Double donation in trigonal planar iron-carbodiphosphorane complexes – a concise study on the spectroscopic and electronic properties.

Supplementary Information

Nis-Julian H. Kneusels,[†,‡] Jörn E. Münzer,[†] Kimon Flosdorf,[†] Dandan Jiang,[¶] Bernhard Neumüller,[†] Lili Zhao,[¶,*] Andreas Eichhöfer,[§,*] Gernot Frenking[†,¶,*] and Istemi Kuzu[†,*]

[†]*Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Strasse 4, D-35032 Marburg, Germany. Email: istemi.kuzu@chemie.uni-marburg.de; frenking@chemie.uni-marburg.de*
¶Institute of Advanced Synthesis, School of Chemistry and Molecular Engineering, Jiangsu National Synergetic Innovation Center for Advanced Materials, Nanjing Tech University, Nanjing 211816, China. Email: ias_llzhao@njtech.edu.cn
[‡]*Current address: Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, CB2 1EW, England.*
[§]*Institut für Nanotechnologie, Karlsruher Institut für Technologie (KIT), Campus Nord, Hermann-von-Helmholtz-Platz 1, 76344, Eggenstein-Leopoldshafen, Germany. Email: andreas.eichhoefer@kit.edu*

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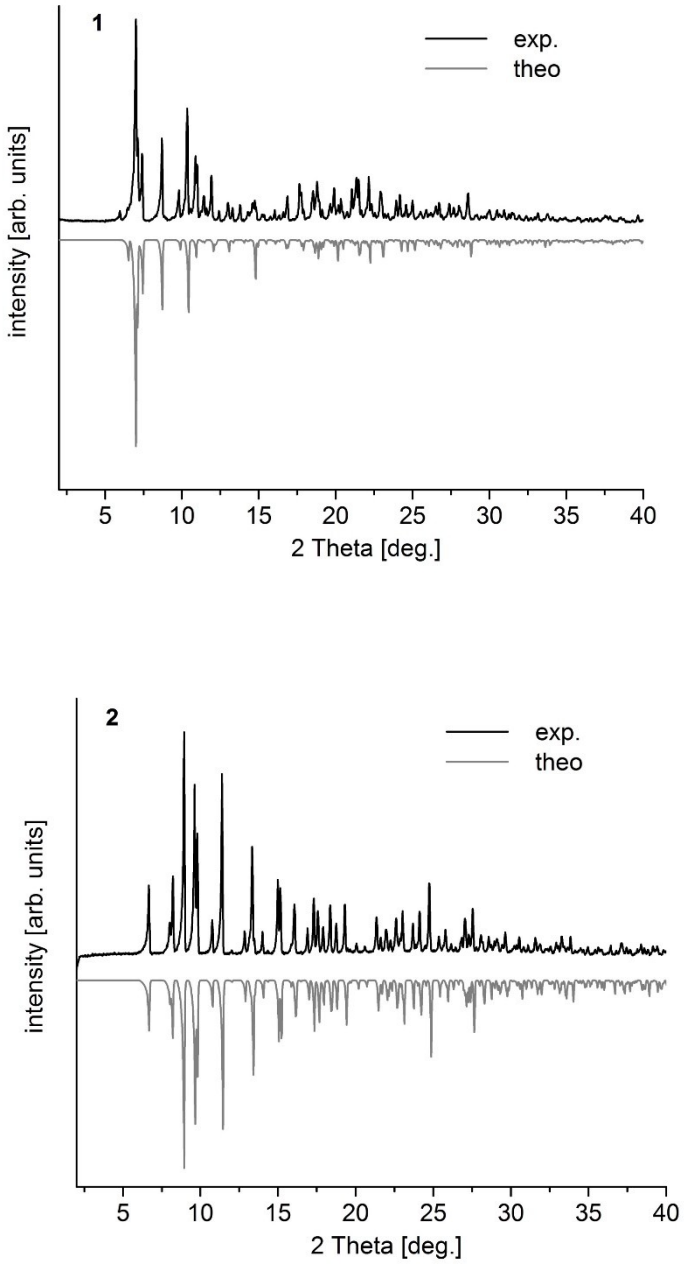


Figure S1. Measured (black) and simulated (grey) X-ray powder diffraction pattern (XRD) of [CDP^{Ph}-Fe{N(SiMe$_3$)$_2$}$_2$]·toluene (**1**·toluene, above) and [CDP^{Me}-Fe{N(SiMe$_3$)$_2$}$_2$] (**2**, below).

