Electronic Supporting Information

Deciphering the Direct Heterometallic Interaction in κ^3-bis(donor)ferrocenyl-transition-metal Complexes

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Table S1 Different Fe-M distances reported in the literature

Name given by the authors	Functional	Basis set	M	d_{Fe-M} [Å]	d_{Fe-M} [Å]	h_{rel} [-]	ref.
$[Pd(dppdtbpf)(PPh_3)]^{2+}$	PBE	TZP-ZORA	Pd	2.93	3.20	0.0922	[13]
$[Pd(dppdtbpf)(PPh_3)]^{2+}$	PBE-D3	TZP-ZORA	Pd	2.93	3.20	0.0922	[13]
$[Pd(dcpf)(PPh_3)]^{2+}$	PBE	TZP-ZORA	Pd	2.93	3.17	0.0819	[13]
$[Pd(dcpf)(PPh_3)]^{2+}$	PBE-D3	TZP-ZORA	Pd	2.93	3.17	0.0819	[13]
$[Pt(dppr)(PPh_3)]^{2+}$	PBE	TZP-ZORA	Pt	2.89	3.12	0.0796	[13]
$[Fc'(PPh_2)(NMe_2)\cdot Pd(PPh_2)Fc'(NMe_2)][BF_4]_2$	B3LYP	def2TZVP	Pd	2.82	3.04	0.0793	[14]
$[Pt(dppr)(PPh_3)]^{2+}$	PW91	TZP-ZORA	Pt	2.89	3.11	0.0761	[13]
$[Fc'(PPh_2)(NMe_2)\cdot Pd(PPh_2)Fc'(NMe_2)][BF_4]_2$	BP86	def2TZVP	Pd	2.82	3.02	0.0715	[14]
$[Fc'(PMes_2)(P\mathit{t}Bu_2)\cdot PdCl][SbF_6]$	B3LYP-D3	def2TZVP	Pd	2.84	3.03	0.0691	[14]
$[Fc'(PMes_2)(P\mathit{t}Bu_2)\cdot PdCl][SbF_6]$	M06-2X	def2TZVP	Pd	2.84	3.03	0.0673	[14]
$[Pd(dppr)(PPh_3)]^{2+}$	PBE	TZP-ZORA	Pd	2.89	3.08	0.0657	[13]
$[Pd(dppr)(PPh_3)]^{2+}$	PBE-D3	TZP-ZORA	Pd	2.89	3.08	0.0657	[13]
$[Fc'(PPh_2)(NMe_2)\cdot PdP(\mathit{p}\text{-}OMe\text{-}C_6H_4)_3][BF_4]_2$	B3LYP	def2TZVP	Pd	2.83	3.02	0.0656	[14]
$[Fc'(PPh_2)(NMe_2)\cdot Pd(PPh_2)Fc'(NMe_2)][BF_4]_2$	B3LYP-D3	def2TZVP	Pd	2.82	3.00	0.0651	[14]
$[Fc'(PPh_2)(NMe_2)\cdot Pd(PPh_2C_5H_5)][SbF_6]_2$	B3LYP	def2TZVP	Pd	2.81	2.99	0.0647	[14]
$[Fc'(PPh_2)(NMe_2)\cdot Pd(PPh_2)Fc'(NMe_2)][BF_4]_2$	M06-2X	def2TZVP	Pd	2.82	3.00	0.0637	[14]
$[Fc'(PPh_2)(NMe_2)\cdot PdCl][SbF_6]_2$	M06-2X	def2TZVP	Pd	2.74	2.91	0.0630	[14]
$[Fc'(PPh_2)(NMe_2)\cdot PdP(\mathit{p}\text{-}OMe\text{-}C_6H_4)_3][BF_4]_2$	M06-2X	def2TZVP	Pd	2.83	3.01	0.0618	[14]
$[Pd(dcpf)(PPh_3)]^{2+}$	PW91	TZP-ZORA	Pd	2.93	3.11	0.0614	[13]
$[Fc'(PPh_2)(NMe_2)\cdot Pd(PPh_2)Fc'(NMe_2)][BF_4]_2$	B3LYP	def2TZVP	Pd	2.83	3.00	0.0605	[14]
$[Fc'(PPh_2)(NMe_2)\cdot PdCl][SbF_6]_2$	B3LYP-D3	def2TZVP	Pd	2.74	2.90	0.0590	[14]
$[Fc'(PPh_2)(NMe_2)\cdot PdP(\mathit{p}\text{-}OMe\text{-}C_6H_4)_3][BF_4]_2$	B3LYP-D3	def2TZVP	Pd	2.83	3.00	0.0589	[14]
$[Pd(dppr)(PPh_3)]^{2+}$	PW91	TZP-ZORA	Pd	2.89	3.06	0.0588	[13]

$[Pt(dppr)(PPh_3)]^{2+}$	PBE-D3	TZP-ZORA	Pt	2.89	3.06	0.0588	[13]
$[Fc'(PPh_2)(NMe_2)\cdot PdP(p\text{-}OMe\text{-}C_6H_4)_3][BF_4]_2$	BP86	def2TZVP	Pd	2.83	3.00	0.0582	[14]
$[Pd(dppdtbpf)(PPh_3)]^{2+}$	PW91	TZP-ZORA	Pd	2.93	3.10	0.0580	[13]
$[Fc'(PPh_2)(NMe_2)\cdot Pd(PPh_2C_5H_5)][SbF_6]_2$	M06-2X	def2TZVP	Pd	2.81	2.97	0.0580	[14]
$[Fc'(PMes_2)(PtBu_2)\cdot PdCl][SbF_6]$	B3LYP	def2TZVP	Pd	2.84	3.00	0.0568	[14]
$[Fc'(PPh_2)(NMe_2)\cdot Pd(PPh_2C_5H_5)][SbF_6]_2$	BP86	def2TZVP	Pd	2.81	2.97	0.0559	[14]
$[Fc'(PPh_2)(NMe_2)\cdot Pd(PPh_2)Fc'(NMe_2)][BF_4]_2$	M06-2X	def2TZVP	Pd	2.83	2.99	0.0552	[14]
$[Fc'(PPh_2)(NMe_2)\cdot Pd(PPh_2C_5H_5)][SbF_6]_2$	B3LYP-D3	def2TZVP	Pd	2.81	2.97	0.0548	[14]
$[Fc'(PPh_2)(NMe_2)\cdot Pd(PPh_2)Fc'(NMe_2)][BF_4]_2$	B3LYP-D3	def2TZVP	Pd	2.83	2.98	0.0527	[14]
$[Fc'(PPh_2)(NMe_2)\cdot Pd(PPh_2)Fc'(NMe_2)][BF_4]_2$	PBEh1PBE	def2TZVP	Pd	2.82	2.97	0.0520	[14]
$[Pd(dtbpf)Cl]^+$	PBE-D3	TZP-ZORA	Pd	2.94	3.09	0.0510	[13]
$[Pt(dcpf)(PPh_3)]^{2+}$	PW91	TZP-ZORA	Pt	2.94	3.09	0.0510	[13]
$[Pt(dcpf)(PPh_3)]^{2+}$	PBE	TZP-ZORA	Pt	2.94	3.09	0.0510	[13]
$[Pd(dcpf)(PMe_3)]^{2+}$	PBE-D3	TZP-ZORA	Pd	2.95	3.10	0.0508	[13]
$[Pd(dcpf)(PMe_3)]^{2+}$	PW91	TZP-ZORA	Pd	2.95	3.10	0.0508	[13]
$[Fc'(PPh_2)(NMe_2)\cdot Pd(PPh_2)Fc'(NMe_2)][BF_4]_2$	BP86	def2TZVP	Pd	2.83	2.97	0.0506	[14]
$[Pd(dtbpf)Cl]^+$	PBE	TZP-ZORA	Pd	2.94	3.08	0.0476	[13]
$[Fc'(PMes_2)(PtBu_2)\cdot PdCl][SbF_6]$	B3LYP	def2TZVP	Pd	2.74	2.86	0.0455	[14]
$[Pt(dcpf)(PPh_3)]^{2+}$	PBE-D3	TZP-ZORA	Pt	2.94	3.07	0.0442	[13]
$[Pd(dcpf)(PMe_3)]^{2+}$	PBE-D3	TZP-ZORA	Pd	2.95	3.08	0.0441	[13]
$Pd(dppf\text{-}\kappa^3P,P',Fe)(PPh_3)][BF_4]_2$	M11/LANL2DZ-ECP(Fe,Pd)	6-31$^+$G(d,p)	Pd	2.76	2.88	0.0438	[35]
$[Pd(dppf)(PPh_3)]^{2+}$	PBE-D3	TZP-ZORA	Pd	2.89	3.01	0.0415	[13]
$[Pd(dppf)(PPh_3)]^{2+}$	PBE-D3	TZP-ZORA	Pd	2.89	3.01	0.0415	[13]
$[Fc'(PMes_2)(PtBu_2)\cdot PdCl][SbF_6]$	BP86	def2TZVP	Pd	2.84	2.95	0.0402	[14]
$[Fc'(PMes_2)(PtBu_2)\cdot PdCl][SbF_6]$	ωB97X-D	def2TZVP	Pd	2.84	2.95	0.0381	[14]
$[Pd(dppf)(PPh_3)]^{2+}$	PBE	TZP-ZORA	Pd	2.89	3.00	0.0381	[13]
$[Pd(dtbpf)I]^+$	PBE-D3	TZP-ZORA	Pd	2.92	3.03	0.0377	[13]

