Electronic Supplementary Material (ESI) for Dalton Transactions.

Synthesis of phosphinoferrocene amides and thioamides from carbamoyl chlorides and the structural chemistry of Group 11 metal complexes with these mixed-donor ligands

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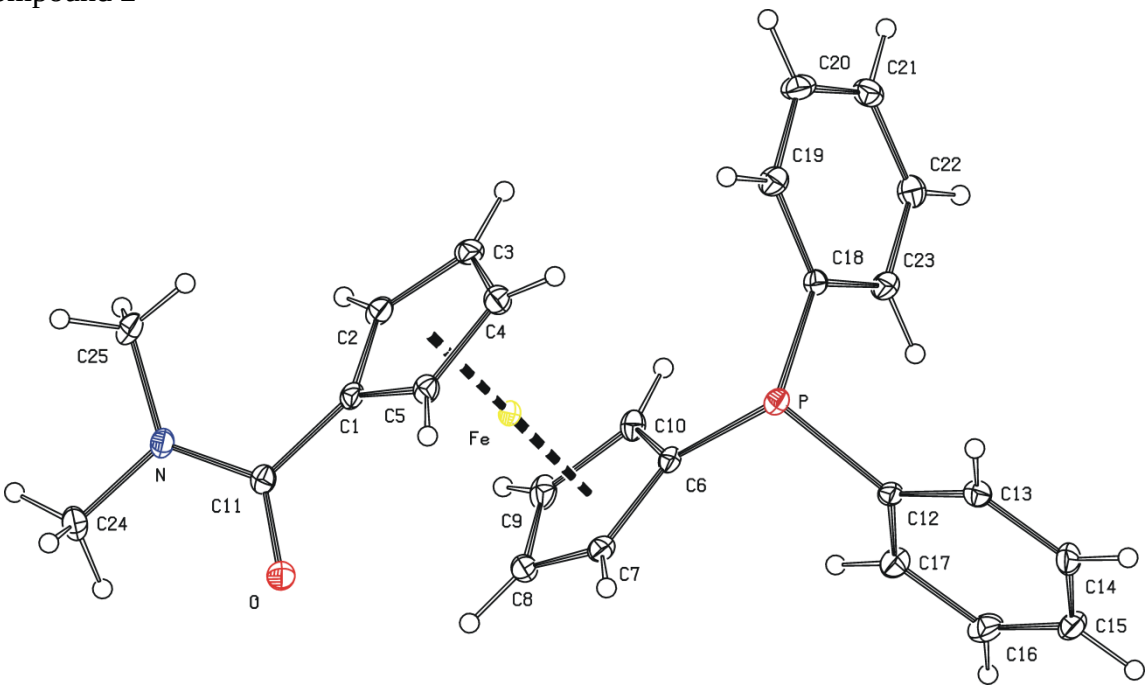
Martin Štícha and Petr Štěpnička*

Supporting Information

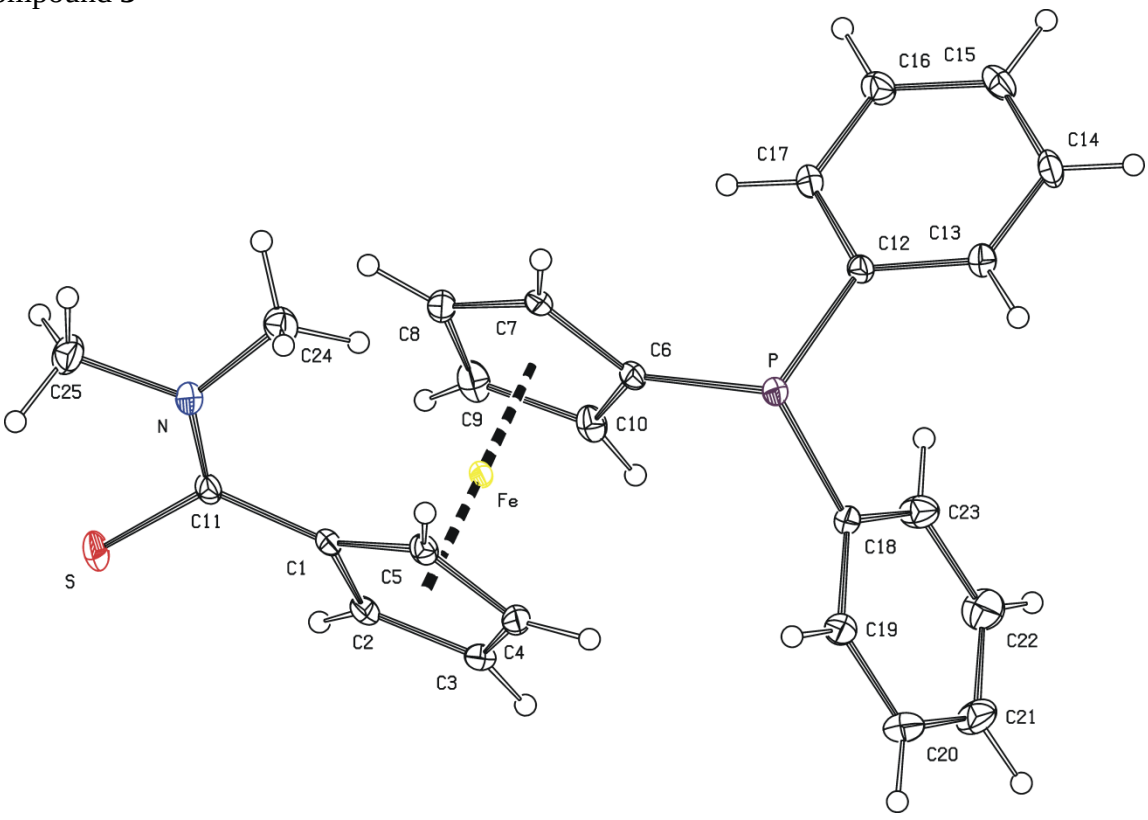
Contents

Displacement ellipsoid plots (at the 30% probability level)

