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Synthesis of 1,1′,2-Trisubstituted Aryl-Based Ferrocenyl Phosphines as Precursors for Immobilized Ligands

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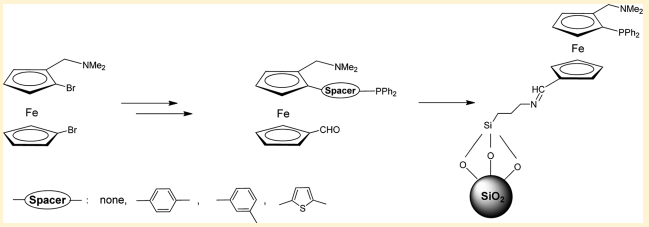
Supporting Information

ABSTRACT: Ferrocenylaryl or ferrocenylheteroaryl phosphines bearing a carboxaldehyde group, [Fe{1-PPh_2(spacer)-2-$NMe_2CH_2C_5H_3$}(C_5H_4CHO)] (spacer = none (*rac*-**12**), 1,4-phenylene (*rac*-**13**), 1,3-phenylene (*rac*-**14**), 2,5-thienylene (*rac*-**15**)), were prepared in a facile four-step sequence starting with dibromination of *N*,*N*-dimethylaminomethylferrocene (**1**) followed by Negishi cross-coupling between 1,1′-dibromo-2-*N*,*N*-dimethylaminomethylferrocene (*rac*-**2**) and aryl or heteroaryl bromide phosphine oxides, Br-spacer-P(O)Ph_2 (spacer = 1,4-phenylene, 1,3-phenylene, 2,5-thienylene), reduction with trichlorosilane, and functionalization of the 1′-position of the cyclopentadienyl ring. All products were fully characterized by spectroscopy (^{1}H, ^{13}C, and ^{31}P NMR, MS, IR) and for *rac*-**3**, *rac*-**7** and *rac*-**11** also by X-ray crystallography. Furthermore, preliminary studies on the grafting of *rac*-**12** on silica were conducted.



INTRODUCTION

One of the most obvious disadvantages of homogeneous catalysis is the difficult separation of the catalyst from the product. This generates costs and sometimes even excludes the application of catalysts on an industrial scale.[1] An attractive strategy to solve this drawback is the immobilization of the active metal complexes on insoluble or water-soluble supports (e.g., SBA-15,[2d] MCM-41,[3] HMS-type SiO_2,[4] Grace 332,[2a] Stöber nanoparticles[2b]). This not only allows facile product separation and catalyst recycling but also incorporates most of the advantages of molecular catalysts, such as high activity, mild reaction conditions, and access to mechanistic studies, into the immobilized system.[5] To immobilize a compound on a solid support, a suitable substituent (anchoring group) for reaction with a functional group (linker) of the surface is required. Depending on the nature of the compounds and their applications, various linkers and anchoring groups have been used for immobilization.[2]

Ferrocene has proved to be a versatile substituent for phosphanes because of its rich chemistry, stability, and redox properties and thus plays a significant role as a backbone or substituent in ancillary ligands.[6] Phosphorus-bearing ferrocenes allow the design of ligands with various electronic and steric properties in order to increase their efficiency in catalysis.[6e,7] Some chiral ferrocenyl bis-phosphines were also immobilized and their activity was tested: e.g., in the hydroxylation of benzene[2d] and ring-closing metathesis,[8] Ir-catalyzed imine hydrogenation,[2a] Pd-catalyzed hydrogenation of ethyl nicotinate,[2c] and Rh-catalyzed hydrogenation of olefins.[2j]

A number of unsymmetrically 1,1′-substituted ferrocene derivatives have been reported and their properties as ligands studied.[6] Their preparation relies on stepwise transmetalation/functionalization reactions or halogen exchange on suitable symmetrically 1,1′-substituted precursors.[6c] These are obtained in good yield by the reaction of 1,1′-dilithioferrocene-*N*,*N*,*N*′,*N*′-tetramethyl-1,2-diaminoethane adduct[9] with ^{n}Bu_3SnCl,[10] a bromine source ($C_2Br_2F_4$ or $C_2H_2Br_4$),[11] or rarely with iodine.[11d] An alternative approach involves highly reactive phosphorus-bridged [1]ferrocenophanes, which undergo facile ring-opening reactions with organolithium reagents.[12]

Even though the 1,1′-substitution of *N*,*N*-dimethylaminomethylferrocene[13] or *N*,*N*-dimethyl-1-ferrocenylethylamine[14] can proceed in a way similar to that described above, it has hardly been investigated. The synthesis of (*R*)-*N*,*N*-dimethyl-1-[(*S*)-1′,2-bis(halogen)ferrocenyl]ethylamine has been reported in a patent.[15] The stepwise synthesis starts with the preparation of the dilithio derivative of Ugi's amine (in the presence of an amine, e.g., TMEDA), followed by reaction with a halogenating agent. The products are obtained in reasonable yields, and their further reaction with 1 equiv of *n*-butyllithium results in a monolithioferrocene derivative. Of the two possible lithiation products, the *ortho*-substituted compound is favored due to stabilization via the amino group (*ortho* effect).[16] Reaction with an electrophile yields a monohalogenated product. The

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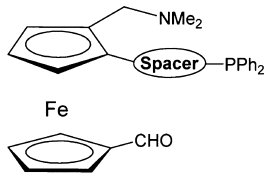
remaining halogen atom can then be substituted by addition of ^{n}BuLi and reaction with an electrophile in very good to excellent yield.

We now report the synthesis of 1,1′,2-trisubstituted aryl-based ferrocenyl phosphines with different spacers (1,4-phenylene, 1,3-phenylene, and 2,5-thienylene) between the ferrocenyl framework and phosphorus atom and a carboxaldehyde group at the 1′-position for further immobilization (Scheme 1).

Scheme 1. 1,1′,2-Trisubstituted Aryl-Based Ferrocenyl Phosphines with a Carboxaldehyde Moiety as Anchoring Group



Spacer:
no spacer: *rac*-**12**
1,4-phenylene: *rac*-**13**
1,3-phenylene: *rac*-**14**
2,5-thienylene: *rac*-**15**

RESULTS AND DISCUSSION

Dilithiation of *N,N*-dimethylaminomethylferrocene (**1**) with ^{n}BuLi in the presence of *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) at the 2- and 1′-positions and further reaction with $C_2H_2Br_4$ leads to 1,1′-dibromo-2-*N,N*-dimethylaminomethylferrocene (*rac*-**2**), which is an excellent starting material for the selective, consecutive substitution of both bromine atoms with various electrophiles and thus for the synthesis of 1,1′,2-trisubstituted unsymmetrical compounds.

Since previously described 1,2-disubstituted aryl-based ferrocene derivatives[17] were obtained only in moderate yields, preliminary studies on the corresponding 1,1′,2-trisubstituted compounds focused on the synthesis of 1-diphenylphosphino-1′-bromo-2-*N,N*-dimethylaminomethylferrocene (*rac*-**3**). Due to the formation of a nitrogen−lithium donor bond, lithiation of *rac*-**2** is preferred at the 2-position, and thus the following reaction with chlorodiphenylphosphine leads to formation of *rac*-**3** in 65% yield (Scheme 2).

Despite many attempts to improve the selectivity of the reaction, the side products 1-bromo-1′-(diphenylphosphino)-2-*N,N*-dimethylaminomethylferrocene (*rac*-**4**) and 1,1′-bis-(diphenylphosphino)-2-*N,N*-dimethyl-aminomethylferrocene (*rac*-**5**) were also always formed (in ca. 28 and 3% yields, respectively) and could be separated from the product by column chromatography.

The structures of compounds *rac*-**3**−**5** were verified by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. The chemical shift in the ^{31}P{^{1}H} NMR spectrum of *rac*-**4** (δ −17.6 ppm) was in agreement with the chemical shift for similar compounds, e.g., 1-diphenylphosphino-1′-*N,N*-dimethylaminomethylferrocene.[18]

In the ^{31}P{^{1}H} NMR spectrum of *rac*-**5**, two signals were observed at −24.5 (1-PPh$_2$) and −16.1 ppm (1′-PPh$_2$).

The molecular structure of *rac*-**3** was determined by single-crystal X-ray crystallography (Figure 1). Room-temperature (293 K) and low-temperature (130 K) measurements were performed.

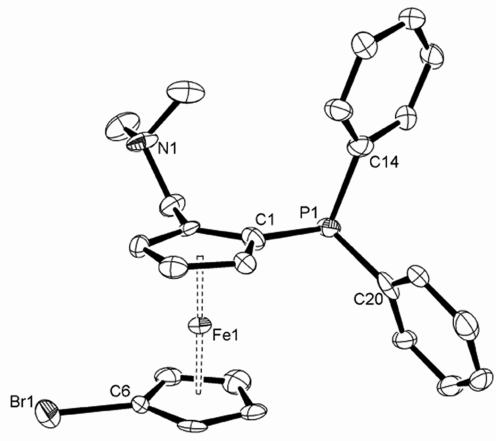


Figure 1. Molecular structure of *rac*-**3** (at 293 K) with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity.