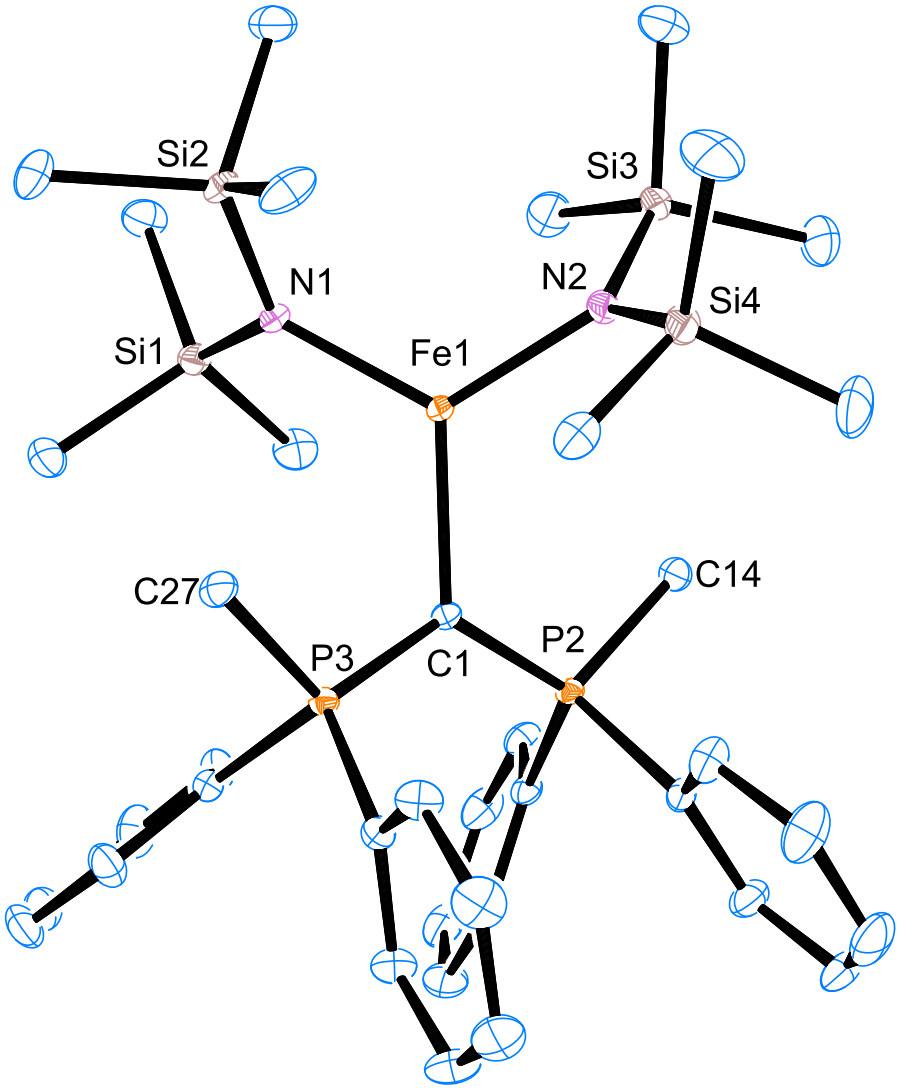


Figure S2. Molecular structure of recrystallized [CDP^{Me}-Fe{N(SiMe$_3$)$_2$}$_2$] (**2**) with 30 % probability for thermal ellipsoids. H atoms are omitted for clarity. Selected bond lengths [pm] and angles [°]: C1–P2 170.1(2), C1–P3 17.0(3), C1–Fe1 211.4(2), Fe1–N1 199.24(17), Fe1–N2 198.91(19); P2–C1–P3 121.94(13), P2–C1–Fe1 119.99(12), P3–C1–Fe1 118.05(11), N1–Fe1–N2 120.80(8), N2–Fe1–C1 119.37(8), N1–Fe1–C1 119.81(8), N1–Fe1–C1–P3 46.1, N2–Fe1–C1–P2 45.7.