[Fc′(PPh_2)(NMe_2)·PdP(*p*-OMe-C_6H_4)$_3$][BF_4]$_2$	PBEh1PBE	def2TZVP	Pd	2.83	2.94	0.0371	[14]
[Fc′(PPh_2)(NMe_2)·Pd($PPh_2C_5H_5$)][SbF_6]$_2$	PBEh1PBE	def2TZVP	Pd	2.81	2.92	0.0370	[14]
[Pd(dtbpf)I]$^+$	PBE	TZP-ZORA	Pd	2.92	3.02	0.0342	[13]
[Fc′(PPh_2)(NMe_2)·PdCl][SbF_6]$_2$	ωB97X-D	def2TZVP	Pd	2.74	2.83	0.0342	[14]
[Fc′($PMes_2$)($PtBu_2$)·PdCl][SbF_6]	PBEh1PBE	def2TZVP	Pd	2.84	2.93	0.0335	[14]
[Fc′(PPh_2)(NMe_2)·Pd(PPh_2)Fc′(NMe_2)][BF_4]$_2$	PBEh1PBE	def2TZVP	Pd	2.83	2.92	0.0326	[14]
[Fc(NCNDIPP)$_2$Li]$^-$	BP86-D4	def2TZVPP	Li	2.85	2.76	0.0313	[34]
[Fc′(PPh_2)(NMe_2)·PdCl][SbF_6]$_2$	BP86	def2TZVP	Pd	2.74	2.82	0.0313	[14]
[Pd(dppf)(P($pC_6H_4CF_3$)$_3$)][BF_4]$_2$	PW91	TZP-ZORA	Pd	2.89	2.98	0.0311	[5]
[Pd(dtbpf)I]$^+$	PW91	TZP-ZORA	Pd	2.92	3.01	0.0308	[13]
[Pd(dippf)(PMe_3)]$^{2+}$	PBE	TZP-ZORA	Pd	3.02	3.11	0.0298	[13]
[Pd(dippf)(PMe_3)]$^{2+}$	PBE-D3	TZP-ZORA	Pd	3.02	3.11	0.0298	[13]
[{fc(NIm_2)}$NiCl_2$]	B97D	6-311G**	Ni	3.80	3.91	0.0297	[15]
[Fc′(PPh_2)(NMe_2)·PdCl][SbF_6]$_2$	PBEh1PBE	def2TZVP	Pd	2.74	2.82	0.0291	[14]
[Fc(NCNDIPP)$_2$Ag]$^-$	B3LYP-D4	def2TZVPP	Ag	3.15	3.24	0.0284	[34]
κ^3-dppf_1 (1p$^+$)	TPSS-D3	def2TZVP	Fe	4.22	4.34	0.0282	[21]
[Fc′(PPh_2)(NMe_2)·Pd(PPh_2)Fc′(NMe_2)][BF_4]$_2$	ωB97X-D	def2TZVP	Pd	2.82	2.90	0.0272	[14]
[Fc(NCNDIPP)$_2$Ag]$^-$	B3LYP-D3	def2TZVPP	Ag	3.15	3.23	0.0258	[34]
[{fc(NIm_2)}Pd(NCMe)]$^{2+}$	B97D	6-311G**	Pd	2.63	2.70	0.0252	[15]
[Pd(dtbpf)Cl]$^+$	PW91	TZP-ZORA	Pd	2.92	2.99	0.0240	[28]
[Pd(dtbpf)I]$^+$	PW91	TZP-ZORA	Pd	2.92	2.99	0.0240	[28]
[Pd(dtbpf)Br]$^+$	PW91	TZP-ZORA	Pd	2.92	2.99	0.0240	[28]
[Pd(dtbpf)Cl]$^+$	PW91	TZP-ZORA	Pd	2.94	3.01	0.0238	[13]
[Fc(NCNDIPP)$_2$Ag]$^-$	B3LYP	def2TZVPP	Ag	3.15	3.22	0.0217	[34]
[Fc′(PPh_2)(NMe_2)·PdP(p-OMe-C_6H_4)$_3$][BF_4]$_2$	ωB97X-D	def2TZVP	Pd	2.83	2.90	0.0216	[14]
[fc($NPEt_3$)$_2$PdMe]$^+$	PW91	TZP-ZORA	Pd	2.78	2.84	0.0214	[37]
[Fc′(PPh_2)(NMe_2)·Pd($PPh_2C_5H_5$)][SbF_6]$_2$	ωB97X-D	def2TZVP	Pd	2.81	2.87	0.0210	[14]
[Pd(dippf)(PMe_3)]$^{2+}$	PW91	TZP-ZORA	Pd	3.02	3.08	0.0199	[13]
[Fc(NCNDIPP)$_2$Ag]$^-$	BP86	def2TZVPP	Ag	3.15	3.21	0.0195	[34]

[Fc′(PPh_2)(NMe_2)·Pd(PPh_2)Fc′(NMe_2)][BF_4]$_2$	ωB97X-D	def2TZVP	Pd	2.83	2.88	0.0191	[14]
[{fc(NIm_2)$_2$}NiCl]$^+$	B97D	6-311G**	Ni	2.63	2.68	0.0187	[15]
[Fc(NCNDIPP)$_2$Ag]$^-$	BP86-D4	def2TZVPP	Ag	3.15	3.21	0.0185	[34]
[Fc(NCNDIPP)$_2$Cu]$^-$	BP86-D3	def2TZVPP	Cu^I	3.17	3.22	0.0170	[34]
[Fc(NCNDIPP)$_2$Cu]$^-$	B3LYP-D3	def2TZVPP	Cu^I	3.17	3.22	0.0167	[34]
[Fc(NCNDIPP)$_2$Cu]$^-$	B3LYP-D4	def2TZVPP	Cu^I	3.17	3.22	0.0167	[34]
[{fc(NIm_2)$_2$}Ni(NCMe)]$^{2+}$	B97D	6-311G**	Ni	2.63	2.67	0.0153	[15]
[Fc(NCNDIPP)$_2$Cu]	BP86-D3	def2TZVPP	Cu^{II}	3.12	3.07	0.0149	[34]
[Fc(NCNDIPP)$_2$Li]$^-$	B3LYP	def2TZVPP	Li	2.85	2.89	0.0148	[34]
[{fc(NIm_2)$_2$}PdCl]$^+$	B97D	6-311G**	Pd	2.67	2.71	0.0142	[15]
[Fc(NCNDIPP)$_2$Ag]$^-$	BP86-D3	def2TZVPP	Ag	3.15	3.20	0.0141	[34]
[Fc(NCNDIPP)$_2$Cu]$^-$	BP86-D4	def2TZVPP	Cu^I	3.17	3.21	0.0136	[34]
[Fc(NCNDIPP)$_2$Li]$^-$	B3LYP-D4	def2TZVPP	Li	2.85	2.81	0.0130	[34]
[Fc(NCNDIPP)$_2$Li]$^-$	BP86	def2TZVPP	Li	2.85	2.88	0.0130	[34]
[Fc(NCNDIPP)$_2$Cu]	BP86	def2TZVPP	Cu^{II}	3.12	3.15	0.0117	[34]
[Fc(NCNDIPP)$_2$Li]$^-$	BP86-D3	def2TZVPP	Li	2.85	2.81	0.0109	[34]
[PdCl({Fe(η^5-$C_5H_4NvC(NR_2)_2$}$_2$-κ^3 N, N′,Fe)]$_2$[$PdCl_4$]	M11/LANL2DZ-ECP (Fe,Pd)	6-31$^+$G(d,p)	Pd	3.79	3.75	0.0102	[35]
[Fc(NCNDIPP)$_2$Cu]	B3LYP-D4	def2TZVPP	Cu^{II}	3.12	3.15	0.0101	[34]
[Fc(NCNDIPP)$_2$Cu]	B3LYP	def2TZVPP	Cu^{II}	3.12	3.15	0.0095	[34]
[Fc(NCNDIPP)$_2$Cu]	BP86-D4	def2TZVPP	Cu^{II}	3.12	3.09	0.0088	[34]
[fc($NPPh_3$)$_2$PdMe]$^+$	PW91	TZP-ZORA	Pd	2.80	2.82	0.0087	[37]
[{fc(NIm_2)$_2$}Pd(PMe_3)]$^{2+}$	B97D	6-311G**	Pd	2.75	2.77	0.0073	[15]
[{fc(NIm_2)$_2$}Ni(PMe_3)]$^{2+}$	B97D	6-311G**	Ni	2.74	2.76	0.0066	[15]
1	TPSS	def2TZVP	Ni	4.24	4.27	0.0057	[21]
[fc($NPPh_3$)$_2$NiPh]$^+$	PW91	TZP-ZORA	Ni	2.82	2.81	0.0051	[37]
[Fc(NCNDIPP)$_2$Cu]$^-$	BP86	def2TZVPP	Cu^I	3.17	3.19	0.0047	[34]
[Fc(NCNDIPP)$_2$Cu]	B3LYP-D3	def2TZVPP	Cu^{II}	3.12	3.13	0.0047	[34]
[Fc(NCNDIPP)$_2$Cu]$^-$	B3LYP	def2TZVPP	Cu^I	3.17	3.18	0.0038	[34]
[{fc(NIm_2)$_2$}$PdCl_2$]	B97D	6-311G**	Pd	4.00	3.99	0.0025	[15]

Table S2 CCDC numbers for **1-6**

Structure	CCDC#	reference
1	980227	[13]
2	277349	[38]
3	1569204	[37]
4	1117672	[39]
5	114238	[36]
6	114239	[36]

Table S3 The obtained d_{Fe-M} (in Å) applying different basis sets using TPSSh DFT functional

Structure	$d_{Fe-M,exp}$ [Å]	3-21G	def2-TZVP	6-311+G** and for metal atoms LANL2DZ	def2-TZVP and for metal atoms TZP-ZORA
1	2.939	2.836	2.935	2.919	2.876
2	2.663	2.666	2.713	2.718	2.690
3	2.781	2.769	2.808	2.818	2.767
4	2.879	2.793	2.940	2.919	2.883
5	2.886	2.552	2.892	2.853	2.891

Table S4. Computed and experimental values of Fe-M distances (d_{Fe-M}) in Å for structures **1-6**

Structure	d_{Fe_M}	TPSSh	M06-2X	CAM-B3LYP	CAM-B3LYP-D3	PW91	B3LYP	B3LYP-D3	ωb97X-D	BP86
1	2.94	3.05	3.08	2.99	3.00	2.94	3.06	3.01	3.03	2.98
2	2.66	2.77	2.78	2.75	2.74	2.71	2.83	2.75	2.76	2.73
3	2.78	2.89	2.9	2.84	2.84	2.81	2.94	2.86	2.87	2.83
4	2.88	3.04	3.05	2.96	2.99	2.94	3.03	2.99	3.00	2.97
5	2.89	3.00	2.98	2.91	2.93	2.89	2.95	2.96	2.95	2.90
6	4.27	4.29	4.20	4.16	4.29	4.25	4.1	4.24	4.16	4.27

Table S5 Computed ring tilts for structures with an eclipsed geometry in conjunction of the def2-TZVP basis set with pseudopotentials on the metal atoms.