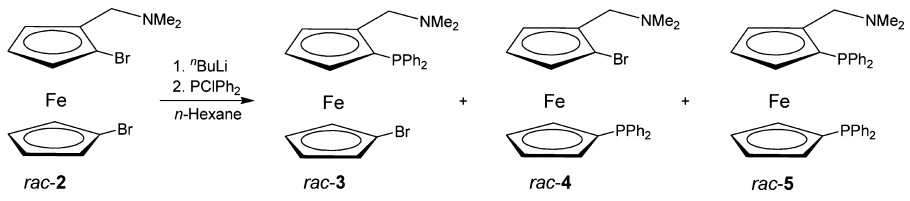
Twinning of the crystal was observed at low temperature as a result of a so-called *translationengleiche* phase transition from the monoclinic space group ($P2_1/c$ at room temperature) to the triclinic space group ($P\bar{1}$ at low temperature). The phase transition temperature was not determined. The structural differences between the two phases are very small and are not described here in detail. The densities of the two phases of *rac*-**3** clearly indicate a closer-packed structure for the low-temperature phase; the NMe$_2$ substituent was no longer disordered in the low-temperature phase. Selected bond lengths and bond angles (measurement at 293 K) are presented in Table 1.

Table 1. Selected Bond Lengths (pm) and Bond Angles (deg) in *rac*-3[a]

Bond Lengths			
P1−C1	181.4(5)	P1−C20	184.6(5)
P1−C14	183.9(5)	Br1−C6	187.4(6)
Bond Angles			
C1−P1−C14	102.2(2)	C14−P1−C20	101.2(2)
C1−P1−C20	102.4(2)		

[a]Measurement at 293 K.

Scheme 2. Products Obtained in the Reaction of 1,1′-Dibromo-2-*N,N*-dimethylaminomethylferrocene (*rac*-2) with Chlorodiphenylphosphine



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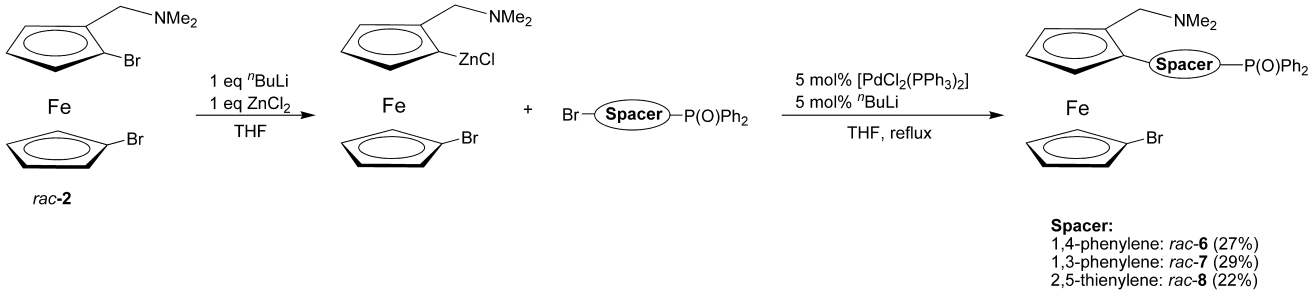
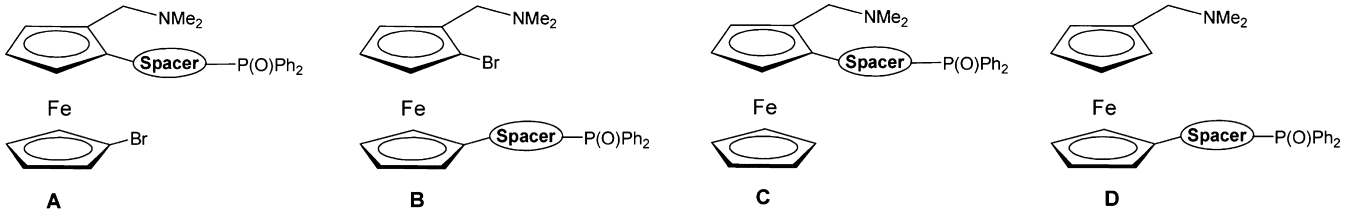
Scheme 3. Synthesis of 1,1′,2-Trisubstituted Ferrocenyl Phosphine Oxides by Negishi Cross-Coupling Reaction



Scheme 4. Four Types of Products Obtained in the Negishi Cross-Coupling of 1,1′-Dibromo-2-*N*,*N*-dimethylaminomethylferrocene (*rac*-2) with Aryl and Heteroaryl Bromide Phosphine Oxides[a]



[a]spacer = 1,4-phenylene, 1,3-phenylene, 2,5-thienylene.

The same selective bromine substitution sequence as described for the synthesis of *rac*-**3** was used for the synthesis of trisubstituted ferrocene derivatives with a 1,4-phenylene, 1,3-phenylene, or 2,5-thienylene spacer. Here, Negishi cross-coupling[19] with the respective aryl or heteroaryl bromide phosphine oxides (Br-spacer-P(O)Ph_2; spacer = 1,4-phenylene, 1,3-phenylene, 2,5-thienylene), which were prepared according to known procedures,[20] was applied (Scheme 3).

The formation of the main products, 1-diphenylphosphine oxide(spacer)-1′-bromo-2-*N*,*N*-dimethylaminomethylferrocene (**A**; spacer = 1,4-phenylene (*rac*-**6**), 1,3-phenylene (*rac*-7), 2,5-thienylene (*rac*-**8**)), is always accompanied by three other compounds, **B**–**D** (Scheme 4). **A**–**D** were separated by column chromatography, and their structures could be determined by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy and mass spectrometry.

The chemical shifts in the ^{31}P{^{1}H} NMR spectra of products of type **A** and **B** are similar and do not indicate whether the coupling reaction took place at the 2- or 1′-position. However, an analysis of the chemical shifts of the diastereotopic methylene protons (CH_2N) in the ^{1}H NMR spectrum allowed assignment of the structure to type **A** or **B**. For the compound *rac*-**2**, the diastereotopic protons have chemical shifts of 3.36 and 3.43 ppm. Similar distances between both doublets of the methylene protons were observed in the ^{1}H NMR spectra of compounds of type **B**, while compounds of type **A** showed these signals at 3.09 and 3.62 ppm. Furthermore, a single-crystal structure determination confirmed the structure of one product of type **A** (*rac*-**7**). In addition, the formation of trisubstituted ferrocene derivatives was proved by mass spectrometry. Formation of the 1,2-disubstituted products **C** and **D** in the syntheses of *rac*-**6**–**8** indicates that the monobrominated ferrocene derivatives were created in one of the synthesis steps. A characteristic singlet for the unsubstituted cyclopentadienyl ring was observed in the ^{1}H NMR spectra of compounds **C**.

Compound *rac*-**7** crystallizes in the triclinic space group $P\bar{1}$ with two molecules in the unit cell (Figure 2). Selected bond lengths and bond angles are summarized in Table 2.

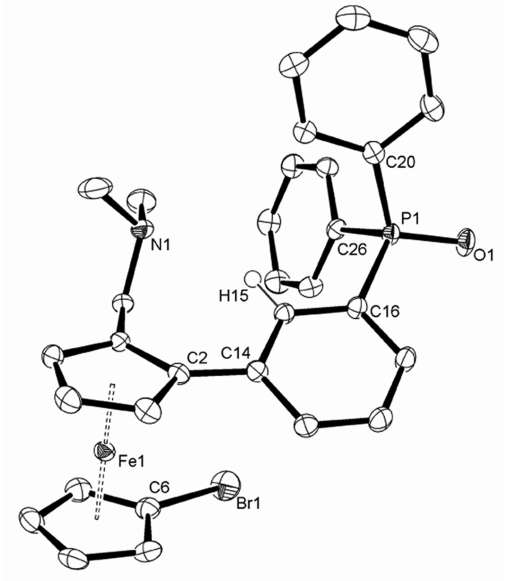


Figure 2. Molecular structure of *rac*-**7** with thermal ellipsoids at the 50% probability level. Hydrogen atoms (other than H15) are omitted for clarity.

The dihedral angle between the plane of the disubstituted cyclopentadienyl ring and the plane of the phenylene spacer is 27.2(7)°; turning of the plane of the spacer toward the *N*,*N*-dimethylamino substituent indicates an N1···H15 interaction (N1···H15 = 236.8 pm; the sum of the van der Waals radii is 264 pm[21]). The dihedral angle is clearly smaller than those found for the 1,2-disubstituted counterparts, and this could be explained by the presence of the bulky bromo substituent at the 1′-position.[14]

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Table 2. Selected Bond Lengths (pm) and Bond Angles (deg) of *rac*-7

Bond Lengths			
C2–C14	147.3(2)	C26–P1	181.2(1)
C16–P1	180.5(1)	P1–O1	148.9(1)
C20–P1	181.3(1)	C6–Br1	188.6(1)
Bond Angles			
C16–P1–C20	107.9(6)	C20–P1–C26	104.9(5)
C16–P1–C26	105.5(6)	C20–P1–O1	112.3(6)
C16–P1–O1	112.4(6)	C26–P1–O1	113.3(6)

Reduction of compounds *rac*-**6**–**8** was performed by employing the same reaction conditions as described for the synthesis of 1,2-disubstituted ferrocenyl phosphines.[17,22] The $^{31}P\{^{1}H\}$ NMR spectra of the reaction mixtures after heating to reflux overnight showed completion of the reaction. The products *rac*-**9**–**11** were isolated in very high yields (Scheme 5).

Compound *rac*-**11** crystallizes in the monoclinic space group $P2_1/c$ with four molecules in the unit cell (Figure 3). Selected bond lengths and bond angles are summarized in Table 3.

The tilt angle of 3.4° between the cyclopentadienyl rings in the trisubstituted ferrocene derivative *rac*-**11** is similar to that of its 1,2-disubstituted counterpart, (5-diphenylphosphino)-thienyl-2-*N*,*N*-dimethylaminomethylferrocene (2.44°),[17] while the dihedral angle between the plane of the disubstituted cyclopentadienyl ring and the plane of the thienylene spacer is smaller in *rac*-**11** (21.9 vs 26.3° in (5-diphenylphosphino)-thienyl-2-*N*,*N*-dimethylaminomethylferrocene[17]).

