C20 = 66.54(12); **8**, Fe−Ct1 = 1.6601(9); Fe−Ct2 = 1.6593(9); Ct1−Fe−Ct2 = 176.40(4); C11−Ct1−Ct2−C21 = 146.87(7); **9**, Fe−Ct = 1.6583(6); Ct−Fe−Ct^{i} = 179.08(4); C6−Ct−Ct^{i}−C6^{i} = 50.95(5). Symmetry transformation: (i) 1−*x*, *y*, 1/2−*z*.

Table 1. Multinuclear NMR Data for 6−11

compound	$\delta(^1H)$ Cp-CH_2 (ppm)/J_{AB} (Hz)	$\delta(^{13}C)$ Cp-CH_2 (ppm)	$\delta(^1H)$ Cp (ppm)	$\delta(^{13}C)$ Cp (ppm)	$\delta(^{15}N)$ CH_2-*N* (ppm)[a]
6	3.39, 3.48/13.5	52.0	3.74, 3.91, 4.04	65.1, 69.0, 70.2, 81.2, 101.8	−327.8
7	3.35, 3.45/12.3	54.7	3.78, 3.93, 4.07	64.4, 67.6, 68.9, 81.4, 101.0	−318.4
8	3.29, 3.36/12.9	59.3	3.75, 3.89, 4.05	65.5, 69.3, 70.5, 81.0, 102.0	−324.2
9	3.41, 3.50/13.5	52.5	3.55, 3.89, 4.05	65.1, 69.5, 70.1, 81.6, 101.7	−327.2
10	8.02[b]	160.3[b]	4.13, 4.38, 4.58	66.9, 67.8, 68.8, 80.2, 105.1	−58.1[b]
11	3.44, 3.50/12.9	48.6	3.80, 3.89, 4.05	64.1, 65.9, 67.4, 84.5, 100.6	−332.0

[a]CH_3NO_2 at 0.0 ppm was used as reference. [b]Chemical shift for (Cp-*CH*=*N*) imino fragment.

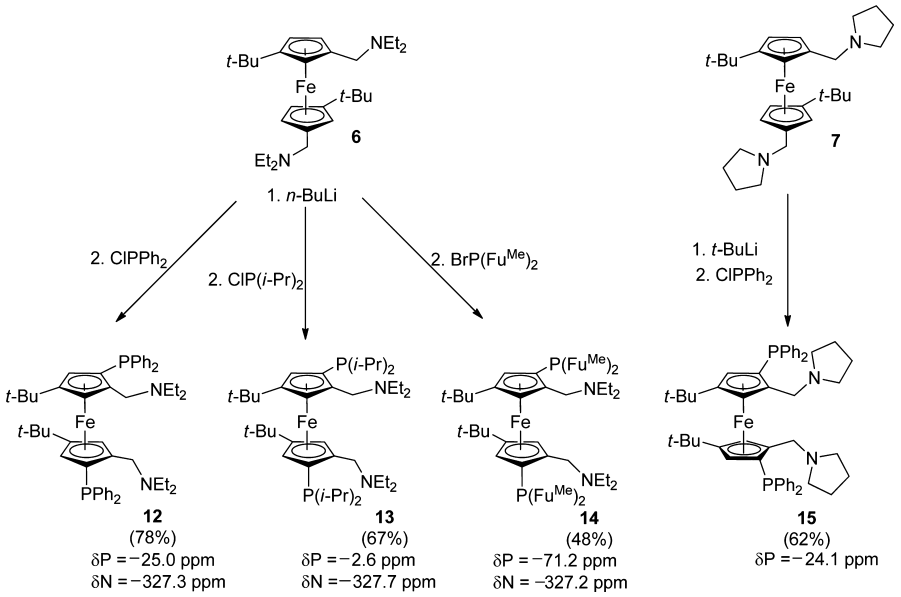
Scheme 8. [(*n*-Butyl)aminomethyl]ferrocene 11 via Ferrocenylimine 10 (Isolated Yields, %)



phines by using acyclic (from compound **6**) and cyclic (from compound **7**) amino groups. A selective bis-metalation in one *ortho*-position of the two possible was achieved in good to excellent yield using *n*-BuLi. This is noteworthy since the initial Mandyphos synthesis using the same lithiation agents had mostly given moderate yields of around 30−40%.[7] We checked the successive reactions of *ortho*-lithiation/phosphination starting from the non-*tert*-butylated analogue of **6**, and we evidenced the absence of diastereoselectivity in this reaction (see X-ray structure of the isolated *meso* compound **12′** in the SI). We were pleased to establish that our reaction conditions with **6** and **7** avoid the formation of many possible lithiated intermediates. However, in our hands, the lithiation of benzyl analogue **9** was conversely found incomplete (or unselective under forcing conditions) by using various amounts of *n*-BuLi or *t*-BuLi in the presence or absence of TMEDA. Therefore, subsequent phosphination reactions using $ClPPh_2$ mainly led to intractable mixtures of phosphinated products. The difficulties

DOI: 10.1021/acs.organomet.5b00601
Organometallics 2015, 34, 5015−5028

Scheme 9. Synthesis of Compounds 12−15 (Isolated Yields, %)



encountered for phosphination of **9** correlate with early reports of the Mandyphos synthesis[7] and suggest that steric hindrance in the *β*-position of the nitrogen atom may be a serious limitation to proper *ortho*-lithiation reactions in these species. Table 2 summarizes the ^{31}P, ^{1}H, and ^{15}N features of **12−15**,

Table 2. Multinuclear NMR Data for 12−15

compound	$\delta(^1H)$ Cp-CH_2 (ppm)/ J_{AB} (Hz)	$\delta(^1H)$ Cp (ppm)	$\delta(^{13}C)$ Cp (ppm)	$\delta(^{31}P)$ (ppm)	$\delta(^{15}N)$ CH_2-*N* (ppm)[a]
12	3.71, 3.80/15.0	3.78, 4.12	67.8, 72.9, 73.7, 90.8, 106.7	−25.0	−327.3
13	3.22, 3.46/12.9	3.91, 4.11	69.7, 72.1, 78.8, 87.5, 104.0	−2.6	−327.7
14	4.01, 4.25/15.5	4.43, 4.64	69.7, 71.9, 72.4, 91.0, 106.7	−71.2	−327.2
15	3.69, 3.78/12.4	3.76, 4.09	68.1, 72.4, 73.6, 91.4, 106.7	−24.1	

[a] CH_3NO_2 at 0.0 ppm was used as reference.

with typical ^{31}P NMR chemical shifts depending on the nature of the P substituents. Conversely, ^{15}N shift is not affected, suggesting little or no direct P/N interactions.

X-ray diffraction analyses were conducted on single crystals of **12** and **15** (Figure 5). The conformation obtained for these *rac* diastereomers fit our expectations since the arrangement of the two *tert*-butyl groups and the four donor atoms is similar to the one obtained for analogous hexasubstituted *tert*-butylated-ferrocenyl tetraphosphines.[24,25,29] The *cisoid* conformation found for compounds **12** and **15** is characterized by a dihedral angle C11−Ct1−Ct2−C32 = −21.85(6)° and −25.92(6)°, respectively. Another structure, **12B**, was obtained, which presents minor conformational differences with **12** (see the SI). A comparison of X-ray structures determined for **15** and its precursor **7** clearly indicates that a rotation of the ferrocene backbone occurred to accommodate a near-eclipsed conformation of the carbon atoms holding methylamino groups (Table 3, C−Ct−Ct′−C′[(a)] = −25.92° and 66.54°, respectively). This rotation is apparently a common and general feature since for the (*N*,*N*′)-diaminomethyl,(*P*,*P*′)-*tert*-butylated ferrocenylphosphines (**5**, **12**, and **15**) very similar conformations were found with 20° < |C−Ct−Ct′−C′[(a)]| < 26° (Table 3). A noticeable consequence of this rotation is a closer mutual proximity of the nitrogen atoms in **12**, **15**, and **5** in comparison with compounds **7**−**9**, as well as with the non-*tert*-butylated compounds **3** (Table 3). Mostly *d*N1···N2 are found around 6.0 Å or below for **12**, **15**, and **5**, whereas values above 6.2 Å (and mostly >8.0 Å) are observed with the other ferrocenes.

In the course of our studies concerning the coordination chemistry and reactivity of these new *tert*-butylated ferrocenes,[30] we observed that the simple reaction of the aminomethylferrocene **6** with $[PdCl_2(PhCN)_2]$ at room temperature (RT) in CH_2Cl_2 led to the formation of the unexpected zwitterionic cyclopalladate **16** (Scheme 10). While the formation of *ortho*-palladated ferrocene complexes is known[31] and has been applied in metal catalysis,[32] they have been mostly described as dimers that are formed in the presence of an excess of external base such as sodium acetate. Complex **16**, for which the formation was supported by an X-ray diffraction structure (Figure 6), is a unique example of a zwitterionic intramolecular ferrocene supported palladacycle.

Our attempts to achieve this kind of intramolecularly assisted cyclopalladation using the non-*tert*-butylated analogue of **6** failed. This difference in reactivity may be attributed to the ring in ferrocene **6**, which, due to electronic effects of *t*-Bu, would be much more susceptible to electrophilic attack. The steric influence of *t*-Bu groups may also favor a concerted deprotonation/metalation of the Cp ring with regard to the necessary proximity of aminomethyl moieties for the proton transfer in the absence of any other external base. Further studies are ongoing to take advantage of this previously unseen intramolecular reactivity, especially for catalytically selective C−H functionalization of ferrocene.[33]

■ CONCLUSION

We investigated the respective interest of "diverging" (successive functionalization of preformed ferrocene) and "converging" (assembly from cyclopentadienyl rings) synthetic