Structure	Functional	d_{Fe-M} [Å]	$\alpha_{exp.}$ [°]	$\alpha_{calc.}$ [°]	h_{rel} [-]
3	B3LYP	2.781	15.324	12.900	0.158
3	B3LYP-D3	2.781	15.324	12.481	0.186
3	BP86	2.781	15.324	14.266	0.069
3	CAM-B3LYP	2.781	15.324	12.827	0.163
3	CAM-B3LYP-D3	2.781	15.324	12.688	0.172
3	M06-2X	2.781	15.324	13.556	0.115
3	PW91	2.781	15.324	14.406	0.060
3	TPSSh	2.781	15.324	14.373	0.062
3	b97X-D	2.781	15.324	14.333	0.065
4	B3LYP	2.879	20.045	17.665	0.119
4	B3LYP-D3	2.879	20.045	17.496	0.127
4	BP86	2.879	20.045	19.372	0.034
4	CAM-B3LYP	2.879	20.045	17.434	0.130
4	CAM-B3LYP-D3	2.879	20.045	17.347	0.135
4	M06-2X	2.879	20.045	15.289	0.237
4	PW91	2.879	20.045	19.588	0.023
4	TPSSh	2.879	20.045	19.171	0.044
4	ωb97X-D	2.879	20.045	17.597	0.122
5	B3LYP	2.886	15.139	13.248	0.125
5	B3LYP-D3	2.886	15.139	13.627	0.100
5	BP86	2.886	15.139	15.292	0.010
5	CAM-B3LYP	2.886	15.139	13.088	0.135
5	CAM-B3LYP-D3	2.886	15.139	13.325	0.120
5	M06-2X	2.886	15.139	11.221	0.259
5	PW91	2.886	15.139	15.537	0.026
5	TPSSh	2.886	15.139	15.030	0.007
5	ωb97X-D	2.781	15.139	13.494	0.109

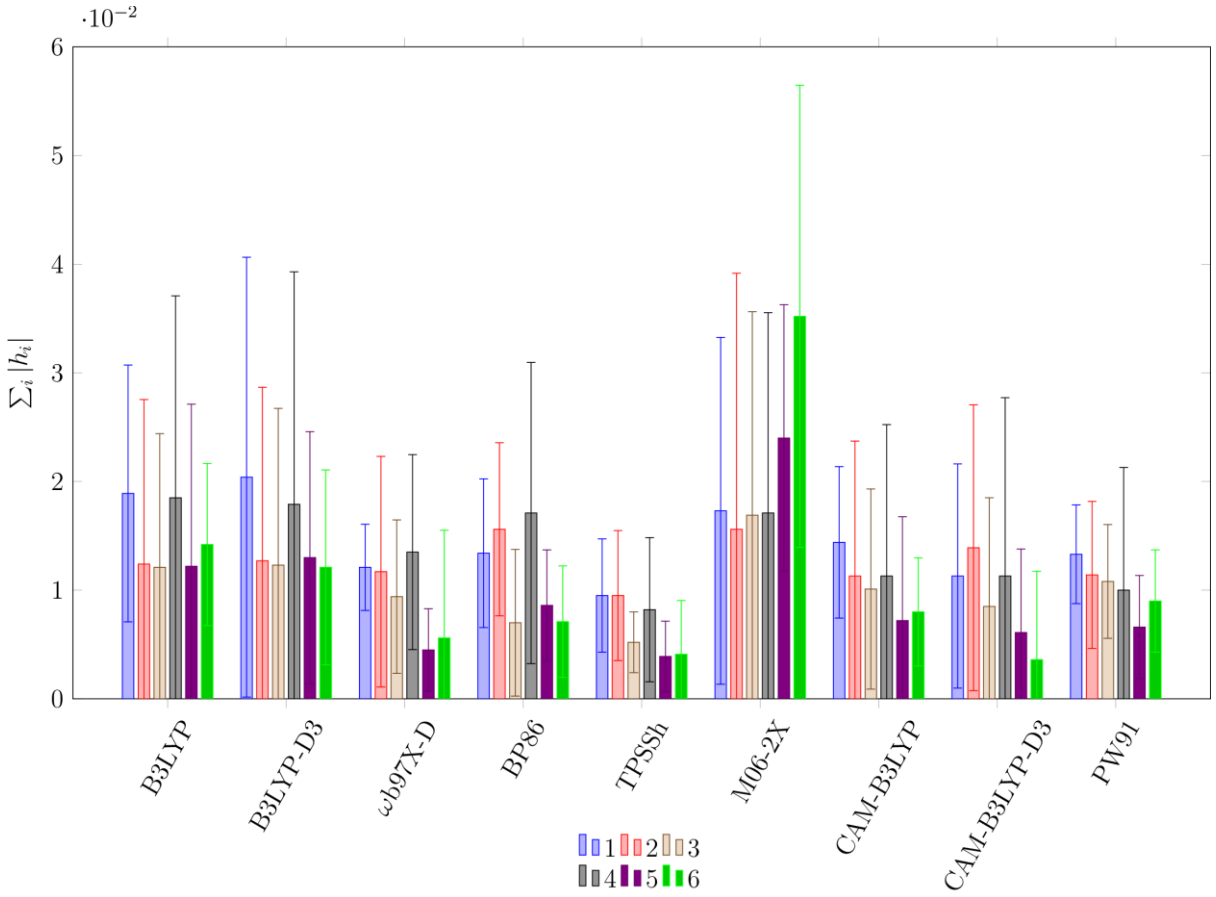


Fig. S1 Mean absolute values of relative errors including bond lengths depicted in **Fig. S2**

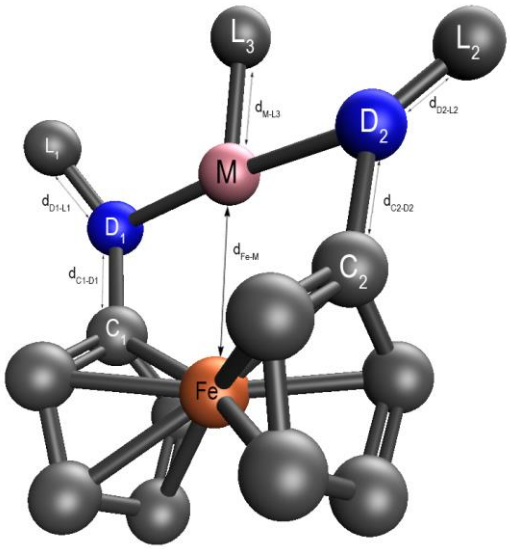


Fig. S2 General ball-stick figure of the κ^3-bis(donor)-ferrocenophanes with notable bond lengths (d) discussed in **Fig. S1**

Table S6 Experimental, and calculated bond lengths of **1**

B3LYP	$d_{exp,1}$ [Å]	$d_{calc,1}$ [Å]	h_{rel} [-]
Pd-Cl	2.316	2.306	-0.004
P-Pd	2.278	2.324	0.020
P-Pd	2.271	2.332	0.026
P-C	1.798	1.816	0.010
P-C	1.796	1.822	0.015
Fe-Pd	2.939	3.048	0.036
TPSSh	$d_{exp,1}$ [Å]	$d_{calc,1}$ [Å]	h_{rel} [-]
Pd-Cl	2.316	2.293	-0.010
P-Pd	2.278	2.314	0.015
P-Pd	2.271	2.303	0.014
P-C	1.798	1.815	0.009
P-C	1.796	1.808	0.007
Fe-Pd	2.939	2.936	-0.001
ωb97X-D	$d_{exp,1}$ [Å]	$d_{calc,1}$ [Å]	h_{rel} [-]
Pd-Cl	2.316	2.293	-0.010
P-Pd	2.278	2.314	0.015
P-Pd	2.271	2.303	0.014
P-C	1.798	1.815	0.009
P-C	1.796	1.808	0.007
Fe-Pd	2.939	2.988	0.017
BP86	$d_{exp,1}$ [Å]	$d_{calc,1}$ [Å]	h_{rel} [-]
Pd-Cl	2.316	2.312	-0.002
P-Pd	2.278	2.308	0.013
P-Pd	2.271	2.313	0.018
P-C	1.798	1.817	0.011
P-C	1.796	1.823	0.015
Fe-Pd	2.939	3.002	0.021
M06-2X	$d_{exp,1}$ [Å]	$d_{calc,1}$ [Å]	h_{rel} [-]
Pd-Cl	2.316	2.302	-0.006
P-Pd	2.278	2.287	0.004
P-Pd	2.271	2.345	0.031
P-C	1.798	1.820	0.012
P-C	1.796	1.808	0.007
Fe-Pd	2.939	3.062	0.040

CAM-B3LYP	$d_{exp,1}$ [Å]	$d_{calc,1}$ [Å]	h_{rel} [-]
Pd-Cl	2.316	2.277	-0.017
P-Pd	2.278	2.303	0.011
P-Pd	2.271	2.315	0.019
P-C	1.798	1.814	0.009
P-C	1.796	1.807	0.006
Fe-Pd	2.939	3.011	0.024
PW91	$d_{exp,1}$ [Å]	$d_{calc,1}$ [Å]	h_{rel} [-]
Pd-Cl	2.316	2.307	-0.004
P-Pd	2.278	2.303	0.011
P-Pd	2.271	2.309	0.016
P-C	1.798	1.819	0.012
P-C	1.796	1.813	0.010
Fe-Pd	2.939	2.983	0.015
CAM-B3LYP-D3	$d_{exp,1}$ [Å]	$d_{calc,1}$ [Å]	h_{rel} [-]
Pd-Cl	2.316	2.275	-0.018
P-Pd	2.278	2.301	0.010
P-Pd	2.271	2.288	0.007
P-C	1.798	1.804	0.003
P-C	1.796	1.813	0.009
Fe-Pd	2.939	3.033	0.031
B3LYP-D3	$d_{exp,1}$ [Å]	$d_{calc,1}$ [Å]	h_{rel} [-]
Pd-Cl	2.316	2.300	-0.007
P-Pd	2.278	2.310	0.014
P-Pd	2.271	2.302	0.013
P-C	1.798	1.895	0.051
P-C	1.796	1.820	0.013
Fe-Pd	2.939	3.077	0.045