For the following immobilization studies, functionalization of the solid support (silica gel) with commercially available 3-aminopropyltrimethoxysilane (APTMS) was conducted.[23] The reactive NH_2 group undergoes a fast and selective condensation reaction with carboxaldehydes, yielding only water as a side product.

For this purpose, the remaining bromine atom in *rac*-**3** and *rac*-**9**–**11** was selectively replaced with a CHO group to give compounds *rac*-**12**–**15** in excellent yields (Scheme 6).

Compounds *rac*-**12**–**15** were purified by column chromatography and obtained as red powders. The characteristic signals for aromatic aldehydes were detected in the low-field region in the ^{1}H NMR spectrum. Additional characterization included $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR spectroscopy, EI MS, IR spectroscopy, and elemental analysis.

Initial studies on the immobilization on chemically modified silica gel were performed with *rac*-**12** as a representative derivative. This procedure was described in the literature for other compounds.[24] Grafting of APTMS (linker) on dried SiO_2 was followed by a condensation reaction between the carboxaldehyde moiety (anchoring group) of *rac*-**12** and the primary amino group of the linker, yielding a ferrocenyl phosphine immobilized on silica gel (Scheme 7).

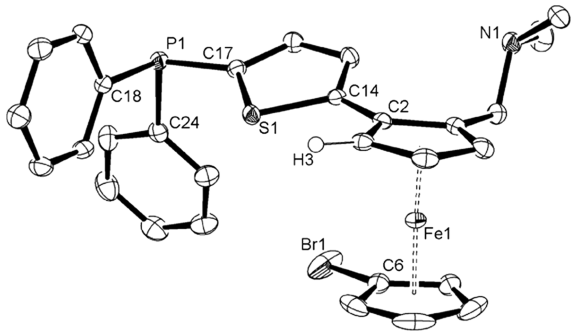


Figure 3. Molecular structure of *rac*-**11** with thermal ellipsoids at the 45% probability level. Hydrogen atoms (other than H3) are omitted for clarity.

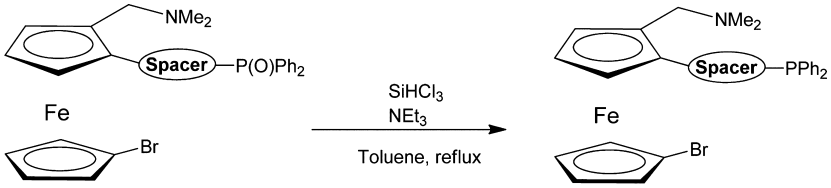
Table 3. Selected Bond Lengths (pm) and Bond Angles (deg) of *rac*-11

Bond Lengths			
C2–C14	145.8(3)	C24–P1	184.2(3)
C17–P1	180.9(3)	C6–Br1	187.2(3)
C18–P1	183.8(3)		
Bond Angles			
C17–P1–C18	99.4(1)	C18–P1–C24	102.4(1)
C17–P1–C24	101.8(1)		

The performed reactions were monitored by DRIFT IR and ^{1}H, ^{29}Si, ^{31}P, and ^{13}C solid-state NMR spectroscopy.[23] The lower intensity of the OH stretching vibration of the silica surface at 3741 cm^{-1} shows that these hydroxyl groups are involved in the formation of chemical bonds with the APTMS molecules.[25]

The signal in the solid-state ^{31}P NMR spectrum of immobilized *rac*-**12** (−29.9 ppm) is slightly shifted in comparison to the signal in the $^{31}P\{^{1}H\}$ NMR spectrum of *rac*-**12** dissolved in $CDCl_3$ (−25.8 ppm). In the ^{29}Si MAS NMR spectra, three main types of units present on the surface of silica (difunctional (D), trifunctional (T), and signals of silica gel (Q)) can be detected. Trifunctional units show resonances at δ −49 (T^1), −56 (T^2), and −65 ppm (T^3). Signals of the silica gel appear at δ −92 (Q^2), −101 (Q^3), and −110 ppm (Q^4).[26] The presence of the T^3 (δ −66.2 ppm) and T^2 (δ −58.6 ppm) units in the ^{29}Si MAS NMR spectrum of a 3-aminopropylsilyl (APS)-modified SiO_2 surface confirmed the incorporation of

Scheme 5. Synthesis of 1,1′,2-Trisubstituted Ferrocenyl Phosphines



Spacer:
1,4-phenylene: *rac*-**6**
1,3-phenylene: *rac*-**7**
2,5-thienylene: *rac*-**8**

Spacer:
1,4-phenylene: *rac*-**9** (95%)
1,3-phenylene: *rac*-**10** (94%)
2,5-thienylene: *rac*-**11** (90%)

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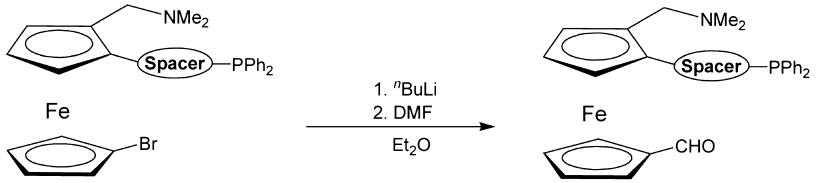
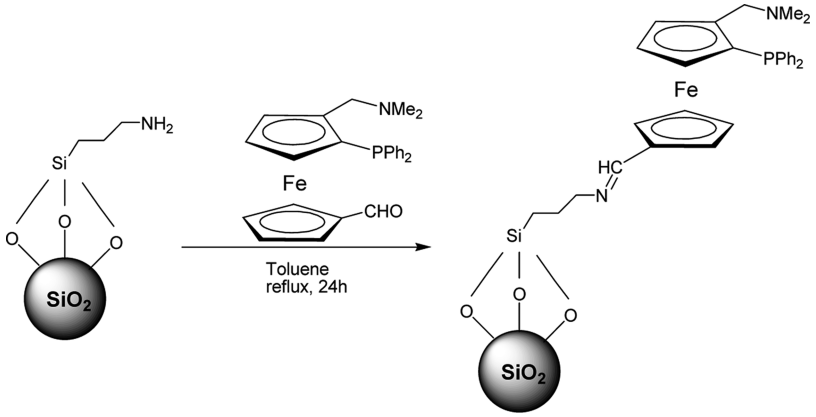
Scheme 6. Synthesis of Carboxaldehyde-Functionalized Ferrocenyl Phosphines as Precursors for Immobilization Reactions



Spacer:
no spacer: *rac*-**3**
1,4-phenylene: *rac*-**9**
1,3-phenylene: *rac*-**10**
2,5-thienylene: *rac*-**11**

Spacer:
no spacer: *rac*-**12** (87%)
1,4-phenylene: *rac*-**13** (84%)
1,3-phenylene: *rac*-**14** (86%)
2,5-thienylene: *rac*-**15** (83%)

Scheme 7. Immobilization of a Ferrocenyl Phosphine Derivative on Modified Silica Gel



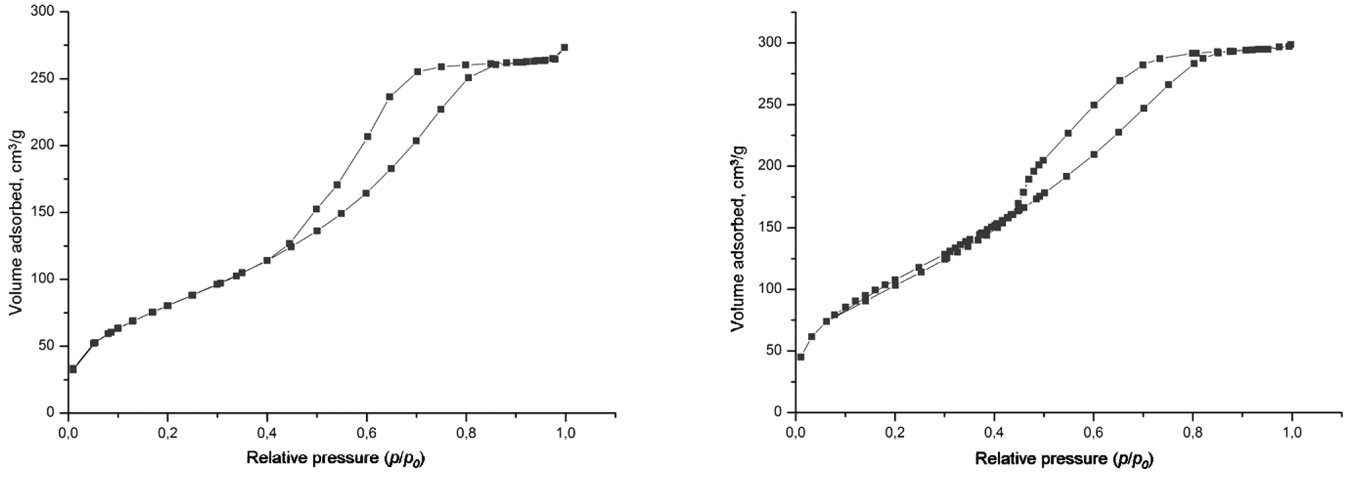


Figure 4. N_2 adsorption−desorption isotherms of APS-modified silica gel (left) and *rac*-**12**-modified silica gel (right).

the APS groups via covalent bonds as a part of the silica gel structure.[24] The ^{13}C CP MAS NMR spectra of such modified silica gels clearly display three signals in the region of aliphatic carbon atoms (δ 8.4 ($SiCH_2$), 24.3 (CH_2), and 43.7 ppm (d, $^1J_{CN}$ = 134.3 Hz, CH_2NH_2)).[27]

