## Kinetics of the $S_N1$ dissociation of ligands L (nitriles, phosphines) in the complexes [CpFe(P-P)L]PF<sub>6</sub> with variable chelate ring size. A surprising bimolecular substitution in the non-chelate complex [CpFe(PPh<sub>2</sub>Me)<sub>2</sub>L]PF<sub>6</sub>

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Complex	[CpFe(dppe)NCMe]PF <sub>6</sub>	[CpFe(dppe)PPh <sub>2</sub> - (OMe)]PF <sub>6</sub>	[CpFe(dppe)PPh <sub>2</sub> - (OEt)]PF <sub>6</sub>	[CpFe(dppe)PPh <sub>2</sub> - (O <i>i</i> Pr)]PF <sub>6</sub> CHCl <sub>3</sub>	[CpFe(dppe)P(OM) <sub>3</sub> ] PF <sub>6</sub>
Empirical formula	C <sub>33</sub> H <sub>32</sub> FeNP <sub>2</sub> , F <sub>6</sub> P	$C_{44}H_{42}FeOP_3, F_6P$	$C_{45}H_{44}FeP_3, F_6P$	$\frac{C_{46}H_{46}FeOP_3, CHCl_3,}{F_6P}$	$C_{34}H_{38}FeO_3P_3, F_6P$
Formula weight	705.35	880.5	894.53	1027.93	788.37
Crystal system	monoclinic	monoclinic	Monoclinic	triclinic	monoclinic
Space group	$P2_1/n$	C2/c	C2/c	PĪ	$P2_1/c$
<i>a</i> (Å)	12.4692(5)	38.785(13)	37.9260(12)	10.8369(8)	11.1635(4)
b (Å)	15.5620(6)	12.895(4)	12.6048(5)	12.6462(9)	16.6012(6)
c (Å)	16.9467(5)	16.767(4)	18.0209(6)	17.9320(14)	19.9065(7)
$\alpha$ (°)	90	90	90	77.660(2)	90
$\beta(^{\circ})$	99.3700(10)	104.747(10)	105.1740(10)	79.840(2)	107.2940(10)
γ (°)	90	90	90	75.172(2)	90
$V(\text{\AA})^3$	3244.6(2)	8109(4)	8314.4(5)	2301.4(3)	3522.4(2)
Ζ	4	8	8	2	4
pcalcd (Mg/m <sup>3</sup> )	1.4424	1.442	1.429	1.483	1.487
Abs coeff $(mm^{-1})$	0.672	0.592	0.579	0.702	0.676
Abs correct	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan
Transmiss max/min	1.0000/0.7731	1.0000/0.5305	1.0000/0.5305	1.0000/0.6457	1.0000/0.4249
F(000)	1448	3632	3696	1056	1624
Crystal size (mm)	0.25 x 0.17 x 0.15	0.24 x 0.07 x 0.05	0.23 x 0.20 x 0.14	0.38 x 0.17 x 0.10	0.38 x 0.18 x 0.08
<i>Θ</i> range (°)	3.013-24.999	3.07-24.997	3.02-25	3.08-27.408	3.10-25
Rflns/unique	24949/5702	27894/6912	30802/7298	22240/10310	26969/6195
R <sub>int</sub>	0.0528	0.1417	0.0835	0.0619	0.0745
Data/params	5702/398	6912/506	7298/514	10310/561	6195/436
Goodness of fit $F^2$	1.039	0.909	1.087	1.088	1.058
$R_1/wR_2$ ( $I > 2\sigma(I)$ )	0.0396/0.0850	0.084/0.1786	0.051/0.1182	0.0529/0.1133	0.0413/0.1009
$R_1/wR_2$ (all data)	0.0544/0.0916	0.1411/0.2155	0.0835/0.1382	0.0922/0.137	0.0549/0.1087
Abs. struct. param	-	-	-	-	-
Largest diff. peak and hole (e $\text{\AA}^{-3}$ )	0.473/-0.321	0.424/-0.484	0.505/-0.427	0.709/-0.682	0.619/-0.47
CCDC No.	1535363	1535364	1535365	1535366	1535367

