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Dioxaneferrocenylimine Cyclometalated Compounds as Precursors to Novel Functionalized Di- and Tetranuclear Metallacycles Leading to 1,3-Double Palladation of an η^5-C_5H_5 Ring

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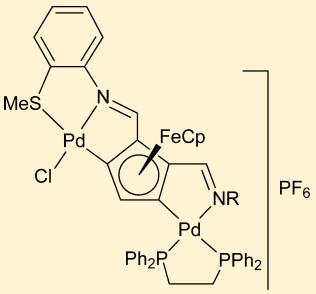
ABSTRACT: Reaction of the Schiff base ligands CpFe[η^5-C_5H_2{C(H)O$(CH_2)_3$O}C(H)=NR] (R = 2,4,6-$Me_3C_6H_2$, **a**; R = Cy, **b**) derived from the 1,2-disubstituted formylferrocene CpFe[(CHO){C(H)O$(CH_2)_3$O}-η^5-C_5H_3] **1**, with $Li_2[PdCl_4]$ in methanol at room temperature for 48 h, gave the chlorine-bridged complexes [Pd{CpFe[η^5-C_5H_2{C(H)O$(CH_2)_3$O}C(H)=NR]}(Cl)]$_2$, **1a** and **1b**, after C−H activation of the cyclopentadienyl ring bearing the cyclic acetal. The reactions of **1a** and **1b** with the $Ph_2P(CH_2)_nPPh_2$ diphosphines in a 1:2 ratio, plus addition of ammonium hexafluorophosphate, gave the dinucelar compounds [Pd{CpFe[η^5-C_5H_2{C(H)O$(CH_2)_3$O}C(H)=NR]}-($Ph_2P(CH_2)_nPPh_2$-*P*,*P*)][PF_6] **2a**, **3a** and **2b**, **3b** with the diphosphine in a chelating mode, as 1:1 electrolytes. Treatment of the latter with aqueous acetic acid gave the corresponding functionalized compounds with transformation of the 1,3-dioxane ring into a formyl group on the metalated ring, **4a**, **5a** and **4b**, **5b**.



The Schiff base condensation reaction of **5b** with 2-(methylthio)aniline in refluxing chloroform gave [Pd($Ph_2P(CH_2)_2PPh_2$)-{(CpFe)η^5-C_5H_2[C(H)=NCy][C(H)=N(2-$SMeC_6H_4$]}][PF_6] **6b**, with regeneration of the C=N double bond, which, when treated with lithium tetrachloropalladate in methanol for 48 h, gave the novel compound [Pd($Ph_2P(CH_2)_2PPh_2$){(CpFe)η^5-C_5H[C(H)=NCy][C(H)=N(2-$SMeC_6H_4$]}PdCl][PF_6] **7b**, which is the first ferrocene metallacycle displaying 1,3-double cyclopalladation.

1. INTRODUCTION

Despite that cyclometalated complexes, particularly palladacyles, have been abundantly researched for the past decades, they continue to constitute one of the major topics within organometallic chemistry, and they are well documented for a great variety of ligands.[1] They have been successfully used in organic synthesis,[2] photochemistry,[3] optical resolution processes,[4,5] catalysis,[6] as potential biologically active materials,[7] and liquid crystals.[8] One of the milestones that has greatly contributed to widening the scope of these species is ferrocene; in fact, although the preparation and characterization of ferrocene, as well as the description of the metal-ring bonding,[9] dates from the early 1950s, it is still a cornerstone for an ample range of derivatives. Electrophilic substitution at the ring yields species with added donor atoms that support coordination of the ferrocene moiety to a metal center, thus greatly extending its chemistry.[10] One of the developments in this area has been the cyclometalated ferrocene derivatives containing bidentate [C(sp^2, ferrocene), N]$^-$ and terdentate [C(sp^2, ferrocene), N, X]$^-$ (X = N, S, O) ligands; typical examples are the ferrocenylimine[11] and ferrocenylthiosemicarbazone[12] palladacyles. Their importance is put forward, to name but a few, in their use as building blocks in macromolecular chemistry,[13] or as chiral discriminators,[4] due to the prochiral nature that activation of the C(sp^2)H bond introduces in the ferrocenyl unit.[14]

Nevertheless, regardless of the profuse chemistry related to ferrocene palladacycles,[15] examples of 2-fold cyclopalladation on a single cyclopentadienyl ring remain outstanding, that is, complexes with a tetradentate [2C(sp^2, ferrocene), N, X]$^{2-}$ or with a multidenate [2C(sp^2, ferrocene), N, X, N, X]$^{2-}$ ligand; albeit for phenyl rings, as much as a 3-fold cyclopalladation of a single benzene ring has been reported.[16] To achieve this, it would first be necessary to introduce the donor atoms, other than carbon, on the five-membered ring to give the 1,2-disubstituted ferrocene. We reasoned that substitution by formyl groups, followed by condensation with the appropriate NH_2 moieties, would be an adequate route for introducing the appropriate nitrogen and sulfur donors, via formation of the corresponding C=N double bonds, followed by double palladation. An alternative route would be the preparation of ferrocene palladacyles bearing a free formyl group, in a similar fashion to complexes reported by us earlier,[17] condensation and ulterior metalation. We envisaged the latter method as an adequate route to meet our goal and, accordingly, herein we report the results of the research that has led to the synthesis of a series of new metallacycles: functionalized ferrocenylimine cyclometalated palladium(II) complexes leading to the first 1,3-dicyclopalladated bis(imine)ferrocene.