DOI: 10.1021/acs.organomet.5b00601
Organometallics 2015, 34, 5015−5028

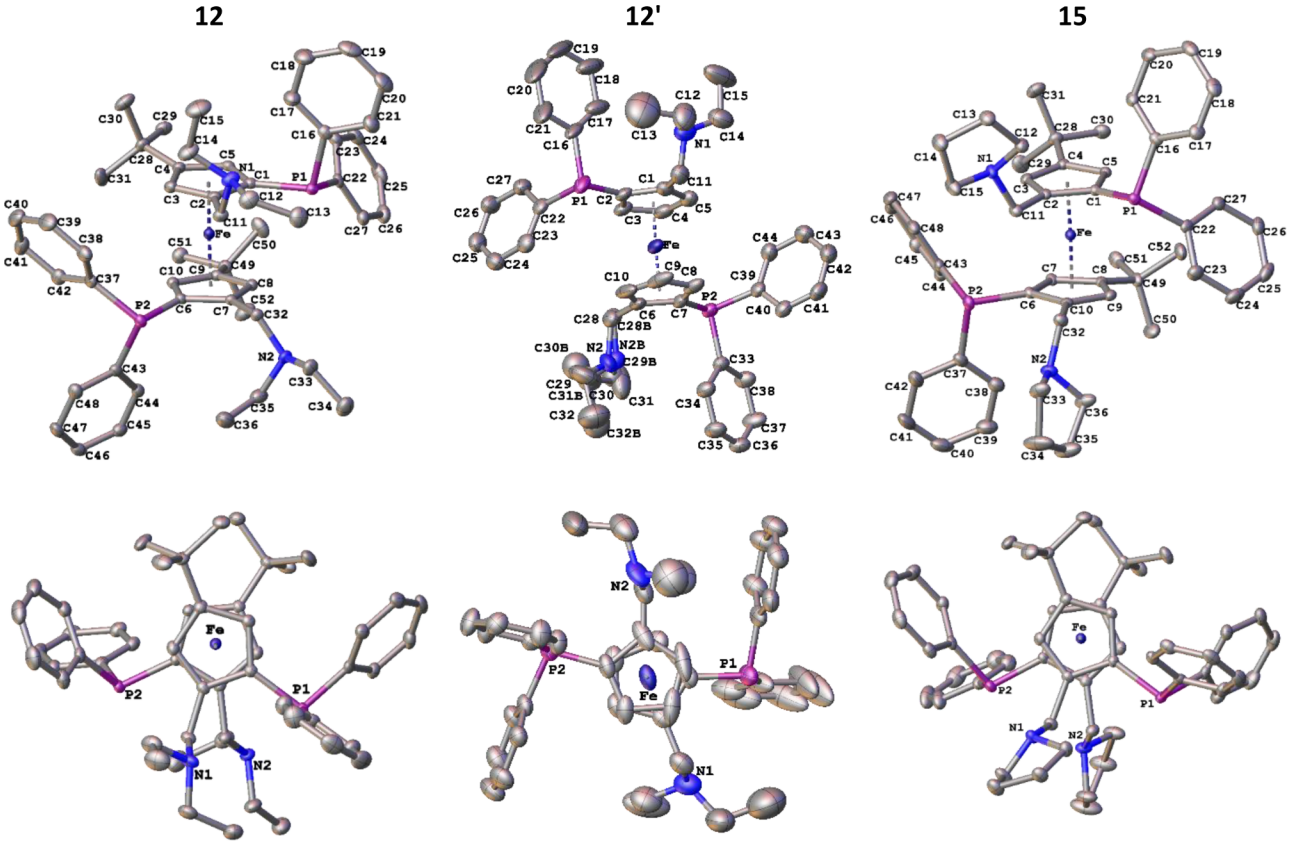


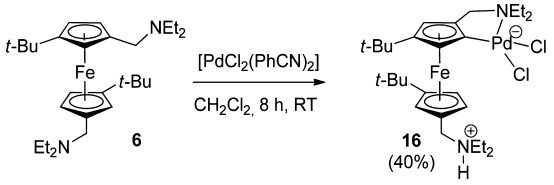
Figure 5. Molecular structures of compounds **12**, **12′**, and **15**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): **12**, Fe−Ct1 = 1.6714(8); Fe−Ct2 = 1.6709(8); C1−P1 = 1.8186(18); C6−P2 = 1.8136(18); Ct1−Fe−Ct2 = 177.85(5); C11−Ct1−Ct2−C32 = −21.85(6); P1−Ct1−Ct2−P2 = 119.93(3); **12′**, Fe−Ct1 = 1.642(2); Fe−Ct2 = 1.647(3); C2−P1 = 1.820(5); C7−P2 = 1.817(5); Ct1−Fe−Ct2 = 178.22(14); C11−Ct1−Ct2−C28 = 159.6(2); C11−Ct1−Ct2−C28B = 168.4(4); P1−Ct1−Ct2−P2 = 162.39(8); **15**, Fe−Ct1 = 1.6719(8); Fe−Ct2 = 1.6758(8); C1−P1 = 1.8152(16); C6−P2 = 1.8132(15); Ct1−Fe−Ct2 = 177.72(4); C11−Ct1−Ct2−C32 = −25.92(6); P1−Ct1−Ct2−P2 = 117.26(2).

Table 3. Key Conformation Parameters for Ferrocenes 3, 5, 7, 8, 9, 12, 12′, 15, and 16

	*d*N1···N2 (Å)	C−Ct−Ct′−C′[a] (deg)	P−Ct−Ct′−P′[b] (deg)	Ctb−Ct−Ct′−Ctb′[c] (deg)
***rac*-3**	6.211(3) (N,N^{i})	28.05(7)	169.82(3)	
***meso*-3**	8.840(2) (N,N^{i})	180	180	
***rac*-5**	6.080(10) (N1,N2)	23.9(3) (C11,C30)	119.51(11) (P1,P2)	51.6(3) (C26,C45)
	5.897(10) (N3,N4)	20.0(3) (C59,C78)	−122.87(12) (P3,P4)	10.43(9) (C74,C93)
7	6.553(4) (N1,N2)	66.54(12)		139.83(12)
8	8.520(2) (N1,N2)	146.87(7)		78.06(7)
9	6.5593(13) (N,N^{i})	50.95(5)		124.75(6)
12	5.972(2) (N1,N2)	−21.85(6)	119.93(3)	52.88(7)
12′	8.718(9) (N1,N2)	159.6(2) (C11,C28)	162.39(8)	
	8.900(15) (N1−N2b)	168.4(4) (C11−C28B)		
15	6.099(3) (N1,N2)	−25.92(6)	117.26(2)	49.65(6)
	6.164(5) (N1−N2b)			
16	7.837(6) (N1,N2)	147.84(16)		81.77(16)

[a]C: carbon atom bearing N(1); C′: carbon atom bearing N(2, ^{i}). [b]P,P′: phosphorus atoms. [c]Ctb: tertiary carbon atom of the *tert*-butyl group.

Scheme 10. Intramolecular Cyclopalladation of 6 to Zwitterion 16



routes to form hexasubstituted tetradentate ferrocenes bearing aminomethyl and phosphino groups and hindering *tert*-butyl moieties. We identified the "diverging" route as more efficient. This strategy starting from 1,1′-di-*tert*-butylferrocene especially allows the diastereoselective introduction on ferrocene of first aminomethyl groups, then the regioselective introduction of phosphino groups. We evidenced the conformation control provided to *rac*-(*N*,*N*′)-diaminomethyl-(*P*,*P*′)-*tert*-butylated-ferrocenyldiphosphines by identifying the key conformational

DOI: 10.1021/acs.organomet.5b00601
Organometallics 2015, 34, 5015−5028

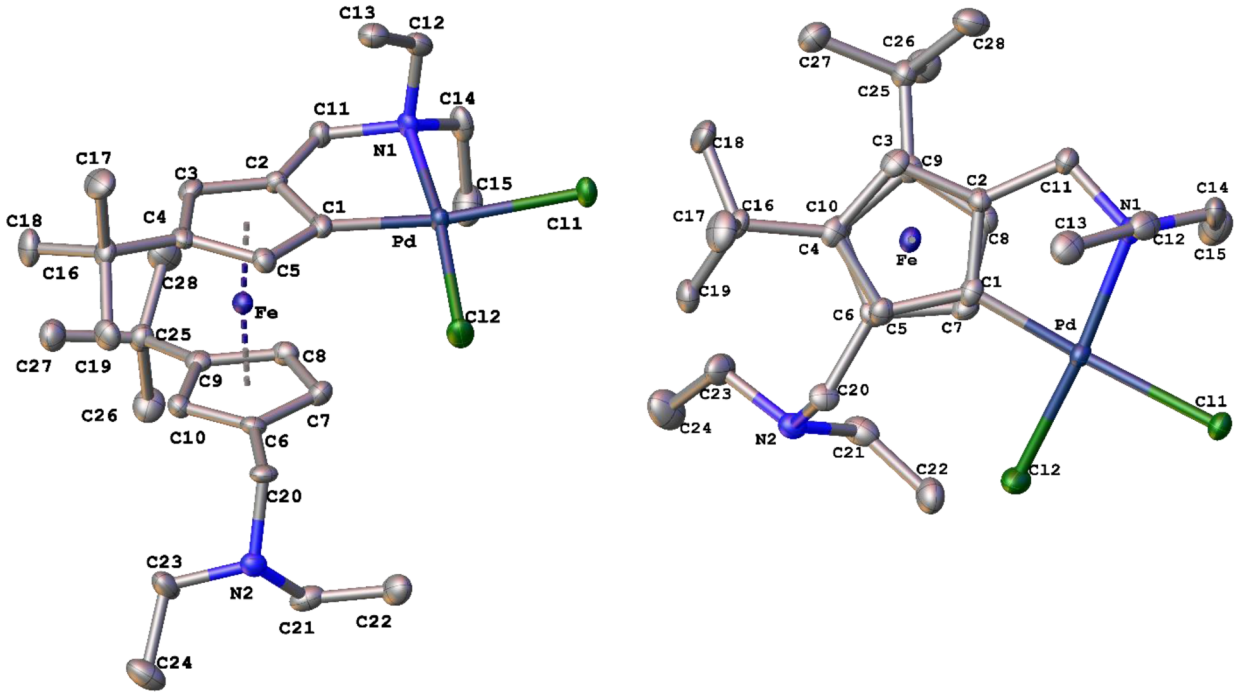


Figure 6. Molecular structures of cyclopalladate **16**. Hydrogen atoms and dichloromethane solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): **16**, Fe−Ct1 = 1.657(2); Fe−Ct2 = 1.652(2); C1−Pd = 1.952(5); N1−Pd = 2.129(4); Pd−Cl1 = 2.4569(12); Pd−Cl2 = 2.3214(12); Ct1−Fe−Ct2 = 174.79(11); C11−Ct1−Ct2−C20 = 147.84(16).

parameters and in particular the systematic near-eclipsed conformation of aminomethyl groups. Such kind of control is supposed to be at the origin of the reaction of the *tert*-butylated aminomethylferrocene **6** with $[PdCl_2(PhCN)_2]$ (in the absence of external strong base) that led to a previously unseen intramolecular palladium-mediated Cp C−H activation. This reaction is presumably concerted due to the formation of a zwitterionic cyclopalladate in good yield, and the conditions apparently prevent the formation of dimeric orthopalladate classically reported.