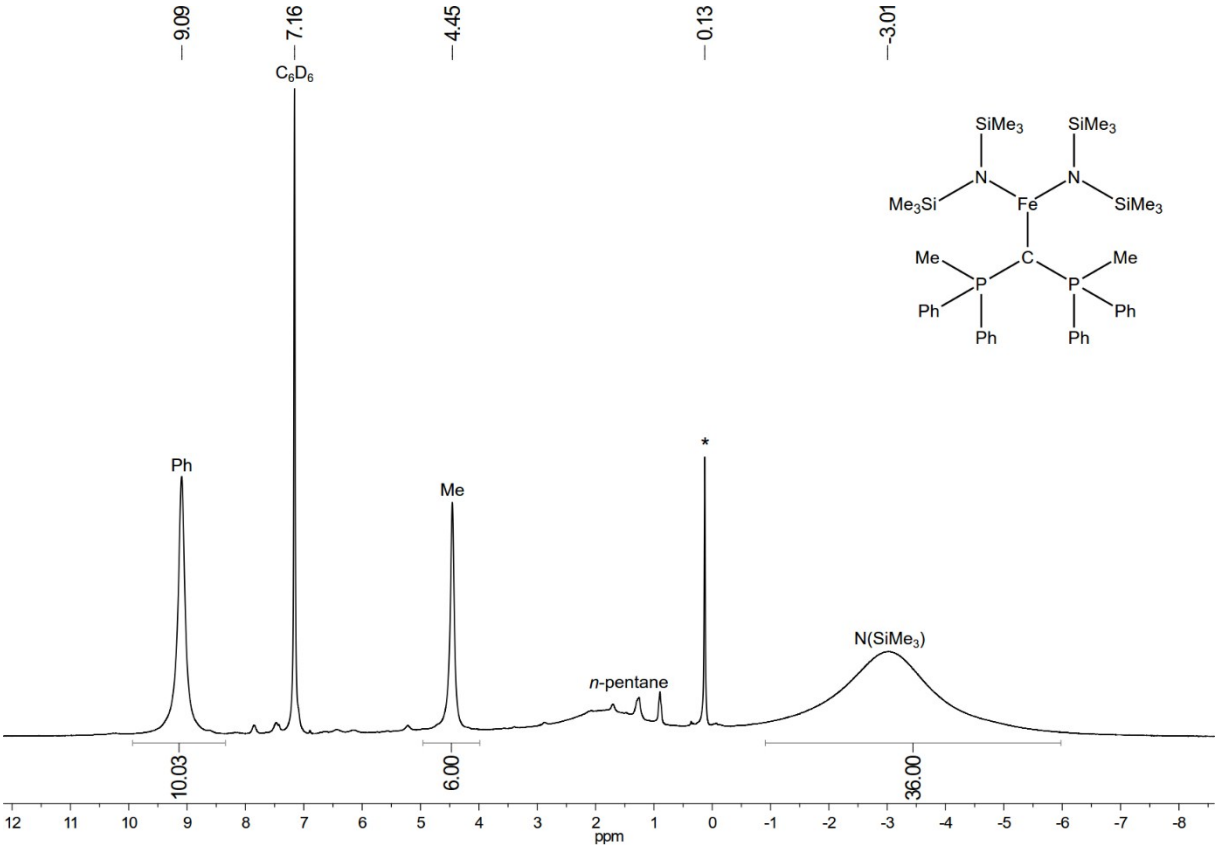


Figure S3. ^{1}H NMR spectrum of [CDP^{Me}-Fe{N(SiMe$_3$)$_2$}$_2$] (**2**) in C_6D_6 (300 K). (*) denotes impurity.