The progress of the condensation reaction between the carboxaldehyde groups and the primary amines was followed by IR spectroscopy.[20,23] The absorbance IR spectra of APS-functionalized silica gel recorded in the range of 1500−1700 cm^{-1} showed two strong vibration bands at 1598 ($\delta(NH_2)$) and 1668 cm^{-1} ($\delta_{asm.}(NH_3^+)$). The second band appeared due to formation of hydrogen bonds between the NH_2 groups of the linker and the OH groups of the silica gel, resulting in $SiOH\cdots NH_2$ units.[28] In the DRIFT spectra of the APS-modified silica gel after the condensation reaction, no bands previously assigned to $\delta(NH_2)$ and $\delta_{asm.}(NH_3^+)$ vibrations were present. Instead, a new band at 1643 cm^{-1}, which was assigned to the C═N stretching vibration, appeared.[29]

The N_2 adsorption−desorption isotherms of both materials, measured at 77 K, are shown in Figure 4. Each displays a characteristic type IV isotherm with H1 hysteresis loop (IUPAC classification), indicating that the mesoporous structure is present also after functionalization.[30] The surface area calculated by the BET method, as well as the pore volume (V_p) and average pore diameter (d_p), decreased after the ferrocenyl derivative was anchored at the surface (Figure 5, Table 4), which means that the molecules are present not only on the surface but in the pores as well.[24b]

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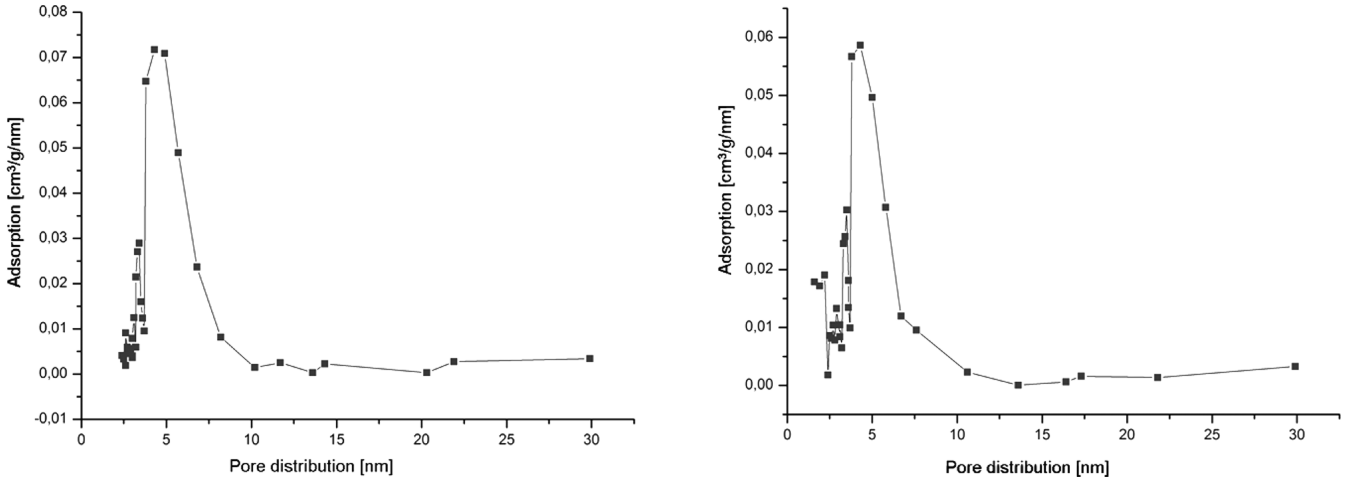

Figure 5. Pore distribution of APS-modified silica gel (left) and *rac*-**12**-modified silica gel (right).

Table 4. Structural Parameters of Modified Silica Gels

sample	BET surface area (m^2/g)	V_p (cm^3/g)	d_p (nm)
APS-modified silica gel	430.75	0.532	4.195
rac-**12**-modified silica gel	411.86	0.462	4.020

The number of molecules immobilized on the modified silica gel was determined by elemental analysis and atomic absorption spectroscopy (Table 5).

Table 5. Elemental Analysis and Atomic Absorption Spectroscopy (AAS) of APS- and *rac*-12-Modified Silica Gel

sample	C, %	H, %	N, %	NH_2 loading (mmol/g)	Fe (mmol/g)[a]
APS-modified silica gel	5.48	1.54	1.52	1.09	
rac-**12**-modified silica gel	8.41	1.88	1.69		1.21

[a]Value obtained by AAS.

The amount of iron and thus the number of immobilized ferrocenyl phosphine molecules was determined by atomic absorption spectroscopy. In case of *rac*-**12**-modified silica gel, the amount of iron in the sample is higher than the number of NH_2 groups available for the condensation reaction. Despite many attempts to remove the unconverted ferrocene derivative from the silica gel pores, about 10% of *rac*-**12**, which is not chemically bonded but is absorbed on the silica gel, was retained in the sample.

CONCLUSION

Aryl- or heteroaryl-based 1,1′,2-trisubstituted ferrocene derivatives *rac*-**12**−**15**, which have a carboxaldehyde anchoring group, were synthesized and characterized. The synthetic approach developed here should also be applicable for other derivatives as well as for diastereomerically pure ligands starting from Ugi's amine, (*S*)- or (*R*)-[$Fe(NMe_2CHMeC_5H_3)(C_5H_5)$].[14] Moreover, preliminary studies showed that these 1,1′,2-trisubstituted ferrocene derivatives can be grafted onto silica gel to prepare immobilized ligands for future catalytic applications.

EXPERIMENTAL SECTION

General Considerations. All manipulations were carried out by standard Schlenk techniques under an atmosphere of dry, high-purity nitrogen. Toluene, THF, diethyl ether, and dichloromethane were dried with an MB SPS-800 Solvent Purification System and stored over activated 4 Å molecular sieves. Et_3N was distilled from $MgSO_4$; TMEDA was heated to reflux with sodium and distilled under a nitrogen atmosphere. Deuterated solvents for NMR spectroscopy were dried as follows: $CDCl_3$ was distilled from P_2O_5 and stored over activated 4 Å molecular sieves; C_6D_6 was dried with sodium, filtered, and stored over potassium mirror.

The compounds *N*,*N*-dimethylaminomethylferrocene (**1**),[13] $[PdCl_2(PPh_3)_2]$,[31] (4-bromophenyl)diphenylphosphine oxide,[20a] (3-bromophenyl)diphenylphosphine oxide,[20b] and (5-bromo-2-thienyl)-diphenylphosphine oxide[20c] were synthesized according to literature procedures. All other chemicals were obtained from commercial sources and used as supplied.

Spectra were recorded on a Bruker AVANCE DRX 400 NMR spectrometer at 400.13 (^{1}H NMR), 161.98 (^{31}P NMR), or 100.61 MHz (^{13}C NMR). TMS was used as an internal standard for ^{1}H NMR spectra, and spectra of other nuclei were referenced to TMS on the δ scale.[32] The signals in the ^{13}C NMR spectra were assigned by $^{13}C\{^{31}P\}$ NMR experiments. EI mass spectra were recorded on a ZAB-HSQ-VG12-520 Analytical Manchester spectrometer or a MASPEC II spectrometer; ESI mass spectra were recorded on a Bruker-Daltonics FT-ICR-MS APEX II spectrometer (*m*/*z* values are given for ^{79}Br in cases where there is a single bromine atom). FTIR spectra were recorded on a Perkin-Elmer Spectrum 2000 spectrometer. C, H, N analyses were performed with a Heraeus VARIO EL Analyzer; air-sensitive samples were prepared for analysis in a glovebox. Melting points were determined in sealed glass capillaries under nitrogen and are uncorrected.

1,1′-Dibromo-2-*N*,*N*-dimethylaminomethylferrocene (*rac*-2). A 68.2 mL portion (1.66 M, 1.1 equiv, 0.11 mol) of ^{n}BuLi in *n*-hexane was added dropwise at −78 °C to a solution of 25 g (0.10 mol) of *N*,*N*-dimethylaminomethylferrocene (**1**) in 250 mL of diethyl ether. The mixture was stirred at room temperature overnight and then cooled to −78 °C, and 16.6 mL (1.1 equiv, 0.11 mol) of TMEDA was added slowly. After the mixture was stirred in a liquid nitrogen/propan-2-ol bath for 1 h, 68.2 mL (1.66 M, 1.1 equiv, 0.11 mol) of ^{n}BuLi in *n*-hexane was added dropwise and the reaction mixture was stirred at room temperature overnight.

The dark red reaction mixture was then cooled to −78 °C, and a diethyl ether solution (ca. 50 mL) of 1,1,2,2-tetrabromoethane (24.5 mL, 0.21 mol, 2.1 equiv) was added dropwise over 6 h in such a manner that the temperature of the mixture did not exceed −70 °C. After complete addition, the brown, cloudy reaction mixture was stirred at room temperature overnight. A 100 mL portion of water was

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added, and the mixture was extracted with 50 mL of ethyl acetate. The organic phases were collected, dried with $MgSO_4$, and concentrated by using a rotary evaporator. The dark brown crude product was purified by column chromatography (silica gel, eluent acetone/NEt_3 (1000/1)) to give *rac*-**2** as a brown oil in 62% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.22 (s, 6H), 3.36 (d, 1H, $^2J_{HH}$ = 12.8 Hz), 3.43 (d, 1H, $^2J_{HH}$ = 12.8 Hz), 4.07 (s, 2H), 4.17 (s, 1H), 4.22 (s, 1H), 4.29 (s, 1H), 4.32 (s, 1H), 4.43 ppm (s, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 45.1 (s), 56.1 (s), 69.3 (s), 70.3 (s), 70.7 (s), 71.1 (s), 72.7 (s), 72.7 (s), 73.2 (s), 78.7 (s), 81.2 (s), 83.7 ppm (s). EI MS: *m*/*z* (relative intensity, %) 401 (100) $[M]^+$, 357 (87), 184 (48), 141 (98), 115 (65), 58 (58). Anal. Calcd for $C_{13}H_{15}Br_2FeN$: C, 39.04; H, 3.53; N, 3.50. Found: C, 39.03; H, 3.75; N, 3.62.

