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Thioether-Functionalized Ferrocenyl-bis(phosphonite), Fe{$(C_5H_4)P(–OC_{10}H_6(\mu\text{-}S)C_{10}H_6O–)$}$_2$: Synthesis, Coordination Behavior, and Application in Suzuki-Miyaura Cross-Coupling Reactions

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The thioether-functionalized metalloligand ferrocenyl-bis(phosphonite), $Fe(C_5H_4PR)_2$ (**4**, R = $–OC_{10}H_6(\mu\text{-}S)C_{10}H_6O–$) is synthesized in three steps starting from ferrocene, and its coordination behavior toward various transition-metal derivatives is described. The reactions of **4** with $[Rh(CO)_2Cl]_2$ or $M(COD)Cl_2$ afforded the chelate complexes, *cis*-[Rh(CO)Cl{$Fe(C_5H_4PR)_2$-$\kappa P,\kappa P$}] (**5**) or *cis*-[MCl_2{$Fe(C_5H_4PR)_2$-$\kappa P,\kappa P$}] (**6**, M = Pd^{II}; **7**, M = Pt^{II}), respectively. However, treatment of **4** with CuX (X = Cl, Br, and I) produces binuclear complexes, [$Cu_2(\mu\text{-}X)_2$(MeCN){$Fe(C_5H_4PR)_2$-$\kappa P,\kappa P$}] (**8**, X = Cl; **9**, X = Br; **10**, X = I) where the sulfur atom on one side of the ligand is involved in a weak interaction with the copper center. Reaction of **4** with 1 equiv of $Ag(PPh_3)OTf$ gives the mononuclear chelate complex [$Ag(OTf)PPh_3${$Fe(C_5H_4PR)_2$-$\kappa P,\kappa P$}] (**11**), whereas treatment with 2 equiv of $AuCl(SMe_2)$ produces the dinuclear gold complex [Au(Cl){$Fe(C_5H_4PR)_2$-$\kappa P,\kappa P$}Au(Cl)] (**12**). The crystal structures of **10** and **12** are reported, where a strong metallophilic interaction is observed between the closed-shell metal centers. The palladium complex **6** catalyzes the Suzuki cross-coupling reactions of aryl bromides with phenylboronic acid with excellent turnover numbers (TON up to 1.36×10^5).

Introduction

Metal-containing ligands, particularly those based on the ferrocene scaffold, have played important roles in catalysis and material science[1] and also in medicinal applications.[2] Ferrocenyl-phosphine ligands are able to form complexes with transition metals in a variety of coordination geometries and oxidation states, which have proven to be efficient catalysts for many organic transformations.[3] Several ferrocenyl-phosphines such as monophosphines,[4] diphosphines (1,1′-, 1,2-, 1,3-disubstitution),[5] polyphosphines[6] with different steric and electronic properties, and also chiral ferrocenyl ligands[7] have been well-studied and have shown good catalyst activity. In contrast, the readily modifiable ferrocenyl-phosphonite or -phosphite derivatives have been much-less explored although they offer an attractive alternative to ferrocenyl-phosphine ligands. Recently, Reetz and co-workers and Pastor and co-workers have reported[8] the

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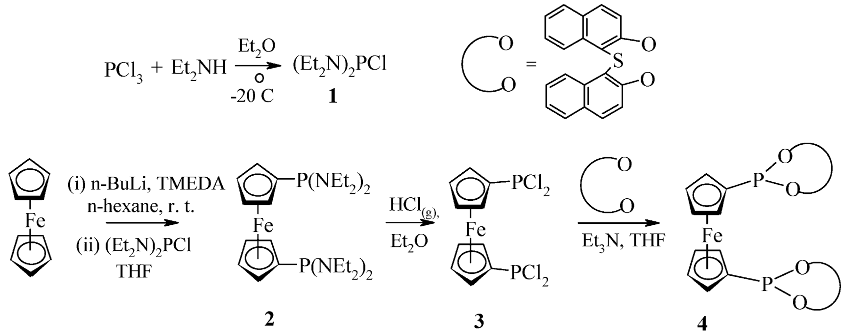
Scheme 1



synthesis of ferrocenyl-bis(phosphonites) containing sterically congested BINOL and tetralkyl-substituted dibenzo[d,f]-[1,3,2]-dioxaphosphepin ring systems, which are highly efficient catalysts in hydrogenation and cross-coupling reactions.

Ferrocenyl-bis(phosphines) or -bis(phosphonites) containing hemilabile backbones such as P,N−[4c,9] P,O−[4a,b,10] compounds have been found to show high activity in several catalytic processes, and their reactivity offers interesting structural possibilities. Despite the considerable current interest in the chemistry of mixed-donor ferrocenyl functional ligands and the catalytic properties of their metal complexes, there are very few reports of ferrocene-based P,S-donor ligands.[11] In our recent work on mesocyclic-thioether-phosphonites, we observed sulfur → phosphorus coordination that influences the coordinating ability and also the geometry of the phosphorus atoms. In this context, we sought to make more derivatives to examine their coordination behavior and catalytic properties. In view of this and as a part of our interest in designing new inexpensive ligands and studying their coordination behavior[12] and catalytic applications,[13] we report on the synthesis and characterization of a new type of mixed P,S-ferrocenyl ligand and its coordination behavior toward various transition-metal derivatives. The palladium(II) complex of this ligand exhibits excellent catalytic activity in the Suzuki−Miyaura cross-coupling reaction.