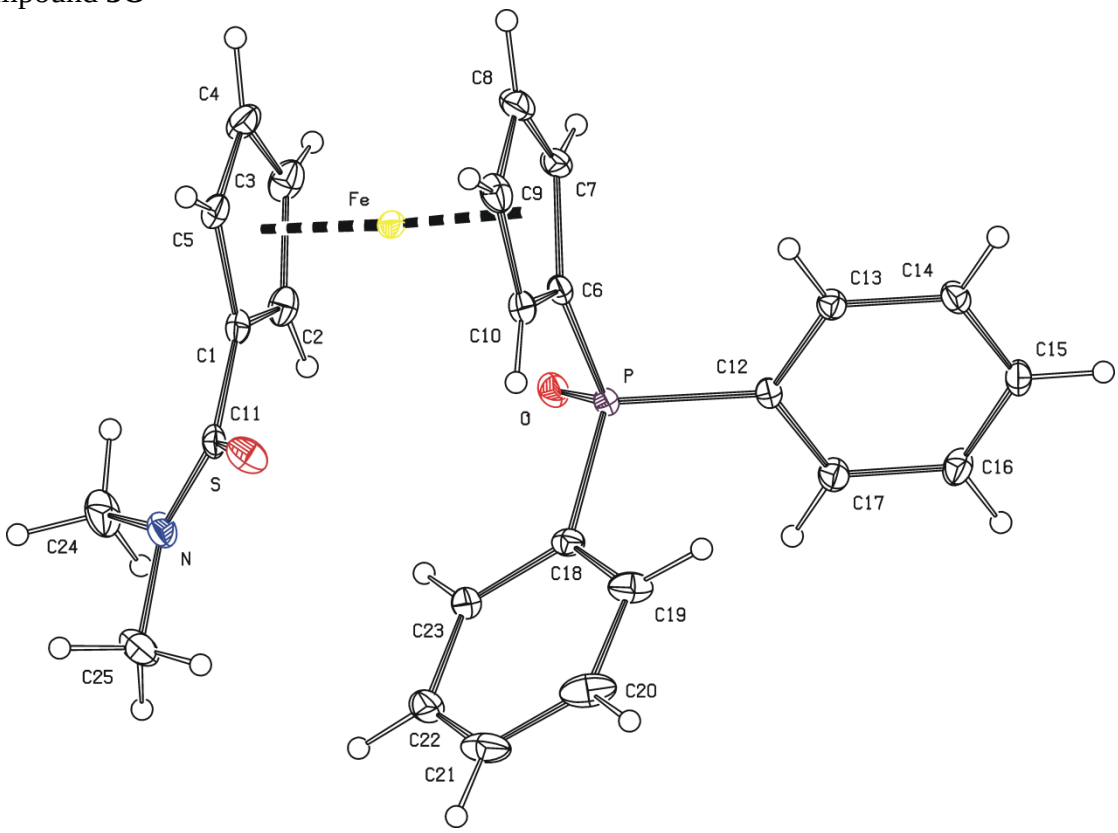
Compound **2**



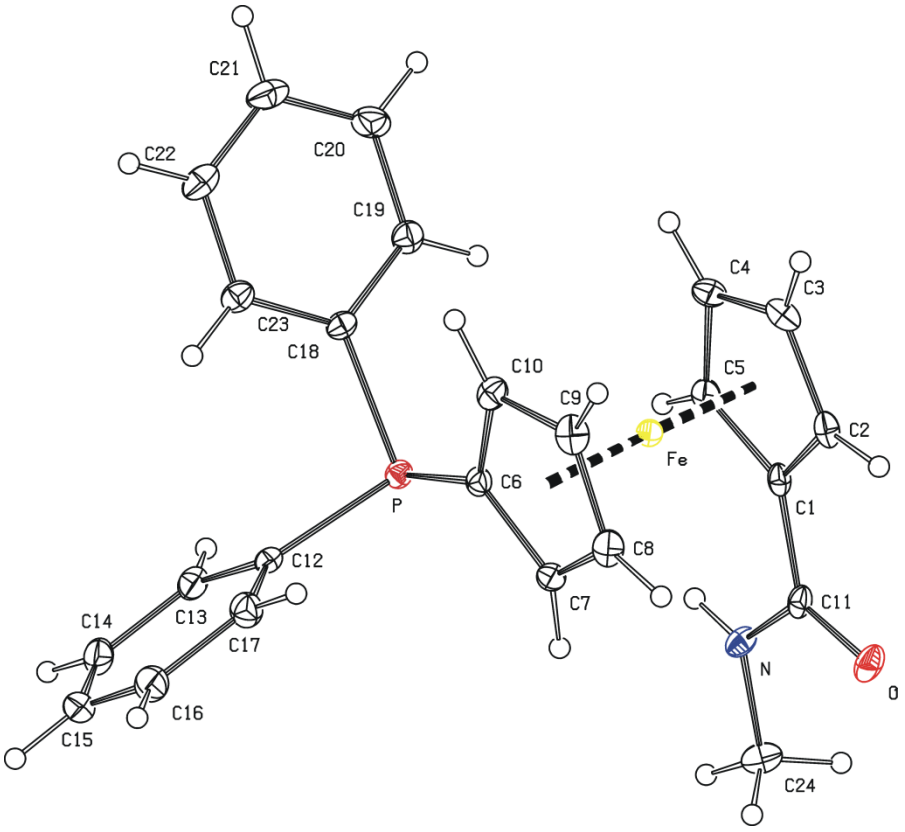
Compound **3**



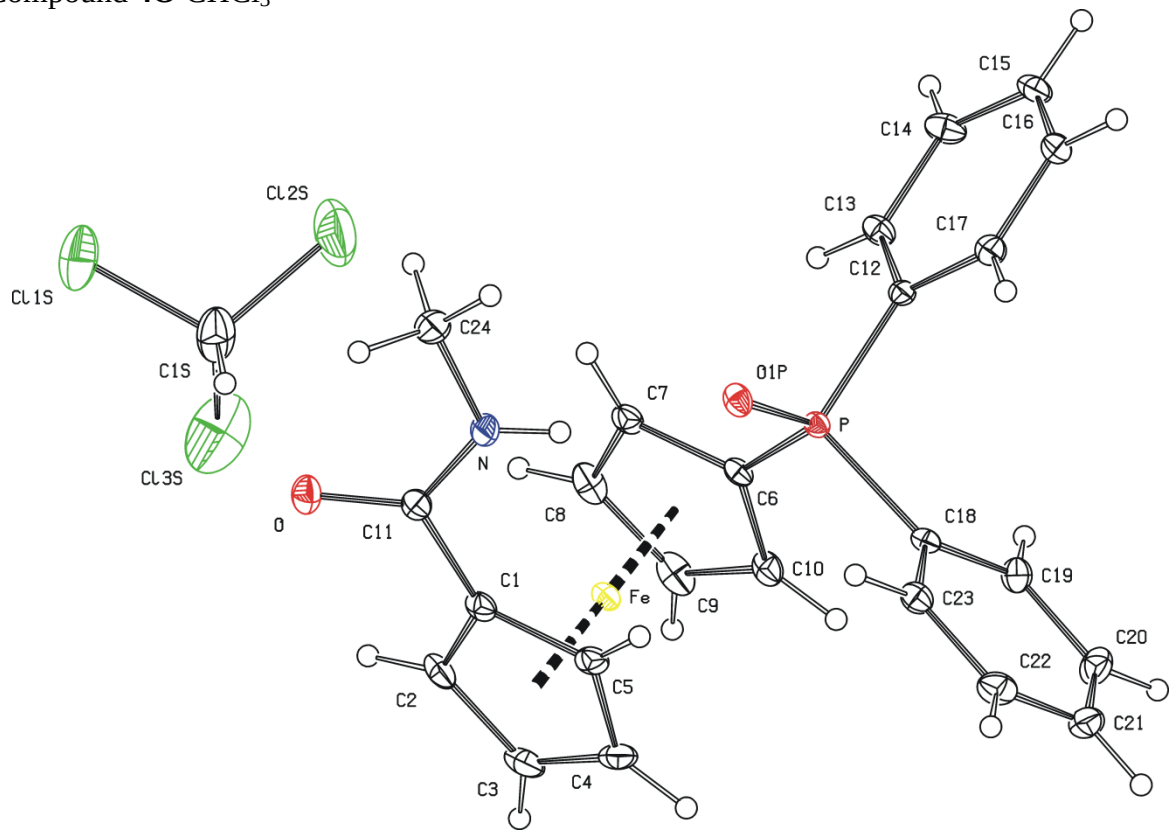
Compound **3O**



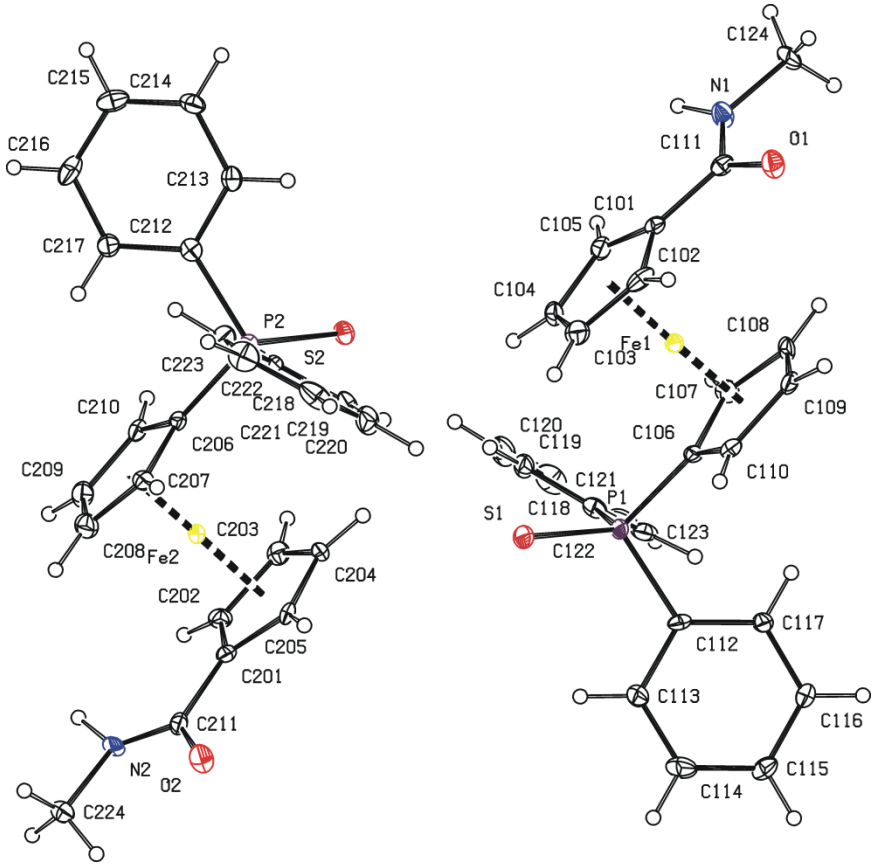
Compound **4**