1-Diphenylphosphino-1′-bromo-2-*N*,*N*-dimethylaminomethylferrocene (*rac*-3). A 4.7 mL portion of ^{n}BuLi in *n*-hexane (1.66 M, 7.86 mmol, 1.05 equiv) was added dropwise at −40 °C to a solution of 3.0 g (7.48 mmol) of 1,1′-dibromo-2-*N*,*N*-dimethylaminomethylferrocene (*rac*-**2**) in 50 mL of *n*-hexane. The reaction mixture was stirred in such a manner that the temperature of the reaction did not exceed −10 °C. After 4 h, the clear orange solution was cooled to −40 °C and 1.4 mL of chlorodiphenylphosphine (7.86 mmol) was added. A yellow suspension was obtained that was stirred overnight at room temperature. Approximately 20 mL of water was added, and the reaction mixture was extracted with ethyl acetate (3 × 20 mL). The organic phases were combined, dried with $MgSO_4$, and concentrated by using a rotary evaporator. The crude orange product was purified by column chromatography (silica gel, eluent acetone/NEt_3 (1000/1)) to give *rac*-**3** as an orange oil in 65% yield. Crystals suitable for X-ray diffraction appeared in the oil after a few weeks. Mp: 54−57 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.02 (s, 6H), 3.47 (d, 1H, $^2J_{HH}$ = 12.8 Hz), 3.60 (d, 1H, $^2J_{HH}$ = 12.8 Hz), 3.77 (s, 1H), 3.79 (s, 1H), 3.98 (s, 1H), 4.06 (s, 1H), 4.26 (s, 1H), 4.36 (s, 1H), 4.57 (s, 1H), 7.21−7.58 ppm (m, 10H). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 161 MHz): δ −25.8 ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 44.9 (s), 56.7 (d, $^3J_{CP}$ = 9.2 Hz), 68.7 (s), 69.5 (s), 70.9 (s), 72.2 (s), 73.1 (s), 73.3 (d, $^3J_{CP}$ = 4.5 Hz), 76.4 (d, $^3J_{CP}$ = 3.8 Hz), 77.9 (d, $^1J_{CP}$ = 10.8 Hz), 92.0 (d, J_{CP} not determined, overlapped signals), 92.1 (d, J_{CP} not determined, overlapping signals), 127.7 (s), 127.8 (d, $^3J_{CP}$ = 6.2 Hz), 128.2 (d, $^3J_{CP}$ = 8.1 Hz), 129.3 (s), 132.4 (d, $^2J_{CP}$ = 18.2 Hz), 135.3 (d, $^2J_{CP}$ = 21.9 Hz), 138.0 (d, $^1J_{CP}$ = 8.3 Hz), 139.9 ppm (d, $^1J_{CP}$ = 8.4 Hz). EI MS: *m*/*z* (relative intensity, %) 505 (100) $[M]^+$, 426 (27), 320 (32), 305 (65), 202 (28), 183 (73), 120 (83), 58 (28). Anal. Calcd for $C_{25}H_{25}BrFeNP$: C, 59.32; H, 4.98; N, 2.77. Found: C, 59.52; H, 5.04; N, 2.64.

1-(4-Diphenylphosphine oxide)phenyl-1′-bromo-2-*N*,*N*-dimethylaminomethylferrocene (*rac*-6). The compound was obtained by a Negishi coupling reaction. A 3 mL portion of ^{n}BuLi in *n*-hexane (1.66 M, 4.98 mmol, 1 equiv) was added dropwise at −40 °C to a solution of 2 g (4.98 mmol) of 1,1′-dibromo-2-*N*,*N*-dimethylaminomethylferrocene (*rac*-**2**) in 20 mL of THF. The reaction mixture was stirred for 4 h at temperatures between −40 and −20 °C. In the next step, 0.52 g of dry $ZnCl_2$ (5.23 mmol, 1.05 equiv) was added at 0 °C and the obtained orange suspension was warmed to room temperature and stirred for 4 h. A 1 equiv portion of ^{n}BuLi solution (1.66 M, 4.98 mmol, 5 mol %) was added to a suspension of 0.17 g (0.25 mmol, 5 mol %) of $[PdCl_2(PPh_3)_2]$ in THF. The obtained dark purple solution was added to the suspension of the ferrocenyl zinc derivative followed by addition of 1.48 g (4.98 mmol, 1 equiv) of (4-bromophenyl)diphenylphosphine oxide in 20 mL of THF. The reaction mixture was heated to reflux for 20 h under an inert atmosphere. THF was removed under reduced pressure. The remaining solid was dissolved in CH_2Cl_2; H_2O was added and the mixture was extracted with CH_2Cl_2, and then the combined organic phases were dried with $MgSO_4$ and concentrated by using a rotary evaporator. The dark brown crude product was further purified by column chromatography (silica gel, eluent acetone/NEt_3 (1000/1)), giving a brown oil. The brown oil was dissolved in Et_2O, the solution was filtered, and the solvent was evaporated to give *rac*-**6** as an orange powder in 27% yield. Mp: 140−141 °C. ^{1}H NMR ($CDCl_3$ 400 MHz): δ 2.18 (s, 6H), 3.09 (d, 1H, $^2J_{HH}$ = 12.8 Hz), 3.62 (d, 1H, $^2J_{HH}$ = 12.8 Hz), 3.95 (d, 2H, $^3J_{HH}$ = 7.0 Hz), 4.19 (s br, 1H), 4.22 (s br, 1H), 4.34 (s br, 1H), 4.37 (s br, 1H), 4.56 (s br, 1H), 7.50−7.46 (m, 4H), 7.62−7.54 (m, 4H), 7.74−7.69 (m, 4H), 7.89−7.87 ppm (m, 2H). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 161 MHz): δ 29.1 ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 100 MHz): δ 44.6 (s), 57.4 (s), 69.8 (s), 70.1 (s), 70.5 (s), 72.0 (s), 72.1 (s), 73.6 (s), 75.7 (s), 78.4 (s), 83.3 (s), 87.6 (s), 128.2 (d, $^2J_{CP}$ = 12.1 Hz), 129.1 (d, $^2J_{CP}$ = 11.8 Hz), 131.2 (s), 131.7 and 131.7 (d, J_{CP} not determined, overlapping signals), 132.0 (d, $^3J_{CP}$ = 9.8 Hz), 132.1 (d, $^3J_{CP}$ = 9.6 Hz), 134.3 (d, $^1J_{CP}$ = 102.1 Hz), 134.4 (d, $^1J_{CP}$ = 105.6 Hz), 142.3 ppm (d, $^4J_{CP}$ = 2.2 Hz). EI MS: *m*/*z* (relative intensity, %) 597 (36) $[M]^+$, 555 (16), 475 (9), 355 (20), 277 (17), 201 (37), 182 (16), 152 (16), 121 (17), 77 (20), 58 (100), 44 (34). Anal. Calcd for $C_{31}H_{29}BrFeNOP$: C, 62.23; H, 4.89; N, 2.34. Found: C, 62.58; H, 5.30; N, 2.45.

1-(3-Diphenylphosphine oxide)phenyl-1′-bromo-2-*N*,*N*-dimethylaminomethylferrocene (*rac*-7). The compound was obtained by a Negishi coupling reaction starting from 1,1′-dibromo-2-*N*,*N*-dimethylaminomethylferrocene (*rac*-**2**) and (3-bromophenyl)-diphenylphosphine oxide. The same procedure as in the synthesis of *rac*-**6** was used. The compound *rac*-**7** was obtained as an orange-red powder in 29% yield. Mp: 87−89 °C. ^{1}H NMR (C_6D_6, 400 MHz): δ 2.05 (s, 6H), 2.85 (d, 1H, $^2J_{HH}$ = 12.9 Hz), 3.53−3.51 (m, 2H), 3.61 (d, 1H, $^2J_{HH}$ = 12.7 Hz), 3.96 (m, 1H), 3.99 (t, 1H, $^3J_{HH}$ = 2.5 Hz), 4.04−4.02 (m, 2H), 4.27 (br, 1H), 7.15−7.02 (m, 7H), 7.72−7.67 (m, 1H), 7.93−7.82 (m, 4H), 8.04−8.01 (m, 1H), 8.51 ppm (d, 1H, $^2J_{HH}$ = 12.8 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6, 161 MHz): δ 25.4 ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 100 MHz): δ 44.7 (s), 57.3 (s), 69.5 (s), 70.0 (s), 70.2 (s), 71.7 (s), 72.0 (s), 73.0 (s), 75.3 (s), 78.6 (s), 83.5 (s), 88.2 (s), 128.1 (s), 128.3 (d, $^2J_{CP}$ = 12.1 Hz), 130.0 (d, $^2J_{CP}$ = 9.7 Hz), 131.3 (d, $^3J_{CP}$ = 4.7 Hz), 131.3 (s), 132.2 (d, $^3J_{CP}$ = 9.73 Hz), 132.3 (d, J_{CP} not determined, overlapping signals), 133.2 (d, $^2J_{CP}$ = 10.5 Hz), 134.0 (d, $^1J_{CP}$ = 103.0 Hz), 134.2 and 134.4 (d, $^1J_{CP}$ = 116.1 Hz), 134.2 (d, $^1J_{CP}$ = 88.2 Hz), 134.3 (d, $^1J_{CP}$ = 88.2 Hz), 138.7 (d, $^3J_{CP}$ = 12.3 Hz) ppm. EI MS: *m*/*z* (relative intensity, %) 597 (32) $[M]^+$, 555 (19), 475 (11), 277 (21), 201 (40), 182 (14), 121 (23), 77 (25), 58 (100), 44 (43). Anal. Calcd for $C_{31}H_{29}BrFeNOP$: C, 62.23; H, 4.89; N, 2.34. Found: C, 62.11; H, 5.04; N, 2.20.

