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Synthesis, Coordination Chemistry, and Catalytic Application of a Novel Unsymmetrical P/O Ferrocenediyl Ligand

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A novel, unsymmetrical 1,1′-disubstituted ferrocenediyl ligand, 1-(diphenylphosphino)-1′-(methoxy)ferrocene (**3**), featuring phosphine and ether substituents has been synthesized via two different routes and structurally characterized. Its coordination chemistry was investigated by reaction with Rh(I), Cu(I), and group 10 metal precursors. With Ni(II) precursors, chelating complexes are formed in high yield, whereas with Pd(II) and Pt(II) precursors, either chelating complexes or monodentate bis ligand complexes with *trans* phosphorus ligation may be formed depending on the reaction conditions and metal precursor employed. A similar monodentate *trans* phosphorus-ligated complex is observed with Rh(I), whereas with Cu(I) precursors, a phosphorus-ligated monodentate bis ligand complex with a coordinated acetonitrile was obtained. Preliminary studies show that **3**, in combination with either Pd(II) or Pd(0) precursors, can act as a catalyst for the Suzuki coupling reaction.

Introduction

Asymmetric, multidentate ligands that are hemilabile in character have found numerous applications in catalysis.[1] Chelating ligands with a ferrocene backbone are of particular interest, and extensive studies into their coordination chemistry and applications have been made.[2,3] While hemilabile P/S,[4] P/O,[5−7] and N/O[8] ligand systems are well-known and important in catalysis, examples of analogous 1,1′-disubstituted *ferrocenes* are rare.[9−17] We have recently demonstrated that the unsymmetrical 1,1′-P/S ferrocenediyl ligand 1-(diphenylphosphino)-1′-(methylthio)ferrocene (**11**) in combination with $Pd_2(dba)_3$ is an active catalyst system for the Suzuki coupling reaction.[18] Although hemilabile P/O ferrocenyl ligands are rare, Buchwald et al. have shown that 1-[2-(diphenylphosphino)ferrocenyl]ethyl methyl ether, [(*rac*)-PPF-OMe], which has 1,2-unsymmetrical substitution, in combination with Pd precursors can catalyze the amination of aryl bromides, iodides, and triflates.[7,19] Ferrocenediyl compounds containing hydroxyl or ether substituents[20,21] and their application in coordination chemistry[22] are scarce: the tendency of hydroxyferrocenes to decompose in air to cyclopentenone species makes their synthesis and handling a challenge. Ferrocenyl ethers, however, are generally more stable, particularly if the isolation of a hydroxyferrocene intermediate is avoided. We have utilized recently developed synthetic methods in the synthesis of a 1,1′-ferrocenediyl P/O ligand, which is described herein

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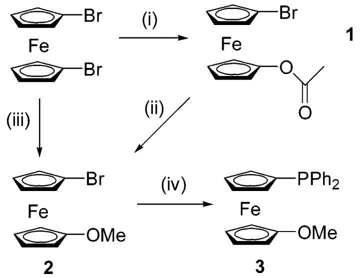
10.1021/om0343768 CCC: $27.50

Scheme 1. Synthesis of Ligand 3[a]



[a] Reagents and conditions: (i) AcOH, Cu_2O cat., MeCN, reflux, 15 h. (ii) NaH, 15-crown-5, MeI, THF, rt, 15 h. (iii) *n*-BuLi, THF, −25 °C, 30 min; TMSOOTMS, −78 °C, 1 h; Me_2SO_4, K_2CO_3, acetone, reflux, 20 h. (iv) *n*-BuLi, THF, −78 °C, 10 min; $ClPPh_2$, rt, 20 h.

together with a study of its coordination chemistry and catalytic efficacy in the Suzuki coupling reaction, highlighting the different properties imparted by an ether—compared to a thioether—substituent (as in **11**). We have recently formed two novel *anionic* 1,1′-ferrocenediyl P/O ligands,[23] and we now report the first example of a *neutral* 1,1′-unsymmetrical P/O ferrocenediyl ligand.

Results and Discussion

Ligand Synthesis. Ligand **3** has been synthesized via two different routes from 1,1′-dibromoferrocene (Scheme 1). Sato et al. have reported the synthesis of 1-(bromo),1′-(stearyloxy)ferrocene, which was achieved by the reaction of 1,1′-dibromoferrocene with stearic acid in the presence of copper(I) oxide in refluxing acetonitrile. (It should be noted that the yield of this reaction was only 13% due to the additional formation of 1,1′-bis(stearyloxy)ferrocene.)[24] In our work, 1-(bromo)-1′-(acetoxy)ferrocene (**1**) was synthesized in 13% yield by the reaction of 1,1′-dibromoferrocene[25] with acetic acid in the presence of copper(I) oxide in refluxing acetonitrile. This reaction is also low yielding due to the formation of 1,1′-bis(acetoxy)ferrocene as a byproduct. Attempts were made to optimize the yield of **1** by varying the amounts of acetic acid and copper(I) oxide and the length of time of reflux, but the maximum yield was always low. A slight improvement in yield was found when the acetic acid was diluted with acetonitrile and added dropwise over a long period of time to help promote monosubstitution. A possible reaction mechanism, proposed by Sato et al.,[26] suggests that the association of copper to the ligand through the bromine and acetate moieties might favor di-substitution, as after one substitution reaction has taken place, the copper center is correctly positioned to catalyze the substitution of the other bromine atom. The ^1H NMR spectrum of **1** shows a singlet corresponding to the methyl group of the acetate. The cyclopentadienyl protons show four pseudo-triplets confirming the unsymmetrical substitution. Reduction of **1** with sodium hydride in the presence of 15-crown-5 and iodomethane yielded 1-(bromo)-1′-(methoxy)ferrocene (**2**).[21] The ^1H NMR spectrum of **2** shows a singlet corresponding to the methyl group of the ether: the proximity to the electronegative oxygen substituent causes a downfield shift compared to **1**. Again, the cyclopentadienyl protons show four pseudo-triplets. The disappointingly low yield of **2** via this route (overall 10% from 1,1′-dibromoferrocene) led us to search for a higher yielding alternative.

The use of bis(trimethylsilyl)peroxide[27] in the preparation of aryl trimethylsilyl ethers,[28] ferrocenyl trimethylsilyl ethers,[29] and ferrocenyl hydroxide derivatives[30] (via hydrolysis) prompted its application in the synthesis of **2**. 1,1-Dibromoferrocene was reacted with 1 equiv of *n*-butyllithium in a cooled THF solution, followed by addition of bis(trimethylsilyl)peroxide. After the reaction mixture had been stirred for 1 h at room temperature, the solvent was removed in vacuo and the residue was redissolved in nitrogen-saturated acetone. Potassium carbonate (to catalyze removal of the trimethylsilyl protecting group) was added, followed by an excess of dimethyl sulfate.[31] After refluxing for 24 h, purification was effected via column chromatography to form **2** in a 56% yield from 1,1-dibromoferrocene.