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2. RESULTS AND DISCUSSION

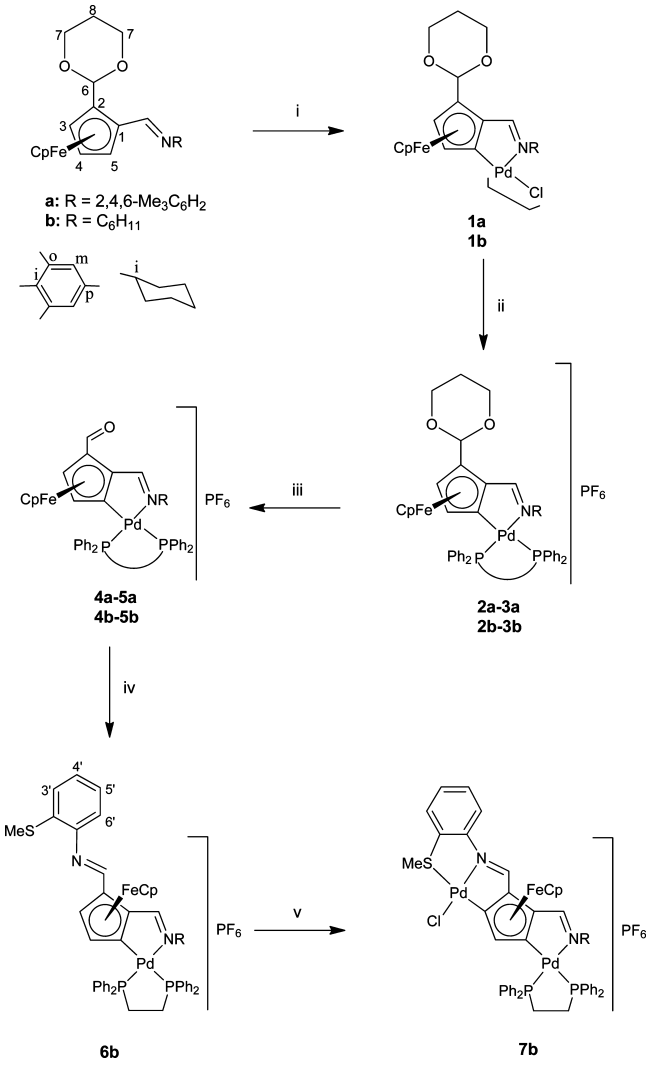
The sequence of reactions leading to the compounds reported in the present paper can be seen in Scheme 1. In our quest to synthesize functionalized ferrocenylimine palladacycles and the subsequent 1,3-dicyclopalladated species, we sought out to prepare a 1,2-disubstituted formylferrocene and the subsequent derivative comprising a protected formyl group, from which to obtain the corresponding imine ligands. To attain this task, we first prepared the 1,2-disubstituted CpFe[(CHO){C(H)O-$(CH_2)_3$O}-η^5-C_5H_3] **1**, following the method of Bunz et al.,[18] where an acetalization reaction protects the second formyl moiety. Treatment of **1** with 2,4,6-trimethylaniline or cyclohexylamine in refluxing chloroform gave ligands **a** and **b**, respectively, as air-stable solids, which were fully characterized (see the Experimental Section). The most important feature was the characteristic υ(C═N) band in the IR spectra at ca. 1630 cm^{-1} and, in the ^{1}H NMR spectra, the *H*C═N and C*H*O_2 resonances at ca. δ8.35 and δ5.63, respectively, as well as four signals of relative intensities 1:1:1:5, three for the cyclopentadienyl resonances H3, H4, and H5 from the substituted ring, with the latter one at the highest frequency due to the anisotropic effect of the C═N double bond, and a singlet for the unsubstituted ring. Reaction of **a** or **b** with $Li_2[PdCl_4]$ in methanol gave **1a** and **1b**, respectively, as air-stable solids, which were fully characterized (preparative details, characterizing microanalytical, IR, and ^{1}H and ^{13}C NMR data are in the Experimental Section). The υ(C═N) band was shifted to lower wavenumbers upon complex formation by ca. 60 cm^{-1}, in agreement with coordination of the palladium atom to the C═N moiety through the nitrogen lone pair.[19,20] The IR spectrum showed two bands at ca. 330 and 260 cm^{-1} assigned to the υ(Pd−Cl) stretches consequent on the differing trans influence of the C,N donors. Accordingly, the ^{1}H NMR showed the characteristic high-frequency shift of the *H*C═N resonance, consequent of Pd−N bond formation,[21] and the absence of the *H*5 resonance after metalation of the cyclopentadienyl ring. The results showed that only one set of resonances was recorded in the ^{1}H NMR spectra, despite that the activation of the $C_{sp}{}^2$−H bond in ferrocene introduces planar chirality (*R*p or *R*s) in the ferrocenyl arrangement.[22] The ^{13}C-{^{1}H} NMR spectra confirmed the assigned structures, with downfield shifts of the C═N, C1, and C5 resonances (the latter, at ca. 30 ppm), confirming metalation of the ring. Also, there was no noticeable quadrupolar broadening of the resonances by coupling with the ^{105}Pd (22% natural abundance, I = 5/2) nucleus for these and for the remaining complexes herein reported.