1-(5-Diphenylphosphine oxide)thienyl-1′-bromo-2-*N*,*N*-dimethylaminomethylferrocene (*rac*-8). The compound was obtained by a Negishi coupling reaction starting from 1,1′-dibromo-2-*N*,*N*-dimethylaminomethylferrocene (*rac*-**2**) and (5-bromothienyl)-2-diphenylphosphine oxide. The same procedure as in the synthesis of *rac*-**6** was used. The compound *rac*-**8** was obtained as an orange-red powder in 22% yield. Mp: 67−72 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.17 (s, 6H), 3.09 (d, 1H, $^2J_{HH}$ = 12.8 Hz,), 3.76 (d, 1H, $^2J_{HH}$ = 12.8 Hz), 3.96 (s br, 1H), 3.98 (s br, 1H), 4.19 (s br, 1H), 4.24 (s br, 1H), 4.33 (m, 2H), 4,58 (s br, 1H), 7.21−7.23 (m, 1H), 7.39−7.38 (m, 1H), 7.50−7.46 (m, 4H), 7.58−7.54 (m, 2H), 7.81−7.74 ppm (m, 4H). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 161 MHz): δ 21.7 ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 100 MHz): δ 44.5 (s), 57.2 (s), 69.8 (s), 70.2 (s), 70.5 (s), 72.0 (s), 72.4 (s), 72.7 (s), 75.2 (s), 78.8 (s), 81.0 (s), 84.1 (s), 127.01 (d, $^2J_{CP}$ = 12.6 Hz), 128.4 (d, $^2J_{CP}$ = 12.3 Hz), 131.5 (d, $^4J_{CP}$ = 2.5 Hz), 131.9 (d, $^3J_{CP}$ = 10.0 Hz), 133.4 (d, $^1J_{CP}$ = 110.5 Hz), 133.5 (d, $^1J_{CP}$ = 110.5 Hz), 134.5 (d, $^1J_{CP}$ = 108.4 Hz), 134.5 (d, $^1J_{CP}$ = 108.4 Hz), 134.6 (d, $^1J_{CP}$ = 108.4 Hz), 136.9 (d, $^3J_{CP}$ = 8.9 Hz), 150.5 ppm (d, $^4J_{CP}$ = 5.2 Hz). EI MS: *m*/*z* (relative intensity, %) 603 (14) $[M]^+$, 559 (7), 361 (17), 283 (9), 223 (11), 201 (47), 183 (22), 115 (28), 77 (38), 58 (100), 44 (38). Anal. Calcd for $C_{29}H_{27}BrFeNOPS$: C, 57.64; H 4.50; N, 2.32. Found: C, 58.15; H, 4.73; N, 2.32.

1-(4-Diphenylphosphino)phenyl-1′-bromo-2-*N*,*N*-dimethylaminomethylferrocene (*rac*-9). A 2.3 mL portion (1.68 mmol, 20 equiv) of NEt_3 and 1.7 mL (1.68 mmol, 20 equiv) of $SiHCl_3$ were added to a toluene solution of 0.5 g (0.84 mmol) of 1-(4-diphenylphosphine oxide)phenyl-1′-bromo-2-*N*,*N*-dimethylaminomethylferrocene (*rac*-**6**). The suspension was heated to reflux overnight under an inert atmosphere. After the mixture was cooled to room temperature, 10 mL of a 30% NaOH solution in degassed water was added and the mixture was stirred at 60 °C for 2 h. The two phases were separated under an inert atmosphere, and the water phase was extracted twice with dry Et_2O. The combined organic phases were

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dried with $MgSO_4$ and filtered, and the solvent was evaporated under vacuum. The obtained orange waxy material was purified by flash column chromatography (eluent acetone/NEt_3 (1000/1)) to give *rac*-**9** as an orange solid in 95% yield. Mp: 111−115 °C. ^{1}H NMR ($CDCl_3$ 400 MHz): δ 2.17 (s, 6H), 3.15 (d, 1H, $^2J_{HH}$ = 12.7 Hz), 3.65 (d, 1H, $^2J_{HH}$ = 12.8 Hz), 3.97−3.93 (m, 2H), 4.18 (br, 1H), 4.24 (br, 1H), 4.32 (m, 2H), 4.50 (t, 1H, $^3J_{HH}$ = 3.4 Hz), 7.28−7.23 (m, 2H), 7.36−7.33 (m, 10H), 7.71 ppm (d, 2H, $^2J_{HH}$ = 7.8 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$, 161 MHz): δ −6.1 ppm. ^{13}C{^{1}H} NMR (C_6D_6, 100 MHz): δ 44.6 (s), 57.3 (s), 69.6 (s), 69.9 (s), 70.2 (s), 71.9 (s), 72.1 (s), 73.0 (s), 75.2 (s), 78.5 (s), 83.4 (s), 88.5 (s), 128.2 (d, J_{CP} not determined, overlapping signals), 128.5 (d, J_{CP} not determined, overlapping signals), 129.5 (d, $^3J_{CP}$ = 7.1 Hz), 133.7 (s, $^2J_{CP}$ = 19.1 Hz), 133.9 (d, $^2J_{CP}$ = 18.9 Hz), 133.9 (d, $^2J_{CP}$ = 19.6 Hz), 135.4 (d, $^1J_{CP}$ = 11.7 Hz), 137.8 (d, $^1J_{CP}$ = 12.0 Hz), 137.9 (d, $^1J_{CP}$ = 12.0 Hz), 139.0 ppm (s). EI MS: *m*/*z* (relative intensity, %) 581 (100) $[M]^+$, 537 (31), 503 (11), 459 (7), 381 (24), 290 (9), 259 (8), 183 (29), 152 (13), 58 (50), 44 (24). Anal. Calcd for $C_{31}H_{29}BrFeNP$: C, 63.94; H, 5.02; N, 2.41. Found: C, 64.02; H, 5.34; N, 2.80.

1-(3-Diphenylphosphino)phenyl-1′-bromo-2-*N*,*N*-dimethylaminomethylferrocene (*rac*-10). The compound was synthesized by using the same procedure as for the synthesis of *rac*-**9**. The compound *rac*-**10** was obtained as an orange powder in 94% yield. Mp: 77−80 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.08 (s, 6H), 3.14 (d, 1H, $^2J_{HH}$ = 12.9 Hz), 3.43 (d, 1H, $^2J_{HH}$ = 12.9 Hz), 3.71 (d, 1H, $^3J_{HH}$ = 3.2 Hz), 3.76 (m, 1H), 4.02 (t, 1H, $^3J_{HH}$ = 2.2 Hz), 4.29 (t, 1H, $^3J_{HH}$ = 2.0 Hz), 4.27−4.26 (m, 2H), 4.38 (t, 1H, $^3J_{HH}$ = 3.6 Hz), 7.29−7.24 (m, 2H), 7.39−7.36 (m, 10H), 7.64−7.57 ppm (m, 2H). ^{31}P{^{1}H} NMR ($CDCl_3$, 161 MHz): δ −5.4 ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 44.7 (s), 56.5 (s), 69.3 (s), 69.9 (s), 70.4 (s), 71.4 (s), 71.8 (s), 72.3 (s), 74.7 (s), 78.2 (s), 83.0 (s), 89.1 (s), 128.2 (d, $^3J_{CP}$ = 8.5 Hz), 128.6 (d, $^3J_{CP}$ = 6.9 Hz), 128.8 (s), 129.7 (s), 132.0 (d, $^2J_{CP}$ = 23.8 Hz), 132.0 (d, $^2J_{CP}$ = 23.8 Hz), 133.8 (d, $^2J_{CP}$ = 19.4 Hz), 134.7 (d, $^1J_{CP}$ = 15.3 Hz), 136.9 (d, $^1J_{CP}$ = 10.9 Hz), 137.2 (d, $^1J_{CP}$ = 11.0 Hz), 137.4 (d, J_{CP} = 11.1 Hz), 138.0 ppm (d, $^3J_{CP}$ = 5.7 Hz). EI MS: *m*/*z* (relative intensity, %) 581 (100) $[M]^+$, 539 (32), 381 (28), 339 (60), 270 (23), 215 (14), 183 (60), 152 (27), 121 (14), 58 (98), 44 (84). Anal. Calcd for $C_{31}H_{29}BrFeNP$: C, 63.94; H, 5.02; N, 2.41. Found: C, 63.51; H, 5.20; N, 2.40.