Table S7 Experimental, and calculated bond lengths of **2**

B3LYP	$d_{exp,2}$ [Å]	$d_{calc,2}$ [Å]	h_{rel} [-]
Pd-Cl	2.345	2.332	-0.006
P-N	1.614	1.619	0.003
P-N	1.614	1.619	0.003
N-Pd	2.049	2.061	0.006
N-Pd	2.030	2.061	0.015
Fe-Pd	2.663	2.775	0.040
TPSSh	$d_{exp,2}$ [Å]	$d_{calc,2}$ [Å]	h_{rel} [-]
Pd-Cl	2.345	2.318	-0.012
P-N	1.614	1.631	0.010
P-N	1.614	1.626	0.007
N-Pd	2.049	2.048	0.000
N-Pd	2.030	2.048	0.009
Fe-Pd	2.663	2.713	0.018
ωb97X-D	$d_{exp,2}$ [Å]	$d_{calc,2}$ [Å]	h_{rel} [-]
Pd-Cl	2.345	2.318	-0.012
P-N	1.614	1.631	0.010
P-N	1.614	1.626	0.007
N-Pd	2.049	2.048	0.000
N-Pd	2.030	2.048	0.009
Fe-Pd	2.663	2.748	0.031
BP86	$d_{exp,2}$ [Å]	$d_{calc,2}$ [Å]	h_{rel} [-]
Pd-Cl	2.345	2.331	-0.006
P-N	1.614	1.641	0.016
P-N	1.614	1.641	0.016
N-Pd	2.049	2.066	0.008
N-Pd	2.030	2.066	0.018
Fe-Pd	2.663	2.738	0.027
M06-2X	$d_{exp,2}$ [Å]	$d_{calc,2}$ [Å]	h_{rel} [-]
Pd-Cl	2.345	2.327	-0.008
P-N	1.614	1.618	0.002
P-N	1.614	1.618	0.002
N-Pd	2.049	2.058	0.004
N-Pd	2.030	2.058	0.014
Fe-Pd	2.663	2.830	0.059

CAM-B3lYP	$d_{exp,2}$ [Å]	$d_{calc,2}$ [Å]	h_{rel} [-]
Pd-Cl	2.345	2.305	-0.017
P-N	1.614	1.608	-0.004
P-N	1.614	1.608	-0.004
N-Pd	2.049	2.032	-0.008
N-Pd	2.030	2.032	0.001
Fe-Pd	2.663	2.754	0.033
PW91	$d_{exp,2}$ [Å]	$d_{calc,2}$ [Å]	h_{rel} [-]
Pd-Cl	2.345	2.329	-0.007
P-N	1.614	1.638	0.014
P-N	1.614	1.638	0.014
N-Pd	2.049	2.062	0.006
N-Pd	2.030	2.062	0.016
Fe-Pd	2.663	2.729	0.024
CAM-B3lYP-D3	$d_{exp,2}$ [Å]	$d_{calc,2}$ [Å]	h_{rel} [-]
Pd-Cl	2.345	2.304	-0.018
P-N	1.614	1.609	-0.003
P-N	1.614	1.609	-0.003
N-Pd	2.049	2.030	-0.010
N-Pd	2.030	2.030	0.000
Fe-Pd	2.663	2.757	0.034
B3LYP-D3	$d_{exp,2}$ [Å]	$d_{calc,2}$ [Å]	h_{rel} [-]
Pd-Cl	2.345	2.329	-0.007
P-N	1.614	1.621	0.004
P-N	1.614	1.621	0.004
N-Pd	2.049	2.057	0.004
N-Pd	2.030	2.057	0.013
Fe-Pd	2.663	2.781	0.043

Table S8 Experimental, and calculated bond lengths of **3**

B3LYP	$d_{exp,3}$ [Å]	$d_{calc,3}$ [Å]	h_{rel} [-]
Pd-N	2.054	2.080	0.012
Pd-N	2.048	2.074	0.012
N-P	1.611	1.611	0.000
N-P	1.626	1.612	-0.008
Fe-Pd	2.781	2.887	0.037
N-C	1.406	1.399	-0.005
TPSSh	$d_{exp,3}$ [Å]	$d_{calc,3}$ [Å]	h_{rel} [-]
Pd-N	2.054	2.060	0.003
Pd-N	2.048	2.054	0.003
N-P	1.611	1.615	0.002
N-P	1.626	1.616	-0.006
Fe-Pd	2.781	2.808	0.010
N-C	1.406	1.399	-0.005
ωb97X-D	$d_{exp,3}$ [Å]	$d_{calc,3}$ [Å]	h_{rel} [-]
Pd-N	2.054	2.060	0.003
Pd-N	2.048	2.054	0.003
N-P	1.611	1.615	0.002
N-P	1.626	1.616	-0.006
Fe-Pd	2.781	2.843	0.022
N-C	1.406	1.399	-0.005
BP86	$d_{exp,3}$ [Å]	$d_{calc,3}$ [Å]	h_{rel} [-]
Pd-N	2.054	2.073	0.009
Pd-N	2.048	2.069	0.010
N-P	1.611	1.630	0.012
N-P	1.626	1.629	0.002
Fe-Pd	2.781	2.841	0.021
N-C	1.406	1.403	-0.002
M06-2X	$d_{exp,3}$ [Å]	$d_{calc,3}$ [Å]	h_{rel} [-]
Pd-N	2.054	2.088	0.016
Pd-N	2.048	2.094	0.022
N-P	1.611	1.605	-0.004
N-P	1.626	1.603	-0.014
Fe-Pd	2.781	2.935	0.053
N-C	1.406	1.411	0.004

CAM-B3LYP	$d_{exp,3}$ [Å]	$d_{calc,3}$ [Å]	h_{rel} [-]
Pd-N	2.054	2.046	-0.004
Pd-N	2.048	2.053	0.003
N-P	1.611	1.602	-0.006
N-P	1.626	1.600	-0.016
Fe-Pd	2.781	2.859	0.027
N-C	1.406	1.401	-0.004
PW91	$d_{exp,3}$ [Å]	$d_{calc,3}$ [Å]	h_{rel} [-]
Pd-N	2.054	2.064	0.005
Pd-N	2.048	2.072	0.012
N-P	1.611	1.626	0.009
N-P	1.626	1.627	0.001
Fe-Pd	2.781	2.828	0.017
N-C	1.406	1.397	-0.006
CAM-B3LYP-D3	$d_{exp,3}$ [Å]	$d_{calc,3}$ [Å]	h_{rel} [-]
Pd-N	2.054	2.050	-0.002
Pd-N	2.048	2.040	-0.004
N-P	1.611	1.600	-0.007
N-P	1.626	1.600	-0.016
Fe-Pd	2.781	2.868	0.030
N-C	1.406	1.397	-0.007
B3LYP-D3	$d_{exp,3}$ [Å]	$d_{calc,3}$ [Å]	h_{rel} [-]
Pd-N	2.054	2.074	0.010
Pd-N	2.048	2.063	0.007
N-P	1.611	1.610	-0.001
N-P	1.626	1.610	-0.010
Fe-Pd	2.781	2.904	0.042
N-C	1.406	1.397	-0.006

Table S9 Experimental, and calculated bond lengths of **4**

B3LYP	$d_{exp,4}$ [Å]	$d_{calc,4}$ [Å]	h_{rel} [-]
P-Pd	2.241	2.274	0.014
Pd-S	2.308	2.342	0.014
S-Pd	2.294	2.329	0.015
S-C	1.719	1.736	0.010
S-C	1.741	1.737	-0.002
Fe-Pd	2.879	3.037	0.052
TPSSh	$d_{exp,4}$ [Å]	$d_{calc,4}$ [Å]	h_{rel} [-]
P-Pd	2.241	2.248	0.003
Pd-S	2.308	2.322	0.006
S-Pd	2.294	2.309	0.006
S-C	1.719	1.732	0.008
S-C	1.741	1.734	-0.004
Fe-Pd	2.879	2.940	0.021
wb97X-D	$d_{exp,4}$ [Å]	$d_{calc,4}$ [Å]	h_{rel} [-]
P-Pd	2.241	2.251	0.004
Pd-S	2.308	2.300	-0.003
S-Pd	2.294	2.314	0.008
S-C	1.719	1.733	0.008
S-C	1.741	1.732	-0.005
Fe-Pd	2.879	2.957	0.026
BP86	$d_{exp,4}$ [Å]	$d_{calc,4}$ [Å]	h_{rel} [-]
P-Pd	2.241	2.254	0.006
Pd-S	2.308	2.322	0.006
S-Pd	2.294	2.335	0.017
S-C	1.719	1.737	0.010
S-C	1.741	1.738	-0.002
Fe-Pd	2.879	2.992	0.038
M06-2X	$d_{exp,4}$ [Å]	$d_{calc,4}$ [Å]	h_{rel} [-]
P-Pd	2.241	2.219	-0.010
Pd-S	2.308	2.318	0.004
S-Pd	2.294	2.334	0.017
S-C	1.719	1.745	0.015
S-C	1.741	1.746	0.003
Fe-Pd	2.879	3.031	0.050

CAM-B3LYP	$d_{exp,4}$ [Å]	$d_{calc,4}$ [Å]	h_{rel} [-]
P-Pd	2.241	2.253	0.005
Pd-S	2.308	2.302	-0.003
S-Pd	2.294	2.314	0.009
S-C	1.719	1.732	0.007
S-C	1.741	1.733	-0.004
Fe-Pd	2.879	2.992	0.038
PW91	$d_{exp,4}$ [Å]	$d_{calc,4}$ [Å]	h_{rel} [-]
P-Pd	2.241	2.249	0.004
Pd-S	2.308	2.318	0.004
S-Pd	2.294	2.330	0.016
S-C	1.719	1.733	0.008
S-C	1.741	1.734	-0.004
Fe-Pd	2.879	2.971	0.031
CAM-B3LYP-D3	$d_{exp,4}$ [Å]	$d_{calc,4}$ [Å]	h_{rel} [-]
P-Pd	2.241	2.241	0.000
Pd-S	2.308	2.313	0.002
S-Pd	2.294	2.301	0.003
S-C	1.719	1.733	0.008
S-C	1.741	1.734	-0.004
Fe-Pd	2.879	3.003	0.041
B3LYP-D3	$d_{exp,4}$ [Å]	$d_{calc,4}$ [Å]	h_{rel} [-]
P-Pd	2.241	2.255	0.006
Pd-S	2.308	2.339	0.013
S-Pd	2.294	2.327	0.014
S-C	1.719	1.739	0.012
S-C	1.741	1.738	-0.001
Fe-Pd	2.879	3.052	0.057