The conversion of **2** to **3** was completed via the addition of 1 equiv of *n*-butyllithium to a cooled THF solution of **2**, followed by quenching with chlorodiphenylphosphine. The ^1H spectrum of **3** again shows four pseudo-triplets for the cyclopentadienyl protons together with signals due to the methyl and phenyl groups. The $^{31}P\{^1H\}$ spectrum shows a singlet at −16.4 ppm. Crystals of **3** were obtained by slow evaporation from a pentane solution. A single-crystal X-ray analysis showed the complex (Figure 1) to have a gross structure very similar to those of the related unsubstituted,[32] carbox-

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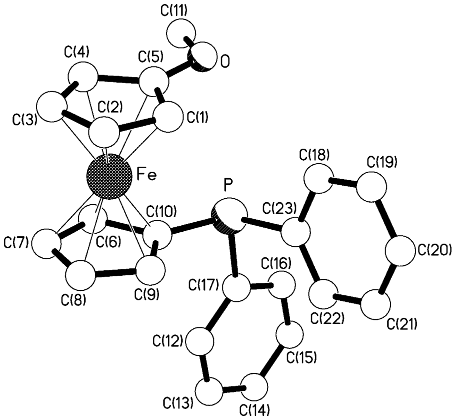
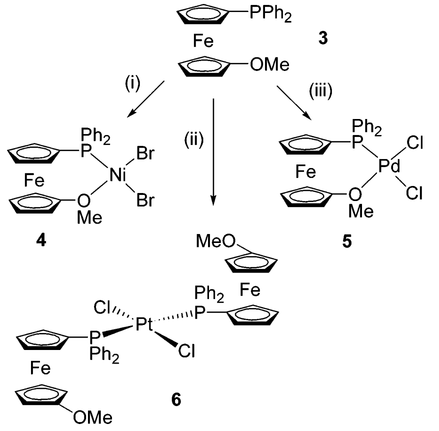


Figure 1. Molecular structure of **3**. Selected bond lengths (Å) and angles (deg): P−C(10) 1.814(3), P−C(17) 1.851(2), P−C(23) 1.857(2), C(10)−P−C(17) 101.62(10), C(10)−P−C(23) 101.40(11), C(17)−P−C(23) 100.32(10).

aldehyde,[33] carboxylic acid,[34] and mercapto,[14] diphenylphosphino analogues. In all of these complexes one of the P−Ph bonds is oriented approximately orthogonally (ca. 88°) to the plane of its associated C_5H_4 ring, while the other is inclined by ca. 15° and angled upward toward the other cyclopentadienyl ring. The relative orientations of the substituents on the two Cp rings appear to be controlled by either intra- or intermolecular interactions. In **3** the cyclopentadienyl rings are inclined by ca. 2° and staggered by ca. 16°, there being a relatively short (2.53 Å) approach of C(18)−H to the methoxy oxygen atom. The angles at phosphorus are all contracted from tetrahedral but do not differ significantly from those observed in, for example, the unsubstituted analogue.[32] The P−Ph bond lengths in **3** are longer than those in the unsubstituted,[32] carboxaldehyde,[33] and carboxylic acid[34] structures but the same as those in the mercapto complex.[14] The P−Cp distance is the same in all of these structures. The only short intermolecular contact of note is between C(8)−H and the C(23) phenyl ring in centrosymmetrically related pairs of molecules; the H⋯π distance is 2.87 Å and the C−H⋯π angle 163°.

Coordination Chemistry. To probe the coordination chemistry of **3**, the ligand was reacted with group 10 metal precursors as shown in Scheme 2. The Ni(II) complex **4** was obtained via the reaction of (1,2-dimethoxyethane)dibromonickel(II) and **3** in CH_2Cl_2. The reaction mixture changed color immediately from pale pink to dark green and was stirred at 35 °C for 24 h, after which time a green precipitate was visible. The solvent was removed in vacuo and the green powder washed with dry hexane. The ^1H NMR showed very broad peaks and could not be properly assigned. The $^{31}P\{^1H\}$ NMR showed a single peak at 29.8 ppm. The broadening of the NMR suggested that the complex was paramagnetic, which is consistent with a tetrahedral geometry at the Ni center. The positive ion FAB mass spectrum did not show the molecular ion but instead a peak for the free ligand (400 amu). However, the microanalysis is consistent with a 1:1 chelate complex. A similar result was obtained upon the reaction of **11** with (1,2-dimethoxyethane)dibromonickel(II).[18] The Pd(II) complex **5** was obtained upon the reaction of dichloro(1,5-cyclooctadiene)palladium(II) dissolved in CH_2Cl_2 with a slight excess of **3** dissolved in toluene. The solution was stirred at room temperature for 20 h, by which time a brown precipitate was visible. The precipitate was filtered and washed with hexane to remove any unreacted ligand, enabling isolation of dichloro[1-(diphenylphosphino)-1′-(methoxy)ferrocene]palladium(II) (**5**) in 70% yield. The ^1H NMR spectrum shows a singlet at 3.71 ppm corresponding to the methoxy group. The peak is shifted downfield compared to the free ligand due to coordination of the oxygen to the metal center. The cyclopentadienyl protons show two poorly resolved multiplets at 4.53 and 4.60 ppm, and the phenyl protons of the PPh_2 group give a multiplet centered at 7.45 ppm. The $^{31}P\{^1H\}$ NMR shows a singlet at 31.9 ppm and indicates a considerable downfield shift compared to the free ligand due to the coordination of the phosphorus to the metal center. The FAB mass spectrum exhibits the molecular ion (578 amu) and the expected fragmentation pattern corresponding to the loss of one chlorine (543 amu) and two chlorines (506 amu).

Scheme 2. Synthesis of Group 10 Metal Complexes of 3[a]



[a] Reagents and conditions: (i) (DME)$NiBr_2$, CH_2Cl_2, 35 °C, 24 h. (ii) $(PhCN)_2PtCl_2$, toluene/CH_2Cl_2, rt, 20 h. (iii) (COD)$PdCl_2$, toluene/CH_2Cl_2, rt, 20 h.