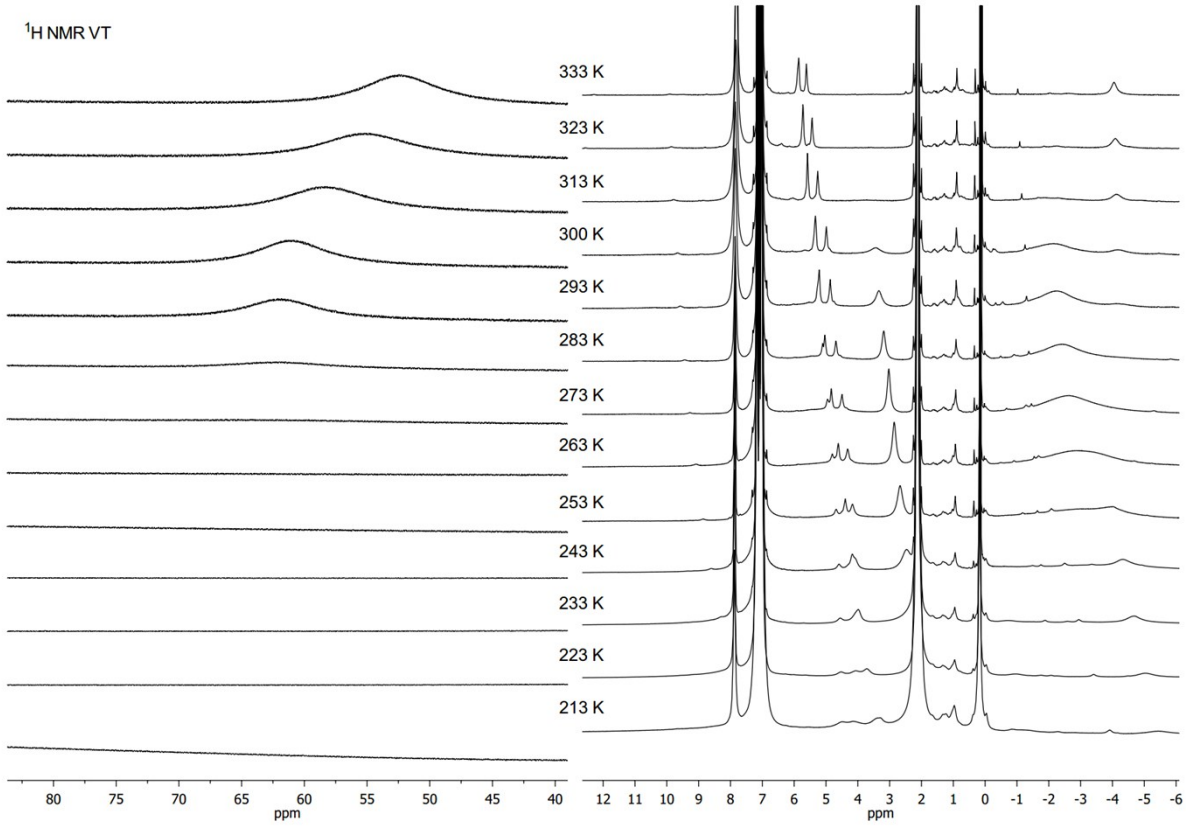


Figure S4. Variable temperature ^{1}H NMR spectrum of [CDP^{Ph}-Fe{N(SiMe$_3$)$_2$}$_2$] (**1**) in toluene-d$_8$.