Table S10 Experimental, and calculated bond lengths of **5**

B3LYP	$d_{exp,5}$ [Å]	$d_{calc,5}$ [Å]	h_{rel} [-]
S-Ni	2.159	2.162	0.001
S-Ni	2.139	2.146	0.003
Ni-P	2.136	2.103	-0.016
Ni-Fe	2.886	3.000	0.038
C-S	1.728	1.742	0.008
C-S	1.736	1.743	0.004
TPSSh	$d_{exp,5}$ [Å]	$d_{calc,5}$ [Å]	h_{rel} [-]
S-Ni	2.159	2.168	0.004
Ni-S	2.139	2.160	0.010
Ni-P	2.136	2.128	-0.004
Ni-Fe	2.890	2.890	0.000
C-S	1.728	1.735	0.004
C-S	1.736	1.735	0.000
ωb97X-D	$d_{exp,5}$ [Å]	$d_{calc,5}$ [Å]	h_{rel} [-]
S-Ni	2.159	2.159	0.000
Ni-S	2.139	2.159	0.009
Ni-P	2.136	2.141	0.003
Ni-Fe	2.890	2.910	0.007
C-S	1.728	1.738	0.006
C-S	1.736	1.738	0.001
BP86	$d_{exp,5}$ [Å]	$d_{calc,5}$ [Å]	h_{rel} [-]
S-Ni	2.159	2.177	0.008
Ni-S	2.139	2.171	0.015
Ni-P	2.136	2.122	-0.006
Ni-Fe	2.890	2.928	0.013
C-S	1.728	1.739	0.006
C-S	1.736	1.739	0.002
M06-2X	$d_{exp,5}$ [Å]	$d_{calc,5}$ [Å]	h_{rel} [-]
S-Ni	2.159	2.204	0.020
Ni-S	2.139	2.204	0.029
Ni-P	2.136	2.231	0.043
Ni-Fe	2.890	2.954	0.022
C-S	1.728	1.753	0.015
C-S	1.736	1.754	0.010

CAM-B3LYP	$d_{exp,5}$ [Å]	$d_{calc,5}$ [Å]	h_{rel} [-]
S-Ni	2.159	2.157	-0.001
Ni-S	2.139	2.157	0.008
Ni-P	2.136	2.138	0.001
Ni-Fe	2.890	2.960	0.024
C-S	1.728	1.738	0.006
C-S	1.736	1.738	0.001
PW91	$d_{exp,5}$ [Å]	$d_{calc,5}$ [Å]	h_{rel} [-]
S-Ni	2.159	2.170	0.005
Ni-S	2.139	2.170	0.014
Ni-P	2.136	2.117	-0.009
Ni-Fe	2.890	2.898	0.003
C-S	1.728	1.735	0.004
C-S	1.736	1.735	-0.001
CAM-B3LYP-D3	$d_{exp,5}$ [Å]	$d_{calc,5}$ [Å]	h_{rel} [-]
S-Ni	2.159	2.156	-0.002
Ni-S	2.139	2.155	0.007
Ni-P	2.136	2.130	-0.003
Ni-Fe	2.890	2.948	0.020
C-S	1.728	1.738	0.006
C-S	1.736	1.738	0.001
B3LYP-D3	$d_{exp,5}$ [Å]	$d_{calc,5}$ [Å]	h_{rel} [-]
S-Ni	2.159	2.184	0.011
Ni-S	2.139	2.176	0.017
Ni-P	2.136	2.145	0.004
Ni-Fe	2.886	2.985	0.033
C-S	1.728	1.742	0.008
C-S	1.736	1.741	0.003

Table S11 Experimental, and calculated bond lengths of **6**

B3LYP	$d_{exp,6}$ [Å]	$d_{calc,6}$ [Å]	h_{rel} [-]
S-Ni	2.200	2.228	0.013
S-Ni	2.206	2.228	0.010
P-Ni	2.178	2.230	0.023
P-Ni	2.178	2.230	0.023
Ni-Fe	4.269	4.287	0.004
C-S	1.748	1.763	0.008
TPSSh	$d_{exp,6}$ [Å]	$d_{calc,6}$ [Å]	h_{rel} [-]
S-Ni	2.200	2.201	0.000
S-Ni	2.206	2.201	-0.002
P-Ni	2.178	2.178	0.000
P-Ni	2.178	2.178	0.000
Ni-Fe	4.269	4.246	-0.006
C-S	1.748	1.759	0.006
ωb97X-D	$d_{exp,6}$ [Å]	$d_{calc,6}$ [Å]	h_{rel} [-]
S-Ni	2.200	2.201	0.000
S-Ni	2.206	2.201	-0.002
P-Ni	2.178	2.178	0.000
P-Ni	2.178	2.178	0.000
Ni-Fe	4.269	4.158	-0.027
C-S	1.748	1.759	0.006
BP86	$d_{exp,6}$ [Å]	$d_{calc,6}$ [Å]	h_{rel} [-]
S-Ni	2.200	2.209	0.004
S-Ni	2.206	2.209	0.001
P-Ni	2.178	2.183	0.002
P-Ni	2.178	2.182	0.002
Ni-Fe	4.269	4.290	0.005
C-S	1.748	1.763	0.008
M06-2X	$d_{exp,6}$ [Å]	$d_{calc,6}$ [Å]	h_{rel} [-]
S-Ni	2.200	2.277	0.034
S-Ni	2.206	2.268	0.027
P-Ni	2.178	2.321	0.062
P-Ni	2.178	2.320	0.061
Ni-Fe	4.269	4.101	-0.041
C-S	1.748	1.759	0.006

CAM-B3LYP	$d_{exp,6}$ [Å]	$d_{calc,6}$ [Å]	h_{rel} [-]
S-Ni	2.200	2.208	0.004
S-Ni	2.206	2.208	0.001
P-Ni	2.178	2.207	0.013
P-Ni	2.178	2.207	0.013
Ni-Fe	4.269	4.241	-0.007
C-S	1.748	1.757	0.005
PW91	$d_{exp,6}$ [Å]	$d_{calc,6}$ [Å]	h_{rel} [-]
S-Ni	2.200	2.205	0.002
S-Ni	2.206	2.206	0.000
P-Ni	2.178	2.174	-0.002
P-Ni	2.178	2.175	-0.001
Ni-Fe	4.269	4.267	-0.001
C-S	1.748	1.758	0.006
CAM-B3LYP-D3	$d_{exp,6}$ [Å]	$d_{calc,6}$ [Å]	h_{rel} [-]
S-Ni	2.200	2.207	0.003
S-Ni	2.206	2.222	0.008
P-Ni	2.178	2.184	0.003
P-Ni	2.178	2.196	0.008
Ni-Fe	4.269	4.164	-0.025
C-S	1.748	1.753	0.003
B3LYP-D3	$d_{exp,6}$ [Å]	$d_{calc,6}$ [Å]	h_{rel} [-]
S-Ni	2.200	2.236	0.016
S-Ni	2.206	2.236	0.014
P-Ni	2.178	2.197	0.009
P-Ni	2.178	2.197	0.009
Ni-Fe	4.269	4.203	-0.016
C-S	1.748	1.761	0.007

Table S12 Comparing the relative error for d_{Fe-M} with TPSSh/def2-TZVP, and 6-311+G**/LANL2DZ

Structure	3-21G	def2-TZVP	6-311+G** and for metal atoms LANL2DZ
1	0.0350	0.0012	0.0067
2	0.0010	0.0187	0.0208
3	0.0041	0.0097	0.0134
4	0.0296	0.0213	0.0142
5	0.1159	0.0020	0.0114

Table S13. QTAIM derived values for structures **1-6** at TPSSh/def2-TZVP and for metal atoms Jorge-TZP was used.

	$d_{Fe-M,\ exp}$ [Å]	$d_{Fe-M,\ calc}$ [Å]	ρ_b [a.u.]	∇^2_b [a.u.]	H_b [a.u.]	V_b [a.u.]	G_b [a.u.]	q_{Fe} [-]	q_M [-]	Δq [-]
1	2.94	2.94	0.0282	0.0327	-0.00544	-0.0191	0.0136	0.688	0.381	0.307
2	2.67	2.71	0.0411	0.0489	-0.01001	-0.0322	0.0222	0.699	0.650	0.049
3	2.78	2.81	0.0342	0.0492	-0.00723	-0.0268	0.0195	0.702	0.557	0.145
4	2.88	2.94	0.0282	0.0305	-0.00514	-0.0179	0.0128	0.725	0.215	0.509
5	2.89	2.89	0.0243	0.0297	-0.00347	-0.0144	0.0109	0.662	0.404	0.258
6	4.27	4.25	-	-	-	-	-	-	-	-