An investigation into the coordination chemistry of **3** with Pt(II) precursors was also undertaken. A slight excess of ligand **3** in toluene was stirred at room temperature with $Pt(PhCN)_2Cl_2$ in DCM for 20 h in an attempt to synthesize a chelating complex. Instead, however, the platinum complex **6** with two monodentate ligands bound through their phosphorus atoms was detected as shown in Scheme 2. The yield of the complex was only 35%. This was improved by using 2 equiv of ligand to ensure that all of the metal precursor reacts. A similar result was obtained by Long et al., who synthesized bis[1-(diphenylphosphino)-1′-(methylsulfanyl)ferrocene]palladium(II) dichloride by stirring 3 equiv of 1-(diphenylphosphino)-1′-(methylsulfanyl)ferrocene with Pd(COD)Cl_2 at room temperature.[18]

The ^1H NMR spectrum gives a singlet at 3.57 ppm corresponding to the methoxy group. This is very similar to the chemical shift of the methoxy group in the free ligand, which is 3.52 ppm, indicating that the oxygen is not bound to the metal center. The cyclopentadienyl

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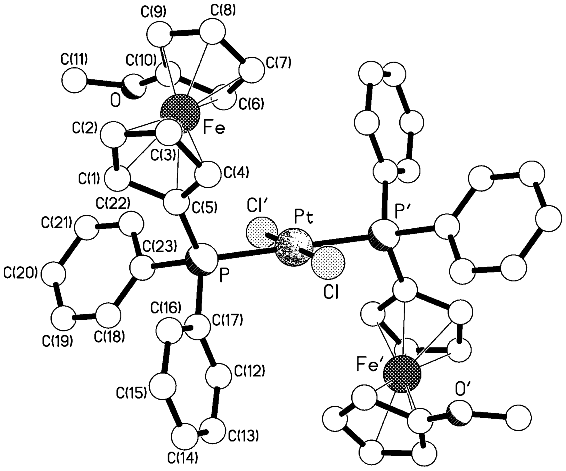

Figure 2. Molecular structure of **6**.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Compound 6

Pt−Cl	2.3121(13)	Pt−P	2.3216(14)
P−C(5)	1.815(7)	P−C(17)	1.827(3)
P−C(23)	1.849(3)		
Cl−Pt−Cl′	180	Cl−Pt−P	87.32(7)
Cl−Pt−P′	92.68(7)	P−Pt−P′	180
C(5)−P−C(17)	105.9(2)	C(5)−P−C(23)	103.0(3)
C(17)−P−C(23)	102.4(2)	C(5)−P−Pt	114.2(2)
C(17)−P−Pt	109.5(2)	C(23)−P−Pt	120.4(2)

protons show a multiplet at 4.28 ppm (due to the presence of two overlapping pseudo-triplets) and pseudo-triplets at 4.45 and 4.59 ppm. The phenyl protons of the PPh_2 group give a multiplet centered at 7.38 ppm. The $^{31}P\{^1H\}$ NMR exhibits only one singlet at 11.0 ppm (indicating that only one isomer of the product formed, later identifed as the *trans*-isomer by crystal structure analysis). Platinum satellites are observed with a $^1J_{Pt-P}$ of 2620 Hz. The $^{13}C\{^1H\}$ NMR shows six signals for the cyclopentadienyl carbons together with signals due to the methyl and phenyl carbons. The *ipso, ortho,* and *meta* phenyl carbons show coupling to the ^{31}P nucleus but appear as triplets rather than the expected doublets. It is postulated that the carbons on different phenyl rings are in slightly different environments, and hence the pseudo-triplets result from two overlapping doublets. The FAB mass spectrum shows the molecular ion (1066 amu) and the expected fragmentation pattern corresponding to the loss of one chlorine atom (1030 amu) and two chlorines (995 amu).

The complex **6**, which is illustrated in Figure 2, has crystallographic inversion symmetry and is isomorphous with its [(methylsulfanyl)ferrocene]palladium(II) analogue.[18] The geometry at platinum is slightly distorted square planar with *cis* angles of 92.68(7)° and 87.32(7)°; the Pt−P bond lengths (Table 1) do not differ significantly from those in, for example, the analogous unsubstituted[35] and carboxylic acid[36] bis-complexes. As observed in **3**, one of the P−Ph bonds lies close (ca. 9°) to the plane of its associated Cp ring, while the other is steeply inclined (by ca. 77°). The cyclopentadienyl rings are virtually eclipsed (ca. 2° stagger) with their planes inclined by ca. 5°. The $P-C_5$ and $O-C_5$ vectors have a gauche (67°) relationship. The closest intramolecular approach to the methoxy oxygen atom is 2.57 Å from C(22)−H. There are no noteworthy intermolecular interactions.

A slight excess of **3** in toluene was refluxed with both $Pt(PhCN)_2Cl_2$ and $Pt(COD)Cl_2$ in CH_2Cl_2 for 20 h in a further attempt to synthesize a chelating complex. It was hoped that the harsher conditions would favor formation of the desired complex. The solution was concentrated and dry hexane added to bring about precipitation of the products. The mixture was filtered and the residue washed with dry hexane. Analysis of the resulting orange powder showed it to be a mixture of chelating and nonchelating complexes. The FAB mass spectrum has a peak corresponding to both the molecular ion of dichloro[1-(diphenylphosphino)-1′-(methoxy)-ferrocene]platinum(II), **7** (666 amu), and the molecular ion of **6** (1066 amu). The ^1H NMR spectrum shows a peak at 3.70 ppm corresponding to the methoxy group of **7** (shifted downfield from the free ligand at 3.52 ppm due to the coordination of the oxygen to the metal), as well as a peak at 3.57 ppm corresponding to the methoxy group of **6**. The ferrocene and phenyl regions could not be fully resolved due to overlapping of the peaks from both complexes. Separation of the two complexes was attempted by both recrystallization and preparative TLC. Recrystallization was not successful, as both complexes precipitated as microcrystalline powders on layering a CH_2Cl_2 solution of the mixture with hexane. Compound **6** was isolated via preparative TLC, but unfortunately **7** decomposed on the TLC plates and could not be isolated. It should be noted that a similar result was obtained when a slight excess of **3** was heated to 35 °C with $Pd(PhCN)_2Cl_2$ in benzene for 20 h. Analysis of the reaction mixture showed it to contain a mixture of **5** and bis[1-(diphenylphosphino)-1′-(methoxy)ferrocene]palladium(II) chloride (**8**). The FAB mass spectrum has a peak corresponding to the molecular ion of both **5** (578 amu) and **8** (978 amu). The ^1H NMR spectrum shows a peak at 3.71 ppm corresponding to the methoxy group of **5** together with a peak at 3.55 ppm due to the methoxy group of **8**, indicating the oxygen heteroatom is not bound to the Pd center. The $^{31}P\{^1H\}$ NMR gives a peak at 15.8 ppm corresponding to **8** and at 31.9 ppm due to **5**.