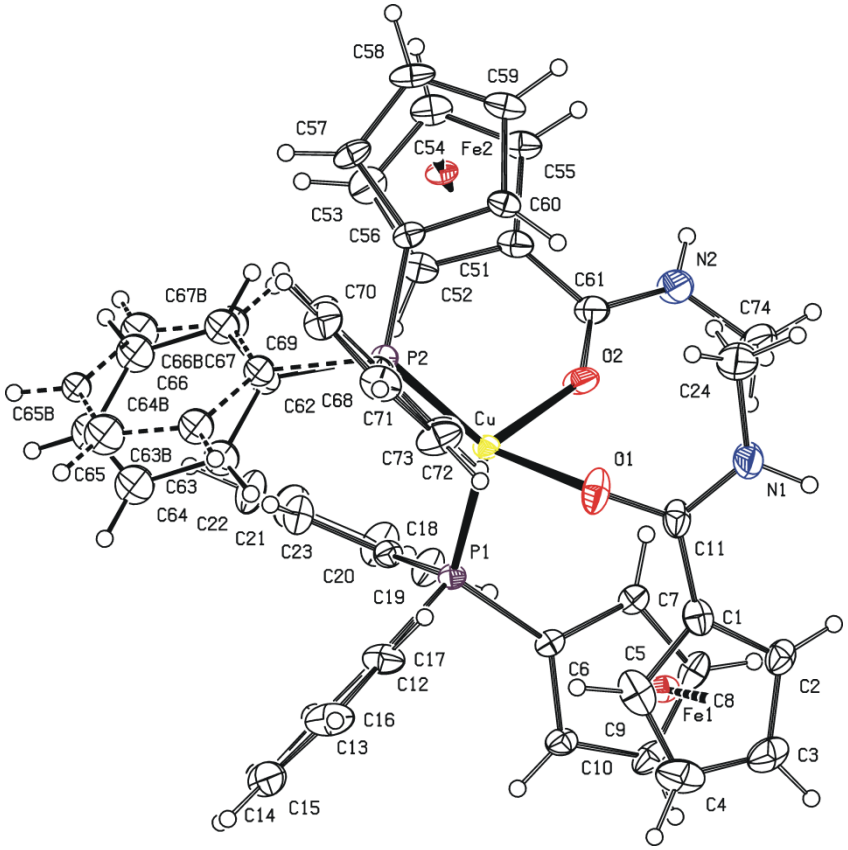
Compound **4O**·$CHCl_3$



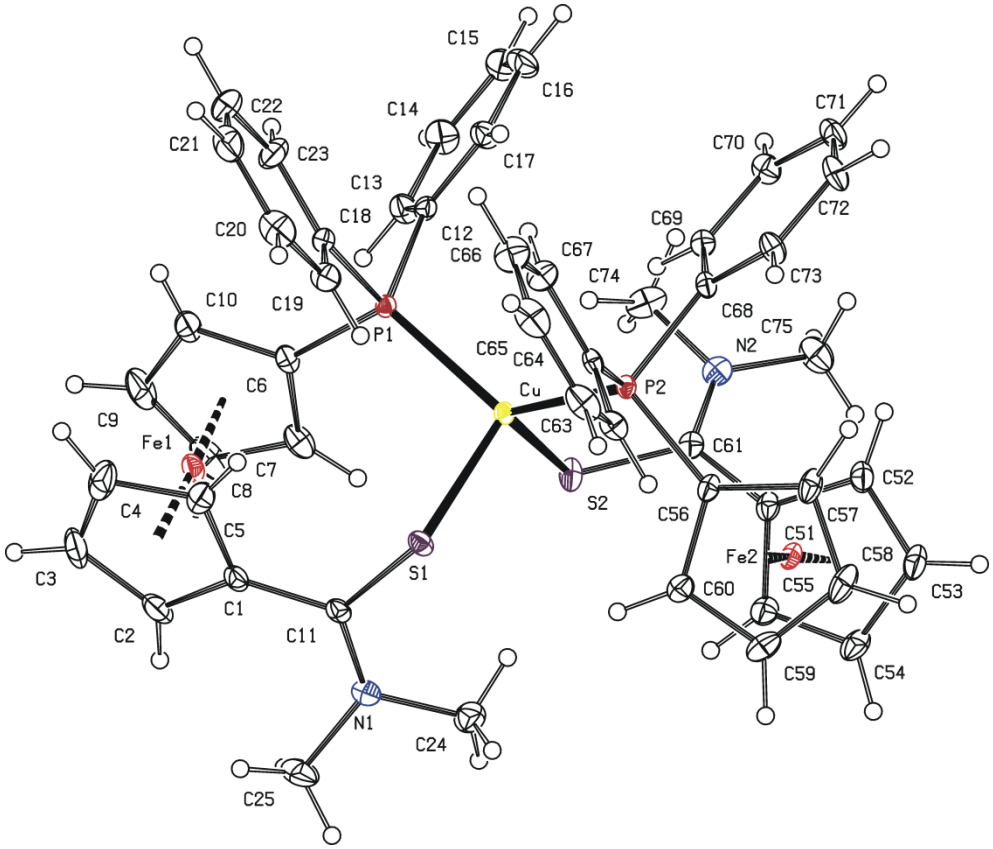
Compound **4S**



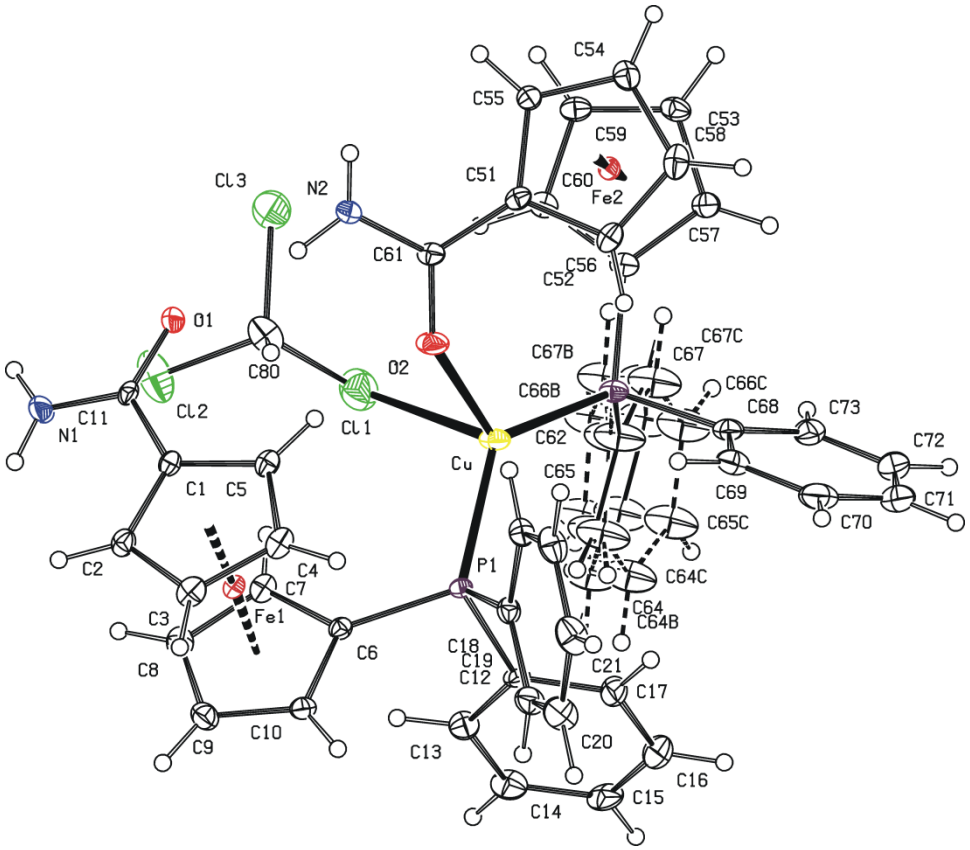
View of the cation in the structure of **6b**·1/4$CHCl_3$