Results and Discussions

Ligand Synthesis. The bis(diethylamino)chlorophosphine, $(Et_2N)_2PCl$ (**1**), was prepared from the reaction of PCl_3 with 4 equiv of diethylamine at −20 °C by a modification of the published procedure.[14] The ferrocenyl derivatives $Fe(C_5H_4P(NEt_2)_2)_2$ (**2**) and $Fe(C_5H_4PCl_2)_2$ (**3**) were also prepared in improved yield by a modification of the published procedure.[8a,15] The ferrocenyl-bis(phosphonite), $Fe(C_5H_4PR)_2$ ($R = -OC_{10}H_6(\mu\text{-}S)C_{10}H_6O-$) (**4**), was synthesized by the reaction of

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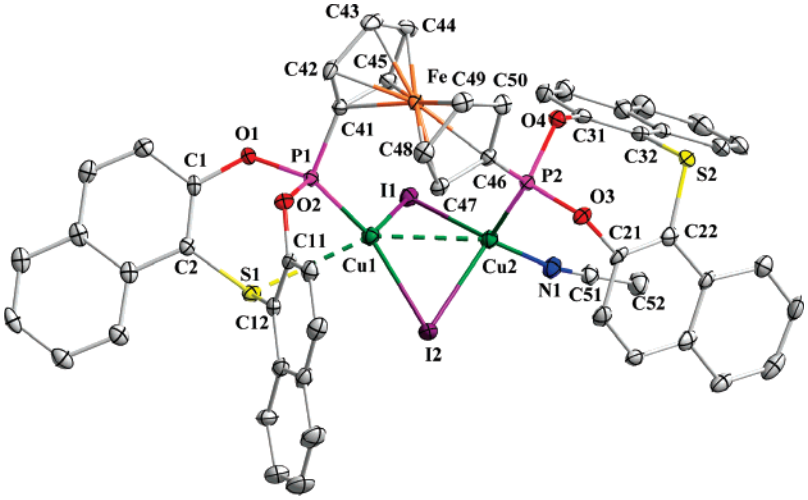

Figure 1. Molecular structure of **10**. For clarity, all of the hydrogen atoms have been omitted.

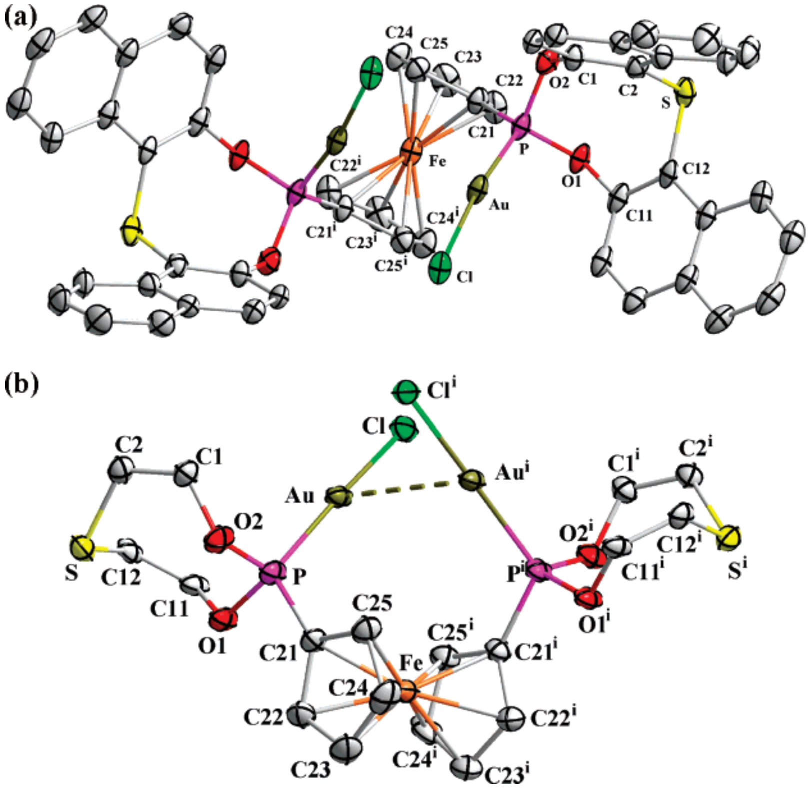

Figure 2. (a) Molecular structure of **12**. For clarity, all of the hydrogen atoms have been omitted. (b) Core view of **12** showing Au−Au aurophillic interaction.

thiobis(2,2′-naphthol) with **3** in the presence of an excess of triethylamine at −15 °C (Scheme 1). Bisphosphonite **4** is a dark-orange colored solid, which is moderately stable in air. The ^{31}P NMR spectrum of **4** consists of a singlet at 175.2 ppm, and the ^{1}H NMR spectrum shows two broad singlets at 4.83 and 4.77 ppm for the protons of the ferrocenyl group.

Metal Complexes. The reaction of ferrocenyl-bis(phosphonite) **4** with $[Rh(CO)_2Cl]_2$ in a 2:1 molar ratio gives the mononuclear chelate complex, *cis*-$[Rh(CO)Cl\{Fe(C_5H_4PR)_2\text{-}\kappa P,\kappa P\}]$ (**5**), in good yield. The IR spectrum of **5** shows a strong CO absorption at 2031 cm^{-1}, which clearly indicates the trans disposition of the CO ligand to one of the phosphorus atoms rather than to chlorine.[16] The ^{31}P NMR spectrum of **5** shows two doublets centered at 180.1 and 140.2 ppm due to the presence of two magnetically nonequivalent phosphorus atoms. The corresponding $^{1}J_{\mathrm{RhP}}$ coupling constants are 177 and 145 Hz, respectively. The $^{2}J_{\mathrm{PP}}$ coupling constant is 33 Hz. Because the carbon monoxide is a good π acceptor, the upfield shift at δ 140.2 ($^{1}J_{\mathrm{Rh-P}} = 145$ Hz) is assigned to the phosphorus atom trans to the carbon monoxide, and the downfield shift at δ 180.1 ($^{1}J_{\mathrm{RhP}} = 177$ Hz) is assigned to the phosphorus atom trans

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Table 1. Crystallographic Data for **10** and **12**