A Rh(I) complex **9** was formed by dissolving 2 equiv of **3** in the minimum amount of diethyl ether and adding this to a solution of tetracarbonyldichlorodirhodium(I) dissolved in methanol (Scheme 3). An orange precipitate formed after 5 min, which was filtered off after 2 h and washed with diethyl ether and methanol. Rather than the expected chelating complex, bis[1-(diphenylphosphino-κP)-1′-(methoxy)ferrocene]carbonylchlororhodium(I) (**9**) was isolated in 47% yield. A similar monodentate bis ligand Rh(I) complex with *trans* phosphorus ligation featuring a P/O-substituted ligand has recently been used in methanol carbonylation catalysis,[37] and the application of **9** in carbonylation catalysis is currently under study. The ^1H NMR spectrum of **9** shows a singlet at 3.52 ppm corresponding to the methoxy protons,

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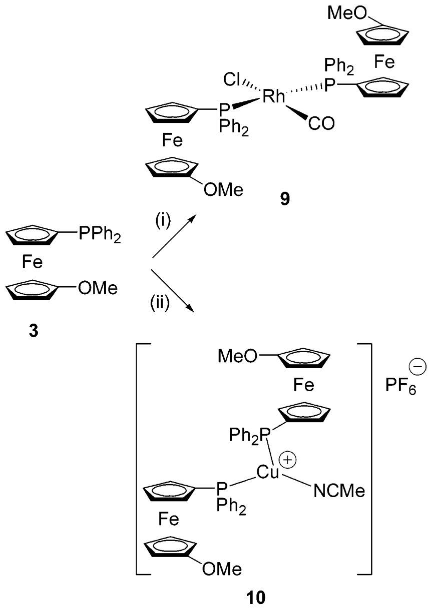
Scheme 3. Synthesis of Rh(I) and Cu(I) Complexes of 3[a]



[a] Reagents and conditions: (i) [RhCl(CO)$_2$]$_2$, methanol/Et$_2$O, rt, 2 h. (ii) Cu(MeCN)$_4$$^+PF_6$$^-$, CH$_2Cl_2$, rt, 2 h.

barely shifted from the free ligand, indicating that the oxygen heteroatom is not interacting with the rhodium center. The ferrocenyl protons give signals at 4.12, 4.21, and 4.48 ppm. The phenyl groups exhibit two multiplets at 7.39 and 7.66 ppm. The ^{31}P{^{1}H} NMR spectrum shows a doublet at 22.74 ppm due to coupling with the Rh nucleus, and the coupling constant $^{1}J_{\mathrm{Rh-P}}$ is 125.8 Hz. This is lower than the value of 168 Hz found for carbonylchloro[1-(diphenylphosphino)-1′-(methylthio)-ferrocene]rhodium(I)[18] and is expected as two P nuclei now couple to the Rh center. The fact that there is only one P environment suggests that the P atoms are *trans* to each other and that the complex has a similar *trans* phosphorus ligation to **6**. The ^{13}C{^{1}H} NMR shows six signals for the cyclopentadienyl carbons together with signals due to the methyl and phenyl carbons. The *ipso, ortho,* and *meta* phenyl again appear as triplets rather than the expected doublets as with **6**. The carbonyl carbon shows a triplet at 135.96 ppm due to coupling to the two equivalent ^{31}P nuclei, but coupling to the ^{103}Rh nucleus was not observed due to the broad nature of the signals. Only one carbonyl peak is seen in the IR spectrum at 1968 cm^{-1}. This is lower than the value of 2006 cm^{-1} found for carbonylchloro[1-(diphenylphosphino)-1′-(methylthio)ferrocene]rhodium(I), as the Rh center has two phosphine donor groups resulting in more back-donation to the CO π* orbitals. The positive ion FAB mass spectrum shows the molecular ion (966 amu) and fragmentation peaks due to M$^+$ − Cl (931 amu) and M$^+$ − CO − Cl (903 amu). A copper(I) complex, **10**, was also synthesized as an analogue to the spiro Cu(I) complexes of **11** previously synthesized.[12] Two equivalents of **3** were dissolved in dry DCM and added to a stirred DCM solution of Cu(MeCN)$_4$$^+$(PF$_6$)$^-$. The reaction mixture was stirred for 2 h and the solvent evaporated. The orange precipitate thus formed was washed with hexane and dried. The ^{1}H NMR of **10** shows a singlet at 2.37 ppm, showing that bound MeCN is still present in the product complex. The methoxy protons give a singlet at 3.45 ppm; surprisingly this represents an upfield shift from the free ligand, again suggesting that the O heteroatom is not coordinated to the Cu atom. The ferrocenyl protons exhibit four signals at 3.60, 3.95, 4.10, and 4.51 ppm, and the phenyl protons show a multiplet centered at 7.34 ppm. The ^{31}P{^{1}H} NMR exhibits a singlet at −6.44 ppm corresponding to the P donor atom in the ligand and a septet at −143.64 ppm corresponding to the PF$_6$$^-$ counterion. The positive ion FAB mass spectrum does not give the molecular ion but the expected fragmentation pattern corresponding to M$^+$ − MeCN (863 amu) and M$^+$ − MeCN − L (463 amu), as well as a signal for L$^+$ (400 amu).

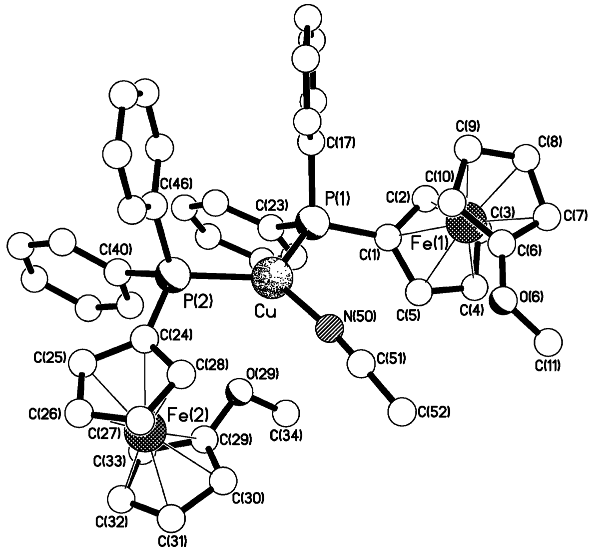


Figure 3. Molecular structure of **10**.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Compound 10

Cu−P(1)	2.2530(13)	Cu−P(2)	2.2491(13)
Cu−N(50)	1.969(5)	P(1)−C(1)	1.802(5)
P(1)−C(17)	1.824(3)	P(1)−C(23)	1.838(3)
P(2)−C(24)	1.803(5)	P(2)−C(40)	1.826(3)
P(2)−C(46)	1.838(2)		
N(50)−Cu−P(2)	116.81(14)	N(50)−Cu−P(1)	116.98(14)
P(2)−Cu−P(1)	125.87(5)	C(1)−P(1)−C(17)	104.7(2)
C(1)−P(1)−C(23)	103.21(19)	C(17)−P(1)−C(23)	102.65(16)
C(1)−P(1)−Cu	118.82(18)	C(17)−P(1)−Cu	112.02(11)
C(23)−P(1)−Cu	113.75(13)	C(24)−P(2)−C(40)	102.6(2)
C(24)−P(2)−C(46)	103.01(18)	C(40)−P(2)−C(46)	103.26(17)
C(24)−P(2)−Cu	116.99(17)	C(40)−P(2)−Cu	116.16(12)
C(46)−P(2)−Cu	112.95(12)		