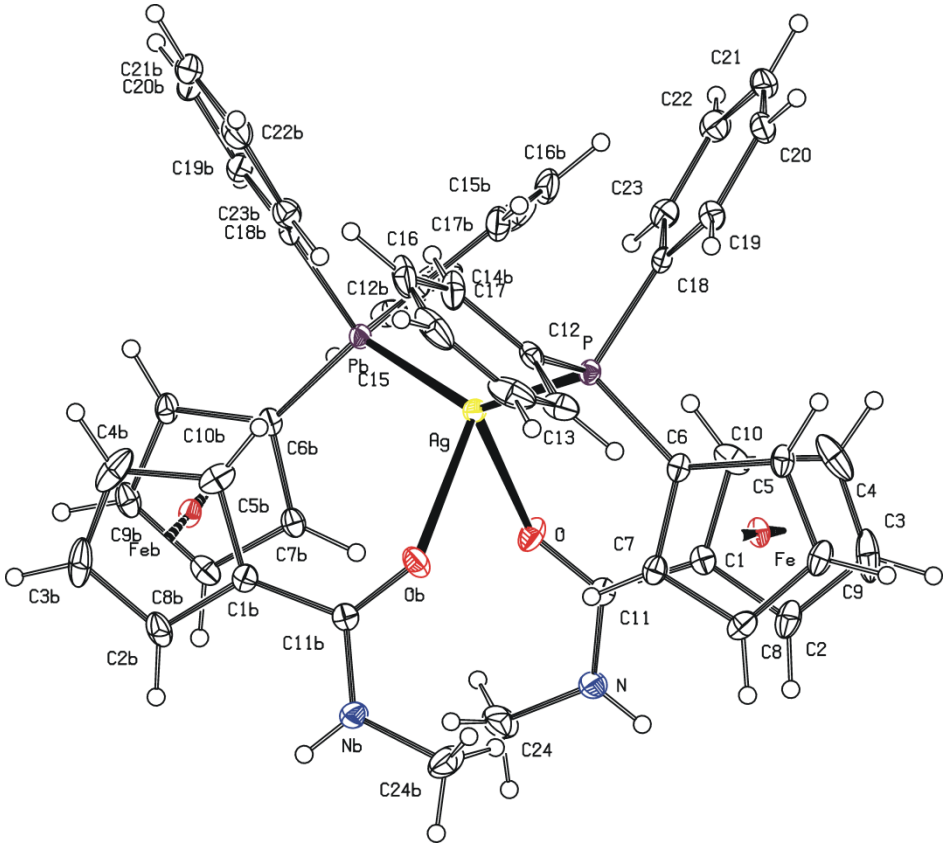
View of the cation in the structure of **6d**·2$CHCl_3$



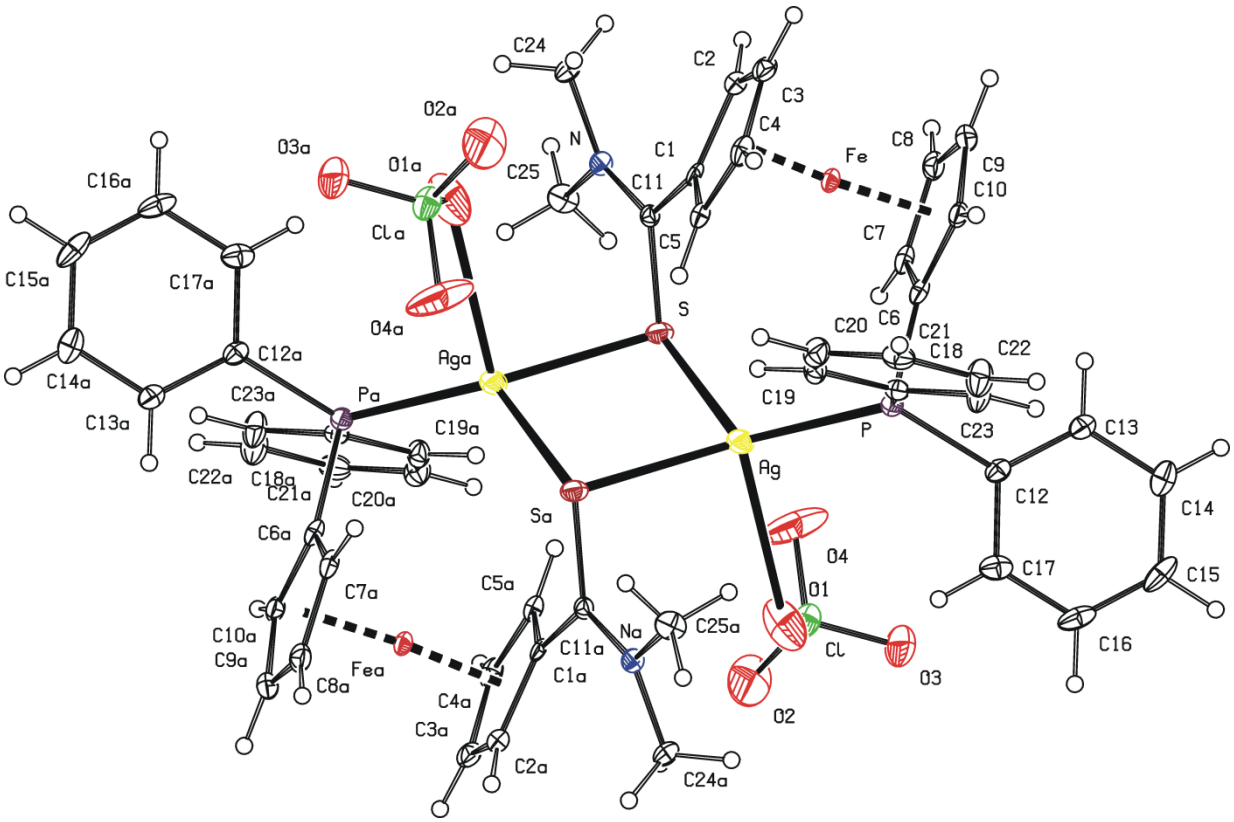
View of the cation in the structure of **6a′**·4$CHCl_3$



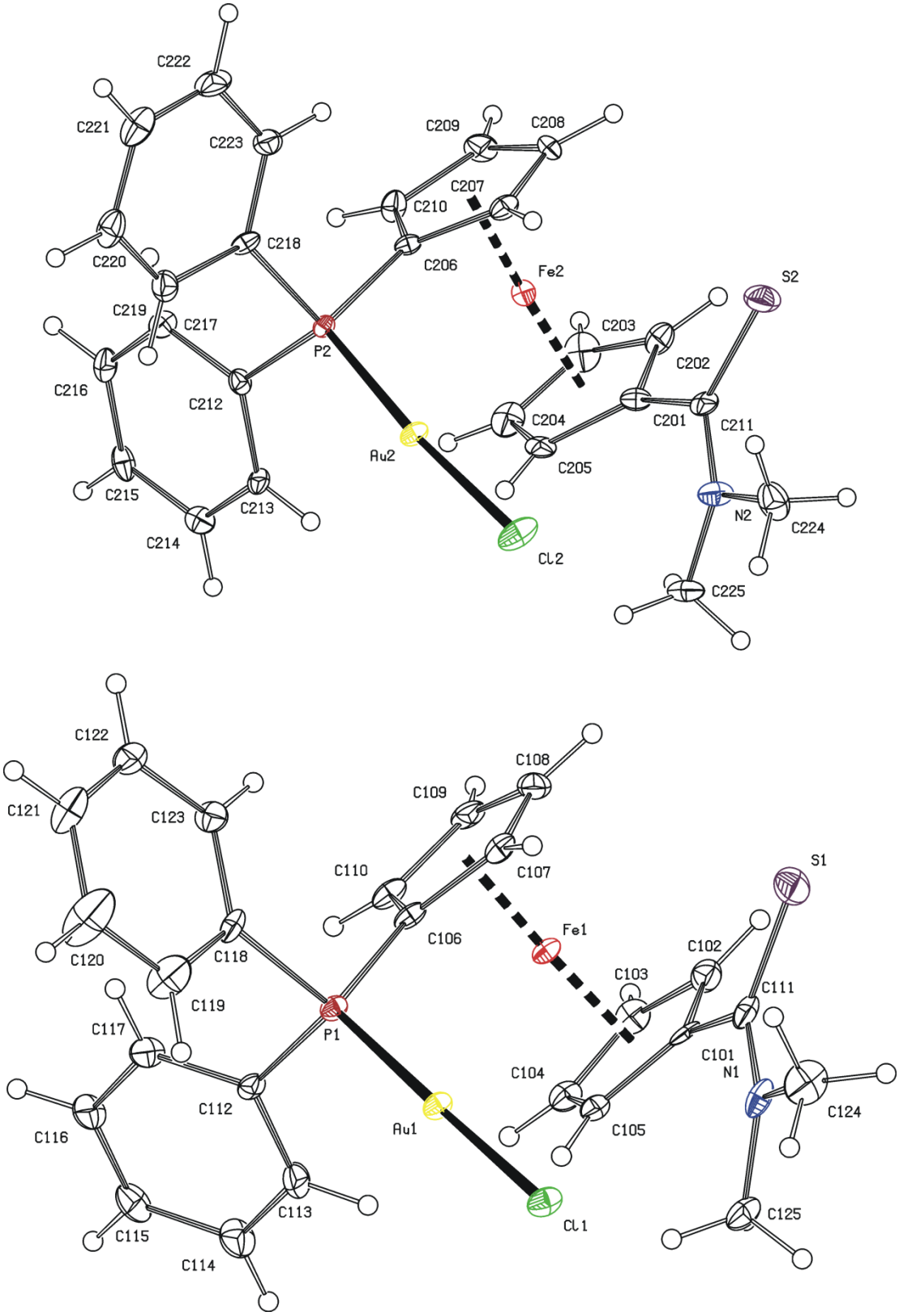
View of the cation in the structure of **7b**·4$CHCl_3$