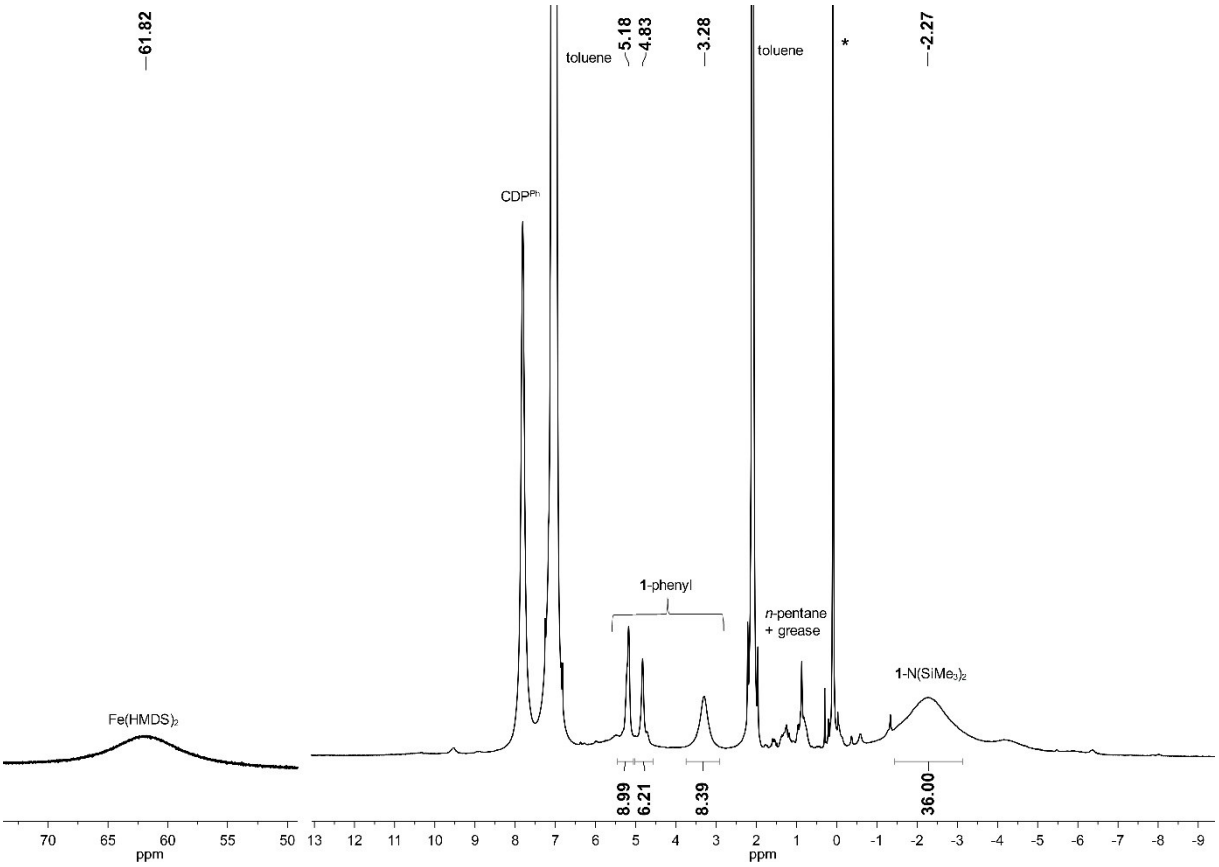


Figure S5. ^{1}H NMR spectrum of [CDP^{Ph}-Fe{N(SiMe$_3$)$_2$}$_2$] (**1**) in toluene-d$_8$ (293 K). (◐) denotes impurity.