1-(5-Diphenylphosphino)thienyl-1′-bromo-2-*N*,*N*-dimethylaminomethylferrocene (*rac*-11). The compound was synthesized by using the same procedure as for the synthesis of *rac*-**9**. The compound *rac*-**11** was obtained as an orange powder in 90% yield. Mp: 47−51 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.18 (s, 6H), 3.14 (d, 1H, $^2J_{HH}$ = 12.8 Hz), 3.79 (d, 1H, $^2J_{HH}$ = 12.9 Hz), 3.95−3.93 (m, 2H), 4.16 (m, 1H), 4.21 (m, 1H), 4.30−4.27 (m, 2H), 4.52 (m, 1H), 7.14−7.11 (m, 1H), 7.28 (m, 1H), 7.34−7.33 (m, 6H), 7.43−7.39 ppm (m, 4H). ^{31}P{^{1}H} NMR ($CDCl_3$, 161 MHz): δ −19.5 ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 44.8 (s), 57.0 (s), 69.6 (s), 70.1 (s), 70.3 (s), 71.7 (s), 72.0 (s), 72.7 (s), 74.8 (s), 78.8 (s), 81.8 (s), 83.1 (s), 126.7 (d, $^3J_{CP}$ = 7.4 Hz), 128.4 (d, $^3J_{CP}$ = 6.9 Hz), 128.8 (s), 133.1 (d, $^1J_{CP}$ = 19.3 Hz), 136.2 (d, $^2J_{CP}$ = 26.9 Hz), 136.7 (d, $^2J_{CP}$ = 25.2 Hz), 137.9 (d, $^3J_{CP}$ = 8.5 Hz), 147.9 ppm (s). EI MS: *m*/*z* (relative intensity, %) 587 (100) $[M]^+$, 543 (22), 507 (9), 464 (6), 403 (15), 387 (32), 294 (11), 267 (14), 202 (15), 183 (15), 115 (13), 58 (45), 44 (16). Anal. Calcd for $C_{29}H_{27}BrFeNPS$: C, 59.20; H, 4.63; N, 2.38. Found: C, 59.63; H, 4.89; N, 2.40.

1-Diphenylphosphino-1′-carboxaldehyde-2-*N*,*N*-dimethylaminomethylferrocene (*rac*-12). A 1.9 mL portion of ^{n}BuLi in *n*-hexane (1.66 M, 3.11 mmol, 1.05 equiv) was added dropwise at −40 °C to a solution of 1.5 g (2.96 mmol) of 1-diphenylphosphino-1′-bromo-2-*N*,*N*-dimethylaminomethylferrocene (*rac*-**3**) in 30 mL of *n*-hexane. The reaction mixture was stirred, and the temperature of the reaction mixture was kept at −10 °C. After 2 h, the clear orange solution was cooled to −40 °C, 0.9 mL of DMF (0.012 mmol, 4 equiv) was added, and the obtained brown suspension was stirred overnight at room temperature. Approximately 20 mL of water was added and the reaction mixture extracted with ethyl acetate (3 × 15 mL). The organic phases were combined, dried with $MgSO_4$, and filtered, and the solution was concentrated by using a rotary evaporator. The dark red crude product was purified by column chromatography (silica gel, eluent acetone/NEt_3 (1000/1)) to give *rac*-**12** as a red-brown oil in 87% yield. Mp: 98−100 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.99 (s, 6H), 3.22 (d, 1H, $^2J_{HH}$ = 13.5 Hz), 3.51 (d, 1H, $^2J_{HH}$ = 13.5 Hz), 4.02 (s br, 1H), 4.29 (s br, 1H), 4.36 (s br, 1H), 4.41 (s br, 1H), 4.46 (s br, 1H), 4.66 (s br, 2H), 7.28−7.21 (m, 5H), 7.46−7.40 (m, 3H), 7.64−7.59 (m, 2H), 9.57 ppm (s, 1H). ^{31}P{^{1}H} NMR ($CDCl_3$, 161 MHz): δ −25.4 ppm. ^{13}C{^{1}H} NMR (C_6D_6, 100 MHz): δ 44.7 (s), 57.3 (d, $^3J_{CP}$ = 8.7 Hz), 70.4 (s), 70.5 (s), 70.8 (s), 72.5 (d, $^3J_{CP}$ = 4.9 Hz), 74.0 (s), 74.2 (d, $^3J_{CP}$ = 3.8 Hz), 74.5 (s), 79.2 (d, $^1J_{CP}$ = 13.5 Hz), 93.0 (d, J_{CP} not determined, overlapping signals), 93.0 (d, J_{CP} not determined, overlapping signals), 127.6 (s), 128.1 (d, $^1J_{CP}$ = 8.3 Hz), 129.2 (s), 132.3 (s), 132.3 (s), 135.4 (s), 135.5 (s), 138.1 (d, $^2J_{CP}$ = 10.1 Hz), 140.4 (d, $^2J_{CP}$ = 10.0 Hz), 191.6 ppm (s). EI MS: *m*/*z* (relative intensity, %) 455 (34) $[M]^+$, 412 (7), 384 (9), 361 (11), 317 (9), 270 (41), 239 (15), 199 (9), 141 (13), 91 (54), 65 (20). Anal. Calcd for $C_{26}H_{26}FeNOP$: C, 68.59; H, 5.76; N, 3.08. Found: C, 68.76; H, 5.98; N, 3.20.

1-(4-Diphenylphosphino)phenyl-1′-carboxaldehyde-2-*N*,*N*-dimethylaminomethylferrocene (*rac*-13). The compound was synthesized by using the same procedure as for the synthesis of *rac*-**12**. The compound *rac*-**13** was obtained as an orange powder in 84% yield. Mp: 116−119 °C. ^{1}H NMR (C_6D_6, 400 MHz): δ 2.00 (s, 6H), 2.73 (d, 1H, $^2J_{HH}$ = 12.6 Hz,), 3.49 (d, 1H, $^2J_{HH}$ = 12.6 Hz), 3.91 (m, 2H), 3.94 (t, 1H, $^3J_{HH}$ = 2.4 Hz), 4.03 (t, 1H, $^3J_{HH}$ =1.5 Hz), 4.26 (t, 1H, $^3J_{HH}$ = 1.2 Hz), 4.34 (t, 1H, $^3J_{HH}$ = 1.1 Hz), 4.42 (t, 1H, $^3J_{HH}$ = 1.2 Hz), 7.09−7.06 (m, 6H), 7.50−7.44 (m, 6H), 7.81−7.79 (m, 2H), 9.73 ppm (s, 1H). ^{31}P{^{1}H} NMR (C_6D_6, 161 MHz): δ −5.8 ppm. ^{13}C{^{1}H} NMR (C_6D_6, 100 MHz): δ 44.5 (s), 57.4 (s), 68.4 (s), 70.8 (s), 71.3 (s), 71.6 (s), 73.5 (s), 75.0 (s), 75.3 (s), 80.5 (s), 83.64 (s), 88.7 (s), 128.5 (d, J_{CP} not determined, overlapped signals), 128.6 (d, J_{CP} not determined, overlapped signals), 128.6 (s), 128.6 (d, J_{CP} not determined, overlapped signals,), 128.3 (d, $^3J_{CP}$ = 6.6 Hz), 133.7 (d, $^2J_{CP}$ = 17.2 Hz), 133.9 (d, $^2J_{CP}$ = 17.2 Hz), 133.9 (d, $^2J_{CP}$ = 19.8 Hz), 135.9 (d, $^1J_{CP}$ = 12.3 Hz), 137.7 (d, $^1J_{CP}$ = 12.5 Hz), 137.3 (d, $^1J_{CP}$ = 12.2 Hz), 138.3 (s), 191.8 ppm (s). EI MS: *m*/*z* (relative intensity, %) 531 (100) $[M]^+$, 516 (47), 502 (38), 459 (13), 302 (20), 274 (21), 265 (13), 183 (28), 152 (13), 121 (15), 58 (30). Anal. Calcd for $C_{32}H_{30}FeNOP$: C, 72.33; H, 5.69; N, 2.64. Found: C, 72.58; H, 5.73; N, 2.73.

1-(3-Diphenylphosphino)phenyl-1′-carboxaldehyde-2-*N*,*N*-dimethylaminomethylferrocene (*rac*-14). The compound was synthesized by using the same procedure as for the synthesis of *rac*-**12**. The compound *rac*-**14** was obtained as an orange powder in 86% yield. Mp: 96−101 °C. ^{1}H NMR (C_6D_6, 400 MHz): δ 1.99 (s, 6H), 2.76 (d, 1H, $^2J_{HH}$ = 12.2 Hz), 3.46 (d, 1H, $^2J_{HH}$ = 13.0 Hz), 3.85−3.83 (m, 2H), 3.89 (t, 1H, $^3J_{HH}$ = 2.5 Hz), 4.04 (t, 1H, $^3J_{HH}$ = 1.8 Hz), 4.17 (t, 1H, $^3J_{HH}$ = 1.8 Hz), 4.31 (t, 1H, $^3J_{HH}$ = 1.1 Hz), 4.36 (t, 1H, $^3J_{HH}$ = 1.3 Hz), 7.14−7.05 (m, 7H), 7.35−7.31 (m, 1H), 7.52−7.43 (m, 4H), 7.80 (d, 1H, $^2J_{HH}$ = 7.8 Hz), 7.94 (d, 1H, $^2J_{HH}$ = 7.6 Hz), 9.69 ppm (s, 1H). ^{31}P{^{1}H} NMR (C_6D_6, 161 MHz): δ −5.5 ppm. ^{13}C{^{1}H} NMR (C_6D_6, 100 MHz): δ 44.6 (s), 57.3 (s), 68.3 (s), 70.5 (s), 71.3 (s), 71.4 (s), 73.2 (s), 74.9 (s), 75.5 (s), 80.4 (s), 83.8 (s), 89.2 (s), 128.2 (s), 128.4 (d, $^3J_{CP}$ = 7.4 Hz), 128.6 (d, $^2J_{CP}$ = 17.2 Hz), 128.6 (d, $^3J_{CP}$ = 4.0 Hz), 128.7 (d, $^3J_{CP}$ = 4.1 Hz), 129.6 (s), 132.2 (d, $^2J_{CP}$ = 21.8 Hz), 133.9 (d, $^2J_{CP}$ = 19.3 Hz), 134.0 (d, $^2J_{CP}$ = 19.3 Hz), 134.2 (d, $^2J_{CP}$ = 17.7 Hz), 137.6 (d, $^1J_{CP}$ = 11.0 Hz), 137.7 (d, $^1J_{CP}$ = 11.3 Hz), 137.9 (d, $^1J_{CP}$ = 11.9 Hz), 137.9 (d, $^3J_{CP}$ = 6.1 Hz), 191.8 ppm (s). EI MS: *m*/*z* (relative intensity, %) 531 (100) $[M]^+$, 516 (34), 503 (36), 486 (61), 460 (49), 394 (20), 339 (14), 302 (18), 274 (18), 257 (20), 183 (40), 152 (18), 121 (14), 58 (32). Anal. Calcd for $C_{32}H_{30}FeNOP$: C, 72.33; H, 5.69; N, 2.64. Found: C, 72.50; H, 5.97; N, 2.75.