The molecular structure of **10** confirmed the presence of a coordinated acetonitrile and showed the geometry at copper to be distorted trigonal planar (Figure 3, Table 2), the other two coordination sites being occupied by the phosphorus atoms of two independent 1-(diphenylphosphino)-1′-(methoxy)ferrocene ligands. The Cu−P bond lengths [2.2491(13) and 2.2530(13) Å] are comparable with those observed in other Cu(I)P$_2$NCMe complexes,[38] but the Cu−N distance [1.969(5) Å] is noticeably shorter than the range of values (1.998−2.038 Å) observed in those complexes. The copper atom is displaced by 0.073 Å out of the plane of its substituents in

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[38] (a) Che, C.-M.; Mao, Z.; Miskowski, V. M.; Tse, M.-C.; Chan, C.-K.; Cheung, K.-K.; Phillips, D. L.; Leung, K.-H. *Angew. Chem., Int. Ed.* **2000**, *39*, 4084. (b) Liu, H.; Calhorda, M. J.; Drew, M. G. B.; Felix, V.; Novosad, J.; Veiros, L. F.; de Biani, F. F.; Zanello, P. *Dalton* **2002**, 4365.

Scheme 4. Reagents and Conditions for Catalyst Testing of the Suzuki Reaction

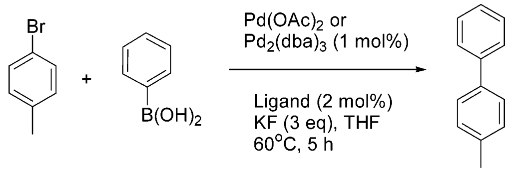

Table 3. Results of Catalysis Testing for the Suzuki Reaction Using 3, 11, and dppf

ligand	isolated yield of 4-phenyltoluene[a] (%)	isolated yield of 4-phenyltoluene[b] (%)
3	73	89
11	55	80
dppf	74	79

[a] Using Pd(OAc)$_2$ reagent. [b] Using Pd$_2$(dba)$_3$ reagent.

the direction of the methoxy oxygen O(29). The Cu···O(29) distance is fairly short at 2.86 Å, although comparable approaches of ethoxy oxygen atoms to trigonal copper(I) centers have been observed previously.[39] Both ferrocenyl units have significantly staggered geometries [ca. 24° for Fe(1) and ca. 16° for Fe(2)], and their P−C$_5$ and O−C$_5$ vectors are inclined by 93° [Fe(1)] and 16° [Fe(2)], respectively. The closer to eclipsed geometry observed at Fe(2) facilitates the formation of an intramolecular C−H···O hydrogen bond between one of the *ortho* hydrogen atoms on the C(40) phenyl ring and the methoxy oxygen atom O(29); the C···O and H···O distances are 3.19 and 2.32 Å, and the C−H···O angle is 149°. There is a small $\pi-\pi$ overlap between the C(23) and C(40) phenyl rings, the centroid···centroid and mean-interplanar separations being 4.68 and 3.31 Å, respectively (the rings are inclined by ca. 8°). The PF$_6$ anion and included DCM are both disordered, and there are no intermolecular interactions of note.

Catalysis Studies. We have recently reported the application of **11** to the Suzuki reaction in conjunction with Pd(0) precursors.[18] Compound **3** was also investigated with Pd(II) and Pd(0) reagents as a possible system for the Suzuki reaction and its activity compared to both **11** and 1,1′-bis(diphenylphosphino)ferrocene (dppf) as a ligand of choice for this reaction. Following the methodology of Buchwald et al.,[40] either Pd(OAc)$_2$ (1 mol %) or Pd$_2$(dba)$_3$·C$_6$H$_6$ (1 mol %; 2 mol % Pd), ligand (2 mol %), and 3 equiv of potassium fluoride were stirred with the starting materials (1 mmol scale) in THF (1 mL). The coupling reaction studied is shown in Scheme 4. The reactions were carried out at 60 °C for 5 h. The crude product was purified by column chromatography and the purity of the product checked by GC analysis. The isolated yield of 4-phenyltoluene was used as a measure of the effectiveness of each catalyst system: the results are shown in Table 3.

With Pd(OAc)$_2$, dppf was found to be a more effective catalyst than **11**. This is thought to be due to the fact that dppf is more effective in reducing Pd(II) to Pd(0), a necessary step before the cross-coupling reaction can take place. Compound **3**, however, was found to have an activity similar to that of dppf. With Pd$_2$(dba)$_3$, under the experimental conditions described here, dppf and **11** were found to have a similar activity, with **3** slightly higher than both.

Conclusions

The synthesis of the novel ligand **3** has been reported via two different routes, which include a new route to unsymmetrical ferrocenyl ethers. The relatively straightforward, highest yielding route affords **3** in an overall yield of 23% from 1,1′-dibromoferrocene. The coordination chemistry of **3** has been explored with group 10 metal halides and Rh(I) and Cu(I) precursors, and chelating complexes were isolated with (COD)PdCl$_2$ and (dme)NiBr$_2$. A monodentate bis ligand complex with *trans* phosphorus ligation was isolated with Pt(PhCN)$_2$Cl$_2$. With Pd(PhCN)$_2$Cl$_2$, evidence was found for the analogous Pd complex, which was formed alongside a chelating complex. Both chelating and phosphorus ligated bis ligand complexes were formed with Pt(COD)Cl$_2$. Similar phosphorus ligated bis ligand complexes were formed with Rh(I) and Cu(I) precursors. The coordination chemistry described herein suggests that **3** may be able to act as a hemilabile ligand with the methoxy group acting as substitutionally labile with soft metal centers, and future studies will focus on the applications of **3** in catalysis together with further study into the coordination chemistry of this ligand. Preliminary studies into the efficacy of **3**, in combination with Pd precursors, as a catalyst for the Suzuki reaction show that **3** is a good ligand for this reaction. The synthesis of other 1,1′-unsymmetrical P/O, S/O, and N/O ferrocenediyl ligands is currently underway.