Treatment of **1a** and **1b** with bidentate tertiary phosphines gave an array of dinuclear compounds after cleavage of the Pd_2X_2 nucleus of the starting material, which kept the dioxane moiety bonded to the ferrocene ring. Thus, reaction of **1a** and **1b** with diphosphines in a 1:2 molar ratio gave compounds **2a**, **3a** and **2b**, **3b** (see the Experimental Section). The complexes were 1:1 electrolytes, as shown by molar conductivity measurements in dry acetonitrile.[23] The ^{31}P NMR spectra showed two doublets for the two nonequivalent phosphorus nuclei; the resonance at lower frequency was assigned to the phosphorus nucleus trans to the carbon atom, in agreement with the differing trans influence of both C,N donors.[24]

The aforementioned phosphine complexes could be used to prepare the hitherto outstanding functionalized ferrocenylimine palladacycles bearing a formyl group on the C2 carbon atom of the metalated cyclopentadienyl ring. This is reminiscent of similar functionalized palladacycles obtained by us earlier;[17,25] then, the HC═O group was spontaneously formed upon metalation of the ligand, although, in a later stage, double palladation was later achieved through oxidative-addition reactions in nonacidic media.[26] However, in the present case, the initial protection of the formyl group by acetalization allowed us to produce the second group at will after the first palladation of the ligand. Thus, treatment of **2a**, **3a** and **2b**, **3b** with a mixture of aqueous acetic acid/acetone gave **4a**, **5a** and **4b**, **5b** as air-stable solids, which were fully characterized (see the Experimental Section and Scheme 1). The main differences with the spectroscopic data for the parent compounds was the presence of the band assigned to the υ(C═O) stretch in the IR spectra; in the ^{1}H NMR spectra, the absence of the resonances for the dioxane ring protons, on the one hand, and a singlet at ca. 10 ppm assignable to the *H*C═O resonance, on the other; and also the HC═O resonance at ca. 194 ppm in the ^{13}C NMR spectra.

2.1. Dicyclometalated Compounds. Dicyclopalladated and dicycloplatinated complexes derived from ferrocene have

Scheme 1. (i) $Li_2[PdCl_4]$, Methanol; (ii) 1:2 $Ph_2P(CH_2)_nPPh_2/NH_4PF_6$, Acetone; (iii) AcOH/$H_2O$; (iv) 2-$SMeC_6H_4NH_2/CHCl_3$; (v) $Li_2[PdCl_4]$/NaAcO/MeOH (2, 4: n = 1; 3, 5: n = 2)



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been previously obtained.[27] However, metalation followed a 1,1′-substitution pattern, with the ensuing metallacycles on different cyclopentadienyl rings, most surely due to the impossibility of situating the corresponding donor atoms, other than carbon, on the same five-membered ring. Notwithstanding, 1,3-dicyclopalladation of ferrocene may be achieved through the functionalized compounds described above, and we now detail our preliminary results concerning the preparation and characterization of these new species that open a new field in the chemistry of cyclometalated compounds. Thus, Schiff base condensation of **5b** with 2-(methylthio)aniline in refluxing chloroform gave **6b** with regeneration of the C═N double bond, as a stable solid, which was completely characterized (see the Experimental Section and Scheme 1). The IR and NMR spectra failed to show any evidence for the formyl group put forward by the absence of the υ(C═O) stretch and the *H*C═O (^{1}H) and HC═O (^{13}C) resonances, respectively. Instead, two υ(C═N) bands were observed at 1624 cm^{-1} (noncoordinated C═N group) and at 1601 cm^{-1} (coordinated C═N group). The NMR data exhibited a singlet resonance at δ8.37 (1H, nonbonded C═N group) and a doublet at δ8.15 (1H, coordinated C═N) with coupling of the imine proton to the ^{31}P nucleus (^4J(PH) = 8.0 Hz); a singlet at δ2.36 was assigned to the S*Me* protons. Likewise, the ^{13}C-{^{1}H} NMR spectrum showed two *C*═N resonances at δ169.9 (coordinated C═N) and 158.3 (noncoordinated C═N). The remaining resonances were assigned accordingly.

Reaction of **6b** with lithium tetrachloropalladate in methanol for 48 h gave the hitherto unknown compound **7b** displaying 1,3-double cyclopalladation of the ferrocene cyclopentadienyl ring, as an air-stable solid (Scheme 1). Characterizing data for **7b** are given in the Experimental Section. Cyclopalladation was readily ascertained by IR and NMR spectroscopies. Accordingly, the shift of the (C═N) stretch toward lower wavenumbers and the upfield shift of the *H*C═N resonance in the ^{1}H NMR spectrum supported nitrogen coordination to the metal center.[19−21] Two signals of relative intensities of 1:5 at δ3.94 and δ4.43 in the ^{1}H NMR spectrum were assigned to the cyclopentadienyl resonances, the former for the sole proton of the metalated ring and the latter for the five equivalent protons of the unsubstituted ring; also, the S*Me* resonance was downfield-shifted by ca. 0.5 ppm, in agreement with Pd−S coordination. The ^{13}C NMR spectrum showed the downfield shift of the C═N, C1, C2, and C3 resonances upon the second metalation of the ferrocene ring, with the most noticeable displacement at C3 at ca. 30 ppm, after metalation.

3. CONCLUSIONS

We have shown that ferrocenylimine palladacycles may be obtained as complexes bearing a formyl group, provided that the organic functionality is protected throughout the metalation process. This is achieved in the present case by an acetalization reaction prior to metalation, following the Bunz method, giving cyclometalated compounds with a dioxane ring, which, after controlled hydrolysis, yield the aforementioned derivatives. The reaction between the functionalized palladacycle and a primary amine, with formation of a C═N double bond, and ulterior treatment with a palladium(II) salt gives a trinuclear compound presenting a 1,3-double metalated cyclopentadienyl ring from the ferrocene moiety, a species that is a novelty in cyclometalation chemistry. The results depicted herein are but the initial step in what we expect to be a new and wide range of cyclometalated complexes, and the ensuing preparations are currently in progress.