EXPERIMENTAL SECTION

General Procedures. All reactions were performed under an atmosphere of dry argon in oven-dried glassware using Schlenk and vacuum line techniques. Solvents were purified and dried by standard methods prior to use. Chromatography was performed on silica gel (220−440 mesh). The identity and purity of the products were established at the "Platform of Chemical Analysis and Molecular Synthesis of the University of Burgundy" (PACSMUB) using high-resolution mass spectrometry, elemental analysis, and multinuclear NMR. The exact masses were obtained from an LTQ-Orbitrap XL (THERMO). Elemental analysis was performed on a CHNS/O Thermo Electron Flash EA 1112 Series analyzer. ^{1}H (300.13, 500.13, or 600.13 MHz), ^{13}C (75.5, 125.8, or 150.9 MHz), and ^{31}P (121.5, 202.5, or 242.9 MHz) NMR spectra were recorded in $CDCl_3$, unless otherwise stated, on a 300 MHz Bruker Avance III NanoBay, a 500 MHz Bruker Avance III, or a 600 MHz Bruker Avance II spectrometer. Chemical shifts (δ) are reported in parts per million downfield relative to internal TMS (for ^{1}H, ^{13}C) and external 85% H_3PO_4 (for ^{31}P). Coupling constants are reported in hertz. The ^{15}N NMR chemical shifts were measured by $^{1}H-^{15}N$ heteronuclear multiple-bond correlation spectroscopy (HMBC) on a 600 MHz Bruker Avance II spectrometer (60.82 MHz). Neat nitromethane has been used as an external standard reference for which the ^{15}N chemical shift is taken to be 0 ppm. X-ray analysis for compounds was achieved from intensity data collected on a Nonius Kappa CCD at 115 K for *rac*-**3**, *meso*-**3**, **4**, **5**, **7**, **8**, **12′**, **12B**, and **16** and on a Bruker D8 Venture triumph at 100 K for **9** (Cu), **12** (Mo), and **15** (Mo). The structures were solved by direct methods (SIR92 for *rac*-**3**, *meso*-**3**, **4**, **5**, **12′**, and **16**, ShelXS 2013 for **7**, **8**, **9**, **12**, and **12B**, and Superflip for **15**)[34,35] and refined with full-matrix least-squares methods based on F^2 (SHELXL-97) with the aid of the OLEX2 program.[36] All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms attached to carbon atoms were included in calculated positions and refined as riding atoms. Crystallographic data are reported in the SI.

All chemicals were used as supplied, without further purification. *N*,*N*-Dimethylformamide-dimethyl sulfate, cyclopentadienylidene-*N*,*N*-dimethylmethanamine (**1**),[37] *tert*-butylcyclopentadienyllithium, (diphenylphosphino)-3-*tert*-butylcyclopentadienyllithium, 1,1′-bis-*tert*-butylferrocene,[38] and 1,1′-bis-*tert*-butyl-3,3′-diformylferrocene[39] were prepared according to reported procedures. Amines from commercial sources were used. Lithium triethylborohydride (LiTEBH) and sodium triacetoxyborohydride (STAB) reducing agents were stored under argon. All compounds synthesized from 1,1′-bis-*tert*-butyl-3,3′-diformylferrocene are racemic and are noted as either *rac*-**x** or simply **x**.

1-Cyclopenta-2,4-dien-1-ylidene-*N*,*N*-dimethylmethanamine (1). Dimethylsulfate (16.36 g, 12.3 mL, 130 mmol) was added to dimethylformamide (9.50 g, 10 mL, 130 mmol), and the reaction mixture was heated at 80 °C for 2 h. Then, the reaction mixture was allowed to cool and vacuum-dried. The *N*,*N*-dimethylformamide-dimethyl sulfate formed as a viscous, pale yellow, ether-insoluble oil in quantitative yield. ^{1}H NMR: δ 2.99, 3.25 (s, 3H each, NCH_3), 3.40 (s, 3H, OCH_3), 4.21 (s, 3H, $[SO_4CH_3]^-$), 8.65 (s, 1H, $CH{=}N^+$) ppm.

N,*N*-Dimethylformamide-dimethyl sulfate (18.50 g, 93.0 mmol) was added slowly to a solution of CpLi (6.70 g, 93.0 mmol) in THF (40 mL) at −20 °C. The mixture was allowed to warm and was stirred at room temperature for 2 h. After removal of the solvent *in vacuo*, the residue was dissolved in CH_2Cl_2 and washed with water. The organic phase was separated and dried over $MgSO_4$, and the solvent evaporated *in vacuo*. The residue was crystallized from hexane (50 mL), affording yellow crystals of pure **1**. Yield: 5.60 g (45.8 mmol, 50%). ^{1}H NMR: δ 3.25 (s, 6H, $N(CH_3)_2$), 6.35, 6.43 (m, 1H each, Cp−C*H*), 6.58 (m, 2H, Cp−C*H*), 7.16 (s, 1H, ═C*H*−N) ppm.

DOI: 10.1021/acs.organomet.5b00601
Organometallics 2015, 34, 5015−5028

1,1′-Bis((*N*,*N*-dimethylamino)methyl)ferrocene (2). A molar solution of superhydride (LiTEBH)[40] in THF (6.1 mL, 6.1 mmol) was added dropwise to a solution of dimethylaminofulvene **1** (0.75 g, 6.1 mmol) in toluene/THF (14 mL/14 mL) at −20 °C. The mixture was allowed to warm to room temperature and stirred for 3 h. This solution was added dropwise to a suspension of $FeCl_2$ (0.39 g, 3.05 mmol) in THF (8 mL) at −40 °C. The suspension was warmed and stirred overnight at room temperature. Water (14 mL) was added to the reaction mixture, the organic layer was separated, and the aqueous layer was washed with Et_2O (2 × 10 mL). Organic layers were combined, dried over Na_2SO_4, and evaporated to dryness. The amber oil product was purified by SiO_2 column chromatography. Unreacted dimethylaminofulvene **1** was eluted with EtOAc. 1,1′-Bis((*N*,*N*-dimethylamino)methyl)ferrocene **2** was eluted with CH_2Cl_2/MeOH/Et_3N (9:0.9:0.1). Yield: 0.66 g (2.2 mmol, 73%). ^{1}H NMR: δ 2.18 (s, 12H, NCH_3), 3.30 (s, 4H, CH_2), 4.07, 4.11 (m, 4H each, Cp−C*H*) ppm.

1,1′-Bis((*N*,*N*-dimethylamino)methyl)-2,2′-bis(diphenylphosphino)ferrocene (3), *rac* and *meso* Compounds. TMEDA (0.4 mL, 2.60 mmol) and *n*-BuLi (2.2 mL of a 1.6 M solution in hexane, 3.30 mmol) were successively added to a solution of 1,1′-bis((*N*,*N*-dimethylamino)methyl)ferrocene (**2**) (0.47 g, 1.57 mmol) in Et_2O (15 mL) at 0 °C. The reaction mixture was allowed to warm and stirred at room temperature for 6 h. The mixture was cooled to −40 °C, and $ClPPh_2$ (0.65 mL, 3.5 mmol) was added dropwise. The reaction mixture was warmed and stirred overnight at room temperature. The reaction mixture was hydrolyzed by the addition of a saturated solution of $NaHCO_3$ (20 mL), the organic layer was separated, and the aqueous layer was extracted with Et_2O (20 mL). Organic layers were combined, dried over Na_2SO_4, and evaporated to dryness. The crude product was purified by SiO_2 column chromatography. Impurities were first eluted with EtOAc/hexane (1:1). The (P,N)-ferrocene derivative *meso*-**3** was then eluted with Et_2O (fraction 1), and the (P,N)-ferrocene derivative *rac*-**3** was eluted with EtOH (fraction 2). Overall yield of compound **3** (fractions 1 + 2): 0.61g (0.91 mmol, 59%). Suitable crystals for X-ray diffraction of *meso*-**3** and *rac*-**3** have been obtained by slow evaporation of compound solution in a CH_2Cl_2/pentane mixture.

*Fraction 1 (meso-**3**).* ^{1}H NMR: δ 1.78 (s, 12H, NCH_3), 2.60 (d, 2H, J = 12 Hz, CH_2), 3.29 (dd, 2H, J = 14 Hz, J = 3 Hz, CH_2), 3.88 (br s, 2H, Cp−C*H*), 4.04, 4.24 (m, 2H each, Cp−C*H*), 7.16−7.65 (m, 20H, Ph) ppm. ^{31}P{^{1}H} NMR: δ −25.5 ppm. ^{13}C{^{1}H} NMR: δ 44.7 (s, NCH_3), 56.7 (d, J_{PC} = 9 Hz, CH_2), 73.1 (d, J_{PC} = 4 Hz, Cp), 73.2 (d, J_{PC} = 4.5 Hz, Cp), 75.1 (d, J_{PC} = 4 Hz, Cp), 90.5 (s, *ipso*-Cp), 90.8 (s, *ipso*-Cp), 127.7 (s, Ph), 127.7 (d, J_{PC} = 6 Hz, Ph), 128.3 (d, J_{PC} = 8 Hz, Ph), 129.4 (s, Ph), 131.6 (d, J_{PC} = 10 Hz, Ph), 135.6 (d, J_{PC} = 22 Hz, Ph), 137.7 (d, J_{PC} = 8 Hz, Ph), 140.2 (d, J_{PC} = 9 Hz, Ph) ppm. HR-MS ($C_{40}H_{42}FeN_2P_2$) ESI: $[M + H]^+$ m/z calcd 669.22461, found 669.22044, [err] 6.13 ppm; $[M + Na]^+$ m/z calcd 691.20655, found 691.20435, [err] 3.08 ppm.

*Fraction 2 (rac-**3**).* ^{1}H NMR: δ 1.97 (s, 12H, NCH_3), 3.23 (br s, 2H, Cp−C*H*), 3.34 (d, 2H, J = 13 Hz, CH_2), 3.56 (dd, 2H, J = 13 Hz, J = 2 Hz, CH_2), 4.04, 4.34 (m, 2H each, Cp), 7.09−7.39 (m, 20H, Ph) ppm. ^{31}P{^{1}H} NMR: δ −25.6 ppm. ^{13}C{^{1}H} NMR: δ 45.0 (s, NCH_3), 57.4 (d, J_{PC} = 9 Hz, CH_2), 72.2 (d, J_{PC} = 2 Hz, Cp), 72.3 (d, J_{PC} = 4.5 Hz, Cp), 76.4 (d, J_{PC} = 4.5 Hz, Cp), 91.5 (s, *ipso*-Cp), 91.9 (s, *ipso*-Cp), 127.6 (s, Ph), 127.8 (d, J_{PC} = 6 Hz, Ph), 128.1 (d, J_{PC} = 8 Hz, Ph), 129.1 (s, Ph), 132.4 (d, J_{PC} = 18 Hz, Ph), 135.1 (d, J_{PC} = 23 Hz, Ph), 137.7 (d, J_{PC} = 8 Hz, Ph), 140.1 (d, J_{PC} = 8 Hz, Ph) ppm. HR-MS ($C_{40}H_{42}FeN_2P_2$) ESI: $[M + H]^+$ m/z calcd 669.22461, found 669.22149, [err] 4.56 ppm; $[M + Na]^+$ m/z calcd 691.20655, found 691.20544, [err] 1.51 ppm. Anal. Calcd for $C_{40}H_{42}FeN_2P_2$ (668.58): C, 71.86; H, 6.33; N, 4.19. Found: C, 71.57; H, 6.58; N, 3.97.