Experimental Section

General Procedures. All preparations were carried out using standard Schlenk techniques.[41] All solvents were distilled over standard drying agents under nitrogen directly before use, and all reactions were carried out under an atmosphere of nitrogen. Chromatographic separations were carried out on silica gel (Kieselgel 60, 70−230 mesh). All NMR spectra were recorded using a Delta upgrade on a JEOL EX270 MHz spectrometer operating at 270.1 MHz (^{1}H) and 101.3 MHz (^{31}P{^{1}H}). Chemical shifts (δ) are reported in ppm using CDCl$_3$ (^{1}H, 7.25 ppm), C$_6$D$_6$ (7.15 ppm), or CD$_2$Cl$_2$ (5.30 ppm) as the reference, while ^{31}P{^{1}H} spectra were referenced to H$_3$PO$_4$. Infrared spectra were recorded using NaCl solution cells (CH$_2$Cl$_2$) using a Perkin-Elmer 983 Fourier transform IR spectrometer. Mass spectra were recorded using positive FAB methods, on an Autospec Q mass spectrometer. Microanalyses were carried out at SACS, University of North London.

Syntheses: 1-(Bromo)-1′-(acetoxy)ferrocene (1). A mixture of 1,1′-dibromoferrocene (2.00 g, 5.82 mmol, 1 equiv), acetic acid dried over molecular sieves (0.17 cm^3, 2.91 mmol, 0.5 equiv), and copper(I) oxide (0.42 g, 2.91 mmol, 0.5 equiv) was heated to reflux in dry acetonitrile (40 cm^3) for 15 h under nitrogen. After cooling, dichloromethane was added (75 cm^3) and the mixture filtered. The precipitate was washed with dichloromethane (30 cm^3). The green filtrate and washings were combined and extracted with water (50 cm^3), and the layers were separated. The orange organic layer was dried (MgSO$_4$) and the solvent removed in vacuo to yield an orange oily solid. The crude mixture was purified by column chromatography (silica, toluene), yielding **1** as an orange oil (0.24 g,

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(40) Wolfe, J. P.; Singer, R. A.; Yang, B. H.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 9550.

(41) Errington, R. J. *Advanced Practical Inorganic and Metalorganic Chemistry*; Blackie: London, 1997.

0.74 mmol, 13%). Anal. Calcd for $C_{12}H_{11}BrFeO_2$: C 44.63, H 3.43. Found: C 44.45, H 3.59. IR (CH_2Cl_2) cm^{-1}: 1755 (s, C=O) 1270 (vs, C−O). ^{1}H NMR δ ($CDCl_3$) ppm: 2.18 (s, 3H, CH_3), 3.99 (br t, 2H, C_5H_4OAc), 4.13 (br t, 2H, C_5H_4Br), 4.44 (br t, 2H, C_5H_4OAc), 4.46 (br t, 2H, C_5H_4Br). *m/z*: 324, 322 (M^+), 282, 280 ($M^+ - CH_3CO$), 244 ($M^+ - Br$).

1-(Bromo)-1′-(methoxy)ferrocene (2). From 1. To a stirred solution of **1** (0.24 g, 0.74 mmol, 1 equiv), 15-crown-5 (0.05 cm^3, 0.24 mmol, 0.33 equiv), and iodomethane (0.16 cm^3, 2.5 mmol, 3.4 equiv) in dry deoxygenated THF (15 cm^3) under nitrogen was added sodium hydride (60% in mineral oil, 0.19 g, 4.0 mmol, 5.4 equiv). The reaction mixture was stirred at room temperature for 15 h. The reaction mixture was then filtered and the solvent removed in vacuo to yield an orange oil. The crude product was purified by column chromatography (silica, toluene), yielding **2** as an orange oil (0.17 g, 0.57 mmol, 77% from **1**, 10% from 1,1′-dibromoferrocene). Anal. Calcd for $C_{11}H_{11}BrFeO$: C 44.79, H 3.76. Found: C 44.89, H 3.58. IR (CH_2Cl_2) cm^{-1}: 1272 (s, C−O). ^{1}H NMR δ ($CDCl_3$) ppm: 3.90 (s, 3H, CH_3) 3.99 (t, 2H, C_5H_4), 4.07 (t, 2H, C_5H_4), 4.11 (t, 2H, C_5H_4), 4.40 (t, 2H, C_5H_4). *m/z*: 296, 294 (M^+), 216 ($M^+ - Br$). Acc. mass calcd for $C_{11}H_{11}BrFeO$: 293.934265, found 293.934616.

2. From 1,1′-Dibromoferrocene. 1,1′-Dibromoferrocene (0.50 g, 1.45 mmol, 1 equiv) was dissolved in dry THF (40 cm^3) and cooled to −25 °C. To this solution was added *n*-butyllithium (1.6 M in hexanes, 0.86 cm^3, 1.38 mmol, 0.95 equiv) and the solution stirred at −25 °C for 30 min. The solution was cooled to −78 °C, and bis(trimethylsilyl) peroxide (0.24 cm^3, 2.18 mmol, 1.5 equiv) was added dropwise slowly. The solution was stirred at −78 °C for 1 h and then allowed to warm to room temperature. The THF was removed in vacuo and the residue redissolved in nitrogen-saturated acetone (35 cm^3). K_2CO_3 (1.24 g, 9.00 mmol, 6.2 equiv) was added and Me_2SO_4 added via syringe (1.03 cm^3, 11.0 mmol, 7.5 equiv). The mixture was refluxed for 20 h, cooled, and filtered, and the solvent was removed in vacuo to yield an orange oil. The crude product was purified by column chromatography (silica, toluene/hexane, 1:1), and **2** was obtained as an orange oil (0.241 g, 0.82 mmol, 56% from 1,1′-dibromoferrocene).