4. EXPERIMENTAL SECTION

4.1. General Remarks. Solvents were purified by standard methods.[28] Reagents were used as supplied; CpFe[(CHO){C(H)O-(CH$_2$)$_3$O}-η^5-C$_5$H$_3$] was synthesized using the Bunz method.[18] All preparations were carried out under dry dinitrogen. Elemental analyses were performed with a Fisons elemental analyzer, model 1108. IR spectra were recorded as Nujol mulls or polythene discs on PerkinElmer 1330, Mattson model Cygnus-100, and Bruker model IFS-66 V spectrophotometers. ^{1}H NMR spectra in solution were recorded in $CDCl_3$ at room temperature on a Varian Mercury 300 spectrometer operating at 300.14 MHz using 5 mm o.d. tubes; chemical shifts, in parts per million, are reported downfield relative to TMS using the solvent signal ($CDCl_3$, δ^1H = 7.26 ppm) as a reference. ^{31}P NMR spectra were recorded at 202.46 MHz on a Bruker AMX 500 spectrometer using 5 mm o.d. tubes and are reported in parts per million relative to external H_3PO_4 (85%). Coupling constants are reported in hertz. The physical measurements were carried out by the RIAIDT services of the Universidad de Santiago de Compostela.

4.2. Synthesis of the Ligands. *CpFe[η^5-C$_5$H$_2${C(H)O(CH$_2$)$_3$O}-C(H)═N-2,4,6-Me$_3$C$_6$H$_2$] (**a**).* CpFe[1-(CHO)-2-{C(H)O(CH$_2$)$_3$O}-η^5-C$_5$H$_3$] (500 mg, 1.666 mmol) and 2,4,6-Me$_3$C$_6$H$_2$NH$_2$ (236 mg, 1.749 mmol) were added in chloroform (40 cm^3). The resulting solution was stirred under reflux for 8 h in a Dean−Stark apparatus. The solvent was then removed under vacum and the product collected as a red solid. Yield: 82%. Found: C, 69.2; H, 6.7; N, 3.5. $C_{24}H_{27}FeNO_2$ (417.32) requires C, 69.1; H, 6.5; N, 3.4. IR ν_{max}/cm^{-1}: 1630 s (C═N). NMR ^{1}H ($CDCl_3$): δ_H = 8.35 (s, 1H, *H*C═N), 6.91 (s, 1H, C$_6$H$_2$), 6.78 (s, 1H, C$_6$H$_2$), 5.63 (s, 1H, CHO$_2$), 4.96 [dd, 1H, H5, ^3J(H4H5) = 2.7 Hz, ^4J(H3H5) = 1.4 Hz], 4.64 [dd, 1H, H3, ^3J(H3H4) = 2.7 Hz, ^4J(H3H5) = 1.4 Hz], 4.44 [t, 1H, H4, ^3J(H4H5) = 2.7 Hz, ^3J(H3H4) = 2.7 Hz], 4.28 (s, 5H, C$_5$H$_5$), 4.19, 3.92, 2.11, 1,38 (m, 6H, CH$_2$), 2.30 (s, 3H, Me), 2.22 (s, 3H, Me), 2.18 (s, 3H, Me). NMR ^{13}C ($CDCl_3$): δ_C = 158.5 (C═N), 146.1 (C$_i$), 129.2 (C$_m$), 128.9 (C$_p$), 126.4 (C$_o$), 100.2 (C$_6$), 85.4 (C$_1$), 70.3 (C$_5$), 70.1 (C$_4$), 69.2 (C$_3$), 67.4 (C$_2$), 66.3 (C$_7$), 25.1 (C$_8$), 21.9, 18.9 (Me), 69.5 (Cp). FAB-MS: m/z = 418 [MH]$^+$.

Ligand **b** was prepared analogously.

*CpFe[η^5-C$_5$H$_2${C(H)O(CH$_2$)$_3$O}C(H)═NCy] (**b**):* Yield: 95%. Found: C, 66.6; H, 6.9; N, 3.6. $C_{21}H_{27}FeNO_2$ (381.29) requires C, 66.2; H, 7.1; N, 3.7. IR ν_{max}/cm^{-1}: 1636 s (C═N). NMR ^{1}H ($CDCl_3$): δ_H = 8.34 (s, 1H, *H*C═N), 5.62 (s, 1H, CHO$_2$), 4.77 [dd, 1H, H5, ^3J(H4H5) = 2.6 Hz, ^4J(H3H5) = 1.7 Hz], 4.51 [dd, 1H, H3, ^3J(H3H4) = 2.6 Hz, ^4J(H3H5) = 1.7 Hz], 4.29 [t, 1H, H4, ^3J(H4H5) = 2.6 Hz, ^3J(H3H4) = 2.6 Hz], 4.14 (s, 5H, C$_5$H$_5$), 4.22, 3.94, 2.19, 1.33 (m, 6H, CH$_2$), 3.05 (m, 1H, H-Cy). NMR ^{13}C ($CDCl_3$): δ_C = 158.8 (C═N), 100.4 (C$_6$), 86.3 (C$_1$), 70.6 (C$_5$), 70.4 (C$_4$), 69.5 (C$_3$), 68.7 (C$_i$), 67.4 (C$_2$), 65.9 (C$_7$), 24.8 (C$_8$), 34.3, 25.6, 24.6 (Cy), 69.3 (Cp). FAB-MS: m/z = 382 [MH]$^+$.