Compound **7d**

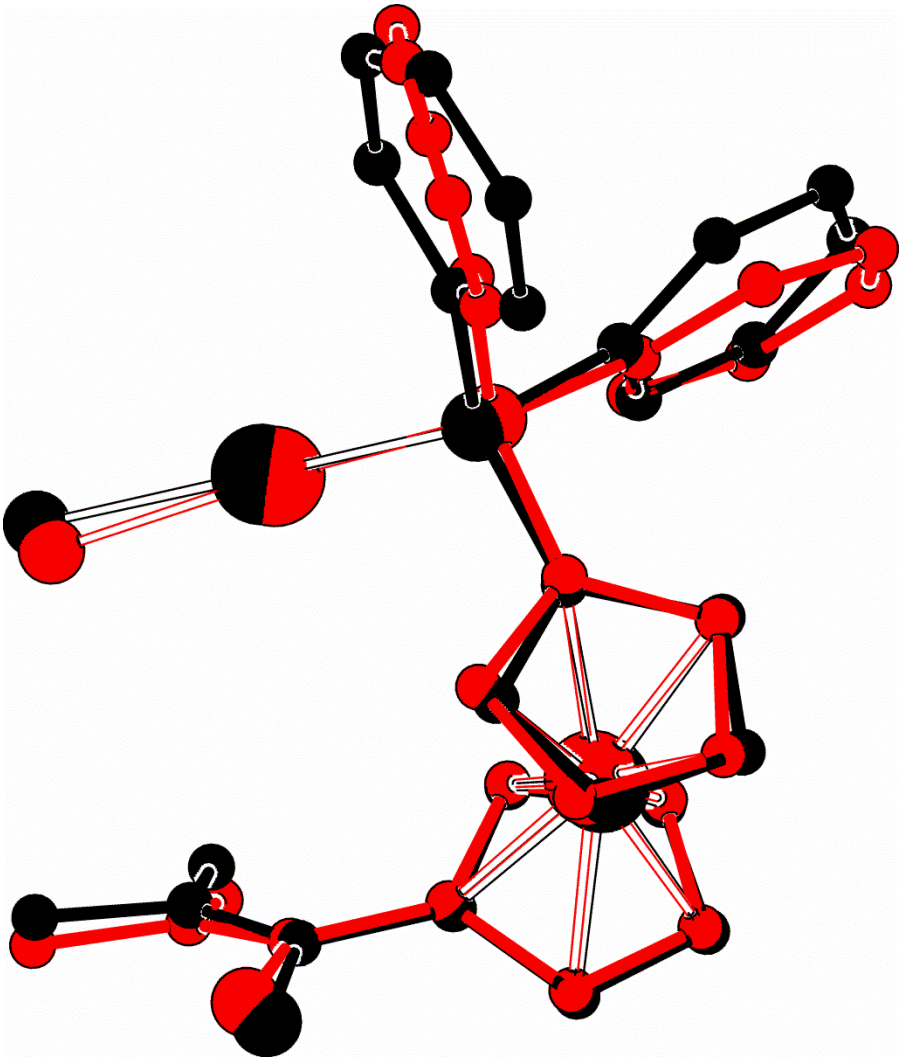

C24
C2
C3
C4
O2a
O3a
O1a
N
C1
C8
Fe
C9
C10
C16a
C25
C11
C7
Cl a
C5
C15a
C17a
S
C20
C6
C21
C18
C22
O4a
Aga
C12a
C19
C14a
C23a
Pa
P
C23
C13
C13a
C19a
Ag
C22a
C18a
C21a
C20a
C12
C14
Sa
C6a
O4
C5a
C17
C15
C7a
O1
C10a
Na
C25a
Cl
C9a
C11a
C16
Fea
C8a
C1a
O3
C4a
O2
C3a
C2a
C24a

Compound **8d**


C222
C221
C223
C209
C208
C207
C210
C218
C206
C220
Fe2
S2
C219
C217
C203
P2
C202
C216
C212
C204
C201
C211
Au2
C205
C215
C213
N2
C224
C214
Cl2
C225
C122
C108
C121
C123
C109
C110
C107
S1
C106
Fe1
C120
C118
C102
C103
C119
C111
C117
P1
C101
N1
C104
C112
C124
Au1
C105
C116
C113
Cl1
C115
C125
C114

Least-squares overlap of the two independent molecules in the crystal structure of **8d**

(Note: molecule 1 in black, molecule 2 in red; hydrogen atoms omitted for clarity)



Crystals suitable for X-ray diffraction analysis were grown by crystallization from chloroform-hexane (**2**: orange block, 0.15 × 0.20 × 0.21 mm^3; **3O**: orange plate, 0.29 × 0.30 × 0.30 mm^3; **6b**·1/4$CHCl_3$: red-orange prism, 0.18 × 0.30 × 0.33 mm^3; **6a′**·$CHCl_3$: orange prism, 0.23 × 0.26 × 0.28 mm^3), chloroform/benzene-hexane (**7b**: orange prism, 0.12 × 0.18 × 0.23 mm3), chloroform-diethyl ether (**8d**: red plate, 0.15 × 0.24 ×0.25 mm^3), dichloromethane-hexane (**3**: red prism, 0.19 × 0.31 × 0.47 mm^3; **4O**·$CHCl_3$: orange plate, 0.13 × 0.23 × 0.32 mm^3), dichloromethane-pentane (**4**: orange prism, 0.13 × 0.28 × 0.60 mm^3) and from ethyl acetate-hexane (**4S**: orange plate, 0.06 × 0.18 × 0.41 mm^3). The crystals of **7d** were obtained by reactive diffusion approach (see main text).

Table S1. Summary of crystallographic data and structure refinement parameters.[a]

Compound	**2**	**3**	**3O**	**4**
Formula	$C_{25}H_{24}FeNOP$	$C_{25}H_{24}FeNPS$	$C_{25}H_{24}FeNOPS$	$C_{24}H_{22}FeNOP$
M	441.27	457.33	473.33	427.25
Crystal system	monoclinic	monoclinic	triclinic	monoclinic
Space group	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)
a/Å	9.5479(2)	11.4811(3)	8.5443(2)	9.0313(3)
b/Å	14.2146(3)	24.8305(7)	10.0465(3)	25.3683(8)
c/Å	15.2152(3)	7.6806(2)	13.2078(3)	9.3612(3)
α/°			87.165(1)	
β/°	94.478(1)	101.066(1)	89.785(1)	109.678(1)
γ/°			71.819(1)	
V/Å^3	2058.70(7)	2148.9(1)	1075.76(5)	2019.5(1)
Z	4	4	2	4
D_{calc} (g mL^{-1})	1.424	1.414	1.461	1.405
μ(Mo Kα)/mm^{-1}	0.827	0.885	0.890	0.840
Diffrns collected	19138	19732	13660	13825
Indep. diffrns	4734	4923	4897	4634
Observed[b] diffrns	3958	4405	4452	3967
R_{int}[c]/%	2.89	2.30	1.53	2.63
No. of parameters	264	264	273	254
R[d] obsd diffrns/%	3.01	2.88	2.67	3.03
R, wR[d] all data/%	4.04, 7.11	3.35, 7.26	3.02, 6.86	3.76, 7.62
Δρ/e Å^{-3}	0.35, –0.29	1.08,[e] –0.25	0.42, –0.25	0.36, –0.25
CCDC entry	1029509	1029510	1029511	1029512