Table S14. QTAIM derived values [a.u.] for model structures depicted in **Fig. 3**. at TPSSh/def2-TZVP+jorge-TZP

	q_{Fe} [-]	q_{M} [-]	d_{Fe-M} [Å]	ρ_b [a.u.]	∇^2_b [a.u.]	H_b [a.u.]	V_b [a.u.]
$Fc(NMe_2)_2[NiCl]$	0.695	0.635	2.621	0.0390	0.0504	-0.00817	-0.0289
$Fc(NMe_2)_2[NiNMe_3]$	0.729	0.722	2.743	0.0335	0.0316	-0.00620	-0.0203
$Fc(NMe_2)_2[NiPMe_3]$	0.709	0.529	2.723	0.0342	0.0364	-0.00641	-0.0219
$Fc(OMe)_2[NiCl]$	0.708	0.762	2.605	0.0404	0.0513	-0.00873	-0.0303
$Fc(OMe)_2[NiNMe_3]$	0.677	0.810	2.643	0.0396	0.0375	-0.00839	-0.0262
$Fc(OMe)_2[NiPMe_3]$	0.676	0.675	2.660	0.0381	0.0413	-0.00774	-0.0258
$Fc(PMe_2)_2[NiCl]$	0.668	0.422	2.842	0.0256	0.0319	-0.00430	-0.0166
$Fc(PMe_2)_2[NiNMe_3]$	0.667	0.542	2.924	0.0242	0.0213	-0.00391	-0.0132
$Fc(PMe_2)_2[NiPMe_3]$	0.662	0.255	2.921	0.0239	0.0258	-0.00370	-0.0139
$Fc(SMe)_2[NiCl]$	0.715	0.557	2.802	0.0278	0.0359	-0.00472	-0.0184
$Fc(SMe)_2[NiNMe_3]$	0.686	0.580	2.932	0.0241	0.0195	-0.00353	-0.0119
$Fc(SMe)_2[NiPMe_3]$	0.709	0.422	2.919	0.0243	0.0243	-0.00349	-0.0131
$Fc(NMe_2)_2[PdCl]$	0.728	0.586	2.736	0.0411	0.0386	-0.01027	-0.0302
$Fc(NMe_2)_2[PdNMe_3]$	0.726	0.476	2.756	0.0393	0.0417	-0.00942	-0.0293
$Fc(NMe_2)_2[PdPMe_3]$	0.724	0.666	2.660	0.0442	0.0601	-0.01101	-0.0371
$Fc(OMe)_2[PdCl]$	0.696	0.627	2.679	0.0449	0.0429	-0.01177	-0.0343
$Fc(OMe)_2[PdNMe_3]$	0.707	0.538	2.722	0.0413	0.0456	-0.00995	-0.0313
$Fc(OMe)_2[PdPMe_3]$	0.736	0.646	2.651	0.0449	0.0613	-0.01105	-0.0374
$Fc(PMe_2)_2[PdCl]$	0.724	0.265	3.002	0.0257	0.0252	-0.00466	-0.0156
$Fc(PMe_2)_2[PdNMe_3]$	0.755	0.361	3.090	0.0244	0.0154	-0.00430	-0.0125
$Fc(PMe_2)_2[PdPMe_3]$	0.727	0.096	3.128	0.0226	0.0179	-0.00379	-0.0121
$Fc(SMe)_2[PdCl]$	0.715	0.495	2.831	0.0330	0.0392	-0.00661	-0.0230
$Fc(SMe)_2[PdNMe_3]$	0.709	0.457	2.901	0.0311	0.0261	-0.00616	-0.0188
$Fc(SMe)_2[PdPMe_3]$	0.693	0.283	2.952	0.0284	0.0276	-0.00525	-0.0174

Fig. S3 Correltaion analysis between QTAIM derived parameters in model structures depicted in **Fig. 3** (TPSSh/def2-TZVP + jorge-TZP).

	Pd							Ni						
TPSSh	d_{Fe-M}	ρ_b	G_b	Δq	V_b	H_b	∇_b^2	d_{Fe-M}	ρ_b	G_b	Δq	V_b	H_b	∇_b^2
d_{Fe-M}	1.00							1.00						
ρ_b	0.97	1.00						0.97	1.00					
G_b	0.95	0.96	1.00					0.97	0.92	1.00				
Δq	0.89	0.88	0.82	1.00				0.56	0.62	0.44	1.00			
V_b	0.96	0.98	0.99	0.84	1.00			0.98	0.95	0.99	0.51	1.00		
H_b	0.94	0.99	0.93	0.84	0.97	1.00		0.97	0.99	0.93	0.62	0.97	1.00	
∇_b^2	0.87	0.84	0.95	0.72	0.91	0.79	1.00	0.87	0.78	0.96	0.29	0.92	0.80	1.00

Further discussion about QTAIM related parameters

A QTAIM-based approach has been proposed by Espinosa and Streubel for anionic O-donors and halides based on the corresponding VSCC minima in relation to the atomic basins of the interacting atoms in molecules.[55,58] Their derived dimensional relative charge concentration bands position parameter proved to be a reliable parameter to distinguish dative, and covalent bonding for the examined structures. However, it has been proposed that when at least one heavy (e.g. transitional metal) is involved in the interaction, the radial shape of the $\nabla^2(r)$ function leaves considerable ambiguity regarding the nature of the interaction.[54] Therefore, the examination of other real space values at the BCP is critical.

Gibbs et al reported that for non-transitional metal-oxygen bonds, the G_b/ρ_b ratio proved to be a versatile descriptor, capable of differentiating between closed and shared shell interactions.[56-57] With good linear correlations with corresponding bond lengths, the G_b/ρ_b ratio was recently used by Espinosa and Streubel to differentiate weak, dative and mostly covalent bonds in phosphinidene complexes.[55] We have found diminished correlation between the G_b/ρ_b ratio and d_{Fe-M} for our transitional metal containing species (see Fig. S4).

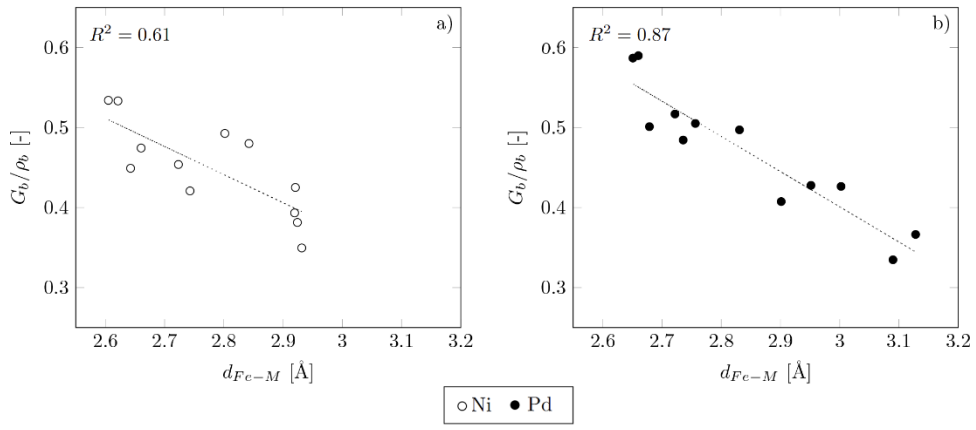


Fig. S4 Correlation between the adimensional G_b/ρ_b ratio and d_{Fe-M} for model molecules with **a)** M = Pd and **b)** M = Ni.

Further discussion about the involvement of the ipso-carbon atoms

The use, and physical interpretation of source function analysis derived values have been comprehensively reviewed by Gatti.[53] For the source function analysis in QTAIM basins, a medium quality grid (with a spacing of 0.1 Bohr) was computed corresponding to the electron density. Then, the source function - with the reference point taken as the position of the corresponding bond critical point

- was integrated into the QTAIM basins with an exact refinement of basin boundary in the Multiwfn program.

Table S15 S% values for Ni complexes TPSSh/def2-TZVP+jorge-TZP (for metal atoms)

	S%(Fe)	S%(Ni)	∑S%(C_{ipso})	∑S%($C_{ipso,ortho}$)
$Fc(NMe_2)_2NiCl$	-5.63	21.77	-13.91	
$Fc(NMe_2)_2NiNMe_3$	-6.37	14.26	-22.15	
$Fc(NMe_2)_2NiPMe_3$	-6.65	10.46	-18.67	
$Fc(OMe)_2NiCl$	-0.08	9.42	-10.91	
$Fc(OMe)_2NiNMe_3$	-4.93	20.82	-12.42	
$Fc(OMe)_2NiPMe_3$	-3.40	15.74	-14.07	
$Fc(PMe_2)_2NiCl$	-20.63	-6.61	-11.52	-2.36
$Fc(PMe_2)_2NiNMe_3$	-23.00	3.35	-14.03	-7.48
$Fc(PMe_2)_2NiPMe_3$	-24.48	-0.27	-15.91	-5.15
$Fc(SMe)_2NiCl$	-13.81	-2.09	-20.80	-2.32
$Fc(SMe)_2NiNMe_3$	-20.20	3.56	-30.07	-3.19
$Fc(SMe)_2NiPMe_3$	-17.63	-0.13	-31.54	-3.56

In all complexes, a notable negative contribution to the resulting electron density can be attributed to the *ipso*-carbon atoms. As they act as sinks of electron density, they facilitate the Fe-M interaction by lowering the kinetic energy arising from the repulsion between filled orbitals of the metal fragments. Although the correlation between the corresponding S%(Fe) and S%(M) values is acceptable, a better correlation can be observed between the sum of S% values for the metal centers and the *ipso*-carbon atoms; and d_{Fe-M}, (see **Fig. S4b**). The contributions of other atoms have not been considered, as resulting complexes do not have orbitals which would correspond to an interaction (SF% > -1%). In case of PMe_2 and SMe_2 donors, the effect of *ortho* carbon atoms become apparent and can no longer be neglected. (see **Fig. S4c**), yielding to a better correlation overall. This suggests that the direct heterobimetallic interaction, and the active involvement of the Cp rings dictate together the distance between metal centers in the resulting complex.

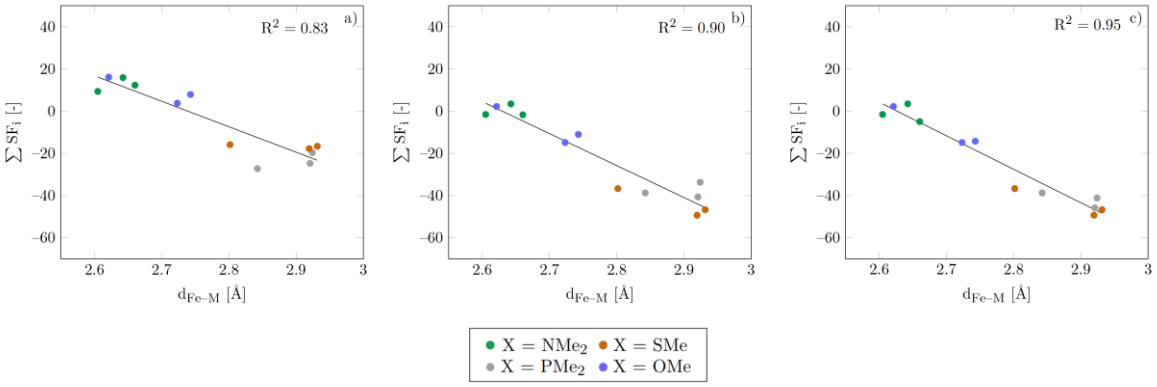


Fig. S5 The sum of S% values for the metal atoms (a), for metal atoms and *ipso*-carbon atoms (b) and for metal atoms coupled with *ipso*, and neighboring carbon atoms (c).