4.3. Synthesis of the Complexes. *[Pd{CpFe[η^5-C$_5$H$_2${C(H)O-(CH$_2$)$_3$O}C(H)═N-2,4,6-Me$_3$C$_6$H$_2$]}(Cl)]$_2$ (**1a**).* In a round-bottom 100 mL Schlenk flask, palladium(II) chloride (85 mg, 0.479 mmol) and lithium chloride (41 mg, 0.958 mmol) were added together in methanol (40 cm^3). The resulting suspension was stirred for 2 h. Ligand **a** (200 mg, 0.479 mmol) and sodium acetate were then added, and the mixture was stirred for 48 h, after which a precipitate formed, which was filtered off, washed with methanol, and dried under vacum. Yield: 72%. Found: C, 51.8; H, 4.8; N, 2.8. $C_{48}H_{52}N_2Cl_2Fe_2O_4Pd_2$ (1116.37 g/mol) requires C, 51.6; H, 4.7; N, 2.5. IR ν_{max}/cm^{-1}: 1577 s (C═N), 334 s, 267 m (Pd−Cl). NMR ^{1}H ($CDCl_3$): δ_H = 7.99 (s, 1H, *H*C═N), 6.96 (s, 1H, C$_6$H$_2$), 6.66 (s, 1H, C$_6$H$_2$), 4.64 (m, 1H, H3), 5.59 (s, 1H, CHO$_2$), 4.59 (m, 1H, H4), 4.33 (s, 5H, C$_5$H$_5$), 4.12, 3.83, 2.52, 1.37 (m, 6H, CH$_2$), 2.95 (s, 3H, Me), 2.30 (s, 3H, Me), 2.24 (s, 3H, Me). NMR ^{13}C ($CDCl_3$): δ_C = 167.6 (C═N), 146.2 (C$_i$), 129.1 (C$_m$), 128.8 (C$_p$), 126.3 (C$_o$), 101.2 (C$_5$), 100.1 (C$_6$), 95.2 (C$_1$), 72.1

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(C_4), 72.0 (C_3), 68.1 (C_2), 66.2 (C_7), 25.2 (C_8), 21.2, 18.9 (Me), 70.7 (Cp). FAB-MS: m/z = 1116 $[MH]^+$, 1081 $[MH - Cl]^+$.

Compound **1b** was prepared similarly.

*[Pd{CpFe[η^5-C_5H_2{C(H)O(CH$_2$)$_3$O}C(H)=NCy]}(Cl)]$_2$ (**1b**):* Yield: 62%. Found: C, 49.5; H, 5.8; N, 2.4. $C_{42}H_{52}N_2Cl_2Fe_2O_4Pd_2$ (1044.31 g/mol) requires C, 48.3; H, 5.0; N, 2.7. IR ν_{max}/cm^{-1}: 1578 s (C=N), 331 s, 250 m (Pd−Cl). NMR ^{1}H ($CDCl_3$): δ_H = 8.04 (s, 1H, *H*C=N), 5.70 (s, 1H, CHO_2), 4.64 (b, 1H, H3), 4.50 (b, 1H, H4), 4.28 (s, 5H, C_5H_5), 4.21, 3.90, 2.41, 0.88 (m, 6H, CH_2), 3.43 (m, 1H, H-Cy). NMR ^{13}C ($CDCl_3$): δ_C = 166.9 (C=N), 100.2 (C_6), 96.1 (C_1), 100.5 (C_5), 71.9 (C_4), 72.0 (C_3), 67.9 (C_2), 67.5 (C_i), 66.0 (C_7), 24.9 (C_8), 34.3, 25.1, 24.8 (Cy), 70.6 (Cp). FAB-MS: m/z = 1044 $[M]^+$.

*[Pd{CpFe[η^5-C_5H_2{C(H)O(CH$_2$)$_3$O}C(H)=N-2,4,6-Me$_3$C$_6$H$_2$]}(Ph$_2$P-(CH$_2$)P-Ph$_2$-P,P)][PF$_6$] (**2a**).* Compound **1a** (30 mg, 0.026 mmol) and $Ph_2P(CH_2)PPh_2$ (20 mg, 0.052 mmol) were added together in acetone (15 cm^3). The mixture was stirred for 24. NH_4PF_6 was then added, and stirring continued for 1 h. Addition of water produced a precipitate that was filtered off, dried under vacum, and recrystallized from dichloromethane/hexane. Yield: 44%. Found: C, 55.7; H, 4.4; N, 1.5. $C_{49}H_{48}NF_6FeO_2P_3Pd$ (1052.09 g/mol) requires C, 55.9; H, 4.6; N, 1.3. IR ν_{max}/cm^{-1}: 1575 m (C=N). NMR ^{1}H ($CDCl_3$): δ_H = 8.34 (d, 1H, *H*C=N, ^4J(PH) = 7.9 Hz), 6.68 (s, 2H, C_6H_2), 5.45 (s, 1H, CHO_2), 4.27 (b, 1H, H3), 4.32, 3.88 (m, 6H, CH_2), 4.15 (s, 5H, C_5H_5), 3.72 (b, 1H, H4), 2.38 (s, 3H, Me), 2.30 (s, 3H, Me), 2.06 (s, 3H, Me). NMR ^{13}C ($CDCl_3$): δ_C = 167.2 (C=N), 146.0 (C_i), 135−126 (PPh_2 + $C_{mesityl}$), 102.0 (C_5), 100.0 (C_6), 95.1 (C_1), 72.3 (C_4), 71.9 (C_3), 68.0 (C_2), 66.1 (C_7), 25.0 (C_8), 20.9, 18.7 (Me), 70.9 (Cp). NMR ^{31}P ($CDCl_3$): δ_P = 51.3 (d, ^2J(PP) = 20.1 Hz), 27.2 (d, ^2J(PP) = 20.1 Hz). FAB-MS: m/z = 907 $[MH - PF_6]^+$.