	10	12
formula	$C_{50}H_{32}I_2O_4P_2S_2FeCu_2.(MeCN)_2$	$C_{50}H_{32}Au_2Cl_2FeO_4P_2S_2$
fw	1341.7	1343.5
cryst syst	triclinic	monoclinic
cryst size (mm^3)	0.06 × 0.08 × 0.13	0.08 × 0.12 × 0.12
space group	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)
a (Å)	11.356(1)	18.585(1)
b (Å)	12.034(1)	9.683(6)
c (Å)	19.243(2)	24.923(2)
α (deg)	86.241(1)	90
β (deg)	77.666(1)	103.520(1)
γ (deg)	74.859(1)	90
V (Å^3)	2479.7(4)	4360.7(5)
Z	2	4
ρ_{calcd} (g cm^{-3})	1.810	2.046
μ (Mo Kα), (mm^{-1})	2.585	7.380
F (000)	1327	2576
T (K)	100	100
$\theta_{min-max}$ (deg)	2.0, 28.4	2.3, 28.3
GOF (F^2)	1.04	1.08
R1^a	0.0450	0.0330
wR2^b	0.1024	0.0756

^{a} $R1 = \sum|F_o| - |F_c|/\sum|F_o|$. ^{b} $wR2 = \{\sum w[(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Table 2. Selected Bond Distances (Angstroms) and Bond Angles (Degrees) for **10** and **12**

10		12	
I1−Cu1	2.581(7)	Au−Cl	2.284(1)
I1−Cu2	2.723(7)	Au−P	2.202(1)
I2−Cu1	2.565(7)	Fe−C21	2.044(4)
I2−Cu2	2.686(7)	Fe−C22	2.049(5)
Cu1−P1	2.185(1)	Fe−C23	2.049(5)
Cu2−P2	2.218(1)	Fe−C24	2.054(5)
Cu2−N1	1.994(4)	Fe−C25	2.042(5)
Fe−C41	2.028(5)	P−O1	1.608(3)
Fe−C42	2.044(5)	P−O2	1.610(3)
Fe−C43	2.053(6)	P−C21	1.755(4)
Fe−C44	2.056(6)	S−C2	1.792(4)
Fe−C45	2.032(5)	S−C12	1.783(6)
P1−C41	1.773(4)		
P2−C46	1.772(5)		
Cu1...S1	2.979(1)		
Cu1−I1−Cu2	60.91(2)	Cl−Au−P	170.95(4)
Cu1−I2−Cu2	61.61(2)	C21−Fe−C22	40.75(2)
I1−Cu1−I2	108.55(2)	C21−Fe−C23	68.29(2)
I1−Cu1−P1	117.87(4)	C21−Fe−C25^i	111.73(2)
I2−Cu1−P1	132.52(4)	C21−Fe−C22^i	164.08(2)
I1−Cu2−I2	101.15(2)	Au−P−O1	111.76(1)
I1−Cu2−P2	122.37(4)	Au−P−O2	116.27(1)
I1−Cu2−N1	98.12(1)	Au−P−C21	119.71(1)
I2−Cu2−P2	110.34(4)	O1−P−C21	100.66(2)
P2−Cu2−N1	112.76(1)	O1−P−O2	105.19(2)
C41−Fe−C42	41.36(2)	C2−S−C12	99.23(2)
C41−Fe−C43	68.54(2)		
C41−Fe−C47	108.57(2)		
C41−Fe−C50	164.70(18)		
Cu1−P1−C41	116.13(2)		
O2−P1−C41	102.17(2)		
O1−P1−C41	98.28(2)		
Cu2−P2−C46	126.61(2)		
O3−P2−C46	96.5(2)		
O4−P2−C46	97.96(2)		

to the chlorine.[16] Treatment of ligand **4** with M(COD)Cl_2 (M = Pd^{II} or Pt^{II}) in dichloromethane produce the complexes, [$MCl_2\{Fe(C_5H_4PR)_2$-$\kappa P,\kappa P\}$] (**6**, M = Pd^{II}; **7**, M = Pt^{II}). Palladium **6** was precipitated out within 20 min from the reaction solution, whereas platinum **7** was crystallized from the reaction solution at room temperature. The ^{31}P NMR spectra of **6** and **7** show single resonances at 94.8 and 76.7 ppm, respectively, with the platinum complex showing satellite peaks with a $^1J_{PtP}$ coupling of 4476 Hz. This high value of the Pt−P coupling constant signifies the mutual cis orientation of the phosphorus atoms around the platinum center. In the ^{1}H NMR spectra, two broad singlets are observed in the region 4.47−4.75 ppm for the ferrocenyl protons in both of the complexes.

The reaction of bis(phosphonite) **4** with an excess of CuX (X = Cl, Br, I) in a dichloromethane/acetonitrile mixture afforded the halide-bridged binuclear complexes, [$Cu_2(\mu$-$X)_2$-(MeCN)$\{Fe(C_5H_4PR)_2$-$\kappa P,\kappa P\}$] (**8**, X = Cl; **9**, X = Br; **10**, X = I) in good yield as dark-orange crystals. The ^{31}P NMR spectra of **8**−**10** show at room temperature as well as at 0 °C only broad singlets at 139.6, 139.3, and 138.4 ppm, respectively. The ^{1}H NMR spectra show two singlets in the region 4.97−5.26 ppm for the ferrocenyl protons and sharp singlets around 2.07−2.49 ppm for the protons of a coordinated acetonitrile ligand. Although the X-ray structure of **10** shows two different environments for copper atoms, the ^{31}P NMR data suggests that the acetonitrile probably does disrupt the thioether−copper interaction and that it does so very rapidly on the NMR time scale and exchanges itself between the two copper centers. Similarly, treatment of **4** with 1 equiv of Ag(PPh_3)OTf afforded the mononuclear chelate complex [Ag(OTf)$PPh_3\{Fe(C_5H_4PR)_2$-$\kappa P,\kappa P\}$] (**11**). The ^{31}P NMR spectrum of **11** shows two doublets centered at 162.4 ppm with Ag−P couplings of 361 ($^1J(^{109}$AgP)) and 312 Hz ($^1J(^{107}$AgP)) for the phosphonite phosphorus and a broad singlet at 11.6 ppm for PPh_3. The resonance for the PPh_3 group was too broad to obtain values for couplings with the ^{107}Ag and ^{109}Ag nuclei. The dinuclear gold complex [Au(Cl)$\{Fe(C_5H_4PR)_2$-$\kappa P,\kappa P\}$Au(Cl)] (**12**) was obtained by the reaction of **4** with 2 equiv of AuCl(SMe_2) in dichloromethane at room temperature. The ^{31}P NMR spectrum of **12** shows a singlet at 142.7 ppm, and the ^{1}H NMR spectrum shows two singlets at 5.50 and 5.31 ppm for the ferrocenyl protons. The proposed formulations for the complexes described above are further supported by elemental analyses and by single-crystal structure determinations for **10** and **12**.