**Table S1.** Crystallographic Data for the Complexes (Mo $K_{\alpha}$  radiation)

Complex	[CpFe(dppe)PPh-	[CpFe(PPh <sub>2</sub> Me) <sub>2</sub> NCMe]	[CpFe(PPh <sub>2</sub> Me) <sub>2</sub> -	[CpFe(PPh <sub>2</sub> Me) <sub>2</sub> -	[CpFe(PPh <sub>2</sub> Me) <sub>2</sub> I]
	$(OMe)_2]PF_6$	PF <sub>6</sub>	$P(OMe)_3]PF_6 CH_2Cl_2$	$PPh(OMe)_2]PF_6$	$CH_2Cl_2$
				CH <sub>2</sub> Cl <sub>2</sub>	
Empirical formula	C <sub>39</sub> H <sub>40</sub> FeO <sub>2</sub> P <sub>3</sub> , F <sub>6</sub> P	$C_{33}H_{34}NP_2Fe$ , $F_6P$	$C_{34}H_{40}FeOP_2$ , $F_6P$ ,	$C_{39}H_{42}FeO_2P_3, F_6P_2$	C <sub>31</sub> H <sub>31</sub> FeIP <sub>2</sub> , CH <sub>2</sub> Cl <sub>2</sub>
			CH <sub>2</sub> Cl <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub>	
Formula weight	830.41	707.37	875.31	921.38	733.17
Crystal system	orthorhombic	triclinic	Monoclinic	monoclinic	triclinic
Space group	Pbca	PĪ	$P2_1/c$	$P2_1/n$	$P\overline{1}$
<i>a</i> (Å)	12.2498(4)	9.493(5)	8.9902(2)	11.6214(11)	10.035(4)
$b(\dot{A})$	19.1993(9)	12.392(5)	22.0037(6)	23.3763(19)	11.862(5)
<i>c</i> (Å)	31.6611(12)	14.053(5)	20.2720(5)	15.6475(13)	13.738(5)
α (°)	90	90.386(16)	90	90	70.821(16)
$\beta(^{\circ})$	90	93.909(16)	103.5440(10)	104.939(2)	86.016(13)
γ (°)	90	102.325(14)	90	90	83.341(15)
$V(\text{\AA})^3$	7446.3(5)	1611.0(12)	3974.32(18)	4107.2(6)	1533.3(11)
Ζ	8	2	4	4	2
pcalcd (Mg/m <sup>3</sup> )	1.481	1.458	1.491	1.490	1.588
Abs coeff $(mm^{-1})$	0.642	0.677	0.751	0.7160	1.798
Abs correct	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan
Transmiss max/min	1.0000/0.9909	1.0000/0.7628	1.0000/0.7531	1.0000/0.52964	1.0000/0.5972
F (000)	3408	728	1800	1896	736
Crystal size (mm)	0.52 x 0.08 x 0.07	0.36 x 0.30 x 0.15	0.70 x 0.24 x 0.18	0.26 x 0.13 x 0.06	0.20 x 0.13 x 0.08
$\Theta$ range (°)	2.087-24.999	3.045-24.999	3.236-24.999	3.07-25.00	3.02-27.485
Rflns/unique	55723/6451	12799/5654	47138/6868	31695/7216	15116/6935
$R_{\rm int}$	0.1841	0.0323	0.045	0.2042	0.0459
Data/params	6451/471	5654/400	6868/465	7216/496	6935/345
Goodness of fit $F^2$	1.047	1.069	0.962	1.035	1.057
$R_1/wR_2$ ( $I > 2\sigma(I)$ )	0.0741/0.1462	0.0412/0.0881	0.0377/0.0917	0.0923/0.1442	0.0429/0.0838
$R_1/wR_2$ (all data)	0.1118/0.1674	0.053/0.0925	0.0464/0.0962	0.1735/0.1766	0.0555/0.0888
Abs. struct. param	-	-	-	-	-
Largest diff. peak and hole (e $Å^{-3}$ )	0.813/-0.691	0.511/-0.334	0.941/-0.608	0.526/-0.528	1.172/-0.843
CCDC No.	1535368	1535369	1535370	1535371	1535372