***N*-{[4-*tert*-Butyl-2-(diphenylphosphino)cyclopenta-2,4-dien-1-ylidene]methyl}-*N*,*N*-dimethylamine (4).** *N*,*N*-dimethylformamide-dimethyl sulfate (2.55 g, 12.8 mmol) was added slowly to a solution of (diphenylphosphino)-3-*tert*-butylcyclopentadienyllithium (4.00 g, 12.8 mmol) in THF (40 mL) at −20 °C. The mixture was allowed to warm and was stirred at room temperature overnight. After removal of the solvent *in vacuo*, the residue was dissolved in CH_2Cl_2 and washed with water. The organic phase was separated, dried ($MgSO_4$), and evaporated to dryness. Yield: 4.00 g (11.0 mmol, 86%). Single crystals suitable for X-ray diffraction studies were obtained from a concentrated solution in hexane kept at room temperature. ^{1}H NMR: δ 1.19 (s, 9H, $C(CH_3)_3$), 3.20 (s, 6H, $N(CH_3)_2$), 6.22 (m, 1H, Cp−C*H*), 6.54 (m, 1H, Cp−C*H*), 7.23−7.36 (m, 10H, PPh_2), 7.67 (d, 1H, J_{PH} = 6.0 Hz, =C*H*−N) ppm. ^{31}P{^{1}H} NMR: δ −29.1 ppm. HR-MS ($C_{24}H_{28}NP$) ESI: $[M + H]^+$ m/z calcd 362.2032, found 362.2049, [err] 4.6 ppm; $[M + Na]^+$ m/z calcd 384.1852, found 384.1867, [err] 4.1 ppm.

1,1′-Bis((*N*,*N*-dimethylamino)methyl)-2,2′-bis-(diphenylphosphino)-4,4′-bis(*tert*-butyl)ferrocene (5), *rac* and *meso* Compounds. $LiHBEt_3$ supplied as a 1 M solution in THF (4.4 mL, 4.4 mmol) was dried by removal of the solvent on heating at 60 °C for 2 h and then for 20 min at 90 °C under reduced pressure (10^{-2} bar). The solid superhydride was dissolved in distilled and dried toluene (40 mL), leading to a cloudy white suspension. A solution of substituted dimethylaminofulvene **4** (1.52 g, 4.2 mmol) in dry toluene (20 mL) was added during 1 h onto the solution of reducing agent at −20 °C. The mixture was allowed to warm to room temperature and stirred for 24 h. After evaporation of the solvent and dissolution of the residue in THF (20 mL), the resulting solution was added dropwise to a suspension of $FeCl_2$ (0.26 g, 2.1 mmol) in THF (15 mL) at −40 °C. The suspension was warmed and boiled overnight with stirring. The solvent was evaporated, and the residue was dissolved in CH_2Cl_2 and washed with water. The organic layer was separated, dried over Na_2SO_4, and evaporated to dryness. The residue was purified, and *rac* and *meso*-**5** isomers were separated by SiO_2 column chromatography with MeOH as eluent. Fraction 2 (R_f = 0.50−0.52, *meso*-**5**): yield 0.44 g (0.56 mmol, 25%). ^{1}H NMR: δ 0.71 (s, 18H, $C(CH_3)_3$), 1.97 (s, 12H, NCH_3), 3.44 (br d, 2H, J = 12.4 Hz, CH_2), 3.76 (br s, 2H, Cp), 3.90−4.05 (br m, 2H, CH_2), 4.15 (br s, 2H, Cp), 7.07−7.12 (m, 10H, Ph), 7.25−7.33 (m, 6H, Ph), 7.57−7.65 (m, 4H, Ph) ppm. ^{31}P{^{1}H} NMR: δ −27.1 (br s) ppm. ^{13}C{^{1}H} NMR: δ 30.2 (s, $C(CH_3)_3$), 31.4 (s, $C(CH_3)_3$), 44.9 (br s, NCH_3), 56.9 (m, CH_2N), 67.5, 72.5 (br s, Cp), 73.4 (d, J_{PC} = 10 Hz, Cp), 127.6, 129.4 (s, *p*-Ph), 127.8, 128.4 (d, J_{PC} = 7 and 8 Hz, *m*-Ph), 132.6, 136.2 (d, J_{PC} = 19 and 22.5 Hz, *o*-Ph), 137.4 and 140.3 (br s, *i*-PPh_2) ppm. Fraction 4 (R_f = 0.23−0.25, *rac*-**5**): yield 0.20 g (0.26 mmol, 12%). ^{1}H NMR: δ 0.92 (s, 18H, $C(CH_3)_3$), 1.83 (s, 12H, NCH_3), 3.43 (br d, 2H, J = 12.8 Hz, CH_2), 3.73 (br s, 2H, Cp), 3.76−3.87 (br m, 2H, CH_2), 4.18 (br s, 2H, Cp), 7.00−7.11 (m, 10H, Ph), 7.23−7.34 (m, 10H, Ph) ppm. ^{31}P{^{1}H} NMR: δ −28.3 ppm. ^{13}C{^{1}H} NMR: δ 30.4 (s, $C(CH_3)_3$), 31.9 (s, $C(CH_3)_3$), 44.9 (br s, NCH_3), 58.1 (m, CH_2N), 67.7, 72.7 (br s, Cp), 76.0 (d, J_{PC} = 13 Hz, Cp), 127.6, 128.9 (s, *p*-Ph), 127.6, 128.2 (d, J_{PC} = 7 and 8 Hz, *m*-Ph), 133.0 (d, J_{PC} = 20 Hz, *o*-Ph), 136.0 (m, *o*-Ph), 137.1, 140.6 (br s, *i*-Ph) ppm. Suitable crystals for X-ray diffraction of *rac*-**5** have been obtained by slow evaporation of a CH_2Cl_2/pentane (1:1) solution.

1,1′-Bis(*tert*-butyl)-3,3′-Bis((*N*,*N*-diethylamino)methyl)-ferrocene (*rac*-6). To a solution of 1,1′-bis-*tert*-butyl-3,3′-diformyl-ferrocene (2.00 g, 5.64 mmol) in dichloroethane (40 mL) was added diethylamine (1.22 mL, 11.84 mmol), and the mixture was stirred for 1 h at room temperature. To this suspension was added 3.58 g of STAB (16.92 mmol). The mixture was stirred at room temperature overnight. The reaction mixture was hydrolyzed by the addition of 1 M NaOH (20 mL), the phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic phases were dried on $MgSO_4$, and the solvent was removed *in vacuo*. Column chromatography on SiO_2 using heptane/EtOAc/Et_3N (90:9:1) gave complex **6** as a red oily product in 95% yield after solvent evaporation (2.50 g, 5.34 mmol). ^{1}H NMR (CD_2Cl_2): δ 0.99 (t, 12H, J_{HH} = 7.5 Hz, CH_2CH_3), 1.22 (s, 18H, $C(CH_3)_3$), 2.40 (q, 8H, J_{HH} = 7.5 Hz, CH_2CH_3), 3.39, 3.48 (ABq, 4H, J_{AB} = 13.5 Hz, Cp−CH_2−N), 3.74, 3.91, 4.04 (m, 2H each, Cp−C*H*) ppm. ^{13}C{H} NMR: δ 11.9 (s, 4C, CH_2CH_3), 30.4 (s, 2C, $C(CH_3)_3$), 31.5 (s, 6C, $C(CH_3)_3$), 46.3 (s, 4C, CH_2CH_3), 52.0 (s, 2C, Cp-CH_2−N), 65.1, 69.0, 70.2 (s, 2C each, 2,4,5-Cp), 81.2 (s, 2C, 3-Cp), 101.8 (s, 2C, 1-Cp) ppm. ^{15}N NMR (CD_2Cl_2): δ −327.8 ppm. HR-MS ($C_{28}H_{48}FeN_2$)

DOI: 10.1021/acs.organomet.5b00601
Organometallics 2015, 34, 5015−5028

ESI: $[M + H]^+$ m/z calcd 469.32400, found 469.32258, [err] 2.958 ppm. Anal. Calcd for $C_{28}H_{48}FeN_2$ (468.32): C, 71.78; H, 10.33; N, 5.98. Found: C, 70.78; H, 9.30; N, 6.06; better EA could not be obtained for this oily product.

1,1′-Bis(*tert*-butyl)-3,3′-Bis((pyrrolidin-1-yl)methyl)ferrocene (*rac*-7). To a solution of 1,1′-bis-*tert*-butyl-3,3′-diformylferrocene (0.50 g, 1.41 mmol) in dichloroethane (20 mL) was added pyrrolidine (0.25 mL, 2.96 mmol), and the mixture was stirred for 1 h. To this suspension was added 0.69 g of STAB (3.20 mmol). The mixture was stirred at room temperature overnight. The reaction mixture was hydrolyzed by the addition of 1 M NaOH (18 mL), the phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic phases were dried on $MgSO_4$, and the solvent was removed *in vacuo*. Column chromatography on deactivated SiO_2 (silica poured in heptane in the presence of 10% of NEt_3 and then dried *in vacuo*) using heptane/EtOAc (3:2) gave complex **7** as a reddish crystalline solid in 74% yield after solvent evaporation (0.48 g, 1.03 mmol). Single crystals suitable for X-ray diffraction studies were obtained from a concentrated solution in pentane kept at room temperature. ^{1}H NMR (CD_2Cl_2): δ 1.21 (s, 18H, C(CH_3)$_3$), 1.70 (m, 8H, py-β-N−CH_2), 2.46 (m, 8H, py-α-N−CH_2), 3.35, 3.45 (ABq, 4H, J_{AB} = 12.3 Hz, Cp-CH_2−N), 3.78, 3.93, 4.07 (m, 2H each, Cp−CH) ppm. ^{13}C{^{1}H} NMR: δ 22.3 (s, 4C, py-β-N−CH_2), 29.5 (s, 2C, $C(CH_3)_3$), 30.5 (s, 6C, C(CH_3)$_3$), 52.8 (s, 4C, py-α-N−CH_2), 54.7 (s, 2C, Cp-CH_2−N), 64.4, 67.6, 68.9 (s, 2C each, 2,4,5-Cp), 81.4 (s, 2C, 3-Cp), 101.0 (s, 2C, 1-Cp) ppm. ^{15}N NMR (CD_2Cl_2): δ −318.4 ppm. HR-MS ($C_{28}H_{44}FeN_2$) ESI: $[M + H]^+$ m/z calcd 465.29270, found 465.29106, [err] 3.456 ppm. Anal. Calcd for $C_{28}H_{44}FeN_2$ (464.29): C, 72.40; H, 9.55; N, 6.03. Found: C, 72.69; H, 9.47; N, 5.75.