Molecular Structures of 10 and 12. Perspective views of the molecular structures of **10** and **12** with atom-numbering schemes are shown in Figures 1 and 2, respectively. The crystallographic data and the details of the structure determinations are given in Table 1 and selected bond lengths and bond angles are listed in Table 2.

10 is dinuclear with both the iodine atoms and the bis(phosphonite) ligand bridging the two copper atoms. One of the copper atoms is tetra-coordinated, being bound to one phosphorus atom, two iodine atoms, and one acetonitrile ligand. The other copper atom is best considered to be pseudo tetra-coordinated because, in addition to coordination by the other phosphorus atom and the two iodine atoms, there is a weak interaction with the sulfur atom as indicated by the S1···Cu1 distance (2.979(1) Å), which is less than the sum of the van der Waals radii for copper and sulfur (3.20 Å).[17] The Cu_2I_2 core adopts a butterfly shape with the iodine atoms at the wing tips, as indicated by the Cu−I−Cu angles [Cu1−

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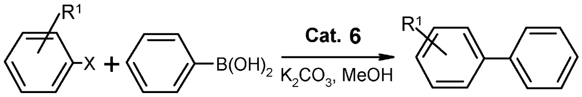
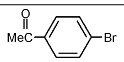
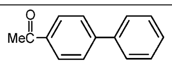
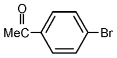
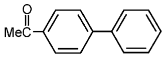
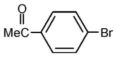
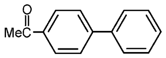
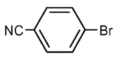
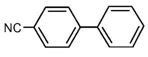
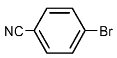
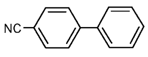
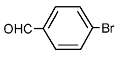
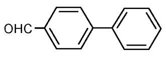
Table 3. Suzuki Cross-Coupling of Aryl Halides with Phenyl Boronic Acid[a]



Entry	Aryl halide	Amount of Cat. (mol %)	Time (h)	Product	Conv. (%)[b]	TON
1		0.05	2		100	2000
2		0.005	12		98	19,600
3		0.0005	24		45	90,000
4		0.005	2		99	19,800
5		0.0005	24		68	1,36,000
6		0.005	24		86	17,200

[a] Aryl halide (0.5 mmol), phenyl boronic acid (0.75 mmol), K_2CO_3 (1 mmol), MeOH (5 mL), at 60 °C. [b] Conversion to coupled product determined by GC, based on aryl halides; average of two runs.

I1−Cu2 = 60.91(2); Cu1−I2−Cu2 = 61.61(2)°]. The four Cu−I bond lengths (Table 2) differ significantly from one another with each copper atom forming a long and a short Cu−I bond. The distance between the two copper centers is 2.691 Å, which indicates the presence of a ligand-supported Cu⋯Cu interaction.[18] The Cu−P bond lengths (Cu1−P1 = 2.185(1), Cu2−P2 = 2.218(1) Å) are slightly shorter than the corresponding distances observed in the analogous complex, $[Cu(\mu\text{-}I)(dppf\text{-}P,P')]_2$ (Cu−P = 2.28(1), 2.286(8) Å), where dppf chelates the copper centers.[19] The bond angles around Cu(1) and Cu(2) range from 108.55(2) to 132.52(4) and 98.13(1) to 122.37(4)°, respectively, indicating the distorted-tetrahedral environment around copper. One of the eight-membered rings containing phosphorus and sulfur is in an anti chairlike conformation, where the sulfur atom remains away from the copper center, whereas the other eight-membered ring is in a syn boatlike conformation, and its sulfur atom shows a coordinative interaction toward the copper center. Previously, binuclear copper iodide complexes of bis(phosphine)s crystallized from solvent systems containing acetonitrile generally have been found to adopt tetrahedral geometries at both copper centers due to the coordination of acetonitrile at both metals.[20] However, in this complex, the coordinative interaction of one thioether moiety with the adjacent copper atom is evidently strong enough to prevent displacement by acetonitrile.

12 has crystallographically imposed 2-fold rotation symmetry with the 2-fold axis passing through the iron atom and the midpoint of the Au1−Au2 vector. The bis(phosphonite) ligand coordinates the metal centers in an open bridging mode with Au−P and Au−Cl bond distances of 2.202(1) and 2.284(1) Å, respectively, which are close to those found in the similar structure of $[Au_2Cl_2(\mu\text{-dppf})]$ (Au−P = 2.226(1) and Au−Cl = 2.282(1) Å).[21] The P−Au−Cl bond angle, 170.95(4)°, is significantly distorted from the expected linear geometry. This may be due to packing interactions because the chlorine atom makes contacts of 2.61 Å with H23 (at $-x$, $-1 + y$, $^1/_2 - z$) and of 2.69 Å with H15 (at $-x$, $1 - y$, $-z$), both of which would be even shorter were the angle to be more linear. The cyclopentadienyl rings adopt an eclipsed conformation. Both the eight-membered rings containing phosphorus and sulfur are in an anti chairlike conformation, where the sulfur atom remains too far from the gold centers for there to be any sulfur-to-gold interactions. This contrasts with what was found previously for complexes of related bis(phosphonite) ligands,[12d,13e] where these eight-membered rings adopted syn boat conformations. The shortest Fe−Au distance is 4.179 Å, indicating that there is no Fe- - -Au interaction. Both of the gold centers are on same side, and there appears to be an aurophilic interaction because the Au⋯Au contact distance is 3.175 Å, which falls within the range of Au−Au distances (2.7−3.7 Å) reported for several gold complexes.[22] These metallophilic interactions in **10** and **12** are due to the