**Table S1.** Crystallographic Data for the Complexes (Mo $K_{\alpha}$  radiation)

Complex	[CpFe(dppp)NCMe] PF <sub>6</sub> CHCl <sub>3</sub>	[CpFe(dppp)- P(OMe) <sub>3</sub> ]PF <sub>6</sub>	[CpFe(dppp)- PPh(OMe) <sub>2</sub> ]PF <sub>6</sub>	[CpFe(dppp)- PPh <sub>2</sub> (OMe)PF <sub>6</sub>	[CpFe(dppp)- PPh <sub>2</sub> (OEt)]PF <sub>6</sub>
Empirical formula	$C_{34}H_{34}FeNP_2, F_6P,$ CHCl <sub>2</sub>	$C_{35}H_{40}FeO_3P_3, F_6P$	$C_{39}H_{40}FeO_2P_3, F_6P$	$C_{45}H_{44}FeOP_3, F_6P$	$C_{46}H_{46}FeOP_3, F_6P$
Formula weight	838.75	802.4	848.46	894.53	908.56
Crystal system	monoclinic	orthorhombic	Orthorhombic	orthorhombic	monoclinic
Space group	C2/c	Pca2 <sub>1</sub>	$P$ na $2_1$	$Pn2_1a$	$P2_1/c$
a (Å)	27.0808(19)	17.1671(6)	14.1022(4)	12.6131(14))	13.3871(10)
b (Å)	12.0515(8)	9.4816(3)	19.7486(4)	16.3705(19)	13.6101(9)
c(Å)	22.5312(16)	21.5862(6)	13.9570(6)	19.791(2)	25.3570(18)
$\alpha$ (°)	90	90	90	90	90
$\beta(^{\circ})$	92.450(2)	90	90	90	104.8700(10)
γ (°)	90	90	90	90	90
$V(A)^3$	7346.7(9)	3513.6(3)	3887.0(2)	4086.4(8)	4465.3(5)
Ζ	8	4	4	4	4
pcalcd (Mg/m <sup>3</sup> )	1.517	1.517	1.45	1.454	1.351
Abs coeff (mm <sup>-1</sup> )	0.818	0.679	0.616	0.589	0.540
Abs correct	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan
Transmiss max/min	1.0000/0.0938	1.0000/0.5765	1.0000/0.6350	1.0000/0.6262	1.0000/0.8813
F (000)	3424	1656	1752	1848	55402
Crystal size (mm)	0.24 x 0.18 x 0.17	0.19 x 0.11 x 0.10	0.30 x 0.14 x 0.11	0.24 x 0.24 x 0.11	0.41 x 0.36 x 0.35
$\Theta$ range (°)	2.992-27.456	3.032-27.431	3.068-24.987	3.009-24.999	2.993-25.00
Rflns/unique	34985/8360	53039/7954	47657/6811	30590/7182	55402/7852
R <sub>int</sub>	0.176	0.1408	0.0826	0.0629	0.0443
Data/params	8360/443	7954/445	6811/471	7182/515	7852/582
Goodness of fit $F^2$	1.032	1.087	1.047	1.052	1.200
$R_1/wR_2(I>2\sigma(I))$	0.082/0.1862	0.0487/0.0945	0.0388/0.0888	0.0467/0.1136	0.1177/0.3143
$R_1/wR_2$ (all data)	0.1625/0.2365	0.0743/0.1071	0.0484/0.0938	0.053/0.1181	0.122/0.3163
Abs. struct. param	-	0.015(12)	0.011(10)	0.014(9)	-
Largest diff. peak and hole (e $(A^{-3})$ )	0.71/-0.836	0.468/-0.575	0.393/-0.327	0.915/-0.389	1.976/-1.093
CCDC No.	1535373	1535374	1535375	1535376	1535377

**Table S1.** Crystallographic Data for the Complexes (Mo $K_{\alpha}$  radiation)

Complex	[CpFe(dppm)-	[CpFe(dppb)-	$[CpFe{PPh_2(OMe)}_2-$	[CpFe(PPh <sub>2</sub> Me)-	$[CpFe{PPh_2(OMe)}_3]$
	$P(OMe)_3]PF_6$	$P(OMe)_3]PF_6, CHCl_3$	NCMe]PF <sub>6</sub>	$\{PPh_2(OMe)\}_2]PF_6,$	$PF_6$ , $CH_2Cl_2$
				2CH <sub>2</sub> Cl <sub>2</sub>	
Empirical formula	$C_{33}H_{36}FeO_3P_3, F_6P$	$2(C_{36}H_{42}FeO_{3}P_{3}),$	$C_{33}H_{34}FeO_2P_3, F_6P_2$	$C_{44}H_{44}FeO_2P_3$ , $F_6P$ ,	$C_{44}H_{44}FeO_3P_3$ , $F_6P_2$ ,
		$3(CHCl_3), 2(F_6P)$		$2(CH_2Cl_2)$	CH <sub>2</sub> Cl <sub>2</sub>
Formula weight	774.35	1990.95	739.37	1068.37	999.45
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	triclinic
Space group	$P2_1/c$	$P2_1/a$	$P2_1/c$	$P\bar{1}$	PĪ
$a(\text{\AA})$	19.3216(4)	14.7697(5)	9.6678(5)	12.1751(16)	12.4693(4)
b(A)	18.9000(4)	31.5883(8)	28.7237(14)	12.9407(19)	13.1771(6)
<i>c</i> (Å)	19.6203(4)	18.7195(5)	12.8949(7)	17.154(2)	16.1150(6)
$\alpha$ (°)	90	90	90	68.006(4)	101.983(2)
$\beta(^{\circ})$	111.7630(10)	97.9320(10)	112.4920(10)	69.407(4)	102.7650(10)
γ (°)	90	90	90	82.255(4)	108.874(2)
$V(\text{\AA})^3$	6654.2 (2)	8650.0(4)	3308.5(3)	2345.9(6)	2329.12(16)
Ζ	8	4	4	2	2
pcalcd (Mg/m <sup>3</sup> )	1.546	1.529	1.484	1.513	1.425
Abs coeff $(mm^{-1})$	0.714	0.837	0.667	0.748	0.639
Abs correct	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan
Transmiss max/min	1.0000/ 0.8467	1.0000/0.8227	1.0000/0.8698	1.0000/0.7954	1.0000/0.8063
F (000)	3184	4072	1520	1096	1028
Crystal size (mm)	0.50 x 0.14 x 0.13	0.55 x 0.16 x 0.10	0.32 x 0.25 x 0.24	0.49 x 0.38 x 0.26	0.42 x 0.39 x 0.04
$\Theta$ range (°)	3.009-25.00	3.046-24.999	3.109-24.996	3.181-25	3.18-25
Rflns/unique	77137/11683	107735/15210	41814/5824	29577/8225	18459/8220
R <sub>int</sub>	0.0752	0.0832	0.0402	0.0568	0.0296
Data/params	11688/853	15210/1027	5825/418	8225/572	8220/562
Goodness of fit $F^2$	1.036	1.045	1.033	1.077	1.044
$R_1/wR_2$ ( $I > 2\sigma(I)$ )	0.0431/0.087	0.078/0.1986	0.0449/0.1095	0.0811/0.2378	0.0856/0.2547
$R_1/wR_2$ (all data)	0.0752/0.0979	0.1122/0.2221	0.0537/0.1152	0.1099/0.2763	0.0979/0.2691
Largest diff. peak and hole (e	0.49/-0.399	1.495/-0.966	1.058/-1.028	1.545/-1.112	4.179/-1.231
Å <sup>-3</sup> )					
Abs. struct. param	-	-	-	-	-
CCDC No.	1535378	1535379	1549806	1549807	1550539