1-(Diphenylphosphino)-1′-(methoxy)ferrocene (3). **2** (0.80 g, 2.71 mmol, 1 equiv) was dissolved in dry THF (25 cm^3) and cooled to −78 °C. To this solution was added *n*-butyllithium (1.6 M in hexanes, 1.69 mL, 2.71 mmol, 1 equiv) and the solution stirred at −78 °C for 10 min. Chlorodiphenylphosphine (0.60 mL, 3.25 mmol, 1.2 equiv) was added and the mixture allowed to warm to room temperature. The solution was stirred at room temperature for 20 h, the solvent was removed in vacuo, and the residue was redissolved in CH_2Cl_2 (50 cm^3). Water was added (50 cm^3) and the layers were separated. The aqueous layer was washed with CH_2Cl_2 (25 cm^3), the organic layers were combined and dried ($MgSO_4$), and the solvent was removed in vacuo to yield an orange oily solid. The crude mixture was purified by column chromatography (silica, hexane/CH_2Cl_2, 2:1) to give an orange oil. Pure **3** was obtained as an orange solid after recrystallization from pentane (0.43 g, 1.09 mmol, 40%). Crystals suitable for X-ray diffraction were grown by slow evaporation from pentane solution. Anal. Calcd for $C_{23}H_{21}FeOP$: C 69.02, H 5.29. Found: C 69.07, H 5.26. ^{1}H NMR δ ($CDCl_3$) ppm: 3.52 (s, 3H, CH_3) 3.70 (t, 2H, C_5H_4), 3.99 (t, 2H, C_5H_4), 4.12 (t, 2H, C_5H_4), 4.40 (t, 2H, C_5H_4), 7.28 (m, 10H, PC_6H_5). $^{31}P\{^1H\}$ NMR δ ($CDCl_3$) ppm: −16.4. $^{13}C\{^1H\}$ NMR δ ($CDCl_3$) ppm: 55.88 (s, C_5H_4), 57.37 (s, OCH_3), 63.17 (s, C_5H_4), 71.35 (s, C_5H_4), 73.16 (d, *ipso*-C_5H_4, $^1J_{C-P}$ 59.48 Hz), 75.9 (s, C_5H_4), 76.1 (s, C_5H_4), 128.24 (d, *ipso*-C_6H_5, $^1J_{C-P}$ 185.6 Hz), 128.09 (d, *m*-C_6H_5, $^3J_{C-P}$ 26 Hz), 128.40, (s, *p*-C_6H_5), 133.45 (d, *o*-C_6H_5, $^2J_{C-P}$ 76 Hz). *m/z*: 400 (M^+).

Dibromo[1-(diphenylphosphino-κP)-1′-(methoxy-κO)-ferrocene]nickel(II) (4). Bis(1,2-dimethoxyethane)dibromonickel(II) (0.04 g, 0.11 mmol, 0.9 equiv) was added to a dry Schlenk tube, in a glovebox, containing **3** (0.05 g, 0.125 mmol, 1 equiv). Dry, deoxygenated CH_2Cl_2 (20 cm^3) was added, causing the solution to turn green. The Schlenk tube was suspended in an oil bath and the reaction mixture stirred for 24 h at 35 °C. The solvent was removed in vacuo, and the green precipitate was washed with dry hexane (10 cm^3), yielding **4** as a green, air-sensitive powder (0.03 g, 0.05 mmol, 43%). Anal. Calcd for $C_{23}H_{21}Br_2FeNiOP$: C 44.65, H 3.42. Found: C 44.63, H 3.56. ^{31}P NMR δ ($CDCl_3$) ppm: 29.8. *m/z*: 400 ($M^+ - NiBr_2$).

Dichloro[1-(diphenylphosphino-κP)-1′-(methoxy-κO)-ferrocene]palladium(II) (5). **3** (0.10 g, 0.25 mmol, 1 equiv) was dissolved in dry toluene (7 cm^3) and added via cannula to dichloro(1,5-cyclooctadiene)palladium(II) (0.07 g, 0.23 mmol, 0.9 equiv) dissolved in dry CH_2Cl_2 (20 cm^3). The solution was stirred for 20 h under nitrogen. The solution was concentrated by half in vacuo, dry hexane (10 cm^3) added, and the mixture filtered. The brown residue was washed with dry hexane (10 cm^3), yielding **5** as a brown powder (0.10 g, 0.18 mmol, 70%). Anal. Calcd for $C_{23}H_{21}Cl_2FeOPPd$: C 47.83, H 3.66. Found: C 47.64, H 3.49. ^{1}H NMR δ ($CDCl_3$) ppm: 3.71 (s, 3H, OCH_3), 4.53 (m, 4H, C_5H_4) 4.60 (m, 4H, C_5H_4), 7.45 (m, 10H, PC_6H_5). $^{31}P\{^1H\}$ NMR δ ($CDCl_3$) ppm: 31.9. *m/z*: 578 (M^+), 543 ($M^+ - Cl$), 506 ($M^+ - 2Cl$).

Bis[1-(diphenylphosphino-κP)-1′-(methoxy)ferrocene]-dichloroplatinum(II) (6). **3** (0.10 g, 0.25 mmol, 2.1 equiv) was dissolved in dry toluene (3 cm^3) and added via cannula to a solution of bis(benzonitrile)platinum dichloride (0.06 g, 0.12 mmol, 1 equiv) in dry DCM (7 cm^3). The solution was stirred for 20 h under nitrogen at room temperature, after which time an orange precipitate was visible. The solution was concentrated in vacuo, dry hexane (10 cm^3) was added, resulting in complete precipitation of the product, and the mixture was filtered. The product was washed with dry hexane (10 cm^3) and filtered to yield **6** as an orange powder (0.10 g, 0.10 mmol, 80%). Crystals suitable for X-ray diffraction were grown by slow evaporation of hexane from a DCM solution of the complex. Anal. Calcd for $C_{46}H_{42}Cl_2Fe_2O_2P_2Pt$: C 51.81, H 3.97. Found: C 51.53, H 3.77. ^{1}H NMR δ ($CDCl_3$) ppm: 3.57 (s, 3H, OCH_3), 4.28 (m, 4H, C_5H_4) 4.45 (t, 2H, C_5H_4), 4.59 (t, 2H, C_5H_4), 7.38 (m, 10H, PC_6H_5). $^{31}P\{^1H\}$ NMR δ ($CDCl_3$) ppm: 11.0 (s, $^1J_{Pt-P}$ 2620 Hz). $^{13}C\{^1H\}$ NMR δ (CD_2Cl_2) ppm: 56.89 (s, C_5H_4), 57.78 (s, OCH_3), 65.29 (s, C_5H_4), 71.10 (s, C_5H_4), 72.65 (s, C_5H_4), 75.51 (br d, C_5H_4), 76.61 (s, C_5H_4), 127.83 (t, *m*-C_6H_5, $^3J_{C-P}$ 19.6 Hz), 130.55, (s, *p*-C_6H_5), 131.16 (t, *ipso*-C_6H_5, $^1J_{C-P}$ 117.2 Hz), 134.58 (t, *o*-C_6H_5, $^2J_{C-P}$ 22.4 Hz). *m/z*: 1066 (M^+), 1030 ($M^+ - Cl$), 995 ($M^+ - 2Cl$).