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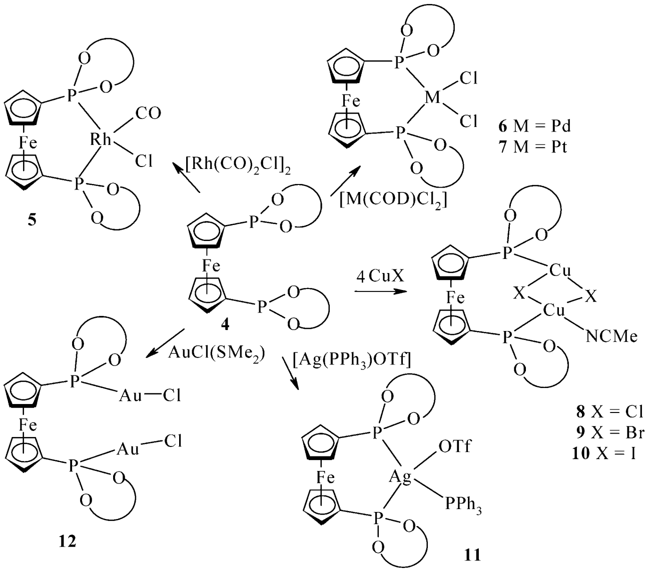
Scheme 2



combination of correlation and relativistic effects with added ionic contributions.[18a,23]

Suzuki Cross-Coupling Reactions using Palladium Complex. The palladium complex **6** catalyzes the cross-coupling reactions of aryl bromides and phenylboronic acid, to yield the desired biaryls in high yields at 60 °C using methanol as solvent (Table 3). Only electron-poor, highly reactive aryl bromides were investigated containing electron-withdrawing π-acceptor substituents in the para position. Using these catalysts, high yields are maintained from catalyst loadings of 0.05 to 0.0005 mol%. In the case of the coupling of 4-bromobenzonitrile with phenyl boronic acid, the highest TON observed is 1.36×10^5 (entry 5). The activity of catalyst **6** is found to be superior to that of the most commonly used catalysts, $PdCl_2$(dppf) and $Pd_2(dba)_3$/(dppf), which catalyze the reaction between 4-bromoacetophenone and phenylboronic acid in toluene at 70 °C in 94 and 86% yields, respectively.[24]

The homogeneous nature of the catalysis was checked by the classical mercury test. Addition of a drop of mercury to the reaction mixtures did not affect the activity of the catalyst, thus showing them to be truly homogeneous systems.[25]

Conclusion

The ferrocenyl-bis(phosphonite) containing the hemilabile thioether-dinaphthyl backbone was synthesized from ferrocene and bis(2-hydroxy-1-napthyl)sulfide. Ferrocenyl-bis(phosphonite), (**4**), shows versatile coordination modes toward various transition-metal derivatives. The bis(phosphonite) forms chelate complexes with rhodium(I), paladium(II), and platinum(II) metals, whereas with copper(I) derivatives, bridged binuclear complexes are obtained. In these binuclear copper complexes, one of the copper centers is coordinated to the sulfur in the ligand backbone, whereas an acetonitrile ligand occupies the corresponding coordination site on the other copper center. Both binuclear complexes **10** and **12** show strong metallophilic interactions between the closed-shell metal centers, which make them ideal candidates for luminescence studies. The palladium complex of the ferrocenyl-bis(phosphonite) is an effective catalyst for the Suzuki cross-coupling reaction (TON up to 1.36×10^5) and is found to be superior to most of the commonly used catalysts. The catalytic activity of this palladium complex toward aryl chlorides and other coupling reactions (e.g., Heck cross-coupling, amination reactions) of different aryl halides is under progress in our laboratory and will be reported in due course.

Experimental Section

All of the experimental manipulations were carried out under an atmosphere of dry nitrogen or argon using Schlenk techniques. Solvents were dried and distilled prior to use by conventional methods. Bis(2-hydroxy-1-napthyl)sulfide,[26] $(Et_2N)_2PCl$,[14] $[Rh(CO)_2Cl]_2$,[27] $M(COD)Cl_2$, (M = Pd, Pt),[28] CuX (X = Cl, Br),[29] $Ag(PPh_3)OTf$,[30] and $AuCl(SMe_2)$[31] were prepared according to the published procedures. Other reagents were obtained from commercial sources and used after purification. The ^1H and $^{31}P\{^1H\}$ NMR (δ in ppm) spectra were obtained on a Varian VRX 400 spectrometer operating at frequencies of 400 and 162 MHz, respectively. The spectra were recorded in $CDCl_3$ (or DMSO-d_6) solutions with $CDCl_3$ (or DMSO-d_6) as an internal lock; TMS and 85% H_3PO_4 were used as internal and external standards for ^1H and $^{31}P\{^1H\}$ NMR, respectively. Positive shifts lie downfield of the standard in all of the cases. Infrared spectra were recorded on a Nicolet Impact 400 FTIR instrument as a KBr disk. Microanalyses were carried out on a Carlo Erba (Model 1106) elemental analyzer. Q-Tof Micromass experiments were carried out using Waters Q-Tof micro(YA-105). Melting points of all of the compounds were determined on a Veego melting point apparatus and are uncorrected. GC analyses were performed on a PerkinElmer Clarus 500 GC fitted with a FID detector and a packed column.

Synthesis of Bis(diethylamino)chlorophosphine, $(Et_2N)_2PCl$ (1). A solution of diethylamine (23.7 mL, 228.9 mmol) in diethyl ether (70 mL) was added dropwise to a solution of PCl_3 (5 mL, 57.2 mmol) in diethyl ether (400 mL) at −20 °C. The solution was slowly warmed to room temperature and stirred for an additional 12 h. The suspension obtained was filtered through celite to remove $Et_2NH{\cdot}HCl$, and the solvent was removed by distillation. The resulted yellow liquid was transferred to a small round-bottom flask and distilled under vacuum to obtain product **1** as a colorless liquid.

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Yield: 73% (17.6 g). ^{1}H NMR (400 MHz, CDCl$_3$): δ 3.17 (quartet, 8H, CH$_2$), 1.14 (t, 12H, CH$_3$). ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$): δ 158.7 (s).