**Table S1.** Crystallographic Data for the Complexes (Mo $K_{\alpha}$  radiation)



**Figure S1.** Time-resolved  ${}^{31}P{}^{1}H$  NMR spectra of the ligand exchange of [CpFe(PPh<sub>2</sub>Me)NCMe]PF<sub>6</sub> with PPh(OMe)<sub>2</sub> (10 eq.) at 293 K in CDCl<sub>3</sub>.



**Figure S2.** Time dependence of the concentrations of reactants and products in the reaction of  $[CpFe(PPh_2Me)_2NCMe]PF_6$  with 5 equivalents of  $PPh_2(OMe)$  in  $CDCl_3$  at 293 K:  $[CpFe(PPh_2Me)_2NCMe]PF_6$  ( $\blacksquare$ ),  $[CpFe(PPh_2Me)_2PPh_2(OMe)]PF_6$  ( $\blacklozenge$ ),  $[CpFe(PPh_2Me)\{PPh_2(OMe)\}_2]PF_6$  ( $\blacktriangle$ ),  $[CpFe(PPh_2Me)\{PPh_2(OMe)\}_2NCMe]PF_6$  ( $\blacklozenge$ ),  $[CpFe\{PPh_2(OMe)\}_2NCMe]$  ( $\bigtriangleup$ ), and  $[CpFe\{PPh_2(OMe)\}_3]$  ( $\diamondsuit$ ).



**Figure S3.** Time-resolved  ${}^{31}P{}^{1}H$  NMR spectra of the ligand exchange of [CpFe(PPh<sub>2</sub>Me)NCMe]PF<sub>6</sub> with PPh<sub>2</sub>(O*i*Pr) (1 eq.) at 293 K in CDCl<sub>3</sub>.



**Figure S4-1.** <sup>1</sup>H NMR Spectrum of [CpFe(dppm)NCMe]PF<sub>6</sub> in acetone-*d*<sub>6</sub> at 293 K.



**Figure S4-2.** <sup>13</sup>C NMR Spectra of [CpFe(dppm)NCMe]PF<sub>6</sub> in acetone- $d_6$  at 293 K (top: DEPT135, bottom: decoupling).



**Figure S4-3.** <sup>31</sup>P{<sup>1</sup>H} NMR Spectrum of [CpFe(dppm)NCMe]PF<sub>6</sub> in acetone- $d_6$  at 293 K.



**Figure S5-1.** <sup>1</sup>H NMR Spectrum of [CpFe(dppe)NCMe]PF<sub>6</sub> in CDCl<sub>3</sub> at 293 K.



**Figure S5-2.** <sup>13</sup>C NMR Spectra of [CpFe(dppe)NCMe]PF<sub>6</sub> in CDCl<sub>3</sub> at 293 K (top: DEPT135, bottom: decoupling).



Figure S5-3. <sup>31</sup>P{<sup>1</sup>H} NMR Spectrum of [CpFe(dppe)NCMe]PF<sub>6</sub> in CDCl<sub>3</sub> at 293 K.



**Figure S5-4.** ORTEP drawing of [CpFe(dppe)NCMe]PF<sub>6</sub>. Hydrogen atoms and hexafluorophosphate anion are omitted for clarity.



**Figure S6-1.** <sup>1</sup>H NMR Spectrum of [CpFe(dppp)NCMe]PF<sub>6</sub> in CDCl<sub>3</sub> at 293 K.



**Figure S6-2.** <sup>13</sup>C NMR Spectra of [CpFe(dppp)NCMe]PF<sub>6</sub> in CDCl<sub>3</sub> at 293 K (top: DEPT135, bottom: decoupling).