Bis[1-(diphenylphosphino-κP)-1′-(methoxy)ferrocene]-carbonylchlororhodium(I) (9). **3** (0.08 g, 0.20 mmol, 2.1 equiv) was dissolved in dry Et_2O (10 cm^3) and added via cannula to a solution of tetracarbonyldichlorodirhodium(I) (0.04 g, 0.10 mmol, 1 equiv) in dry methanol (20 cm^3). The solution was stirred at room temperature for 2 h, after which time an orange precipitate was visible. The solution was concentrated in vacuo and the mixture filtered. The residue was washed with Et_2O (10 cm^3) and methanol (10 cm^3), yielding **9** as an orange powder (0.05 g, 0.05 mmol, 47%). Anal. Calcd for $C_{47}H_{42}ClFe_2O_3P_2Rh$: C 58.39, H 4.38. Found: C 58.56, H 4.49. ^{1}H NMR δ (CD_2Cl_2) ppm: 3.52 (s, 3H, CH_3), 4.12 (t, 2H, C_5H_4), 4.21 (t, 2H, C_5H_4), 4.48 (m, 4H, C_5H_4), 7.39 (m, 6H, PC_6H_5), 7.66 (m, 4H, PC_6H_5). $^{31}P\{^1H\}$ NMR δ (CD_2Cl_2) ppm: 22.74 (d, $^1J_{Rh-P}$ 126 Hz). $^{13}C\{^1H\}$ NMR δ (C_6D_6) ppm: 57.02 (s, C_5H_4), 57.10 (s, OCH_3), 65.56 (s, C_5H_4), 72.32 (s, C_5H_4), 74.69 (s, C_5H_4), 74.95 (s, C_5H_4), 75.42 (s, C_5H_4), 128.91 (br t, *m*-C_6H_5), 129.89, (s, *p*-C_6H_5), 134.50 (t, *o*-C_6H_5, $^2J_{C-P}$ 24.8 Hz), 128.01 (br t, *ipso*-C_6H_5), 135.96 (t, CO, $^2J_{C-P}$ 91.6 Hz). IR (CH_2Cl_2, cm^{-1}): ν(CO) 1968. *m/z*: 966 (M^+), 931 ($M^+ - Cl$), 903 ($M^+ - CO - Cl$).

Bis[1-(diphenylphosphino-κP)-1′-(methoxy)ferrocene]-acetonitrilecopper(I) Hexafluorophosphate (10). **3** (0.08 g, 0.20 mmol, 2.1 equiv) was dissolved in dry CH_2Cl_2 (5 cm^3) and added via cannula to a solution of tetrakis(acetonitrile)-

copper(I) hexafluorophosphate (0.04 g, 0.10 mmol, 1 equiv) in CH_2Cl_2 (10 cm^3). The solution was stirred at room temperature for 2 h. The solvent was removed in vacuo and the precipitate washed with hexane (2 × 10 cm^3) and dried in vacuo, yielding **10** as an orange powder (0.05 g, 0.05 mmol, 56%). Crystals suitable for X-ray analysis were grown by layering a DCM solution of the complex with hexane. Anal. Calcd for $C_{48}H_{45}CuF_6Fe_2NO_2P_3$: C 54.90, H 4.32, N 1.33. Found: C 55.08, H 4.47, N 1.15. ^1H NMR δ ($CDCl_3$) ppm: 2.10 (s, 3H, $C\mathit{H}_3CN$) 3.45 (s, 3H, $OC\mathit{H}_3$), 3.60 (m, 2H, $C_5\mathit{H}_4$), 3.95 (m, 2H, $C_5\mathit{H}_4$), 4.10 (m, 2H, $C_5\mathit{H}_4$), 4.51 (m, 2H, $C_5\mathit{H}_4$) 7.34 (m, 10H, $PC_6\mathit{H}_5$). $^{31}P\{^1H\}$ NMR δ ($CDCl_3$) ppm: −143.64 (septet, $\mathit{P}F_6^-$ $^1J_{P-F}$ 712 Hz) −6.44 (s, $\mathit{P}Ph_2$). $^{13}C\{^1H\}$ NMR δ (CD_2Cl_2) ppm: 30.97 (s, $\mathit{C}H_3CN$), 56.84 (s, C_5H_4), 58.17 (s, $O\mathit{C}H_3$), 64.26 (s, C_5H_4), 72.82 (s, C_5H_4), 72.96 (s, C_5H_4), 73.34 (br d, C_5H_4), 73.89 (s, C_5H_4), 121.54 (s, $CH_3\mathit{C}N$), 129.18 (br s, *ipso*-C_6H_5), 129.28 (br s, *m*-C_6H_5), 131.11 (br s, *p*-C_6H_5), 133.43 (br s, *o*-C_6H_5). *m*/*z*: 863 (M^+ − MeCN), 463 (M^+ − MeCN − L), 400 (L^+).

Crystal data for **3**: $C_{23}H_{21}OPFe$, $M = 400.22$, triclinic, $P\bar{1}$ (no. 2), $a = 8.025(2)$ Å, $b = 10.796(2)$ Å, $c = 11.814(3)$ Å, $\alpha = 100.77(2)°$, $\beta = 96.97(2)°$, $\gamma = 101.507(12)°$, $V = 971.8(4)$ Å^3, $Z = 2$, $D_c = 1.368$ g cm^{-3}, μ(Mo Kα) = 0.866 mm^{-1}, $T = 293$ K, yellow plates; 3409 independent measured reflections, F^2 refinement, $R_1 = 0.039$, $wR_2 = 0.091$, 2745 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max} = 50°$], 211 parameters.

Crystal data for **6**: $C_{46}H_{42}O_2P_2Cl_2Fe_2Pt$, $M = 1066.43$, monoclinic, $P2_1/c$ (no. 14), $a = 9.4390(8)$ Å, $b = 11.460(2)$ Å, $c = 18.440(2)$ Å, $\beta = 93.771(5)°$, $V = 1990.5(4)$ Å^3, $Z = 2$ [C_i symmetry], $D_c = 1.779$ g cm^{-3}, μ(Mo Kα) = 4.479 mm^{-1}, $T = 203$ K, yellow blocks; 3510 independent measured reflections, F^2 refinement, $R_1 = 0.037$, $wR_2 = 0.070$, 2618 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max} = 50°$], 226 parameters.

Crystal data for **10**: $[C_{48}H_{45}CuFe_2NO_2P_2](PF_6)\cdot CH_2Cl_2$, $M = 1134.93$, triclinic, $P\bar{1}$ (no. 2), $a = 12.7069(6)$ Å, $b = 13.2745(7)$ Å, $c = 14.9398(14)$ Å, $\alpha = 78.179(4)°$, $\beta = 83.475(6)°$, $\gamma = 84.346(4)°$, $V = 2443.2(3)$ Å^3, $Z = 2$, $D_c = 1.543$ g cm^{-3}, μ(Mo Kα) = 1.288 mm^{-1}, $T = 293$ K, yellow-orange prisms; 8603 independent measured reflections, F^2 refinement, $R_1 = 0.057$, $wR_2 = 0.126$, 5591 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max} = 50°$], 623 parameters. CCDC 236260−236262.

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Supporting Information Available: Details on the X-ray crystal structures of **3**, **6**, and **10**, including ORTEP diagrams, tables of crystal data and structure refinement, atomic coordinates, bond lengths and angles, and isotropic and anisotropic displacement parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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