Synthesis of Fe{C$_5$H$_4$P(NEt$_2$)$_2$}$_2$ (2). A mixture of *n*-BuLi (37 mL, 59.1 mmol, 1.6 M in hexane) and TMEDA (5.85 mL, 59.1 mmol) in *n*-hexanes (30 mL) was added dropwise to a solution of ferrocene (5 g, 26.9 mmol) also in *n*-hexanes (120 mL) at room temperature. After stirring for 12 h, (Et$_2$N)$_2$PCl (11.3 g, 53.8 mmol) in THF (40 mL) was added dropwise to the resulting orange-colored suspension at −78 °C. The reaction mixture was warmed to room temperature and stirred for an additional 10 h. The suspension obtained was filtered through celite to remove LiCl. The solution was concentrated to dryness to give a pasty crude product of **2**. Yield: 80% (11.5 g). ^{1}H NMR (400 MHz, CDCl$_3$): δ 4.82 (s, 4H, *Fc*), 4.76 (s, 4H, *Fc*), 3.14 (quartet, 16H, CH_2, $^{3}J_{\mathrm{HH}}$ = 7.0 Hz), 1.11 (t, 24H, CH_3, $^{3}J_{\mathrm{HH}}$ = 7.0 Hz). ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$): δ 88.7 (s).

Synthesis of Fe{C$_5$H$_4$PCl$_2$}$_2$ (3). A solution of **2** (11.0 g, 20.6 mmol) in diethyl ether (250 mL) was cooled to −78 °C and saturated with anhydrous HCl(g) for 2 h with continuous stirring. The reaction mixture was then allowed to warm to room temperature and was stirred for an additional 12 h. The resulted suspension was filtered through celite to remove Et$_2$NH·HCl. The solvent was evaporated under vacuum to obtain product **3** as an orange-colored solid. Yield: 92% (7.34 g). ^{1}H NMR (400 MHz, CDCl$_3$): δ 4.72 (s, 8H, *Fc*). ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$): δ 160.7 (s).

Synthesis of Fe(C$_5$H$_4$PR)$_2$ (4, R = −OC$_{10}$H$_6$(μ-S)C$_{10}$H$_6$O−). A solution of **3** (1 g, 2.58 mmol) in THF (30 mL) was added dropwise to the mixture of bis(2-hydroxy-1-napthyl)sulfide (1.64 g, 5.16 mmol) and Et$_3$N (1.62 mL, 11.6 mmol) in THF (50 mL) at −15 °C. The reaction mixture was warmed to room temperature and stirred for 12 h. The solvent was removed under vacuum, and the residue obtained was redissolved in toluene (20 mL) and filtered through celite to remove Et$_3$N·HCl. The orange-colored solution obtained was concentrated to a small volume and cooled to −25 °C to give an analytically pure product of **4** as orange crystals. Yield: 77% (1.75 g). Mp: 168−170 °C. Anal. Calcd for C$_{50}$H$_{32}$O$_4$P$_2$S$_2$Fe: C, 68.34; H, 3.67; S, 7.29. Found: C, 68.29; H, 3.63; S, 7.22. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.79 (d, 4H, *Ar*, $^{3}J_{\mathrm{HH}}$ = 8.4 Hz), 7.75 (d, 4H, *Ar*, $^{3}J_{\mathrm{HH}}$ = 8.0 Hz), 7.70 (d, 4H, *Ar*, $^{3}J_{\mathrm{HH}}$ = 8.8 Hz), 7.59 (t, 4H, *Ar*, $^{3}J_{\mathrm{HH}}$ = 7.2 Hz), 7.41 (t, 4H, *Ar*, $^{3}J_{\mathrm{HH}}$ = 7.2 Hz), 7.20 (d, 4H, *Ar*, $^{3}J_{\mathrm{HH}}$ = 9.2 Hz), 4.83 (br s, 4H, *Fc*), 4.77 (br s, 4H, *Fc*). ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$): δ 175.2 (s).

Synthesis of [Rh(CO)Cl{Fe(C$_5$H$_4$PR)$_2$-$\kappa P,\kappa P$}] (5). A solution of **4** (0.068 g, 0.077 mmol) in THF (10 mL) was added dropwise to a solution of [Rh(CO)$_2$Cl]$_2$ (0.015 g, 0.039 mmol) also in THF (5 mL) at room temperature, and the reaction mixture was stirred for 2 h. The orange-colored solution obtained was concentrated, and petroleum ether (6 mL) was added to precipitate out an orange-colored product, which was then filtered off and dried under vacuum. Yield: 90% (0.072 g). Mp: 182 °C (dec). Anal. Calcd for C$_{51}$H$_{32}$ClO$_5$P$_2$S$_2$FeRh: C, 58.61; H, 3.09; S, 6.14. Found: C, 58.57; H, 3.05; S, 6.09. IR (KBr disc, cm^{-1}): ν_{CO}, 2031. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.70 (d, 4H, *Ar*, $^{3}J_{\mathrm{HH}}$ = 8.4 Hz), 8.12 (d, 4H, *Ar*, $^{3}J_{\mathrm{HH}}$ = 8.4 Hz), 7.91 (d, 4H, *Ar*, $^{3}J_{\mathrm{HH}}$ = 7.2 Hz), 7.29−7.71 (m, 12H, *Ar*), 5.07 (br s, 4H, *Fc*), 4.86 (br s, 4H, *Fc*). ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$): δ 180.1 (br d, $^{1}J_{\mathrm{RhP}}$ = 177 Hz), 140.2 (br d, $^{1}J_{\mathrm{RhP}}$ = 145 Hz).