(Table S1 continued)

Compound	**4O**·$CHCl_3$	**4S**	**6b**·1/4$CHCl_3$	**6d**·2$CHCl_3$
Formula	$C_{25}H_{23}Cl_3FeNO_2P$	$C_{24}H_{22}FeNOPS$	$C_{48.25}H_{44.25}BCl_{1.5}CuF_4Fe_2N_2O_2P_2$	$C_{52}H_{50}BCl_6CuF_4Fe_2N_2P_2S_2$
M	562.61	459.31	1061.27	1303.75
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	*C*2/*c* (no. 15)	*Pc* (no. 7)[f]	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)
a/Å	35.0409(9)	11.803(1)	15.4973(5)	15.1921(4)
b/Å	10.9004(3)	19.326(2)	14.2226(4)	16.1101(3)
c/Å	12.9603(3)	9.6446(8)	20.7615(5)	22.5908(4)
α/°				
β/°	93.644(1)	108.311(3)	91.252(1)	94.686(1)
γ/°				
V/Å^3	4940.3(2)	2088.6(3)	4575.0(2)	5510.5(2)
Z	8	4	4	4
D_{calc} (g mL^{-1})	1.513	1.461	1.541	1.571
μ(Mo Kα)/mm^{-1}	1.023	0.914	1.302	1.379
Diffrns collected	19258	13742	36503	65566
Indep. diffrns	5664	7435	8979	12652
Observed[b] diffrns	4473	5600	7869	10679
R_{int}[c]/%	3.61	4.60	2.10	2.38
No. of parameters	299	526	552	653
R[d] obsd diffrns/%	3.87	4.87	3.92	3.56
R, *wR*[d] all data/%	5.49, 9.96	7.76, 10.9	4.46, 10.4	4.49, 9.45
Δρ/e Å^{-3}	0.75, –0.79	0.75, –0.38	0.81, –0.74	1.49, –0.93[g]
CCDC entry	1029513	1029514	1029515	1029516

(Table S1 continued)

Compound	**6a′**·$CHCl_3$	**7b**·$CHCl_3$	**7d**	**8d**
Formula	$C_{47}H_{41}BCl_3CuF_4$-$Fe_2N_2O_2P_2$	$C_{49}H_{45}AgCl_4$-$Fe_2N_2O_6P_2$	$C_{50}H_{48}Ag_2Cl_2$-$Fe_2N_2O_8P_2S_2$	$C_{25}H_{24}AuClFeNPS$
M	1096.42	1181.18	1329.30	689.75
Crystal system	monoclinic	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/c$ (no. 14)	$C2$ (no. 5)	$P2_1/n$ (no. 14)	$Pca2_1$ (no.29)[h]
a/Å	14.2861(4)	18.0426(3)	7.9090(2)	37.4298(9)
b/Å	11.8455(3)	14.5715(2)	16.0180(5)	9.4501(2)
c/Å	30.249(1)	9.2242(2)	19.5538(6)	13.3460(3)
α/°				
β/°	91.666(1)	91.985(1)	98.075(1)	
γ/°				
V/Å^3	5116.8(3)	2423.66(7)	2452.6(1)	4720.7(2)
Z	4	2	2	8
D_{calc} (g mL^{-1})	1.423	1.619	1.800	1.941
μ(Mo Kα)/mm^{-1}	1.243	1.328	1.683	7.106
Diffrns collected	47156	12514	18097	27368
Indep. diffrns	11722	4906	5350	8998
Observed[b] diffrns	9384	4751	4239	8246
R_{int}[c]/%	3.22	2.16	3.36	3.04
No. of parameters	634	330	318	563
R[d] obsd diffrns/%	6.02	2.42	5.17	3.39
R, wR[d] all data/%	7.34, 17.2	2.58, 5.38	7.02, 12.6	3.92, 7.95
Δρ/e Å^{-3}	2.35, –1.84[g]	0.77, –0.77	3.37[g], –1.46	3.17,[i] –1.26
CCDC entry	1029517	1029518	1029519	1029520

[a] Common details: T = 150(2) K. [b] Diffractions with $I > 2\sigma(I)$. [c] $R_{int} = \Sigma\,|F_o^2 - F_o^2(\text{mean})|\,/\Sigma F_o^2$, where F_o^2(mean) is the average intensity of symmetry-equivalent diffractions. [d] $R = \Sigma\,||F_o| - |F_c||/\Sigma|F_o|$, $wR = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma\, w(F_o^2)^2]^{1/2}$. [e] Electron density maximum due to lone electron pair at the phosphorus atom. [f] Flack's enantiomorph parameter: 0.00(5) . [g] Residual electron density near the heaviest atom. [h] Flack's enantiomorph parameter: 0.002(6).

Table S2. Comparison of DFT calculated and experimental geometry (crystal state) for **2**.

Fe	-C1	2.0456(16)	2.070	C13	-C14	1.394(2)	1.391
Fe	-C2	2.0492(17)	2.066	C14	-C15	1.376(3)	1.395
Fe	-C3	2.0530(17)	2.075	C15	-C16	1.388(3)	1.392
Fe	-C4	2.0418(17)	2.076	C16	-C17	1.385(3)	1.395
Fe	-C5	2.0327(16)	2.061	C18	-C19	1.393(2)	1.401
Fe	-C6	2.0465(16)	2.081	C18	-C23	1.392(2)	1.401
Fe	-C7	2.0319(17)	2.061	C19	-C20	1.386(3)	1.394
Fe	-C8	2.0418(19)	2.068	C20	-C21	1.384(3)	1.393
Fe	-C9	2.0501(18)	2.068	C21	-C22	1.376(2)	1.394
Fe	-C10	2.0520(16)	2.071	C22	-C23	1.391(2)	1.393
P	-C6	1.8195(17)	1.833	C1	-Fe	-C2	40.84(7) 40.58
P	-C12	1.8324(16)	1.856	C1	-Fe	-C3	68.64(7) 67.91
P	-C18	1.8413(16)	1.859	C1	-Fe	-C4	68.65(7) 67.81
O	-C11	1.225(2)	1.226	C1	-Fe	-C5	41.04(7) 40.58
N	-C11	1.356(2)	1.376	C1	-Fe	-C6	161.64(7) 175.47
N	-C24	1.460(2)	1.456	C1	-Fe	-C7	124.05(7) 134.96
N	-C25	1.460(2)	1.456	C1	-Fe	-C8	106.82(7) 108.96
C1	-C2	1.429(2)	1.434	C1	-Fe	-C9	120.33(7) 112.26
C1	-C5	1.429(2)	1.432	C1	-Fe	-C10	155.86(7) 142.43
C1	-C11	1.497(2)	1.496	C2	-Fe	-C3	40.64(7) 40.19
C2	-C3	1.425(3)	1.423	C2	-Fe	-C4	68.36(7) 67.63
C3	-C4	1.419(2)	1.427	C2	-Fe	-C5	68.86(7) 68.03
C4	-C5	1.424(2)	1.421	C2	-Fe	-C6	155.77(7) 143.90
C6	-C7	1.435(2)	1.437	C2	-Fe	-C7	162.33(7) 174.85
C6	-C10	1.429(2)	1.434	C2	-Fe	-C8	126.04(7) 135.37
C7	-C8	1.421(3)	1.421	C2	-Fe	-C9	108.97(7) 110.54
C8	-C9	1.416(3)	1.425	C2	-Fe	-C10	121.69(7) 114.24
C9	-C10	1.424(2)	1.424	C3	-Fe	-C4	40.56(7) 40.20
C12	-C13	1.394(2)	1.403	C3	-Fe	-C5	68.79(7) 67.77
C12	-C17	1.396(2)	1.400	C3	-Fe	-C6	120.30(7) 115.25