Compounds **3a**, **2b**, and **3b** were synthesized analogously.

*[Pd{CpFe[η^5-C_5H_2{C(H)O(CH$_2$)$_3$O}C(H)=N-2,4,6-Me$_3$C$_6$H$_2$]}(Ph$_2$P-(CH$_2$)$_2$P-Ph$_2$-P,P)][PF$_6$] (**3a**):* Yield: 39%. Found: C, 56.8; H, 4.4; N, 1.4. $C_{50}H_{50}NF_6FeO_2P_3Pd$ (1066.11 g/mol) requires C, 56.3; H, 4.7; N, 1.3. IR ν_{max}/cm^{-1}: 1572 w (C=N). NMR ^{1}H ($CDCl_3$): δ_H = 8.34 (d, 1H, *H*C=N, ^4J(PH) = 8.1 Hz), 6.43 (s, 1H, C_6H_2), 6.20 (s, 1H, C_6H_2), 5.44 (s, 1H, CHO_2), 4.59 (b, 1H, H3), 4.17, 3.88, 1.42 (m, 6H, CH_2), 4.04 (s, 5H, C_5H_5), 3.73 (b, 1H, H4), 2.21 (s, 3H, Me), 2.11 (s, 3H, Me), 1.78 (s, 3H, Me). NMR ^{13}C ($CDCl_3$): δ_C = 166.9 (C=N), 146.3 (C_i), 135−125 (PPh_2 + $C_{mesityl}$), 101.7 (C_5), 100.5 (C_6), 96.4 (C_1), 72.4 (C_4), 71.8 (C_3), 68.1 (C_2), 66.4 (C_7), 25.2 (C_8), 22.3, 19.1 (Me), 70.8 (Cp). NMR ^{31}P ($CDCl_3$): δ_P = 56.7 (d, ^2J(PP) = 26.8 Hz), 42.3 (d, ^2J(PP) = 26.8 Hz). FAB-MS: m/z = 922 $[MH - PF_6]^+$.

*[Pd{CpFe[η^5-C_5H_2{C(H)O(CH$_2$)$_3$O}C(H)=NCy]}(Ph$_2$P(CH$_2$)P-Ph$_2$-P,P)][PF$_6$] (**2b**):* Yield: 50%. Found: C, 54.0; H, 4.9; N, 1.6. $C_{46}H_{48}NF_6FeO_2P_3Pd$ (1016.06 g/mol) requires C, 54.4; H, 4.8; N, 1.4. IR ν_{max}/cm^{-1}: 1590 w (C=N). NMR ^{1}H ($CDCl_3$): δ_H = 8.47 (d, 1H, *H*C=N, ^4J(PH) = 8.4 Hz), 5.29 (s, 1H, CHO_2), 4.51 (b, 1H, H3), 3.95, 3.57 (m, 6H, CH_2), 4.04 (s, 5H, C_5H_5), 3.85 (b, 1H, H4), 3.31 (m, 1H, H-Cy). NMR ^{13}C ($CDCl_3$): δ_C = 172.2 (C=N), 133.9, 131.0, 128.3, 127.5 (PPh_2), 101.4 (C_6), 102.1 (C_5), 93.3 (C_1), 72.3 (C_4), 71.8 (C_3), 68.4 (C_2), 67.9 (C_i), 65.8 (C_7), 24.9 (C_8), 34.5, 25.2, 25.0 (Cy), 71.1 (Cp). NMR ^{31}P ($CDCl_3$): δ_P = 30.4 (d, ^2J(PP) = 52 Hz); −4.7 (d, ^2J(PP) = 52.0 Hz). FAB-MS: m/z = 870 $[M - PF_6]^+$.

*[Pd{CpFe[η^5-C_5H_2{C(H)O(CH$_2$)$_3$O}C(H)=NCy]}(Ph$_2$P(CH$_2$)$_2$PPh$_2$-P,P)][PF$_6$] (**3b**):* Yield: 60%. Found: C, 55.3; H, 4.8; N, 1.5. $C_{47}H_{50}NF_6FeO_2P_3Pd$ (1030.08 g/mol) requires C, 54.8; H, 4.9; N, 1.4. IR ν_{max}/cm^{-1}: 1591 w (C=N). NMR ^{1}H ($CDCl_3$): δ_H = 8.52 (d, 1H, *H*C=N, ^4J(PH) = 9.4 Hz), 5.42 (s, 1H, CHO_2), 4.45 (b, 1H, H3), 4.20 (m, 6H, CH_2), 3.93 (s, 5H, C_5H_5), 3.61 (b, 1H, H4), 2.90 (m, 1H, H-Cy). NMR ^{13}C ($CDCl_3$): δ_C = 171.1 (C=N), 101.3 (C_6), 134.2, 130.1, 129.5, 127.1 (PPh_2), 102.3 (C_5), 93.7 (C_1), 72.0 (C_4), 71.8 (C_3), 68.2 (C_2), 67.8 (C_i), 65.9 (C_7), 25.0 (C_8), 34.2, 25.7, 25.1 (Cy), 71.5 (Cp). NMR ^{31}P ($CDCl_3$): δ_P = 57.2 (d, ^2J(PP) = 26.8 Hz); 44.5 (d, ^2J(PP) = 26.8 Hz). FAB-MS: m/z = 884 $[M - PF_6]^+$.