Synthesis of [PdCl$_2${Fe(C$_5$H$_4$PR)$_2$-$\kappa P,\kappa P$}] (6). A solution of Pd(COD)Cl$_2$ (0.03 g, 0.105 mmol) in dichloromethane (6 mL) was added dropwise to a dichloromethane (10 mL) solution of **4** (0.092 g, 0.105 mmol) at room temperature, and the reaction mixture was stirred for 30 min. The orange-colored precipitate formed was filtered off and dried under vacuum. Yield: 83% (0.091 g). Mp: 172−174 °C (dec). Anal. Calcd for C$_{50}$H$_{32}$Cl$_2$O$_4$P$_2$S$_2$FePd: C, 56.87; H, 3.05; S, 6.07. Found: C, 56.79; H, 2.99; S, 6.01. ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ 8.51 (d, 4H, *Ar*, $^{3}J_{\mathrm{HH}}$ = 8.0 Hz), 7.73 (d, 8H, *Ar*, $^{3}J_{\mathrm{HH}}$ = 8.8 Hz), 7.39 (t, 4H, *Ar*, $^{3}J_{\mathrm{HH}}$ = 7.2 Hz), 7.24 (t, 4H, *Ar*, $^{3}J_{\mathrm{HH}}$ = 7.6 Hz), 7.18 (d, 4H, *Ar*, $^{3}J_{\mathrm{HH}}$ = 9.2 Hz), 4.52 (br s, 4H, *Fc*), 4.47 (br s, 4H, *Fc*). ^{31}P{^{1}H} NMR (162 MHz, DMSO-*d*$_6$): δ 94.8 (s).

Synthesis of [PtCl$_2${Fe(C$_5$H$_4$PR)$_2$-$\kappa P,\kappa P$}] (7). A solution of Pt(COD)Cl$_2$ (0.03 g, 0.08 mmol) in dichloromethane (6 mL) was added dropwise to a dichloromethane (10 mL) solution of **4** (0.07 g, 0.08 mmol), and the reaction mixture was stirred for 3 h. The solution was concentrated and layered with petroleum ether (1 mL), which gave a crystalline product (**7**) on slow evaporation. Yield: 85% (0.078 g). Mp: 216−218 °C (dec). Anal. Calcd for C$_{50}$H$_{32}$Cl$_2$O$_4$P$_2$S$_2$FePt: C, 52.46; H, 2.82; S, 5.60. Found: C, 52.39; H, 2.78; S, 5.57. ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ 8.52 (d, 4H, *Ar*, $^{3}J_{\mathrm{HH}}$ = 8.8 Hz), 7.73 (d, 8H, *Ar*, $^{3}J_{\mathrm{HH}}$ = 8.8 Hz), 7.39 (t, 4H, *Ar*, $^{3}J_{\mathrm{HH}}$ = 7.6 Hz), 7.23 (t, 4H, *Ar*, $^{3}J_{\mathrm{HH}}$ = 7.6 Hz), 7.19 (d, 4H, *Ar*, $^{3}J_{\mathrm{HH}}$ = 8.4 Hz), 4.75 (br s, 4H, *Fc*), 4.49 (br s, 4H, *Fc*). ^{31}P{^{1}H} NMR (162 MHz, DMSO-*d*$_6$): δ 76.7 (s), $^{1}J_{\mathrm{PtP}}$ = 4476 Hz.

Synthesis of [Cu$_2$(μ-Cl)$_2$(MeCN){Fe(C$_5$H$_4$PR)$_2$-$\kappa P,\kappa P$}] (8). A solution of CuCl (0.032 g, 0.323 mmol) in acetonitrile (5 mL) was added dropwise to a solution of **4** (0.071 g, 0.081 mmol) in dichloromethane (10 mL) at room temperature, and the reaction mixture was stirred for 3 h. The solution obtained was concentrated under vacuum to give a yellow-colored crystalline product (**8**) upon standing at room temperature. Yield: 79% (0.071 g). Mp: 168−170 °C (dec). Anal. Calcd for C$_{52}$H$_{35}$Cl$_2$NO$_4$P$_2$S$_2$FeCu$_2$: C, 55.87; H, 3.16; N, 1.25; S, 5.74. Found: C, 55.79; H, 3.08; N, 1.21; S, 5.68. ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ 8.77 (d, 4H, *Ar*, $^{3}J_{\mathrm{HH}}$ = 8.0 Hz), 8.00 (d, 8H, *Ar*, $^{3}J_{\mathrm{HH}}$ = 8.4 Hz), 7.35−7.71 (m, 12H, *Ar*), 5.25 (s, 4H, *Fc*), 4.98 (s, 4H, *Fc*), 2.49 (s, 3H, CH_3CN). ^{31}P{^{1}H} NMR (162 MHz, DMSO-*d*$_6$): δ 139.6 (s).

Synthesis of [Cu$_2$(μ-Br)$_2$(MeCN){Fe(C$_5$H$_4$PR)$_2$-$\kappa P,\kappa P$}] (9). This was synthesized by the procedure similar to that for **8**, using CuBr (0.04 g, 0.278 mmol) and **4** (0.061 g, 0.069 mmol). Yield: 74% (0.062 g). Mp: 220−222 °C (dec). Anal. Calcd for C$_{52}$H$_{35}$Br$_2$NO$_4$P$_2$S$_2$FeCu$_2$: C, 51.76; H, 2.92; N, 1.16; S, 5.31. Found: C, 51.71; H, 2.89; N, 1.13; S, 5.29. ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ 7.92 (d, 4H, *Ar*, $^{3}J_{\mathrm{HH}}$ = 8.0 Hz), 7.14 (t, 8H, *Ar*, $^{3}J_{\mathrm{HH}}$ = 9.2 Hz), 6.68−6.86 (m, 8H, *Ar*), 6.49 (d, 4H, *Ar*, $^{3}J_{\mathrm{HH}}$ = 8.4 Hz), 4.89 (s, 4H, *Fc*), 4.43 (s, 4H, *Fc*), 2.50 (s, 3H, CH_3CN). ^{31}P{^{1}H} NMR (162 MHz, DMSO-*d*$_6$): δ 139.3 (s).