It is important to highlight the error of source function computations. Although the source function is a considerably robust descriptor; as it needs to be reintegrated into the electron density grid computed in atomic basins, careful consideration should be taken in determining the trust radius, and positions of nuclear attractors. A direct measure of this is the sum of the integrated SF(A) values for all atoms, which should be close to the computed electron density in the reference point. The relative error for source function computations for Ni complexes is neglibigle (~0.3%, see **Table S16**) in reference to the electron density in the BCP, which validates the use of SF% in these cases. For Pd complexes however, the relative error for the computations grows significantly (~34%, see **Table S16**), which does not lessen upon the utilization of a finer integration grid. The computations were repeated with the midpoints of the metal atoms taken as reference points, and their nuclear positions instead of corresponding (3;-3) critical points yielding similar results.

Table S16 Electron densities [a.u.] and the sum of integrated SF(A) values [a.u.] for model structures and compounds **1-5** with their corresponding relative error (h_{rel,ρ_b} [%]), at the TPSSh/def2-TZVP (jorge-TZP for metal atoms) level of theory.

	ρ_b [a.u.]	$\sum SF_i\,\rho_b$ [a.u.]	h_{rel,ρ_b} [%]
$Fc(NMe_2)_2[NiCl]$	0.0389	0.0390	0.01
$Fc(NMe_2)_2[NiNMe_3]$	0.0333	0.0335	0.50
$Fc(NMe_2)_2[NiPMe_3]$	0.0341	0.0342	0.25
$Fc(OMe)_2[NiCl]$	0.0402	0.0404	0.46
$Fc(OMe)_2[NiNMe_3]$	0.0394	0.0396	0.49
$Fc(OMe)_2[NiPMe_3]$	0.0380	0.0381	0.22
$Fc(PMe_2)_2[NiCl]$	0.0255	0.0256	0.45

$Fc(PMe_2)_2[NiNMe_3]$	0.0241	0.0242	0.52
$Fc(PMe_2)_2[NiPMe_3]$	0.0239	0.0239	0.15
$Fc(SMe)_2[NiCl]$	0.0277	0.0278	0.32
$Fc(SMe)_2[NiNMe_3]$	0.0240	0.0241	0.28
$Fc(SMe)_2[NiPMe_3]$	0.0243	0.0243	0.25
$Fc(NMe_2)_2[PdCl]$	0.0632	0.0442	-30.13
$Fc(NMe_2)_2[PdNMe_3]$	0.0593	0.0411	-30.67
$Fc(NMe_2)_2[PdPMe_3]$	0.0575	0.0393	-31.73
$Fc(OMe)_2[PdCl]$	0.0640	0.0449	-29.78
$Fc(OMe)_2[PdNMe_3]$	0.0636	0.0449	-29.36
$Fc(OMe)_2[PdPMe_3]$	0.0598	0.0413	-30.95
$Fc(PMe_2)_2[PdCl]$	0.0427	0.0257	-39.81
$Fc(PMe_2)_2[PdNMe_3]$	0.0405	0.0244	-39.85
$Fc(PMe_2)_2[PdPMe_3]$	0.0388	0.0226	-41.83
$Fc(SMe)_2[PdCl]$	0.0508	0.0330	-35.04
$Fc(SMe)_2[PdNMe_3]$	0.0483	0.0311	-35.62
$Fc(SMe)_2[PdPMe_3]$	0.0455	0.0284	-37.51
1	0.0456	0.0282	-38.29
2	0.0597	0.0411	-31.11
3	0.0526	0.0342	-35.01
4	0.0455	0.0282	-38.08
5	0.0242	0.0243	0.23

The involvement of the p orbitals of the *ipso*-carbon atoms can be visually represented by considering the Kohn-Sham molecular orbitals that give the largest contribution to the electron density at the bond critical point, consistent with the source function analysis.

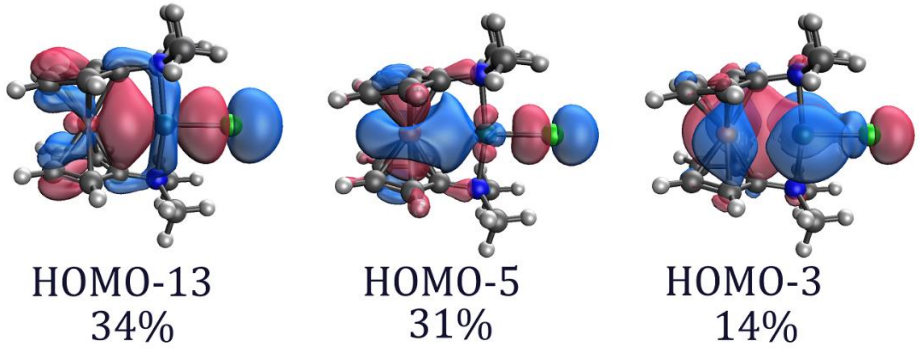


Fig. S6. Kohn-Sham orbitals for $[Fc(NMe2)NiCl]^+$ that give the largest contribution to the electron density at the bond critical point with an isosurface electron density of 0.025 a.u. (TPSSh/def2-TZVP and jorge-TZP for metal atoms)

A notable involvement of the substituent orbitals can be seen in case of SMe_2 and OMe donors. However, the correlation between the resulting SF% sums to $d_{Fe\text{-}M}$ is rather poor, suggesting that the direct effect of the substituents does not contribute to the resulting $d_{Fe\text{-}M}$ directly (see **Fig. S5** and **Table S17).**

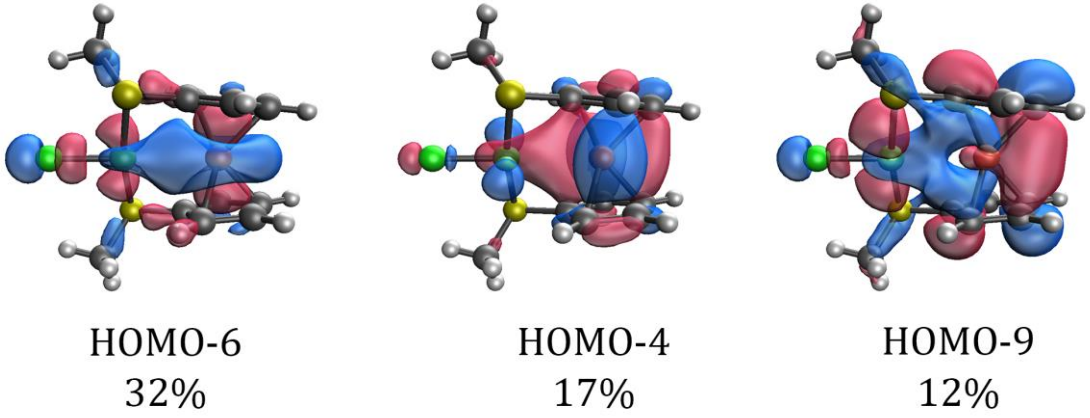


Fig. S7. Kohn-Sham orbitals for $[Fc(SMe)NiCl]^+$ that give the largest contribution to the electron density at the bond critical point (with an isosurface electron density of 0.025 a.u., TPSSh/def2-TZVP and jorge-TZP for metal atoms)

Table S17 S% values for model structures. TPSSh/def2-TZVP+jorge-TZP (for metal atoms)

	S%(Fe)	S%(Ni)	∑S%(D)
$Fc(NMe_2)_2NiCl$	-5.63	21.77	-2.00
$Fc(NMe_2)_2NiNMe_3$	-6.37	14.26	-0.38
$Fc(NMe_2)_2NiPMe_3$	-6.65	10.46	1.63
$Fc(OMe)_2NiCl$	-0.08	9.42	12.66
$Fc(OMe)_2NiNMe_3$	-4.93	20.82	11.21
$Fc(OMe)_2NiPMe_3$	-3.40	15.74	12.61
$Fc(PMe_2)_2NiCl$	-20.63	-6.61	5.84
$Fc(PMe_2)_2NiNMe_3$	-23.00	3.35	2.60
$Fc(PMe_2)_2NiPMe_3$	-24.48	-0.27	4.06
$Fc(SMe)_2NiCl$	-13.81	-2.09	26.12
$Fc(SMe)_2NiNMe_3$	-20.20	3.56	27.51
$Fc(SMe)_2NiPMe_3$	-17.63	-0.13	28.25

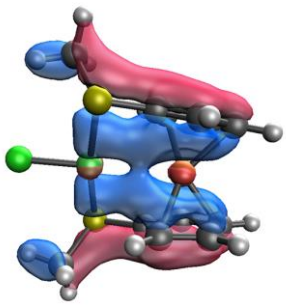
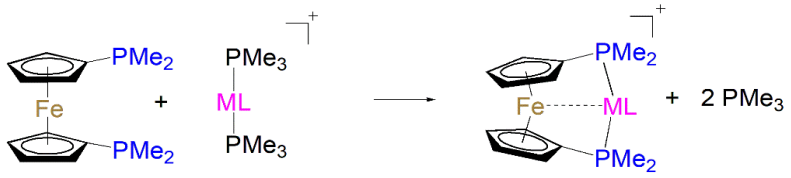


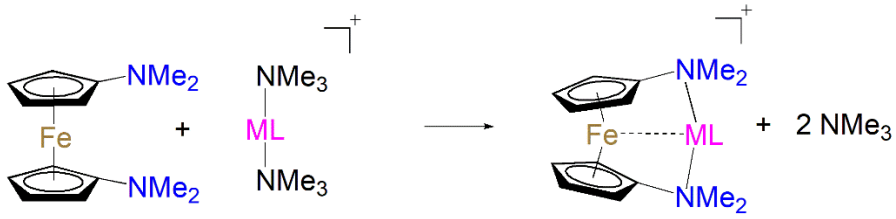
Fig. S8. Kohn-Sham orbital HOMO-31 for $[Fc(SMe)NiCl]^+$ that give the largest contribution to the electron density at the bond critical point (with an isosurface electron density of 0.040 a.u., TPSSh/def2-TZVP and jorge-TZP for metal atoms)