1-(5-Diphenylphosphino)thienyl-1′-carboxaldehyde-2-*N*,*N*-dimethylaminomethylferrocene (*rac*-15). The compound was synthesized by using the same procedure as for the synthesis of *rac*-**12**. The compound *rac*-**15** was obtained as an orange powder in 83% yield. Mp: 56−61 °C. ^{1}H NMR (C_6D_6, 400 MHz): δ 2.01 (s, 6H), 2.75 (d, 1H, $^2J_{HH}$ = 13.1 Hz), 3.65 (d, 1H, $^2J_{HH}$ = 12.1 Hz), 3.84 (t, 1H, $^2J_{HH}$ = 2.4 Hz), 3.95 (s br, 2H), 3.97 (s br, 1H), 4.24 (s, 1H), 4.39−4.37 (m, 2H), 7.18−7.06 (m, 7H), 7.43 (d, 1H, $^3J_{HH}$ = 3.1 Hz), 7.56−7.52 (m,

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Table 6. Crystal Data and Structure Refinement Details for Compounds *rac*-3 (at 293 and 130 K), *rac*-7, and *rac*-11

	rac-3 (293 K)	*rac*-3 (130 K)	*rac*-7	*rac*-11
formula	$C_{25}H_{25}BrFeNP$	$C_{25}H_{25}BrFeNP$	$C_{31}H_{29}BrFeNOP$	$C_{29}H_{27}BrFeNPS$
fw	506.19	506.19	598.28	588.31
T (K)	293(2)	130(2)	130(2)	130(2)
cryst syst	monoclinic	triclinic	triclinic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a (pm)	1027.75(4)	1024.5(1)	852.46(2)	1556.84(4)
b (pm)	2269.76(8)	2231.8(3)	1087.89(4)	1288.09(2)
c (pm)	1092.31(5)	1070.4(1)	1564.66(6)	1305.06(3)
α (deg)	90	88.383(9)	73.740(3)	90
β (deg)	115.071(5)	115.39(1)	88.534(3)	102.172(2)
γ (deg)	90	90.62(1)	71.886(3)	90
V (nm^3)	2.3080(2)	2.2101(4)	1.32095(8)	2.5583(1)
Z	4	4	2	4
D_{calcd} (Mg/m^3)	1.457	1.521	1.504	1.527
μ (mm^{-1})	2.465	2.574	2.169	2.314
$F(000)$	1032	1032	612	1200
cryst size (mm)	0.5 × 0.15 × 0.05	0.5 × 0.15 × 0.05	0.35 × 0.25 × 0.2	0.25 × 0.15 × 0.05
θ range (deg)	2.90−26.37	2.86−26.37	2.90−33.14	3.11−30.51
h,k,l ranges	$-12 \le h \le 12$	$-12 \le h \le 12$	$-13 \le h \le 13$	$-22 \le h \le 22$
	$-28 \le k \le 28$	$-27 \le k \le 27$	$-16 \le k \le 16$	$-18 \le k \le 18$
	$-13 \le l \le 13$	$-13 \le l \le 13$	$-24 \le l \le 24$	$-18 \le l \le 18$
no. of indep rflns [R_{int}]	4708 [0.0450]	13266 [0.0000][a]	10060 [0.0290]	7806 [0.0449]
GOF (F^2)	1.031	0.942	1.056	1.028
$R1$/w$R2$ ($I > 2\sigma(I)$)	0.0634/0.1394	0.0571/0.1223	0.0294/0.0703	0.0457/0.0979
$R1$/w$R2$ (all data)	0.1033/0.1597	0.0867/0.1301	0.0400/0.0762	0.0714/0.1099
residual electron density (e/Å^3)	0.942/−1.060	1.091/−0.838	0.508/−0.730	2.061/−2.235

[a]Twinned crystal.

4H), 9.71 ppm (s, 1H). $^{31}P\{^1H\}$ NMR (C_6D_6, 161 MHz): δ −19.4 ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 100 MHz): δ 44.5 (s), 57.5 (s), 68.3 (s), 70.7 (s), 71.0 (s), 71.5 (s), 73.2 (s), 75.1 (s), 75.6 (s), 80.8 (s), 82.2 (s), 84.0 (s), 128.5 (d, $^3J_{CP}$ = 6.9 Hz), 128.7 (s), 133.3 (d, $^3J_{CP}$ = 3.1 Hz), 133.3 (d, $^3J_{CP}$ = 3.0 Hz), 136.8 (d, $^2J_{CP}$ = 25.1 Hz), 137.3 (d, $^2J_{CP}$ = 28.7 Hz), 138.32 (d, $^1J_{CP}$ = 9.7 Hz), 138.4 (d, $^1J_{CP}$ = 9.8 Hz), 147.7 (s), 191.8 ppm (s). EI MS: m/z (relative intensity, %) 537 (100) $[M]^+$, 522 (26), 509 (29), 492 (26), 352 (19), 308 (26), 280 (22), 267 (14), 183 (19), 121 (17), 58 (31). Anal. Calcd for $C_{30}H_{29}FeNOPS$: C, 67.04; H, 5.25; N, 2.61. Found: C, 67.50; H, 5.72; N, 2.70.

Typical Procedure for Immobilization of 3-Aminopropyltrimethoxysilane (APTMS) on Silica Gel. A 5 g portion of 60A silica gel with particle diameter 0.035−0.070 mm was treated with an aqueous solution of HCl at room temperature. The suspension was stirred for 3 h and then filtered and dried under vacuum at 150 °C for 3−4 h. 3-Aminopropyltrimethoxysilane (2 mmol/g of silica gel) dissolved in dry toluene was added to the dried silica gel under an inert atmosphere. The mixture was stirred at 120 °C overnight and then filtered and dried. The unconverted 3-aminopropyltrimethoxysilane was removed by Soxhlet extraction with diethyl ether. The APS-modified silica gel was dried under vacuum for 5 h. Elemental analysis: 5.48% C, 1.54% H, 1.52% N. NH_2 loading: 1.09 mmol/g. BET surface area: 430.75 m^2/g, V_p = 0.532 cm^3/g, d_p = 4.195 nm. ^{13}C CP MAS NMR: δ 8.4 ($SiCH_2$), 24.3 (CH_2), 43.7 ppm (d, $^1J_{CN}$ = 134.3 Hz, CH_2NH_2). ^{29}Si MAS NMR: δ −58.6 (T^2), −66.2 ppm (T^3).

Typical Procedure for Grafting of *rac*-12 to Modified Silica Gel. The compound *rac*-**12** (0.68 g, 1.5 mmol) was added to 1 g of APS-modified silica gel suspended in dry toluene. The mixture was heated to reflux overnight with stirring, and water was removed by using a Dean−Stark apparatus. The modified silica gel was filtered off and washed seven times with 15 mL of boiling THF. The obtained *rac*-**12**-modified silica gel was dried under vacuum. Elemental analysis: 8.41% C, 1.88% H, 1.69% N. Fe loading: 1.21 mmol/g. BET surface area: 411.86 m^2/g, V_p = 0.462 cm^3/g, d_p = 4.020 nm.

X-ray Structure Determinations. Suitable crystals were mounted on a glass needle with perfluoropolyalkyl ether and cooled under a nitrogen stream. Crystallographic measurements were made with a Gemini diffractometer (Agilent Technologies). Data were collected by using monochromated Mo Kα radiation (λ = 71.073 pm). Structure solution was carried out with SIR92.[33] Anisotropic refinement of all non-hydrogen atoms was achieved with SHELXL-97.[33] Hydrogen atoms were calculated for all structures on idealized positions using the riding model. Twin law for *rac*-**3** (at 130 K): −1.00 0.00 0.00; −0.01 1.00 −0.12; 0.00 0.00 −1.00. Twin domain ratio: 0.509(1):0.491(1). ORTEP[34] was used for molecular visualization. Crystal data and details of data collection and refinement are given in Table 6.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text giving detailed assignments of ^1H, $^{31}P\{^1H\}$, $^{13}C\{^1H\}$ NMR, EI MS, and IR spectroscopic data for compounds *rac*-**2**−**3** and *rac*-**6**−**15** and ^1H, $^{31}P\{^1H\}$ NMR and EI MS data of compounds **B**−**D** having a 1,4-phenylene spacer and CIF files giving crystallographic data for *rac*-**3** (measurement at 293 and 130 K), *rac*-**7**, and *rac*-**11**. This material is available free of charge via the Internet at http://pubs.acs.org. CCDC 939444 (*rac*-**3** (at 293 K)), 939445 (*rac*-**3** (at 130 K)), 939446 (*rac*-**7**) and 939447 (*rac*-**11**) also contain supplementary crystallographic data for this paper. These data can be obtained from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

■ AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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