1,1′-Bis(*tert*-butyl)-3,3′-bis((piperidinyl)methyl)ferrocene (*rac*-8). To a solution of 1,1′-bis-*tert*-butyl-3,3′-diformylferrocene (1.00 g, 2.82 mmol) in dichloroethane (30 mL) was added piperidine (0.61 mL, 6.20 mmol), and the mixture was stirred for 1 h. To this suspension was added 1.37 g of STAB (6.49 mmol). The mixture was stirred at room temperature overnight. The reaction mixture was hydrolyzed by the addition of 1 M NaOH (20 mL), the phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic phases were dried on $MgSO_4$, and the solvent was removed *in vacuo*. Column chromatography on deactivated SiO_2 (silica poured in heptane in the presence of 10% NEt_3 and then dried *in vacuo*) using heptane/EtOAc (7:3) gave complex **8** as a yellow solid in 84% yield after solvent evaporation (1.17 g, 2.38 mmol). Single crystals suitable for X-ray diffraction studies were obtained from a concentrated solution in pentane kept at room temperature. ^{1}H NMR: δ 1.20 (s, 18H, C(CH_3)$_3$), 1.37 (m, 4H, pip-γ-N−CH_2), 1.54 (m, 8H, pip-β-N−CH_2), 2.33 (br s, 8H, pip-α-N−CH_2), 3.29, 3.36 (ABq, 4H, J_{AB} = 12.9 Hz, Cp-CH_2−N), 3.75, 3.89, 4.05 (m, 2H each, Cp−CH) ppm. ^{13}C{H} NMR: δ 24.3 (s, 2C, pip-γ-N−CH_2), 25.8 (s, 4C, pip-β-N−CH_2), 30.6 (s, 2C, $C(CH_3)_3$), 31.6 (s, 6C, C(CH_3)$_3$), 53.9 (s, 4C, pip-α-N−CH_2), 59.3 (s, 2C, Cp-CH_2−N), 65.5, 69.3, 70.5 (s, 2C each, 2,4,5-Cp), 81.0 (s, 2C, 3-Cp), 102.0 (s, 2C, 1-Cp) ppm. ^{15}N NMR (CD_2Cl_2): δ −324.2 ppm. HR-MS ($C_{30}H_{48}FeN_2$) ESI: $[M + Na]^+$ m/z calcd 515.30595, found 515.30352, [err] 4.644 ppm. Anal. Calcd for $C_{30}H_{48}FeN_2$ (492.32): C, 73.15; H, 9.82; N, 5.69. Found: C, 73.69; H, 10.06; N, 5.43.

1,1′-Bis(*tert*-butyl)-3,3′-bis((*N*,*N*-dibenzylamino)methyl)-ferrocene (*rac*-9). To a solution of 1,1′-bis-*tert*-butyl-3,3′-diformyl-ferrocene (1.50 g, 4.23 mmol) in dichloroethane (35 mL) was added dibenzylamine (1.80 mL, 9.31 mmol), and the mixture was stirred for 1 h at room temperature. To this suspension was added 2.06 g of STAB (9.73 mmol). The mixture was stirred at room temperature overnight. The reaction mixture was hydrolyzed by the addition of 1 M NaOH (15 mL), the phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic phases were dried with $MgSO_4$, and the solvent was removed *in vacuo*. Column chromatography on deactivated SiO_2 (silica poured in heptane in the presence of 10% NEt_3 and then dried *in vacuo*) using heptane/EtOAc (6:4) gave complex **9** as a brown crystalline solid in 96% yield after solvent evaporation (2.90 g, 4.05 mmol). Single crystals suitable for X-ray diffraction studies were obtained from a concentrated solution in pentane kept at room temperature. ^{1}H NMR (CD_2Cl_2): δ 1.13 (s, 18H, C(CH_3)$_3$), 3.16 (d, 2H, Cp-CH_2−N, $^2J_{HH}$ = 13.5 Hz), 3.41, 3.50 (ABq, 4H, J_{AB} = 13.5 Hz, Cp-CH_2−Ph), 3.45 (d, 2H, $^2J_{HH}$ = 13.5 Hz, Cp-CH_2−N), 3.55, 3.89, 4.05 (m, 2H each, Cp−CH), 7.25−7.38 (m, 20H, Ph) ppm. ^{13}C{^{1}H} NMR: δ 30.4 (s, 2C, C(CH_3)$_3$), 31.5 (s, 6C, C(CH_3)$_3$), 52.5 (s, 2C, Cp-CH_2−N), 57.3 (s, 4C, N-CH_2−Ph), 65.1, 69.5, 70.1 (s, 2C each, 2,4,5-Cp), 81.6 (s, 2C, 3-Cp), 101.7 (s, 2C, 1-Cp), 126.7 (s, 4C, *p*-Ph), 128.1 (s, 8C, *m*-Ph), 128.8 (s, 8C, *o*-Ph), 140.0 (s, 4C, *ipso*-Ph) ppm. ^{15}N NMR (CD_2Cl_2): δ −327.2 ppm. HR-MS ($C_{48}H_{56}FeN_2$) ESI: $[M]^+$ m/z calcd 716.37884, found 716.37669, [err] 2.866 ppm. Anal. Calcd for $C_{48}H_{56}FeN_2$ (716.38): C, 80.43; H, 7.87; N, 3.91. Found: C, 80.03; H, 7.66; N, 3.88.

1,1′-Bis(*tert*-butyl)-3,3′-bis((*N*-(*n*-butyl)amino)methyl)-ferrocene (*rac*-11) via 1,1′-Bis(*tert*-butyl)-3,3′-bis((*N*-(*n*-butyl)-imino)methyl)ferrocene (*rac*-10). *n*-Butylamine (1.67 mL, 16.94 mmol) was dissolved in 10 mL of THF, and a solution of 2.00 g of 1,1′-bis-*tert*-butyl-3,3′-diformylferrocene (5.64 mmol) in 5 mL of CH_3CN was added dropwise under vigorous stirring over 15 min. The mixture was evaporated to dryness after 2 h of stirring at room temperature, and a brown oil was collected, washed with pentane, and dried *in vacuo* for 2 h to give 2.38 g of complex **10** (5.13 mmol, 91%). ^{1}H NMR: δ 0.95 (t, 6H, J_{HH} = 7.2 Hz, CH_3), 1.23 (s, 18H, C(CH_3)$_3$), 1.39, 1.63, 3.42 (m, 4H each, CH_2), 4.13, 4.38, 4.58 (m, 2H each, Cp−CH), 8.02 (s, 2H, N=CH) ppm. ^{13}C{^{1}H} NMR: δ 13.9 (s, 2C, CH_3), 20.5 (s, 2C, CH_2), 30.6 (s, 2C, $C(CH_3)_3$), 31.4 (s, 6C, C(CH_3)$_3$), 33.1, 61.8 (s, 2C each, CH_2), 66.9, 67.8, 68.8 (s, 2C each, 2,4,5-Cp), 80.2 (s, 2C, 3-Cp), 105.1 (s, 2C, 1-Cp), 160.3 (s, 2C, N=CH) ppm. ^{15}N NMR: δ −58.1 ppm. HR-MS ($C_{28}H_{44}FeN_2$) ESI: $[M + H]^+$ m/z calcd 465.29270, found 465.29261, [err] 0.125 ppm. Anal. Calcd for $C_{28}H_{44}FeN_2$ (464.29): C, 72.40; H, 9.55; N, 6.03. Found: C, 72.10; H, 9.46; N, 5.98. The 1,1′-bis(*tert*-butyl)-3,3′-bis((*N*-(*n*-butyl)imino)-methyl)ferrocene (**10**) (2.38 g, 5.13 mmol) was dissolved in 25 mL of THF, and 0.68 g (18 mmol) of finely divided $LiAlH_4$ was poured into the solution. After 1 h of stirring at room temperature, a portion of pentane (20 mL) was added followed by several drops of aqueous solution of 1 M NaOH. The suspension was filtered, and the filtrate was evaporated to give 2.28 g of complex **11** as an orange oil (4.87 mmol, 95%). ^{1}H NMR: δ 0.88 (t, 6H, J_{HH} = 7.5 Hz, CH_3), 1.18 (s, 18H, C(CH_3)$_3$), 1.28 (br s, 2H, NH), 1.33, 1.43 (m, 4H each, CH_2), 2.60 (br t, 4H, J_{HH} = 7.5 Hz, CH_2), 3.44, 3.50 (ABq, 2H, J_{AB} = 12.9 Hz, Cp-CH_2−N), 3.80, 3.89, 4.05 (m, 2H each, Cp) ppm. ^{13}C{^{1}H} NMR: δ 13.0 (s, 2C, CH_3), 19.5, 29.5 (s, 2C each, CH_2), 30.5 (s, 2C, $C(CH_3)_3$), 31.2 (s, 6C, C(CH_3)$_3$), 48.4 (s, 2C, CH_2), 48.6 (s, 2C, Cp-CH_2−N), 64.1, 65.9, 67.4 (s, 2C each, 2,4,5-Cp), 84.5 (s, 2C, 3-Cp), 100.6 (s, 2C, 1-Cp) ppm. ^{15}N NMR (CD_2Cl_2): δ −332.0 ppm. HR-MS ($C_{28}H_{48}FeN_2$) ESI: $[M + H]^+$ m/z calcd 469.32400, found 469.32327, [err] 1.488 ppm. Anal. Calcd for $C_{28}H_{48}FeN_2$ (468.32): C, 71.78; H, 10.33; N, 5.98. Found: C, 71.36; H, 10.38; N, 5.86.

1,1′-Bis((*N*,*N*-diethylamino)methyl)-2,2′-bis-(diphenylphosphino)-4,4′-bis(*tert*-butyl)ferrocene (*rac*-12). 1,1′-Bis(*tert*-butyl)-3,3′-bis((*N*,*N*-diethylamino)methyl)ferrocene (**6**) (0.67 g, 1.43 mmol) was dissolved in Et_2O (5 mL). Then TMEDA (0.51 mL, 3.43 mmol) and a 1.6 M solution of *n*-BuLi in hexane (2.06 mL, 3.29 mmol) were successively added at −60 °C. The reaction mixture was allowed to warm and stirred at room temperature overnight. Then the mixture was cooled to −40 °C, and the chlorophosphine $ClPPh_2$ (0.64 mL, 3.43 mmol) was added dropwise. After the addition the reaction mixture was warmed and stirred overnight at room temperature. The reaction mixture was hydrolyzed by the addition of a saturated solution of $NaHCO_3$ (20 mL), the phases were separated, and the aqueous layer was extracted with CH_2Cl_2 (20 mL). The combined organic layers were dried with $MgSO_4$, and the solvent was removed *in vacuo*. The crude product (brown oil) was purified by column chromatography on silica (EtOAc/heptane, 1:9). Complex **12** was isolated in a pure form as an orange crystalline solid (0.92 g, 1.10 mmol, 78%). Single crystals suitable for X-ray diffraction studies were obtained from a concentrated solution in pentane kept at room temperature. ^{1}H

DOI: 10.1021/acs.organomet.5b00601
Organometallics 2015, 34, 5015−5028

NMR (CD_2Cl_2): δ 0.78 (s, 18H, $C(CH_3)_3$), 0.86 (t, 12H, J_{HH} = 7.5 Hz, CH_2CH_3), 2.28, 2.40 (ABX_3qd, 8H, J_{AB} = 12.8 Hz, $J_{AX} = J_{BX}$, calcd = 3.8 Hz, NCH_2CH_3), 3.71 (AB spin system, dd, 2H, J_{AB} = 15.0 Hz, J_{PH} = 1.8 Hz, Cp-CH_2−N), 3.78 (br s, 2H, Cp−CH), 3.80 (AB spin system, d, 2H, J_{AB} = 15.0 Hz, Cp-CH_2−N), 4.12 (br s, 2H, Cp−CH), 7.15−7.69 (m, 20H, Ph−CH) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 11.9 (s, 4C, CH_2CH_3), 30.5 (s, 2C, $C(CH_3)_3$), 31.7 (s, 6C, $C(CH_3)_3$), 46.7 (s, 4C, CH_2CH_3), 51.6 (m, 2C, Cp-CH_2−N), 67.8 (m, 2C, 3,5-Cp), 72.9 (br s, 2C, 3,5-Cp), 73.7 (d, 2C, J_{PC} = 10 Hz, 1-Cp), 90.8 (d, 2C, J_{PC} = 27 Hz, 2-Cp), 106.7 (s, 2C, 4-Cp), 127.5 (s, 2C, *p*-Ph), 127.8 (d, 4C, J_{PC} = 6 Hz, *m*-Ph), 128.6 (d, 4C, J_{PC} = 8 Hz, *m*-Ph), 129.7 (s, 2C, *p*-Ph), 132.8 (d, 4C, J_{PC} = 18 Hz, *o*-Ph), 136.8 (d, 4C, J_{PC} = 23 Hz, *o*-Ph), 138.8 (s, 2C, *ipso*-Ph), 142.1 (s, 2C, *ipso*-Ph) ppm. ^{15}N NMR (CD_2Cl_2): δ −327.3 ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −25.0 ppm. HR-MS ($C_{52}H_{66}FeN_2P_2$) ESI: $[M + H]^+$ *m*/*z* calcd 837.41246, found 837.41549, [err] 3.760 ppm. Anal. Calcd for $C_{52}H_{66}FeN_2P_2$ (836.41): C, 74.63; H, 7.95; N, 3.35. Found: C, 74.71; H, 8.08; N, 3.47.