Synthesis of [Cu$_2$(μ-I)$_2$(MeCN){Fe(C$_5$H$_4$PR)$_2$-$\kappa P,\kappa P$}] (10). This was synthesized by the procedure similar to that for **8**, using CuI (0.06 g, 0.315 mmol) and **4** (0.069 g, 0.079 mmol). Yield: 81% (0.083 g). Mp: 208−210 °C (dec). Anal. Calcd for C$_{52}$H$_{35}$I$_2$NO$_4$P$_2$S$_2$FeCu$_2$: C, 48.02; H, 2.71; N, 1.08; S, 4.93. Found: C, 47.98; H, 2.65; N, 1.04; S, 4.83. ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ 8.74 (d, 4H, *Ar*, $^{3}J_{\mathrm{HH}}$ = 8.4 Hz), 7.96−8.01 (m, 8H, *Ar*), 7.69 (t, 4H, *Ar*, $^{3}J_{\mathrm{HH}}$ = 7.2 Hz), 7.53 (t, 4H, *Ar*, $^{3}J_{\mathrm{HH}}$ = 7.2 Hz), 7.36 (d, 4H, *Ar*, $^{3}J_{\mathrm{HH}}$ = 8.8 Hz), 5.26 (s, 4H, *Fc*), 4.99 (s, 4H, *Fc*), 2.07 (s, 3H, CH_3CN). ^{31}P{^{1}H} NMR (162 MHz, DMSO-*d*$_6$): δ 138.4 (s).

Synthesis of [Ag(OTf)PPh$_3${Fe(C$_5$H$_4$PR)$_2$-$\kappa P,\kappa P$}] (11). To a solution of **4** (0.068 g, 0.077 mmol) in dichloromethane (12 mL), Ag(PPh$_3$)OTf (0.04 g, 0.077 mmol) was added, and the reaction mixture was stirred for 4 h. The solution was concentrated and petroleum ether (5 mL) was added to precipitate the pale-yellow product, which was then filtered off and dried under vacuum. Yield: 83% (0.090 g). Mp: 192−194 °C (dec). Anal. Calcd for

$C_{69}H_{47}F_3O_7P_3S_3FeAg$: C, 59.28; H, 3.39; S, 6.88. Found: C, 59.21; H, 3.34; S, 6.81. ^1H NMR (400 MHz, $CDCl_3$): δ 8.44 (d, 4H, *Ar*, $^3J_{HH} = 8.8$ Hz), 7.25−7.66 (m, 20H, *Ar*, 15H, P*Ph*$_3$), 4.62 (s, 4H, *Fc*), 4.50 (s, 4H, *Fc*). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 162.4 (2d, 2P, $^1J(^{109}AgP)$ 361, $^1J(^{107}AgP)$ 312 Hz), 11.6 (br s, 1P, PPh_3).

Synthesis of [{Fe(C$_5$H$_4$PR)$_2$-*κP*,*κP*}Au$_2$Cl$_2$] (12). A solution of $AuCl(SMe_2)$ (0.04 g, 0.136 mmol) in dichloromethane (8 mL) was added dropwise to a solution of **4** (0.06 g, 0.068 mmol) in dichloromethane (10 mL), and the reaction mixture was stirred for 6 h. The yellowish-colored solution was concentrated under vacuum and layered with petroleum ether (1 mL) to give an orange-colored crystalline product of **12** on cooling at −25 °C. Yield: 88% (0.081 g). Mp: 214−216 °C (dec). Anal. Calcd for $C_{50}H_{32}Cl_2O_4P_2S_2FeAu_2$: C, 44.69; H, 2.40; S, 4.77. Found: C, 44.61; H, 2.38; S, 4.72. ^1H NMR (400 MHz, DMSO-d_6): δ 8.97 (d, 4H, *Ar*, $^3J_{HH} = 8.4$ Hz), 8.13 (d, 4H, *Ar*, $^3J_{HH} = 9.2$ Hz), 7.89 (d, 4H, *Ar*, $^3J_{HH} = 8.0$ Hz), 7.58−7.77 (m, 12H, *Ar*), 5.50 (s, 4H, *Fc*), 5.31 (s, 4H, *Fc*). $^{31}P\{^1H\}$ NMR (162 MHz, DMSO-d_6): δ 142.7 (s).

Catalysis. In a two-necked round-bottom flask under an atmosphere of nitrogen was placed the appropriate amount of catalyst solution, and 5 mL of methanol was added to it. The correct amount of catalyst was added as a methanol solution made up by multiple volumetric dilutions of stock solutions. After stirring for 5 min, aryl bromide (0.5 mmol), phenylboronic acid (0.75 mmol), and K_2CO_3 (0.138 g, 1 mmol) were introduced into the reaction flask. The mixture was heated at 60 °C for the required time under an atmosphere of nitrogen (the course of reaction was monitored by GC analysis), following which the solvent was removed under reduced pressure. The residue was diluted with H_2O (8 mL) and Et_2O (8 mL) followed by extraction twice (2 × 6 mL) with Et_2O. The combined organic fractions were dried ($MgSO_4$), stripped of the solvent under vacuum, and the residue redissolved in 5 mL of dichloromethane. An aliquot was taken with a syringe and subjected to GC analysis. Yields were calculated versus aryl bromides or dodecane as an internal standard.

X-ray Crystallography. Crystals of **10** and **12** were mounted in a Cryoloop with a drop of Paratone oil and placed in the cold nitrogen stream of the Kryoflex attachment of the Bruker APEX CCD diffractometer. For each, a full sphere of data was collected using three sets of 400 scans in ω (0.5° per scan) at $\varphi = 0$, 90, and 100° plus two sets of 800 scans in φ (0.45° per scan) at $\omega = -30$ and 210° using the *SMART* software package.[32] The raw data were reduced to F^2 values using the *SAINT+* software,[33] and a global refinement of unit cell parameters using 8200−8700 reflections chosen from the full data set was performed. Multiple measurements of equivalent reflections provided the basis for an empirical absorption correction as well as a correction for any crystal deterioration during the data collection (*SADABS*[34]). The structure of **12** was solved by direct methods, whereas for **10**, the positions of the metal atoms were obtained from a sharpened Patterson function. Both structures were refined by full-matrix least-squares procedures using the *SHELXTL* program package.[35] Hydrogen atoms were placed in calculated positions and included as riding contributions with isotropic displacement parameters tied to those of the attached non-hydrogen atoms.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of **10** and **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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