**Figure S6-3.** <sup>31</sup>P{<sup>1</sup>H} NMR Spectrum of [CpFe(dppp)NCMe]PF<sub>6</sub> in CDCl<sub>3</sub> at 293 K.



**Figure S6-4.** ORTEP drawing of [CpFe(dppp)NCMe]PF<sub>6</sub>· CHCl<sub>3</sub>. Hydrogen atoms, hexafluorophosphate anion, and one CHCl<sub>3</sub> molecule are omitted for clarity.



**Figure S7-1.** <sup>1</sup>H NMR Spectrum of [CpFe(dppb)NCMe]PF<sub>6</sub> in CDCl<sub>3</sub> at 293 K.



**Figure S7-2.** <sup>13</sup>C NMR Spectra of [CpFe(dppb)NCMe]PF<sub>6</sub> in CDCl<sub>3</sub> at 293 K (top: DEPT135, bottom: decoupling).



**Figure S7-3.** <sup>31</sup>P{<sup>1</sup>H} NMR Spectrum of [CpFe(dppb)NCMe]PF<sub>6</sub> in CDCl<sub>3</sub> at 293 K.



**Figure S8-1.** <sup>1</sup>H NMR Spectrum of  $[CpFe(PPh_2Me)_2I]$  in benzene- $d_6$  at 293 K.



**Figure S8-2.** <sup>13</sup>C NMR Spectra of  $[CpFe(PPh_2Me)_2I]$  in benzene-*d*<sub>6</sub> at 293 K (top: DEPT135, bottom: decoupling).



**Figure S8-3.** <sup>31</sup>P{<sup>1</sup>H} NMR Spectrum of  $[CpFe(PPh_2Me)_2I]$  in benzene-*d*<sub>6</sub> at 293 K.



**Figure S8-4.** ORTEP drawing of  $[CpFe(PPh_2Me)_2I]$ ·  $CH_2Cl_2$ . Hydrogen atoms and one  $CH_2Cl_2$  molecule are omitted for clarity.



**Figure S9-1.** <sup>1</sup>H NMR Spectrum of [CpFe(PPh<sub>2</sub>Me)<sub>2</sub>NCMe]PF<sub>6</sub> in CDCl<sub>3</sub> at 293 K.



**Figure S9-2.** <sup>13</sup>C NMR Spectra of [CpFe(PPh<sub>2</sub>Me)<sub>2</sub>NCMe]PF<sub>6</sub> in CDCl<sub>3</sub> at 293 K (top: DEPT135, bottom: decoupling).



**Figure S9-3.** <sup>31</sup>P{<sup>1</sup>H} NMR Spectrum of [CpFe(PPh<sub>2</sub>Me)<sub>2</sub>NCMe]PF<sub>6</sub> in CDCl<sub>3</sub> at 293 K.



**Figure S9-4.** ORTEP drawing of  $[CpFe(PPh_2Me)_2NCMe]PF_6$ . Hydrogen atoms and hexafluorophosphate anion are omitted for clarity.



**Figure S10-1.** <sup>1</sup>H NMR Spectrum of [CpFe(dppm)P(OMe)<sub>3</sub>]PF<sub>6</sub> in acetone-*d*<sub>6</sub> at 293 K.



**Figure S10-2.** <sup>13</sup>C NMR Spectra of  $[CpFe(dppm)P(OMe)_3]PF_6$  in acetone- $d_6$  at 293 K (top: DEPT135, bottom: decoupling).



**Figure S10-3.** <sup>31</sup>P{<sup>1</sup>H} NMR Spectrum of  $[CpFe(dppm)P(OMe)_3]PF_6$  in acetone- $d_6$  at 293 K.



**Figure S10-4.** ORTEP drawing of [CpFe(dppm)P(OMe)<sub>3</sub>]PF<sub>6</sub>. Hydrogen atoms and hexafluorophosphate anion are omitted for clarity.



**Figure S11-1.** <sup>1</sup>H NMR Spectrum of [CpFe(dppe)P(OMe)<sub>3</sub>]PF<sub>6</sub> in CDCl<sub>3</sub> at 293 K.



**Figure S11-2.** <sup>13</sup>C NMR Spectra of [CpFe(dppe)P(OMe)<sub>3</sub>]PF<sub>6</sub> in CDCl<sub>3</sub> at 293 K (top: DEPT135, bottom: decoupling).



**Figure S11-3.** <sup>31</sup>P{<sup>1</sup>H} NMR Spectrum of [CpFe(dppe)P(OMe)<sub>3</sub>]PF<sub>6</sub> in CDCl<sub>3</sub> at 293 K.



**Figure S11-4.** ORTEP drawing of [CpFe(dppe)P(OMe)<sub>3</sub>]PF<sub>6</sub>. Hydrogen atoms and hexafluorophosphate anion are omitted for clarity.