1,1′-Bis((*N*,*N*-diethylamino)methyl)-2,2′-bis(di-isopropylphosphino)-4,4′-bis(*tert*-butyl)ferrocene (*rac*-13). 1,1′-Bis(*tert*-butyl)-3,3′-bis((*N*,*N*-diethylamino)methyl)ferrocene (**6**) (0.63 g, 1.34 mmol) was dissolved in Et_2O (7 mL). Then TMEDA (0.48 mL, 3.22 mmol) and a 1.6 M solution of *n*-BuLi in hexane (1.93 mL, 3.08 mmol) were successively added at −78 °C. The reaction mixture was allowed to warm and stirred at room temperature for 24 h. Then the mixture was cooled to −40 °C, and the chlorodiisopropylphosphine (0.51 mL, 3.22 mmol) in solution in Et_2O (2 mL) was added dropwise. The red-orange reaction mixture was warmed and stirred overnight at room temperature. The reaction mixture was hydrolyzed by the addition of a saturated solution of $NaHCO_3$ (20 mL), the phases were separated, and the aqueous layer was extracted with CH_2Cl_2 (18 mL). The combined organic layers were dried with $MgSO_4$, and the solvent was removed *in vacuo*. The crude product (brown oil) was purified by column chromatography on silica (EtOAc/heptane, 1:9). Complex **13** was isolated in a pure form as an orange crystalline solid (0.63 g, 0.90 mmol, 67%). ^1H NMR (CD_2Cl_2): δ 0.94 (t, 12H, J_{HH} = 7.2 Hz, CH_2CH_3), 1.00−1.22 (m, 12H, $CH(CH_3)_2$), 1.25 (s, 18H, $C(CH_3)_3$), 2.30−2.42 (m, 8H, CH_2CH_3), 2.49−2.60 (m, 2H, $CH(CH_3)_2$), 3.22 (AB spin system, d, 2H, J_{AB} = 12.9 Hz, Cp-CH_2−N), 3.46 (AB spin system, dd, 2H, J_{AB} = 12.9 Hz, J_{PH} = 1.8 Hz, Cp-CH_2−N), 3.91, 4.11 (br s, 2H each, Cp−CH) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 11.4 (s, 4C, CH_2CH_3), 20.4 (d, 2C, J_{PC} = 13 Hz, $CH(CH_3)_2$), 20.9 (d, 2C, J_{PC} = 8 Hz, $CH(CH_3)_2$), 22.5 (d, 2C, J_{PC} = 18 Hz, $CH(CH_3)_2$), 23.2 (d, 2C, J_{PC} = 22 Hz, $CH(CH_3)_2$), 24.3 (d, 2C, J_{PC} = 14 Hz, $CH(CH_3)_2$), 24.7 (d, 2C, J_{PC} = 14 Hz, $CH(CH_3)_2$), 31.0 (s, 2C, $C(CH_3)_3$), 32.3 (s, 6C, $C(CH_3)_3$), 46.2 (s, 4C, CH_2CH_3), 52.6 (m, 2C, Cp-CH_2−N), 69.7 (d, 2C, J_{PC} = 9 Hz, 3,5-Cp), 72.1 (br s, 2C, 3,5-Cp), 78.8, 87.5 (d, 2C each, J_{PC} = 13 Hz, 1,2-Cp), 104.0 (s, 2C, 4-Cp) ppm. ^{15}N NMR (CD_2Cl_2): δ −327.7 ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −2.6 ppm. HR-MS ($C_{40}H_{74}FeN_2P_2$) ESI: $[M + H]^+$ *m*/*z* calcd 701.47451, found 701.46382, [err] 1.599 ppm. Anal. Calcd for $C_{40}H_{74}FeN_2P_2$ (700.41): C, 68.55; H, 10.64; N, 4.00. Found: C, 68.14; H, 10.39; N, 4.12.

1,1′-Bis((*N*,*N*-diethylamino)methyl)-2,2′-bis(bis(5-methyl-2-furyl)phosphino)-4,4′-bis(*tert*-butyl)ferrocene (*rac*-14). 1,1′-Bis-(*tert*-butyl)-3,3′-bis((*N*,*N*-diethylamino)methyl)ferrocene (**6**) (0.50 g, 1.07 mmol) and TMEDA (0.27 mL, 1.82 mmol) were dissolved in pentane (10 mL). Then a 1.6 M solution of *n*-BuLi in hexane (1.54 mL, 2.46 mmol) was added at −78 °C. The reaction mixture was allowed to warm and stirred at room temperature overnight. Then the mixture was cooled to −78 °C, and the bromobis(5-methylfuran-2-yl)phosphine (0.87 g, 3.21 mmol) was added dropwise over 5 min. After the addition the reaction mixture was warmed and stirred overnight at room temperature. The reaction mixture was hydrolyzed by the addition of a saturated solution of $NaHCO_3$ (10 mL), the phases were separated, and the aqueous layer was extracted with CH_2Cl_2 (20 mL). The combined organic layers were dried with $MgSO_4$, and the solvent was removed *in vacuo*. The crude product (amber oil) was purified by column chromatography on silica (EtOAc/heptane, 1:9). Complex **14** was isolated in a pure form as an orange crystalline solid (0.44 g, 0.52 mmol, 48%). ^1H NMR (C_6D_6): δ 1.05 (t, 12H, J_{HH} = 4.5 Hz, CH_2CH_3), 1.16 (s, 18H, $C(CH_3)_3$), 2.03, 1.88 (s, 6H each, CH_3-furyl), 2.37−2.50 (m, 8H, CH_2CH_3), 4.01 (AB spin system, dd, 2H, J_{AB} = 15.5 Hz, J_{PH} = 2.5 Hz, Cp-CH_2−N), 4.25 (AB spin system, dd, 2H, J_{AB} = 15.5 Hz, J_{PH} = 2.5 Hz, Cp-CH_2−N), 4.43, 4.64 (br s, 2H each, Cp−CH), 5.72, 5.81 (m, 2H each, furyl−CH), 6.47 (d, 2H, J_{PH} = 3.5 Hz, furyl−CH), 6.97 (t, 2H, J_{PH} = 6.0 Hz, furyl−CH) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 12.7 (s, 4C, CH_2CH_3), 13.6 (s, 2C, CH_3−furyl), 13.9 (s, 2C, CH_3−furyl), 30.7 (s, 2C, $C(CH_3)_3$), 32.0 (s, 6C, $C(CH_3)_3$), 47.2 (s, 4C, CH_2CH_3), 51.7 (t, 2C, J_{PC} = 7.6 Hz, Cp-CH_2−N), 69.7, 71.9 (d, 2C each, J_{PC} = 5.5 Hz, 3,5-Cp), 72.4 (d, 2C, J_{PC} = 5 Hz, 1-Cp), 91.0 (d, 2C, J_{PC} = 29 Hz, 2-Cp), 106.7 (s, 2C, 4-Cp), 107.1 (d, 2C, J_{PC} = 2.5 Hz, furyl), 107.5 (d, 2C, J_{PC} = 9 Hz, furyl), 119.8 (d, 2C, J_{PC} = 14 Hz, furyl), 123.60 (d, 2C, J_{PC} = 32 Hz, furyl), 151.0 (d, 2C, J_{PC} = 15 Hz, furyl), 152.5, 155.7, 157.2 (s, 2C each, furyl) ppm. ^{15}N NMR (C_6D_6): δ −327.2 ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ −71.2 ppm. HR-MS ($C_{48}H_{66}FeN_2O_4P_2$) ESI: $[M + H]^+$ *m*/*z* calcd 853.39262, found 853.39200, [err] 3.760 ppm. Anal. Calcd for $C_{48}H_{66}FeN_2O_4P_2$ (852.38): C, 67.60; H, 7.80; N, 3.28. Found: C, 67.38; H, 7.64; N, 3.15.

1,1′-Bis((pyrrolidin-1-yl)methyl)-2,2′-bis-(diphenylphosphino)-4,4′-bis(*tert*-butyl)ferrocene (*rac*-15). 1,1′-Bis(*tert*-butyl)-3,3′-bis((pyrrolidin-1-yl)methyl)ferrocene (**7**) (0.50 g, 1.07 mmol) was dissolved in pentane (7 mL). Then a 1.9 M solution of *t*-BuLi in pentane (1.3 mL, 2.46 mmol) was added at −78 °C and stirred for 2 h. The reaction mixture was allowed to warm and stirred at room temperature overnight. Then the mixture was cooled to −78 °C, and the chlorodiphenylphosphine (0.46 mL, 2.46 mmol) in solution in Et_2O (2 mL) was added dropwise. The red-orange reaction mixture was warmed and stirred overnight at room temperature. The reaction mixture was hydrolyzed by the addition of a saturated solution of $NaHCO_3$ (20 mL), the phases were separated, and the aqueous layer was extracted with CH_2Cl_2 (18 mL). The combined organic layers were dried with $MgSO_4$, and the solvent was removed *in vacuo*. The crude product (brown oil) was purified by column chromatography on silica (EtOAc/heptane, 1:9). Complex **15** was isolated in a pure form as an orange crystalline solid (0.55 g, 0.66 mmol, 62%). Single crystals suitable for X-ray diffraction studies were obtained from a concentrated solution in pentane kept at room temperature. ^1H NMR: δ 0.79 (s, 18H, $C(CH_3)_3$), 1.46 (m, 8H, py-β-N−CH_2), 2.31 (m, 8H, py-α-N−CH_2), 3.69 (d, 2H, J_{AB} = 12.4 Hz, Cp-CH_2−N,), 3.78 (d, 2H, *J* = 12.4 Hz, Cp-CH_2−N), 3.76, 4.09 (s, 2H each, Cp−CH), 7.68−7.14 (m, 20H, Ph) ppm. $^{13}C\{^1H\}$ NMR: δ 23.8 (s, 4C, py-β-N−CH_2), 30.5 (s, 2C, $C(CH_3)_3$), 31.7 (s, 6C, $C(CH_3)_3$), 52.9 (m, 4C, py-α-N-CH_2), 53.5 (s, 2C, Cp-CH_2−N), 68.1, 72.4 (br s, 2C each, 3,5-Cp), 73.6 (d, 2C, J_{PC} = 10 Hz, 2-Cp), 91.4 (s, 2C, 1-Cp), 106.7 (s, 2C, 4-Cp), 127.5 (s, 2C, *p*-Ph), 127.8 (d, 4C, J_{PC} = 6 Hz, *m*-Ph), 128.7 (m, 4C, *m*-Ph), 129.6 (s, 2C, *p*-Ph), 132.8 (d, 4C, J_{PC} = 18 Hz, *o*-Ph), 136.6 (d, 4C, J_{PC} = 23 Hz, *o*-Ph), 138.7 (d, 2C, J_{PC} = 11 Hz, *ipso*-Ph), 142.0 (s, 2C, J_{PC} = 11 Hz, *ipso*-Ph) ppm. $^{31}P\{^1H\}$ NMR: δ −24.1 ppm. HR-MS ($C_{52}H_{62}FeN_2P_2$) ESI: $[M + H]^+$ *m*/*z* calcd 833.38116, found 833.38495, [err] 4.690 ppm. Anal. Calcd for $C_{52}H_{62}FeN_2P_2$ (832.37): C, 74.99; H, 7.50; N, 3.36. Found: C, 74.82; H, 7.55; N, 3.38.