*[Pd{CpFe[η^5-C_5H_2{C(H)O}C(H)=N-2,4,6-Me$_3$C$_6$H$_2$]}-(Ph$_2$PCH$_2$PPh$_2$)][PF$_6$] (**4a**):* Yield: 88%. Found: C, 56.1; H, 4.5; N, 1.7. $C_{46}H_{42}NF_6FeOP_3Pd$ (994.01 g/mol) requires C, 55.6; H, 4.3; N, 1.4. IR ν_{max}/cm^{-1}: 1726 w (C=O), 1591 sh,m (C=N). NMR ^{1}H ($CDCl_3$): δ_H = 9.99 (s, 1H, CHO), 8.59 (d, 1H, *H*C=N, ^4J(PH) = 8.1 Hz), 6.69 (s, 1H, C_6H_2), 6.60 (s, 1H, C_6H_2), 4.46 (m, 1H, H3), 4.20 (s, 5H, C_5H_5), 4.06 (m, 1H, H4), 2.35 (s, 3H, Me), 2.32 (s, 3H, Me), 2.25 (s, 3H, Me). NMR ^{13}C ($CDCl_3$): δ_C = 194.4 (C=O), 168.1 (C=N), 145.9 (C_i), 135−126 (PPh_2 + $C_{mesityl}$), 101.2 (C_5), 94.1 (C_1), 71.7 (C_4), 72.1 (C_3), 68.3 (C_2), 21.1, 18.7 (Me), 71.0 (Cp). NMR ^{31}P ($CDCl_3$): δ_P = 54.4 (d, ^2J(PP) = 23.1 Hz), 27.5 (d, ^2J(PP) = 23.1 Hz). FAB-MS: m/z = 848 $[M - PF_6]^+$.

*[Pd{CpFe[η^5-C_5H_2{C(H)O}C(H)=N-2,4,6-Me$_3$C$_6$H$_2$]}(Ph$_2$P-(CH$_2$)$_2$PPh$_2$)][PF$_6$] (**5a**).* Yield: 86%. Found: C, 56.5; H, 4.6; N, 1.7. $C_{47}H_{44}NF_6FeOP_3Pd$ (1008.04 g/mol) requires C, 56.0; H, 4.4; N, 1.4. IR ν_{max}/cm^{-1}: 1667 m (C=O), 1601 w (C=N). NMR ^{1}H ($CDCl_3$): δ_H = 9.99 (s, 1H, CHO), 8.59 (d, 1H, *H*C=N, ^4J(PH) = 7.9 Hz), 6.37 (s, 1H, C_6H_2), 6.23 (s, 1H, C_6H_2), 5.03 (b, 1H, H3), 4.17 (b, 1H, H4), 4.10 (s, 5H, C_5H_5), 2.16 (s, 3H, Me), 2.11 (s, 3H, Me), 1.81 (s, 3H, Me). NMR ^{13}C ($CDCl_3$): δ_C = 193.9 (C=O), 167.7 (C=N), 145.8 (C_i), 135−126 (PPh_2 + $C_{mesityl}$), 100.1 (C_5), 94.5 (C_1), 72.3 (C_4), 70.9 (C_3), 68.4 (C_2), 21.0, 18.7 (Me), 71.3 (Cp). NMR ^{31}P ($CDCl_3$): δ_P = 57.6 (d, ^2J(PP) = 25.2 Hz), 44.3 (d, ^2J(PP) = 25.2 Hz). FAB-MS: m/z = 862 $[M - PF_6]^+$.

*[Pd{CpFe[η^5-C_5H_2{C(H)O}C(H)=NCy]}(Ph$_2$PCH$_2$PPh$_2$)][PF$_6$] (**4b**):* Yield: 78%. Found: C, 54.7; H, 4.3; N, 1.8. $C_{43}H_{42}NF_6FeOP_3Pd$ (957,98 g/mol) requires C, 53.9; H, 4.4; N, 1.5. IR ν_{max}/cm^{-1}: 1721 w (C=O), 1590 m (C=N). NMR ^{1}H ($CDCl_3$): δ_H = 9.91 (s, 1H, CHO), 5.21 [d, 1H, H3, ^3J(H3H4) = 2.4 Hz], 4.41 (s, 5H, C_5H_5), 4.28 [d, 1H, H4, ^3J(H3H4) = 2.4 Hz]. NMR ^{13}C ($CDCl_3$): δ_C = 194.1 (C=O), 167.5 (C=N), 135.1, 131.3, 128.4, 125.1 (PPh_2),101.4 (C_5), 95.1 (C_1), 73.0 (C_4), 72.0 (C_3), 68.9 (C_2), 68.2 (C_i), 33.9, 25.9, 24.7 (Cy), 71.4 (Cp). NMR ^{31}P ($CDCl_3$): δ_P = 28.4 (d, ^2J(PP) = 52.0 Hz), −2.2 (d, ^2J(PP) = 52.0 Hz). FAB-MS: m/z = 812 $[M - PF_6]^+$.