Table S18 Comparison of the DFT results with LNO-CCSD(T)/def2-QZVP//TPSSh/def2-TZVP level of theory (for $Fc(NMe_2)_2$ based systems)



level of theory	ΔE [kcal/mol]					
	PdCl	NiCl	$Pd(PMe_3)$	$Ni(PMe_3)$	$Pd(NMe_3)$	$Ni(NMe_3)$
TPSSh/def2-TZVP	-10.1	-11.1	-24.1	-25.4	-32.2	-28.7
LNO-CCSD(T)/def2-QZVP// TPSSh/def2-TZVP	-10.8	-*	-24.8	-*	-36.0	-24.4

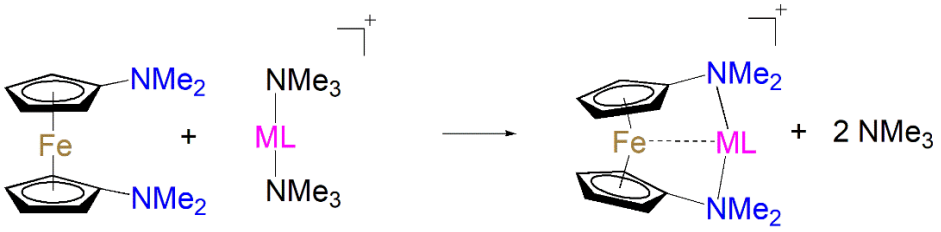
Table S19 Comparison of the DFT results with LNO-CCSD(T)/def2-QZVP//TPSSh/def2-TZVP level of theory (for $Fc(NMe_2)_2$ based systems)



level of theory	ΔE [kcal/mol]					
	PdCl	NiCl	$Pd(PMe_3)$	$Ni(PMe_3)$	$Pd(NMe_3)$	$Ni(NMe_3)$
TPSSh/def2-TZVP	-25.7	-27.9	-34.3	-33.5	-42.2	-34.6
LNO-CCSD(T)/def2-QZVP// TPSSh/def2-TZVP	-36.1	-29.0	-37.9	-33.3	-48.8	-33.6

* LNO-CCSD(T) failed to reach convergence

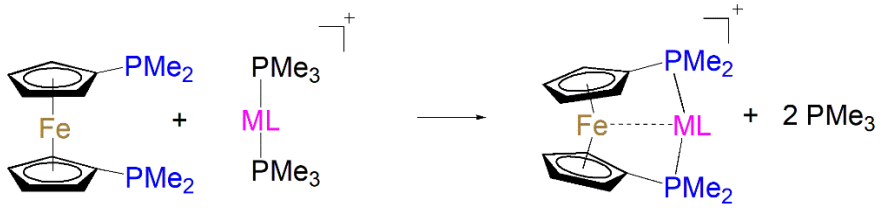
Table S20 Comparison of different DFT functionals (for $Fc(NMe_2)_2$ based system)



ΔE [kcal/mol]

ML	TPSSh/def2-TZVP	LNO-CCSD(T)/def2-QZVP// TPSSh/def2-TZVP	ωB97X-D/def2-TZVP	M06-2X/def2-TZVP	B3LYP/def2-TZVP	CAM-B3LYP/def2-TZVP	B3LYP-D3/def2-TZVP	BP86/def2-TZVP
NiCl	-27.9	-29.0	-18.7	-10.3	-21.2	-16.3	-19.6	-28.6

Table S21 Comparison of different DFT functionals (for $Fc(PMe_2)_2$ based system)



ΔE [kcal/mol]

ML	TPSSh/def2-TZVP	LNO-CCSD(T)/def2-QZVP// TPSSh/def2-TZVP	ωB97X-D/def2-TZVP	M06-2X/def2-TZVP	B3LYP/def2-TZVP	CAM-B3LYP/def2-TZVP	B3LYP-D3/def2-TZVP	BP86/def2-TZVP
PdCl	-10.1	-10.8	-1.2	3.2	-6.5	7.4	-2.9	-12.7
PdPMe3	-24.1	-24.8	-15.8	-10.7	-20.8	-18.8	-17.9	-25.3
Ni(PMe3)	-25.4	-	-16.9	-10.9	-21.8	-6.0	-18.8	-27.3

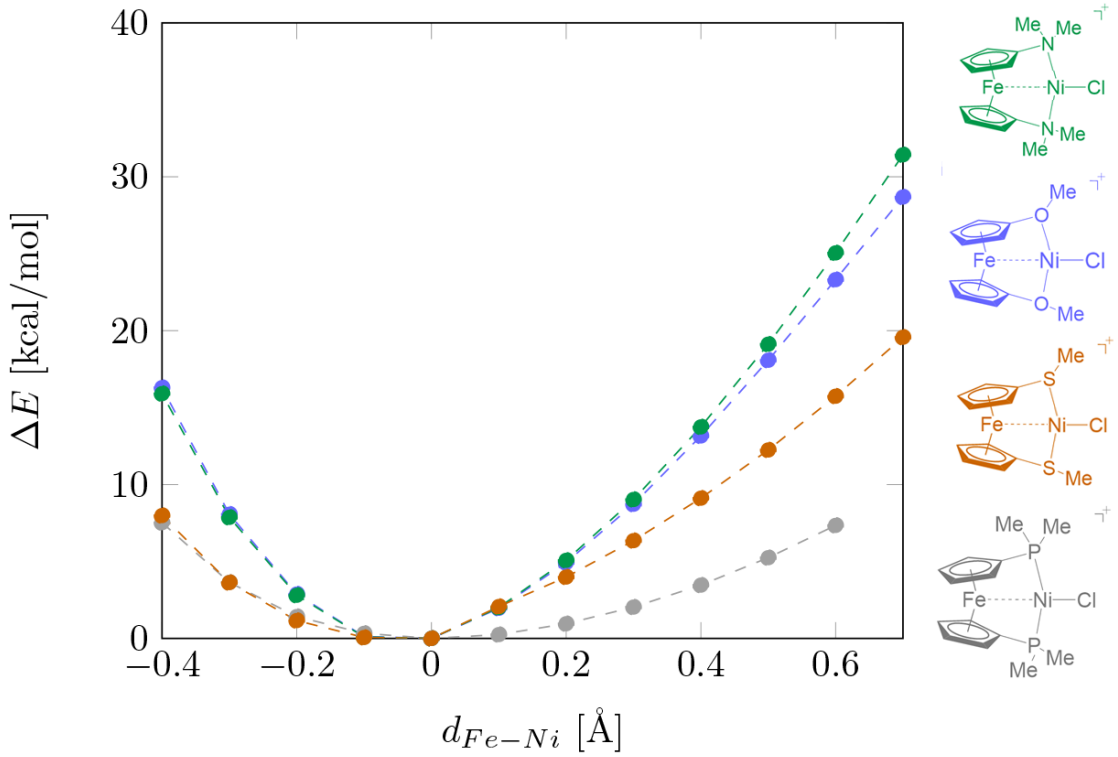


Fig. S9 PES scans for $Fc(OMe)_2[NiCl]^+$, $Fc(NMe_2)_2[NiCl]^+$, $Fc(SMe)_2[NiCl]^+$ $Fc(PMe_2)_2[NiCl]^+$ (at TPSSh/def2-SVP level of theory)

Table S22 Energy difference between scan point **1** and **7** (for single point calculations the geometry obtained after the scan calculations at TPSSh/def2-SVP were used, the Fe-Pd bond was elongated by 0.7 Å). Utilization of DKH Hamiltonians is indicated as DKH0 or DKH2.

	ΔE [kcal/mol]			
	$Fc(NMe_2)_2[PdCl]$	$Fc(OMe)_2[PdCl]$	$Fc(SMe)_2[PdCl]$	$Fc(PMe_2)_2[PdCl]$
def2-TZVP	37.3	31.5	23.0	21.0
jorge-TZP	42.3	37.1	28.7	25.2
jorge-TZP DKH0	46.2	43.1	31.1	26.4
jorge-TZP DKH2	46.1	42.8	31.1	26.4
jorge-TZP-DKH	40.6	34.1	26.3	23.7
jorge-TZP-DKH DKH0	43.8	39.5	27.7	24.2
jorge-TZP-DKH DKH2	43.7	39.1	27.7	24.2
LNO-CCSD(T)/ def2-QZVP// TPSSh/def2-TZVP	43.3	40.8	29.1	26.8

Table S23 Computed BSSE [kcal/mol] for model structures with L = Cl.

BSSE [kcal/mol]	
for system $Fc(NMe_2)_2[PdCl]/ Pd(NMe_3)$	0.1
for system $Fc(PMe_2)_2[PdCl]/Pd(PMe_3)$	0.4
for system $Fc(NMe_2)_2[NiCl]/ Ni(NMe_3)$	0.2
for system $Fc(PMe_2)_2[NiCl]/ Ni(PMe_3)$	0.4

Table S24 Computed adiabatic local mode force constants for the corresponding Fe-M bond [mDyn/Å]

	k_a [mDyn/Å]
$Fc(NMe_2)_2[NiCl]$	1.080
$Fc(NMe_2)_2[NiNMe_3]$	0.808
$Fc(NMe_2)_2[NiPMe_3]$	0.862
$Fc(OMe)_2[NiCl]$	1.076
$Fc(OMe)_2[NiNMe_3]$	0.828
$Fc(OMe)_2[NiPMe_3]$	0.858
$Fc(PMe_2)_2[NiCl]$	0.313
$Fc(PMe_2)_2[NiNMe_3]$	0.259
$Fc(PMe_2)_2[NiPMe_3]$	0.236
$Fc(SMe)_2[NiCl]$	0.591
$Fc(SMe)_2[NiNMe_3]$	0.450
$Fc(SMe)_2[NiPMe_3]$	0.496
$Fc(NMe_2)_2[PdCl]$	1.415
$Fc(NMe_2)_2[PdNMe_3]$	1.137
$Fc(NMe_2)_2[PdPMe_3]$	1.096
$Fc(OMe)_2[PdCl]$	1.306
$Fc(OMe)_2[PdNMe_3]$	1.101
$Fc(OMe)_2[PdPMe_3]$	1.012
$Fc(PMe_2)_2[PdCl]$	0.626
$Fc(PMe_2)_2[PdNMe_3]$	0.551
$Fc(PMe_2)_2[PdPMe_3]$	0.54
$Fc(SMe)_2[PdCl]$	0.779
$Fc(SMe)_2[PdNMe_3]$	0.637
$Fc(SMe)_2[PdPMe_3]$	0.622