Palladacycle 16. Bis(benzonitrile)palladium(II) chloride (0.24 g, 0.64 mmol) was added to a solution of 1,1′-bis(*tert*-butyl)-3,3′-bis((*N*,*N*-diethylamino)methyl)ferrocene (**6**) (0.3 g, 0.64 mmol) in dichloromethane (10 mL). The reaction mixture was stirred at room temperature for 8 h and then filtered over Celite. After removal of the solvent *in vacuo*, a red oil was obtained. Treatment with ether (3 mL) afforded complex **16** as a brown powder (0.155 g, 0.24 mmol, 40%). Single crystals suitable for X-ray diffraction studies were obtained from low diffusion of pentane in a concentrated solution of complex **16** in dichloromethane. ^1H NMR: δ 1.14 (s, 9H, $C(CH_3)_3$), 1.22 (s, 9H, $C(CH_3)_3$), 1.44 (s, 3H, CH_2CH_3), 1.51 (s, 3H, CH_2CH_3), 1.62 (s, 3H, CH_2CH_3), 1.73 (s, 3H, CH_2CH_3), 2.53, 3.44 (ABX_3qd, 2H, J_{AB} = 52.0 Hz, $J_{AX} = J_{BX}$ calcd = 7.0 Hz, CH_2CH_3), 2.79 (s, 1H, CH_2CH_3), 2.86 (s, 2H, CH_2CH_3), 2.95 (s, 1H, CH_2CH_3), 2.96 (s, 1H, CpCH_2N), 3.27 (s, 2H, CH_2CH_3), 3.72 (m, 2H, Cp−CH), 3.91 (m, 1H, Cp−CH), 3.96 (s, 1H, Cp−CH), 4.09 (s, 1H, CpCH_2N), 4.10 (s, 1H, CpCH_2N), 4.34 (m, 1H, CpCH_2N), 5.09 (d, 1H, Cp−CH, *J* = 23.0 Hz), 11.55 (br

DOI: 10.1021/acs.organomet.5b00601
Organometallics 2015, 34, 5015−5028

s, 1H, N*H*) ppm. $^{13}C\{^1H\}$ NMR: δ 9.9, 10.1, 13.0 (s, CH_2CH_3), 31.8, 31.9 (s, $C(CH_3)_3$), 44.2, 45.8, 46.7 (s, NCH_2CH_3), 49.1, 49.3, 59.3 (s, $CpCH_2N$), 60.8, 65.9, 67.3, 73.6, 73.8 (s, Cp) ppm. EA were unsatisfactory. HR-MS ($C_{28}H_{48}Cl_2FeN_2Pd$) ESI: $[M - Cl]^+$ m/z calcd 609.18950, found 609.19062, [err] 3.515 ppm.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00601.

Experimental details for the modified synthesis of 1,1′-bis-*tert*-butylferrocene (**a**), 1,1′-bis-*tert*-butyl-3,3′-diformylferrocene (**b**), and 1,1′-bis((*N*,*N*-diethylamino)-methyl)-2,2′-bis(diphenylphosphino)ferrocene (**12′**); ^1H, $^{13}C\{^1H\}$*, $^{31}P\{^1H\}$* NMR and (^1H, ^{15}N)* 2D NMR spectra and HR-MS analysis* for complexes **a**, **b**, **1**−**12**, and **13**−**16**; crystal data and structure refinement for complexes *rac*-**3**, *meso*-**3**, **4**, **5**, **7**, **8**, **9**, **12**, **12′**, **12B**, **15**, and **16** (*if applicable) (PDF)

Crystallographic data (CIF)

Crystallographic data (CIF)

Crystallographic data (CIF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: nadine.pirio@u-bourgogne.fr.

*E-mail: jean-cyrille.hierso@u-bourgogne.fr. Fax: +33-380 393 682.

Author Contributions

[#]F. Allouch and N. Dwadnia contributed equally.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Thanks are due to A. Kanj and A. Job for their help in this project. The "Conseil Régional de Bourgogne" supported this work through the program PARI IME-SMT08 with a Ph.D. grant for F.A., shared with the Lebanese Foundation "Azm et Saada". The cooperation between the Université de Bourgogne and the Université Libanaise benefited from the CEDRE program 2010−2012 (project 09 SCI F 33/L 50). This work was also supported by the CMCU (Comité Mixte pour la Coopération Universitaire Franco-Tunisien) through the PHC Utique program 13G1209 (Ministères des Affaires Etrangères de la République Française et Ministère de l'Enseignement Supérieur et de la Recherche Scientifique de la République Tunisienne) with financial support for a Ph.D. grant to N.D.

■ REFERENCES

(1) (a) Gan, K. S.; Hor, T. S. A. In *Ferrocenes: Homogeneous Catalysis, Organic Synthesis, Material Science*; Togni, A.; Hayashi, T., Eds.; VCH: Weinheim, 1995. (b) Štěpnička, P., Ed.; *Ferrocenes: Ligands, Materials and Biomolecules*; John Wiley & Sons Ltd: Chichester, 2008. (c) Dai, L.-X.; Hou, X.-L., Eds. *Chiral Ferrocenes in Asymmetric Catalysis: Synthesis and Applications*; Wiley-VCH, 2010. (d) *Medicinal Organometallic Chemistry*; Jaouen, G., Metzler-Nolte, N., Eds.; Springer: Berlin, 2010; Topics in Organometallic Chemistry 32.

(2) See for illustrative examples: (a) Atkinson, R. C. J.; Gibson, V. C.; Long, N. J. *Chem. Soc. Rev.* **2004**, *33*, 313. (b) Fihri, A.; Meunier, P.; Hierso, J.-C. *Coord. Chem. Rev.* **2007**, *251*, 2017. (c) You, J.; Drexler, H.-J.; Zhang, S.; Fischer, C.; Heller, D. *Angew. Chem., Int. Ed.* **2003**, *42*, 913. (d) Berens, U.; Burk, M. J.; Gerlach, A.; Hems, W. *Angew. Chem., Int. Ed.* **2000**, *39*, 1981. (e) Mandell, C. L.; Kleinbach, S. S.; Dougherty, W. G.; Kassel, W. S.; Nataro, C. *Inorg. Chem.* **2010**, *49*, 9718.

(3) For examples of ferrocenyl polyphosphines from our group, see: (a) Beaupérin, M.; Fayad, E.; Amardeil, R.; Cattey, H.; Richard, P.; Brandès, S.; Meunier, P.; Hierso, J.-C. *Organometallics* **2008**, *27*, 1506. (b) Smaliy, R. V.; Beaupérin, M.; Cattey, H.; Meunier, P.; Hierso, J.-C.; Roger, J.; Doucet, H.; Coppel, Y. *Organometallics* **2009**, *28*, 3152. (c) Roy, D.; Mom, S.; Beaupérin, M.; Doucet, H.; Hierso, J.-C. *Angew. Chem., Int. Ed.* **2010**, *49*, 6650. (d) Zinovyeva, V. A.; Luo, C.-H.; Fournier, S.; Devillers, C. H.; Cattey, H.; Doucet, H.; Hierso, J.-C.; Lucas, D. *Chem. - Eur. J.* **2011**, *17*, 9901. (e) Roy, D.; Mom, S.; Lucas, D.; Cattey, H.; Hierso, J.-C.; Doucet, H. *Chem. - Eur. J.* **2011**, *17*, 6453. (f) Roy, D.; Mom, S.; Royer, S.; Lucas, D.; Hierso, J.-C.; Doucet, H. *ACS Catal.* **2012**, *2*, 1033.

(4) For recent examples of nitrogen-containing ferrocenes, see: (a) Dwadnia, N.; Allouch, F.; Pirio, N.; Roger, J.; Cattey, H.; Fournier, S.; Penouilh, M.-J.; Devillers, C. H.; Lucas, D.; Naoufal, D.; Ben Salem, R.; Hierso, J.-C. *Organometallics* **2013**, *32*, 5784. (b) Rittinghaus, S.; Faerber, C.; Bruhn, C.; Siemeling, U. *Dalton Trans.* **2014**, *43*, 3508. (c) Strehler, F.; Hildebrandt, A.; Korb, M.; Rueffer, T.; Lang, H. *Organometallics* **2014**, *33*, 4279. (d) Solarova, H.; Cisarova, I.; Stepnicka, P. *Organometallics* **2014**, *33*, 4131. (e) Kienz, T.; Foerster, C.; Heinze, K. *Organometallics* **2014**, *33*, 4803. (f) Wu, H.; An, Q.; Liu, D.; Zhang, W. *Tetrahedron* **2015**, *71*, 5112. (g) Petrov, A. R.; Derheim, A.; Oetzel, J.; Leibold, M.; Bruhn, C.; Scheerer, S.; Oßwald, S.; Winter, R. F.; Siemeling, U. *Inorg. Chem.* **2015**, *54*, 6657. (h) Dey, S.; Quail, J. W.; Muller, J. *Organometallics* **2015**, *34*, 3039. (i) Brosmer, J. L.; Diaconescu, P. L. *Organometallics* **2015**, *34*, 2567. (j) Skoch, K.; Cisarova, I.; Štěpnička, P. *Organometallics* **2015**, *34*, 1942.