**Figure S12-1.** <sup>1</sup>H NMR Spectrum of [CpFe(dppp)P(OMe)<sub>3</sub>]PF<sub>6</sub> in CDCl<sub>3</sub> at 293 K.



**Figure S12-2.** <sup>13</sup>C NMR Spectra of [CpFe(dppp)P(OMe)<sub>3</sub>]PF<sub>6</sub> in CDCl<sub>3</sub> at 293 K (top: DEPT135, bottom: decoupling).



**Figure S12-3.** <sup>31</sup>P $\{^{1}H\}$  NMR Spectrum of [CpFe(dppp)P(OMe)<sub>3</sub>]PF<sub>6</sub> in CDCl<sub>3</sub> at 293 K.



**Figure S12-4.** ORTEP drawing of [CpFe(dppp)P(OMe)<sub>3</sub>]PF<sub>6</sub>. Hydrogen atoms and hexafluorophosphate anion are omitted for clarity.



**Figure S13-1.** <sup>1</sup>H NMR Spectrum of [CpFe(dppb)P(OMe)<sub>3</sub>]PF<sub>6</sub> in CDCl<sub>3</sub> at 293 K.



**Figure S13-2.** <sup>13</sup>C NMR Spectra of [CpFe(dppb)P(OMe)<sub>3</sub>]PF<sub>6</sub> in CDCl<sub>3</sub> at 293 K (top: DEPT135, bottom: decoupling).



Figure S13-3. <sup>31</sup>P{<sup>1</sup>H} NMR Spectrum of [CpFe(dppb)P(OMe)<sub>3</sub>]PF<sub>6</sub> in CDCl<sub>3</sub> at 293 K.



**Figure S13-4.** ORTEP drawing of  $2([CpFe(dppp)P(OMe)_3]PF_6) \cdot 3CHCl_3$ . Hydrogen atoms, hexafluorophosphate anion, and three CHCl\_3 molecules are omitted for clarity.



Figure S14-1. <sup>1</sup>H NMR Spectrum of [CpFe(PPh<sub>2</sub>Me)<sub>2</sub>P(OMe)<sub>3</sub>]PF<sub>6</sub> in CDCl<sub>3</sub> at 293 K.



**Figure S14-2.** <sup>13</sup>C NMR Spectra of [CpFe(PPh<sub>2</sub>Me)<sub>2</sub>P(OMe)<sub>3</sub>]PF<sub>6</sub> in CDCl<sub>3</sub> at 293 K (top: DEPT135, bottom: decoupling).



Figure S14-3.  ${}^{31}P{}^{1}H$  NMR Spectrum of  $[CpFe(PPh_2Me)_2P(OMe)_3]PF_6$  in CDCl<sub>3</sub> at 293 K.



**Figure S14-4.** ORTEP drawing of  $[CpFe(PPh_2Me)_2P(OMe)_3]PF_6$ · CH<sub>2</sub>Cl<sub>2</sub>. Hydrogen atoms, hexafluorophosphate anion, and one CH<sub>2</sub>Cl<sub>2</sub> molecule are omitted for clarity.



Figure S15-1. <sup>1</sup>H NMR Spectrum of [CpFe{P(OMe)<sub>3</sub>}<sub>3</sub>]PF<sub>6</sub> in CDCl<sub>3</sub> at 293 K.



**Figure S15-2.** <sup>13</sup>C NMR Spectra of  $[CpFe{P(OMe)_3}_3]PF_6$  in CDCl<sub>3</sub> at 293 K (top: DEPT135, bottom: decoupling).



Figure S15-3.  ${}^{31}P{}^{1}H$  NMR Spectrum of [CpFe{P(OMe)<sub>3</sub>}]PF<sub>6</sub> in CDCl<sub>3</sub> at 293 K



**Figure S15-4.** ORTEP drawing of  $[CpFe{P(OMe)_3}_3]PF_6$ . Hydrogen atoms and hexafluorophosphate anion are omitted for clarity.



**Figure S16-1.** <sup>1</sup>H NMR Spectrum of [CpFe(dppe)PPh(OMe)<sub>2</sub>]PF<sub>6</sub> in CDCl<sub>3</sub> at 293 K.



**Figure S16-2.** <sup>13</sup>C NMR Spectra of [CpFe(dppe)PPh(OMe)<sub>2</sub>]PF<sub>6</sub> in CDCl<sub>3</sub> at 293 K (top: DEPT135, bottom: decoupling).



Figure S16-3. <sup>31</sup>P{<sup>1</sup>H} NMR Spectrum of [CpFe(dppe)PPh(OMe)<sub>2</sub>]PF<sub>6</sub> in CDCl<sub>3</sub> at 293 K.



**Figure S16-4.** ORTEP drawing of [CpFe(dppe)PPh(OMe)<sub>2</sub>]PF<sub>6</sub>. Hydrogen atoms and hexafluorophosphate anion are omitted for clarity.