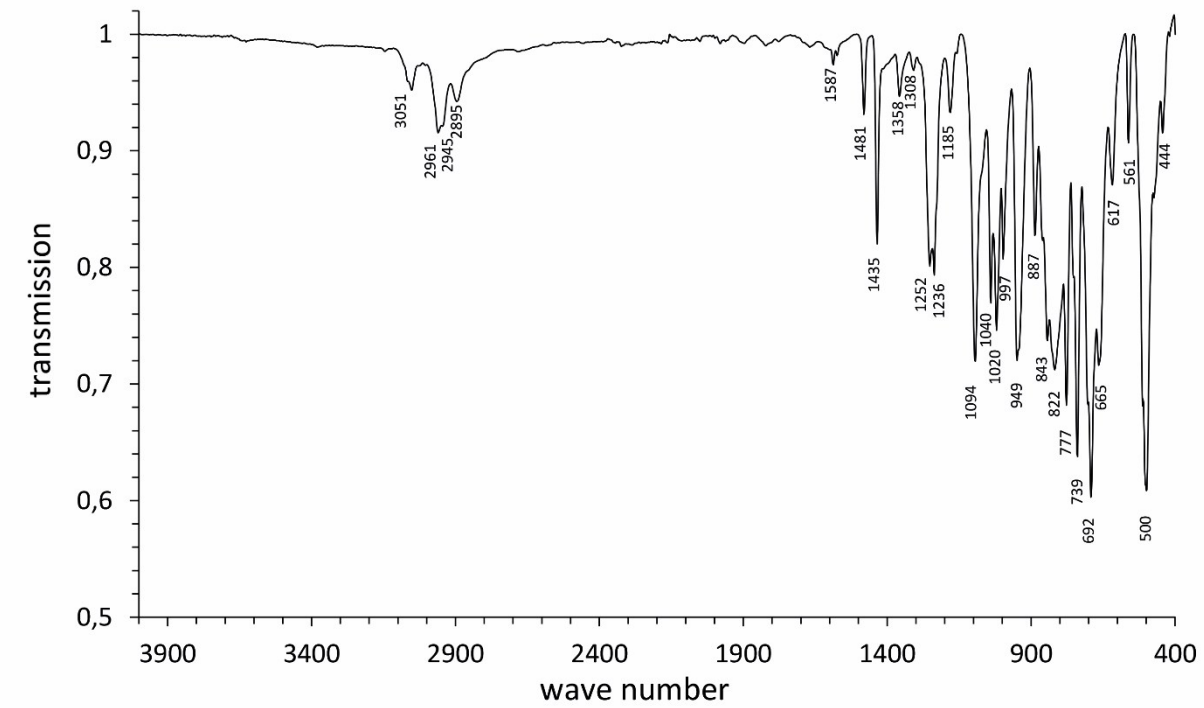


Figure S6. FT-IR spectrum of [CDP^{Ph}-Fe{N(SiMe$_3$)$_2$}$_2$]·toluene (**1**·toluene).