C3	-Fe	-C7	154.52(7)	144.22	C7	-C8	-C9	108.33(16)	107.83
C3	-Fe	-C8	163.91(7)	175.51	Fe	-C9	-C8	69.43(10)	69.87
C3	-Fe	-C9	127.32(7)	137.12	Fe	-C9	-C10	69.76(10)	70.00
C3	-Fe	-C10	109.16(7)	112.51	C8	-C9	-C10	108.00(16)	108.22
C4	-Fe	-C5	40.91(7)	40.17	C4	-Fe	-C9	164.10(7)	177.28
C4	-Fe	-C6	106.85(7)	112.23	C4	-Fe	-C10	126.33(7)	138.20
C4	-Fe	-C7	118.88(7)	114.30	C5	-Fe	-C6	124.03(7)	136.62
C4	-Fe	-C8	153.78(7)	142.40	C5	-Fe	-C7	105.32(7)	110.09
C5	-C1	-C11	122.96(15)	122.69	C5	-Fe	-C8	118.63(7)	112.19
Fe	-C2	-C1	69.45(9)	69.84	C5	-Fe	-C9	154.23(7)	141.52
Fe	-C2	-C3	69.82(10)	70.22	C5	-Fe	-C10	162.49(7)	176.99
C1	-C2	-C3	108.18(15)	108.24	C6	-Fe	-C7	41.20(6)	40.60
Fe	-C3	-C2	69.54(10)	69.59	C6	-Fe	-C8	68.91(7)	68.08
Fe	-C3	-C4	69.30(10)	69.95	C6	-Fe	-C9	68.78(7)	67.94
C2	-C3	-C4	107.83(15)	108.01	C6	-Fe	-C10	40.80(7)	40.40
Fe	-C4	-C3	70.14(10)	69.85	C7	-Fe	-C8	40.83(7)	40.26
Fe	-C4	-C5	69.20(9)	69.37	C7	-Fe	-C9	68.60(7)	67.71
C3	-C4	-C5	108.52(15)	108.16	C7	-Fe	-C10	68.66(7)	67.82
Fe	-C5	-C1	69.97(9)	70.03	C8	-Fe	-C9	40.50(8)	40.31
Fe	-C5	-C4	69.89(9)	70.46	C8	-Fe	-C10	68.28(7)	67.78
C1	-C5	-C4	107.75(15)	108.28	C9	-Fe	-C10	40.61(7)	40.25
Fe	-C6	-P	123.88(9)	127.22	C6	-P	-C12	101.15(7)	101.79
Fe	-C6	-C7	68.85(9)	68.96	C6	-P	-C18	100.66(7)	102.29
Fe	-C6	-C10	69.81(9)	69.44	C12	-P	-C18	100.67(7)	101.25
P	-C6	-C7	123.93(13)	122.36	C11	-N	-C24	117.87(14)	118.10
P	-C6	-C10	128.92(12)	130.79	C11	-N	-C25	125.29(14)	125.26
C7	-C6	-C10	107.08(14)	106.84	C24	-N	-C25	116.29(13)	114.92
Fe	-C7	-C6	69.95(9)	70.43	Fe	-C1	-C2	69.72(9)	69.57
Fe	-C7	-C8	69.96(10)	70.15	Fe	-C1	-C5	69.00(9)	69.40
C6	-C7	-C8	108.16(15)	108.70	Fe	-C1	-C11	126.81(12)	123.25
Fe	-C8	-C7	69.21(10)	69.60	C2	-C1	-C5	107.72(14)	107.31
Fe	-C8	-C9	70.07(11)	69.82	C2	-C1	-C11	129.33(15)	129.89

Fe	-C10	-C6	69.39(9)	70.16	C15	-C16	-C17	120.08(17)	120.35
Fe	-C10	-C9	69.62(9)	69.75	C12	-C17	-C16	120.48(16)	120.57
C6	-C10	-C9	108.43(15)	108.42	P	-C18	-C19	117.61(12)	117.57
O	-C11	-N	121.69(15)	121.57	P	-C18	-C23	124.49(12)	123.92
O	-C11	-C1	121.41(15)	120.59	C19	-C18	-C23	117.90(15)	118.49
N	-C11	-C1	116.90(15)	117.83	C18	-C19	-C20	121.42(16)	120.92
P	-C12	-C13	117.04(12)	117.12	C19	-C20	-C21	119.63(17)	119.98
P	-C12	-C17	124.16(13)	124.28	C20	-C21	-C22	120.03(16)	119.68
C13	-C12	-C17	118.79(15)	118.53	C21	-C22	-C23	120.13(16)	120.25
C12	-C13	-C14	120.48(15)	120.87	C18	-C23	-C22	120.89(15)	120.66
C13	-C14	-C15	119.99(16)	120.08					
C14	-C15	-C16	120.16(16)	119.58					

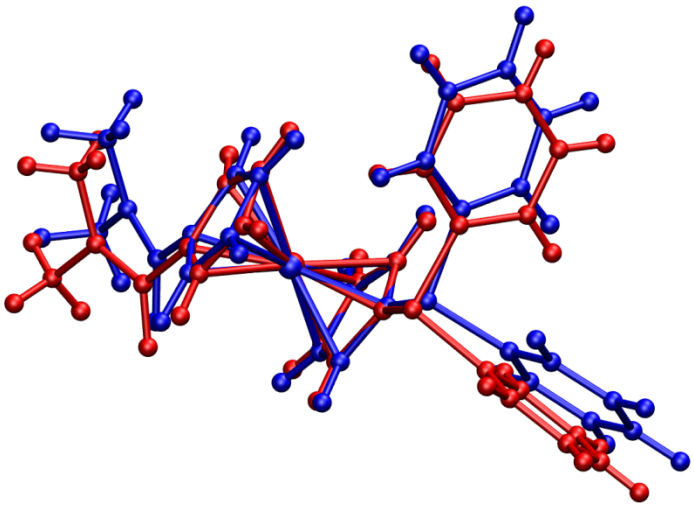
Table S3. Comparison of DFT calculated and experimental geometry (crystal state) for **3**.

Fe	-C1	2.0432(16)	2.086
Fe	-C2	2.0349(16)	2.068
Fe	-C3	2.0520(16)	2.074
Fe	-C4	2.0695(15)	2.081
Fe	-C5	2.0591(16)	2.079
Fe	-C6	2.0531(16)	2.081
Fe	-C7	2.0477(16)	2.068
Fe	-C8	2.0514(18)	2.078
Fe	-C9	2.0393(18)	2.072
Fe	-C10	2.0440(18)	2.068
S	-C11	1.6891(16)	1.685
P	-C6	1.8108(16)	1.836
P	-C12	1.8353(16)	1.856
P	-C18	1.8389(16)	1.858
N	-C11	1.333(2)	1.356
N	-C24	1.465(2)	1.461
N	-C25	1.464(2)	1.462
C1	-C2	1.438(2)	1.435
C1	-C5	1.440(2)	1.443
C1	-C11	1.482(2)	1.486
C2	-C3	1.419(2)	1.416
C3	-C4	1.417(2)	1.424
C4	-C5	1.419(2)	1.418
C6	-C7	1.437(2)	1.436
C6	-C10	1.430(2)	1.433
C7	-C8	1.425(3)	1.424
C8	-C9	1.416(3)	1.424
C9	-C10	1.425(3)	1.424
C12	-C13	1.402(2)	1.403
C12	-C17	1.392(2)	1.400
C13	-C14	1.388(2)	1.391
C14	-C15	1.383(3)	1.394
C15	-C16	1.383(2)	1.392
C16	-C17	1.395(2)	1.395
C18	-C19	1.393(2)	1.401
C18	-C23	1.395(2)	1.401
C19	-C20	1.388(3)	1.394
C20	-C21	1.386(3)	1.393
C21	-C22	1.380(3)	1.394
C22	-C23	1.385(3)	1.393
C1	-Fe	-C2	41.30(6)	40.42
C1	-Fe	-C3	68.92(7)	67.81
C1	-Fe	-C4	68.54(6)	67.70
C1	-Fe	-C5	41.09(6)	40.53
C1	-Fe	-C6	162.17(6)	164.40
C1	-Fe	-C7	124.58(7)	127.79
C1	-Fe	-C8	106.98(7)	109.78
C1	-Fe	-C9	119.87(7)	120.96
C1	-Fe	-C10	155.33(6)	154.40
C2	-Fe	-C3	40.64(7)	40.00
C2	-Fe	-C4	68.09(7)	67.25
C2	-Fe	-C5	68.68(6)	67.51
C2	-Fe	-C6	156.16(7)	153.81
C2	-Fe	-C7	158.13(7)	163.07
C2	-Fe	-C8	119.88(8)	125.21
C2	-Fe	-C9	102.53(8)	106.33
C2	-Fe	-C10	118.38(6)	118.69
C3	-Fe	-C4	40.22(6)	40.08
C3	-Fe	-C5	68.07(6)	67.34
C3	-Fe	-C6	122.55(7)	119.96