*[Pd{CpFe[η^5-C_5H_2{C(H)O}C(H)=NCy]}(Ph$_2$P(CH$_2$)$_2$PPh$_2$)][PF$_6$] (**5b**):* Yield: 79%. Found: C, 55.1; H, 4.5; N, 1.7. $C_{44}H_{44}NF_6FeOP_3Pd$ (972.00 g/mol) requires C, 54.4; H, 4.6; N, 1.4. IR ν_{max}/cm^{-1}: 1719 m (C=O), 1601 m (C=N). NMR ^{1}H ($CDCl_3$): δ_H =10.36 (s, 1H, CHO), 5.22 [d, 1H, H3, ^3J(H3H4) = 2.7 Hz], 4.40 (s, 5H, C_5H_5), 3.97 (b, 1H, H4). NMR ^{13}C ($CDCl_3$): δ_C = 194.2 (C=O), 170.0 (C=N), 135.0, 130.2, 128.5, 126.1 (PPh_2), 102.3 (C_5), 94.8 (C_1), 72.9 (C_4), 71.7 (C_3), 68.8 (C_2), 68.0 (C_i), 33.8, 25.8, 24.9 (Cy), 71.7 (Cp). NMR ^{31}P ($CDCl_3$): δ_P = 57.4 (d, ^2J(PP) = 26.3 Hz); 42.3 (d, ^2J(PP) = 26.3 Hz). FAB-MS: m/z = 826 $[M - PF_6]^+$.

*[Pd(Ph$_2$P(CH$_2$)$_2$PPh$_2$){(CpFe)η^5-C_5H_2[C(H)=NCy][C(H)=N(2-SMeC$_6$H$_4$)}]][PF$_6$] (**6b**).* Compound **5b** (40 mg, 0.041 mmol) and 2-methylthioaniline (5.7 mg, 0.042 mmol) in benzene were heated together under reflux in a Dean−Stark apparatus. After cooling and evaporation of the solvent, the desired product was obtained as a red solid. Yield: 81%. Found: C, 56.1; H, 4.6; N, 2.6; S, 2.8. $C_{51}H_{51}N_2F_6FeP_3PdS$ (1093.19 g/mol) requires C, 56.0; H, 4.7; N, 2.6; S, 2.9. IR ν_{max}/cm^{-1}: 1624 m, 1601 m (C=N). NMR ^{1}H ($CDCl_3$): δ_H = 8.37 (s, 1H, *H*C=N), 8.15 (d, 1H, *H*C=N, ^4J(PH) = 8.0 Hz), 7.00 (m, 4H), 5.28 [d, 1H, H3, ^3J(H3H4) = 2.9 Hz], 4.38 (s, 5H, C_5H_5), 4.01 (b, 1H, H4), 2.36 (s, 3H, S*Me*). NMR ^{13}C ($CDCl_3$): δ_C = 169.9, 158.3 (C=N), 150.1 ($C_{1'}$), 135−124 (PPh_2 + $C_{thioaniline}$), 118.0 ($C_{3'}$), 101.4 (C_5), 93.9 (C_1), 84.9 (C_2), 71.8 (C_4), 71.5 (C_3), 68.1 (C_i), 34.0, 25.0, 24.9 (Cy), 24.5 (SMe), 71.9 (Cp). NMR ^{31}P ($CDCl_3$): δ_P = 57.2 (d, ^2J(PP) = 26.0 Hz), 42.5 (d, ^2J(PP) = 26.0 Hz). FAB-MS: m/z = 947 $[M - PF_6]^+$.

*[Pd(Ph$_2$P(CH$_2$)$_2$PPh$_2$){(CpFe)η^5-C_5H[C(H)=NCy][C(H)=N(2-SMeC$_6$H$_4$)}PdCl]-[PF$_6$] (**7b**).* Compound **6b** (50 mg, 0.046 mmol), $Li_2[PdCl_4]$ (11.3 mg, 0.043 mmol) (prepared in situ from $PdCl_2$ and LiCl), and sodium acetate (24.6 mg, 0.3 mmol) were added in methanol (30 cm^3). The mixture was stirred for 48 h at room temperature under nitrogen. The resulting red precipitate was filtered off, washed with ethanol, and dried. Yield: 52%. Found: C, 49.4; H, 4.2; N, 2.2; S, 2.6. $C_{51}H_{50}N_2ClF_6FeP_3Pd_2S$ (1234.03 g/mol) requires C, 49.6; H, 4.1; N, 2.3; S, 2.6. IR ν_{max}/cm^{-1}: 1605 m, 1601 m (C=N). NMR ^{1}H ($CDCl_3$): δ_H = 8.17 (s, 1H, *H*C=N), 8.10 (d, 1H, *H*C=N, ^4J(PH) = 7.9 Hz), 8.04 (d, 1H, H6′, ^3J(H6′H5′) = 7.9 Hz), 7.95 (d, 1H, H3′, ^3J(H3′H4′) = 8.1 Hz), 3.91 (b, 1H, H4), 4.43 (s, 5H, C_5H_5), 2.81 (s, 3H, S*Me*). NMR ^{13}C ($CDCl_3$): δ_C = 172.2, 170.1 (C=N), 147.9 ($C_{1'}$), 135.6−123 (PPh_2 + $C_{thioaniline}$), 117.5 ($C_{3'}$), 102.7 (C_3), 101.8 (C_5), 99.5 (C_1), 90.4 (C_2), 73.6 (C_4), 67.8 (C_i), 33.7, 25.3, 24.8

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(Cy), 26.7 (SMe), 71.5 (Cp). NMR ^{31}P ($CDCl_3$): δ_P = 57.0 (d, ^2J(PP) = 26.2 Hz), 42.1 (d, ^2J(PP) = 26.2 Hz). FAB-MS: m/z = 1089 $[M - PF_6]^+$.

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