(5) (a) Schaarschmidt, D.; Lang, H. *Organometallics* **2013**, *32*, 5668. (b) Noël, T.; Van der Eycken, J. *Green Process. Synth.* **2013**, *2*, 297. (c) Gómez Arrayás, R.; Adrio, J.; Carretero, J. C. *Angew. Chem., Int. Ed.* **2006**, *45*, 7674. (d) Dai, L.-X.; Tu, T.; You, S.-L.; Deng, W.-P.; Hou, X.-L. *Acc. Chem. Res.* **2003**, *36*, 659. (e) Richards, C. J.; Locke, A. J. *Tetrahedron: Asymmetry* **1998**, *9*, 2377. (f) Kagan, H. B.; Diter, P.; Gref, A.; Guillaneux, D.; Masson-Syzmczak, A.; Rebiere, F.; Riant, O.; Samuel, O.; Taudien, S. *Pure Appl. Chem.* **1996**, *68*, 29.

(6) (a) Iftime, G.; Daran, J.-C.; Manoury, E.; Balavoine, G. G. A. *Organometallics* **1996**, *15*, 4808. (b) Balavoine, G. G. A.; Daran, J.-C.; Iftime, G.; Manoury, E. *J. Organomet. Chem.* **1998**, *567*, 191. (c) Deng, W.-P.; Hou, X.-L.; Dai, L.-X.; Yu, Y.-H.; Xia, W. *Chem. Commun.* **2000**, 285. (d) Deng, W.-P.; You, S.-L.; Hou, X.-L.; Dai, L.-X.; Yu, Y.-H.; Xia, W.; Sun, J. *J. Am. Chem. Soc.* **2001**, *123*, 6508. (e) Chesney, A.; Bryce, M. R.; Chubb, R. W. J.; Batsanov, A. S.; Howard, J. A. K. *Synthesis* **1998**, 413. (f) Butler, I. R.; Müssig, S.; Plath, M. *Inorg. Chem. Commun.* **1999**, *2*, 424. (g) Pugin, B.; Landert, H.; Pioda, G. Patent WO 9815565 A1, 1998. (h) Hayashi, T.; Kanehira, K.; Hagihara, T.; Kumada, M. *J. Org. Chem.* **1988**, *53*, 113. (i) Butler, I. R.; Hobson, L. J.; Macan, S. M. E.; Williams, D. J. *Polyhedron* **1993**, *12*, 1901.

(7) Schwink, L.; Knochel, P. *Chem. - Eur. J.* **1998**, *4*, 950.

(8) (a) Perea, J. J. A.; Lotz, M.; Knochel, P. *Tetrahedron: Asymmetry* **1999**, *10*, 375. (b) Spindler, F.; Malan, C.; Lotz, M.; Kesselgruber, M.; Pittelkow, U.; Rivas Nass, A.; Briel, O.; Blaser, H.-U. *Tetrahedron: Asymmetry* **2004**, *15*, 2299.

(9) Ito, Y.; Sawamura, M.; Hayashi, T. *J. Am. Chem. Soc.* **1986**, *108*, 6405.

(10) Wang, M.-C.; Liu, L.-T.; Hua, Y.-Z.; Zhang, J.-S.; Shi, Y.-Y.; Wang, D.-K. *Tetrahedron: Asymmetry* **2005**, *16*, 2531.

(11) Fukuzawa, S.-I.; Oki, H.; Hosaka, M.; Sugasawa, J.; Kikuchi, S. *Org. Lett.* **2007**, *9*, 5557.

(12) Hu, X.-P.; Chen, H.-L.; Zheng, Z. *Adv. Synth. Catal.* **2005**, *347*, 541.

DOI: 10.1021/acs.organomet.5b00601
Organometallics 2015, 34, 5015−5028

(13) Konno, T.; Shimizu, K.; Ogata, K.; Fukuzawa, S.-I. *J. Org. Chem.* **2012**, *77*, 3318.
(14) Marchenko, A.; Hurieva, A.; Koidan, H.; Rampazzi, V.; Cattey, H.; Pirio, N.; Kostyuk, A. N.; Hierso, J.-C. *Organometallics* **2012**, *31*, 5986.
(15) (a) Hierso, J.-C.; Amardeil, R.; Bentabet, E.; Broussier, R.; Gautheron, B.; Meunier, P.; Kalck, P. *Coord. Chem. Rev.* **2003**, *236*, 143 and references therein. (b) Hierso, J.-C.; Beaupérin, M.; Meunier, P. *Eur. J. Inorg. Chem.* **2007**, 3767 and references therein. (c) See ref 20d for tridentate coordination of a ferrocenyltriphosphine. (d) Evrard, D.; Lucas, D.; Mugnier, Y.; Meunier, P.; Hierso, J.-C. *Organometallics* **2008**, *27*, 2643. (e) Zinovyeva, V. A.; Mom, S.; Fournier, S.; Devillers, C. H.; Cattey, H.; Doucet, H.; Hierso, J.-C.; Lucas, D. *Inorg. Chem.* **2013**, *52*, 11923.
(16) Hashmi, A. S. K.; Haufe, P.; Schmid, C.; Rivas Nass, A.; Frey, W. *Chem. - Eur. J.* **2006**, *12*, 5376.
(17) Hayashi, T.; Mise, T.; Fukushima, M.; Kagotani, M.; Nagashima, N.; Hamada, Y.; Matsumoto, A.; Kawakami, S.; Konishi, M.; Yamamoto, K.; Kumada, M. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1138.
(18) (a) Hierso, J.-C.; Ivanov, V. V.; Amardeil, R.; Richard, P.; Meunier, P. *Chem. Lett.* **2004**, *33*, 1296. (b) Ivanov, V. V.; Hierso, J.-C.; Amardeil, R.; Meunier, P. *Organometallics* **2006**, *25*, 989.
(19) For copper chemistry see ref 3a and: Beaupérin, M.; Job, A.; Cattey, H.; Royer, S.; Meunier, P.; Hierso, J.-C. *Organometallics* **2010**, *29*, 2815.
(20) For Pd-catalyzed C−H arylation see: (a) Roy, D.; Mom, S.; Lucas, D.; Cattey, H.; Hierso, J.-C.; Doucet, H. *Chem. - Eur. J.* **2011**, *17*, 6453. (b) Roger, J.; Mom, S.; Beaupérin, M.; Royer, S.; Meunier, P.; Ivanov, V. V.; Doucet, H.; Hierso, J.-C. *ChemCatChem* **2010**, *2*, 296. (c) For sp^2-C−O coupling see: Platon, M.; Cui, L.; Mom, S.; Richard, P.; Saeys, M.; Hierso, J.-C. *Adv. Synth. Catal.* **2011**, *353*, 3403. (d) For sp^2-C−S coupling see: Platon, M.; Wijaya, N.; Rampazzi, V.; Cui, L.; Rousselin, Y.; Saeys, M.; Hierso, J.-C. *Chem. - Eur. J.* **2014**, *20*, 12584. (e) For dichloroarene amination see: Platon, M.; Roger, J.; Royer, S.; Hierso, J.-C. *Catal. Sci. Technol.* **2014**, *4*, 2072.
(21) Butler, I. R.; Hobson, L. J.; Macan, S. M. E.; Williams, D. J. *Polyhedron* **1993**, *12*, 1901.
(22) (a) Braunstein, P.; Naud, F. *Angew. Chem., Int. Ed.* **2001**, *40*, 680. (b) Wang, X.; Thevenon, A.; Brosmer, J. L.; Yu, I.; Khan, S. I.; Mehrkhodavandi, P.; Diaconescu, P. L. *J. Am. Chem. Soc.* **2014**, *136*, 11264.
(23) We use these terms to easily differentiate the two synthetic strategies in the present discussion.
(24) Beaupérin, M.; Smaliy, R.; Cattey, H.; Meunier, P.; Ou, J.; Toy, P. H.; Hierso, J.-C. *Chem. Commun.* **2014**, *50*, 9505.
(25) Hierso, J.-C.; Fihri, A.; Ivanov, V. V.; Hanquet, B.; Pirio, N.; Donnadieu, B.; Rebière, B.; Amardeil, R.; Meunier, P. *J. Am. Chem. Soc.* **2004**, *126*, 11077.
(26) Hierso, J.-C. *Chem. Rev.* **2014**, *114*, 4838.
(27) Lerayer, E.; Renaut, P.; Roger, J.; Hierso, J.-C. Patent FR 3014871 A1 20150619.
(28) (a) Siemeling, U.; Kuhnert, O.; Neumann, B.; Stammler, A.; Stammler, H.-G.; Bildstein, B.; Malaun, M.; Zanello, P. *Eur. J. Inorg. Chem.* **2001**, *2001*, 913. (b) Shafir, A.; Power, M. P.; Whitener, G. D.; Arnold, J. *Organometallics* **2001**, *20*, 1365. (c) Elliott, A. G.; Green, A. G.; Diaconescu, P. L. *Dalton Trans.* **2012**, *41*, 7852.
(29) Beaupérin, M.; Smaliy, R.; Cattey, H.; Meunier, P.; Ou, J.; Toy, P. H.; Hierso, J.-C. *ChemPlusChem* **2015**, *80*, 119.
(30) Investigations are ongoing and will be published in due time.
(31) (a) Gaunt, J. C.; Shaw, B. L. *J. Organomet. Chem.* **1975**, *102*, 511. (b) Kasahara, A.; Izumi, T.; Maemura, M. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1878. (c) Sokolov, V. I.; Troitskaya, L. L.; Reutov, O. A. *J. Organomet. Chem.* **1979**, *182*, 537.
(32) (a) Izumi, T.; Endo, K.; Saito, O.; Shimizu, I.; Maemura, M.; Kasahara, A. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 663. (b) Gong, J.; Liu, G.; Du, C.; Zhu, Y.; Wu, Y. *J. Organomet. Chem.* **2005**, *690*, 3963. (c) Dupont, J.; Consorti, C. S.; Spencer, J. *Chem. Rev.* **2005**, *105*, 2527.
(33) Singh, K. S.; Dixneuf, P. H. *Organometallics* **2012**, *31*, 7320.
(34) (a) SIR92: Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343. (b) SUPERFLIP: Palatinus, L.; Chapuis, G. *J. Appl. Crystallogr.* **2007**, *40*, 786.
(35) ShelX: Sheldrick, G. M. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, *A64*, 112.
(36) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Crystallogr.* **2009**, *42*, 339.
(37) Hafner, K.; Vöpel, K. H.; Ploss, G.; König, C. *Organic Syntheses*; John Wiley and Sons: New York, 1973; Vol. *5*, p 431.
(38) Compton, D. L.; Rauchfuss, T. B. *Organometallics* **1994**, *13*, 4367.
(39) Masson, G.; Lough, A. J.; Manners, I. *Macromolecules* **2008**, *41*, 539.
(40) By using $LiAlH_4$ the desired compound **2** was not obtained. An excess of reducing agent forms methylcyclopentadienide, which interacts with iron dichloride, leading to the formation of 1,1′-dimethylferrocene; see: Herberich, G. E.; Gaffke, A.; Eckenrath, H. J. *Organometallics* **1998**, *17*, 5931.

DOI: 10.1021/acs.organomet.5b00601
Organometallics 2015, 34, 5015−5028