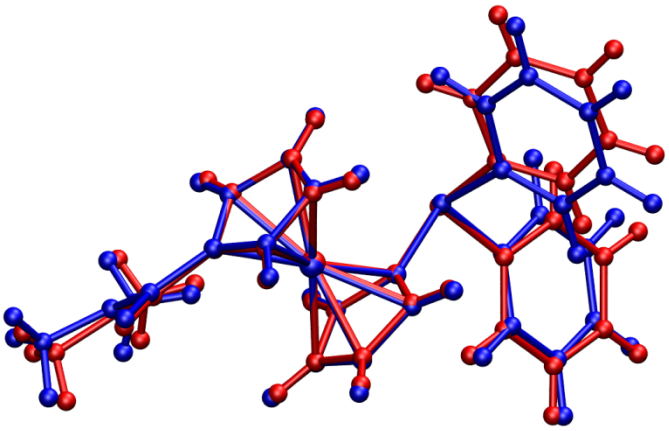
C3	-Fe	-C7	161.19(7)	156.65	C7	-C8	-C9	108.26(16)	108.05
C3	-Fe	-C8	154.83(8)	159.95	Fe	-C9	-C8	70.20(11)	70.17
C3	-Fe	-C9	118.44(8)	122.59	Fe	-C9	-C10	69.76(10)	69.75
C3	-Fe	-C10	104.49(7)	105.59	C8	-C9	-C10	108.21(17)	107.98
C4	-Fe	-C5	40.21(6)	39.86	C4	-Fe	-C9	155.89(8)	159.51
C4	-Fe	-C6	110.35(6)	108.69	C4	-Fe	-C10	122.55(7)	124.10
C4	-Fe	-C7	127.70(6)	123.83	C5	-Fe	-C6	126.58(6)	127.09
C4	-Fe	-C8	163.35(7)	159.21	C5	-Fe	-C7	112.21(6)	111.68
C5	-C1	-C11	129.65(14)	129.44	C5	-Fe	-C8	126.08(7)	124.73
Fe	-C2	-C1	69.66(9)	70.48	C5	-Fe	-C9	158.90(7)	157.79
Fe	-C2	-C3	70.33(9)	70.24	C5	-Fe	-C10	160.23(7)	161.76
C1	-C2	-C3	108.39(14)	108.93	C6	-Fe	-C7	41.03(7)	40.50
Fe	-C3	-C2	69.03(9)	69.76	C6	-Fe	-C8	68.70(7)	67.83
Fe	-C3	-C4	70.55(9)	70.25	C6	-Fe	-C9	68.85(7)	67.93
C2	-C3	-C4	108.21(14)	107.97	C6	-Fe	-C10	40.85(6)	40.41
Fe	-C4	-C3	69.23(9)	69.67	C7	-Fe	-C8	40.68(8)	40.18
Fe	-C4	-C5	69.50(9)	70.00	C7	-Fe	-C9	68.57(8)	67.66
C3	-C4	-C5	108.43(14)	108.22	C7	-Fe	-C10	68.67(7)	67.72
Fe	-C5	-C1	68.87(9)	69.98	C8	-Fe	-C9	40.51(8)	40.13
Fe	-C5	-C4	70.29(9)	70.15	C8	-Fe	-C10	68.38(7)	67.49
C1	-C5	-C4	108.22(13)	108.46	C9	-Fe	-C10	40.85(7)	40.23
Fe	-C6	-P	128.07(8)	127.08	C6	-P	-C12	101.60(7)	101.59
Fe	-C6	-C7	69.28(9)	69.24	C6	-P	-C18	105.45(7)	101.81
Fe	-C6	-C10	69.24(9)	69.29	C12	-P	-C18	100.43(7)	101.43
P	-C6	-C7	122.40(12)	122.74	C11	-N	-C24	126.13(15)	125.37
P	-C6	-C10	130.35(13)	130.39	C11	-N	-C25	119.84(15)	119.93
C7	-C6	-C10	107.21(14)	106.86	C24	-N	-C25	113.66(15)	114.25
Fe	-C7	-C6	69.68(9)	70.27	Fe	-C1	-C2	69.04(9)	69.10
Fe	-C7	-C8	69.80(10)	70.29	Fe	-C1	-C5	70.05(9)	69.50
C6	-C7	-C8	108.03(14)	108.47	Fe	-C1	-C11	130.44(11)	133.57
Fe	-C8	-C7	69.52(10)	69.52	C2	-C1	-C5	106.75(14)	106.41
Fe	-C8	-C9	69.29(11)	69.70	C2	-C1	-C11	123.31(14)	123.42

Fe	-C10	-C6	69.92(9)	70.31	C15	-C16	-C17	120.11(16)	120.32
Fe	-C10	-C9	69.40(10)	70.03	C12	-C17	-C16	120.73(15)	120.57
C6	-C10	-C9	108.28(15)	108.63	P	-C18	-C19	117.35(12)	117.68
S	-C11	-N	121.44(12)	121.03	P	-C18	-C23	123.72(12)	123.81
S	-C11	-C1	117.55(11)	118.78	C19	-C18	-C23	118.51(15)	118.50
N	-C11	-C1	120.94(14)	120.10	C18	-C19	-C20	120.81(17)	120.92
P	-C12	-C13	118.25(12)	116.94	C19	-C20	-C21	119.82(19)	119.97
P	-C12	-C17	123.23(12)	124.47	C20	-C21	-C22	120.0(2)	119.70
C13	-C12	-C17	118.45(15)	118.55	C21	-C22	-C23	120.26(19)	120.25
C12	-C13	-C14	120.45(16)	120.86	C18	-C23	-C22	120.61(17)	120.64
C13	-C14	-C15	120.44(16)	120.08					
C14	-C15	-C16	119.77(16)	119.61					

An overlap of the experimentally determined (crystal state; **red**) and DFT coptimized (gas phase; **blue**) geometries of **2** and **3**.

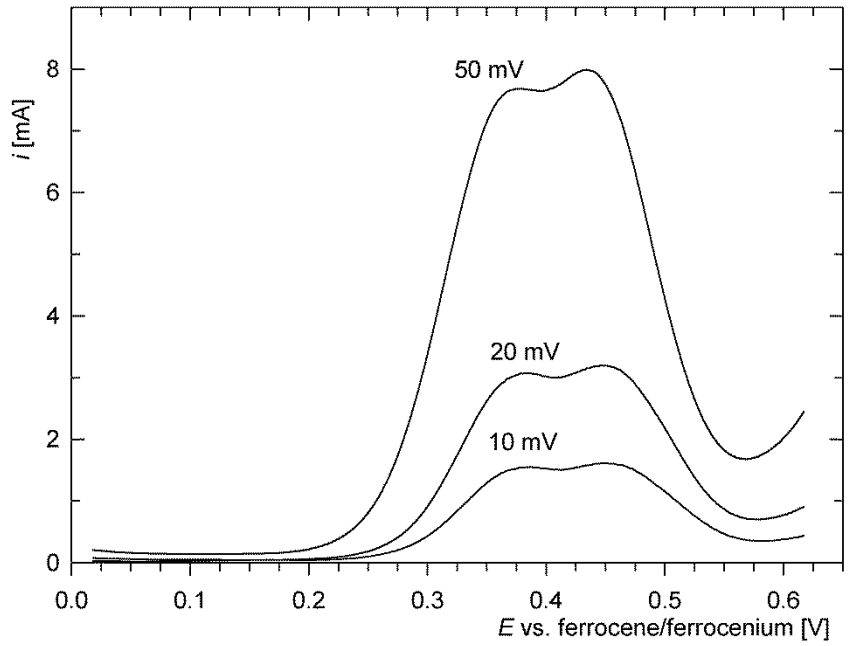


2



3

Differential pulse voltammograms of complex **6c**



The voltammograms were recorded with different modulation amplitude (given in the Figure) at glassy carbon disc electrode in 1,2-dichloroethane containing 0.1 M $Bu_4N[PF_6]$ as the supporting electrolyte.