Figure S17-1. <sup>1</sup>H NMR Spectrum of [CpFe(dppe)PPh<sub>2</sub>(OMe)]PF<sub>6</sub> in CDCl<sub>3</sub> at 293 K.



**Figure S17-2.** <sup>13</sup>C NMR Spectra of [CpFe(dppe)PPh<sub>2</sub>(OMe)]PF<sub>6</sub> in CDCl<sub>3</sub> at 293 K (top: DEPT135, bottom: decoupling).



Figure S17-3. <sup>31</sup>P{<sup>1</sup>H} NMR Spectrum of [CpFe(dppe)PPh<sub>2</sub>(OMe)]PF<sub>6</sub> in CDCl<sub>3</sub> at 293 K.



**Figure S17-4.** ORTEP drawing of [CpFe(dppe)PPh<sub>2</sub>(OMe)]PF<sub>6</sub>. Hydrogen atoms and hexafluorophosphate anion are omitted for clarity.



Figure S18-1. <sup>1</sup>H NMR Spectrum of [CpFe(dppe)PPh<sub>2</sub>(OEt)]PF<sub>6</sub> in CDCl<sub>3</sub> at 293 K.



**Figure S18-2.** <sup>13</sup>C NMR Spectra of [CpFe(dppe)PPh<sub>2</sub>(OEt)]PF<sub>6</sub> in CDCl<sub>3</sub> at 293 K (top: DEPT135, bottom: decoupling).



Figure S18-3. <sup>31</sup>P{<sup>1</sup>H} NMR Spectrum of [CpFe(dppe)PPh<sub>2</sub>(OEt)]PF<sub>6</sub> in CDCl<sub>3</sub> at 293 K.



**Figure S18-4.** ORTEP drawing of [CpFe(dppe)PPh<sub>2</sub>(OEt)]PF<sub>6</sub>. Hydrogen atoms and hexafluorophosphate anion are omitted for clarity.



**Figure S19-1.** <sup>1</sup>H NMR Spectrum of [CpFe(dppe)PPh<sub>2</sub>(O*i*Pr)]PF<sub>6</sub> in CDCl<sub>3</sub> at 293 K.



**Figure S19-2.** <sup>13</sup>C NMR Spectra of [CpFe(dppe)PPh<sub>2</sub>(O*i*Pr)]PF<sub>6</sub> in CDCl<sub>3</sub> at 293 K (top: DEPT135, bottom: decoupling).



Figure S19-3.  ${}^{31}P{}^{1}H$  NMR Spectrum of [CpFe(dppe)PPh<sub>2</sub>(O*i*Pr)]PF<sub>6</sub> in CDCl<sub>3</sub> at 293 K.



**Figure S19-4.** ORTEP drawing of  $[CpFe(dppe)PPh_2(OiPr)]PF_6$ · CHCl<sub>3</sub>. Hydrogen atoms, hexafluorophosphate anion, and one CHCl<sub>3</sub> molecule are omitted for clarity.



Figure S20-1. <sup>1</sup>H NMR Spectrum of [CpFe(PPh<sub>2</sub>Me)PPh(OMe)<sub>2</sub>]PF<sub>6</sub> in CDCl<sub>3</sub> at 293 K.



**Figure S20-2.** <sup>13</sup>C NMR Spectra of [CpFe(PPh<sub>2</sub>Me)<sub>2</sub>PPh(OMe)<sub>2</sub>]PF<sub>6</sub> in CDCl<sub>3</sub> at 293 K (top: DEPT135, bottom: decoupling).



**Figure S20-3.** <sup>31</sup>P{<sup>1</sup>H} NMR Spectrum of  $[CpFe(PPh_2Me)_2PPh(OMe)_2]PF_6$  in CDCl<sub>3</sub> at 293 K.



**Figure S20-4.** ORTEP drawing of  $[CpFe(PPh_2Me)_2PPh(OMe)_2]PF_6$ · CH<sub>2</sub>Cl<sub>2</sub>. Hydrogen atoms, hexafluorophosphate anion, and one CH<sub>2</sub>Cl<sub>2</sub> molecule are omitted for clarity.



Figure S21-1. <sup>1</sup>H NMR Spectrum of [CpFe(dppp)PPh<sub>2</sub>(OMe)]PF<sub>6</sub> in CDCl<sub>3</sub> at 293 K.



**Figure S21-2.** <sup>13</sup>C NMR Spectra of [CpFe(dppp)PPh<sub>2</sub>(OMe)]PF<sub>6</sub> in CDCl<sub>3</sub> at 293 K (top: DEPT135, bottom: decoupling).



Figure S21-3. <sup>31</sup>P{<sup>1</sup>H} NMR Spectrum of [CpFe(dppp)PPh<sub>2</sub>(OMe)]PF<sub>6</sub> in CDCl<sub>3</sub> at 293 K.



**Figure S21-4.** ORTEP drawing of [CpFe(dppp)PPh<sub>2</sub>(OMe)]PF<sub>6</sub>. Hydrogen atoms and hexafluorophosphate anion are omitted for clarity.



Figure S22-1. <sup>1</sup>H NMR Spectrum of [CpFe(dppp)PPh<sub>2</sub>(OEt)]PF<sub>6</sub> in CDCl<sub>3</sub> at 293 K.



**Figure S22-2.** <sup>13</sup>C NMR Spectra of [CpFe(dppp)PPh<sub>2</sub>(OEt)]PF<sub>6</sub> in CDCl<sub>3</sub> at 293 K (top: DEPT135, bottom: decoupling).



Figure S22-3. <sup>31</sup>P{<sup>1</sup>H} NMR Spectrum of [CpFe(dppp)PPh<sub>2</sub>(OEt)]PF<sub>6</sub> in CDCl<sub>3</sub> at 293 K.



**Figure S22-4.** ORTEP drawing of [CpFe(dppp)PPh<sub>2</sub>(OEt)]PF<sub>6</sub>. Hydrogen atoms and hexafluorophosphate anion are omitted for clarity.



**Figure S23-1.** <sup>1</sup>H NMR Spectrum of [CpFe(dppp)PPh(OMe)<sub>2</sub>]PF<sub>6</sub> in CDCl<sub>3</sub> at 293 K.



**Figure S23-2.** <sup>13</sup>C NMR Spectra of [CpFe(dppp)PPh(OMe)<sub>2</sub>]PF<sub>6</sub> in CDCl<sub>3</sub> at 293 K (top: DEPT135, bottom: decoupling).



Figure S23-3.  ${}^{31}P{}^{1}H$  NMR Spectrum of [CpFe(dppp)PPh(OMe)<sub>2</sub>]PF<sub>6</sub> in CDCl<sub>3</sub> at 293 K.



**Figure S23-4.** ORTEP drawing of [CpFe(dppp)PPh(OMe)<sub>2</sub>]PF<sub>6</sub>. Hydrogen atoms and hexafluorophosphate anion are omitted for clarity.



**Figure S24-1.** <sup>1</sup>H NMR Spectrum of [CpFe(PPh<sub>2</sub>Me){PPh<sub>2</sub>(OMe)}<sub>2</sub>]PF<sub>6</sub> in CDCl<sub>3</sub> at 293 K.



Figure S24-2. <sup>31</sup>P{<sup>1</sup>H} NMR Spectrum of  $[CpFe(PPh_2Me){PPh_2(OMe)}_2]PF_6$  in CDCl<sub>3</sub> at 293 K.



**Figure S24-3.** ORTEP drawing of  $[CpFe(PPh_2Me){PPh_2(OMe)}_2]PF_6 \cdot 2CH_2Cl_2$ . Hydrogen atoms, hexafluorophosphate anion and  $CH_2Cl_2$  molecules are omitted for clarity.



**Figure S25-1.** <sup>1</sup>H NMR Spectrum of [CpFe{PPh<sub>2</sub>(OMe)}<sub>2</sub>NCMe]PF<sub>6</sub> in CDCl<sub>3</sub> at 293 K.



**Figure S25-2.** <sup>13</sup>C NMR Spectra of [CpFe{PPh<sub>2</sub>(OMe)}<sub>2</sub>NCMe]PF<sub>6</sub> in CDCl<sub>3</sub> at 293 K (top: DEPT135, bottom: decoupling).



Figure S25-3.  ${}^{31}P{}^{1}H$  NMR Spectrum of [CpFe{PPh<sub>2</sub>(OMe)}<sub>2</sub>NCMe]PF<sub>6</sub> in CDCl<sub>3</sub> at 293 K.



**Figure S25-4.** ORTEP drawing of  $[CpFe{PPh_2(OMe)}_2NCMe]PF_6$ . Hydrogen atoms and hexafluorophosphate anion are omitted for clarity.



**Figure S26-1.** <sup>1</sup>H NMR Spectrum of [CpFe{PPh<sub>2</sub>(OMe)}<sub>3</sub>]PF<sub>6</sub> in CDCl<sub>3</sub> at 293 K.



**Figure S26-2.** <sup>13</sup>C NMR Spectra of  $[CpFe{PPh_2(OMe)}_3]PF_6$  in CDCl<sub>3</sub> at 293 K (top: DEPT135, bottom: decoupling).



Figure S26-3.  ${}^{31}P{}^{1}H$  NMR Spectrum of [CpFe{PPh<sub>2</sub>(OMe)}]PF<sub>6</sub> in CDCl<sub>3</sub> at 293 K.



**Figure S26-4.** ORTEP drawing of  $[CpFe{PPh_2(OMe)}_3]PF_6$ . Hydrogen atoms, hexafluorophosphate anion,  $CH_2Cl_2$  molecule are omitted for clarity.