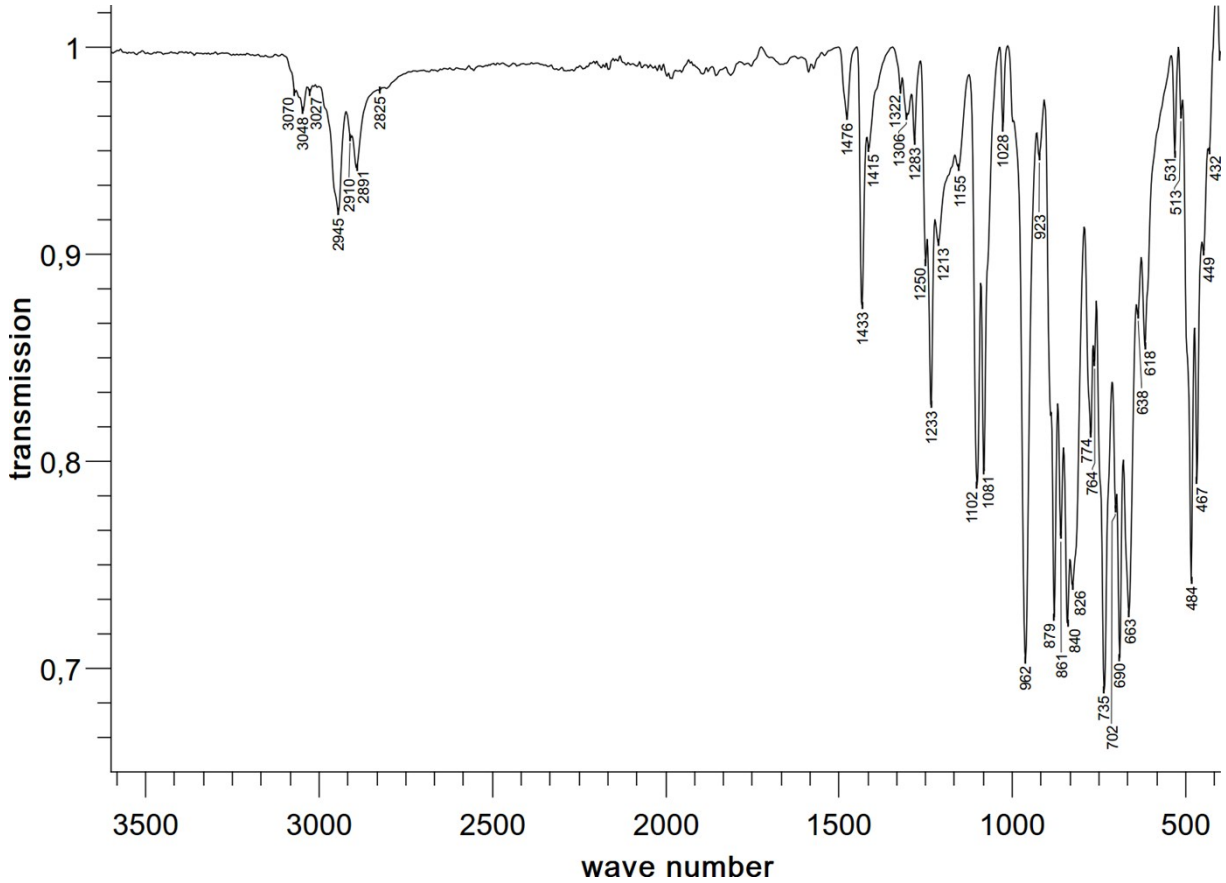


Figure S7. FT-IR spectrum of [CDP^{Me}-$Fe\{N(SiMe_3)_2\}_2$] (**2**).

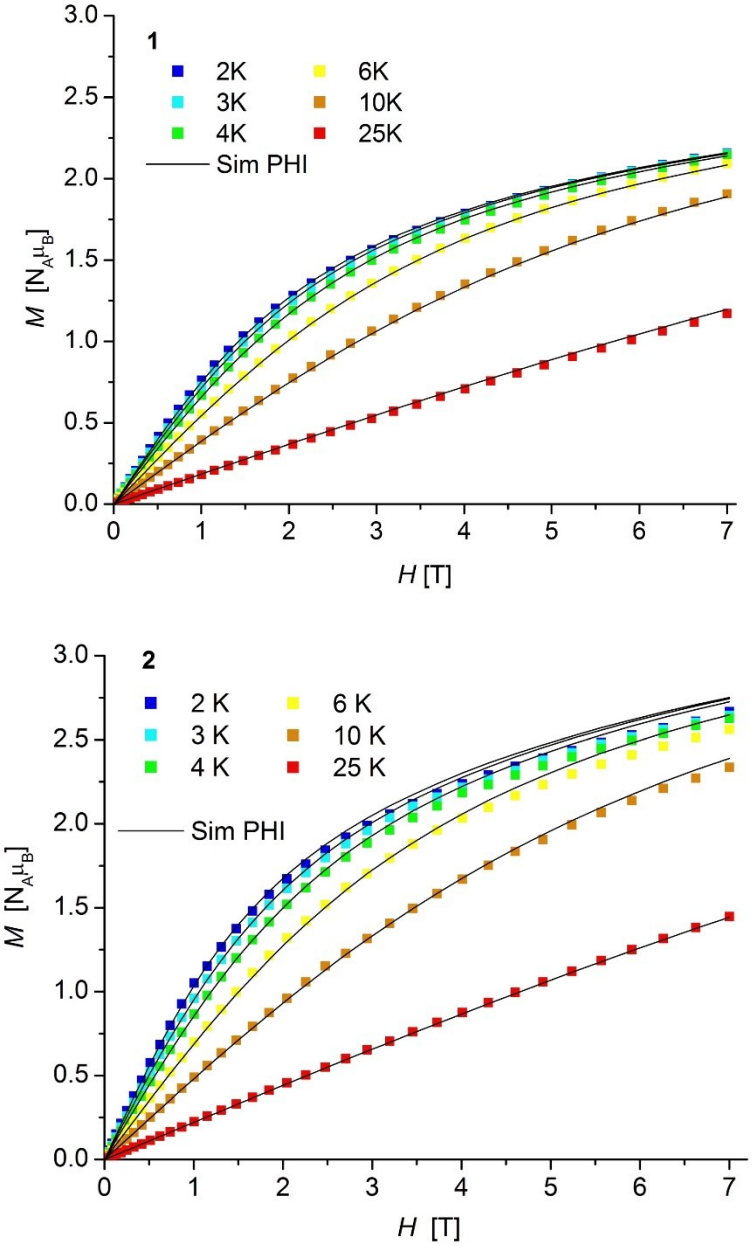


Figure S8. Plots of magnetization *M* versus *H* between 2 and 25 K for **1** (above) and **2** (below). Solid lines represents the results of the simultaneous curve fitting with the χT data, according to a spin Hamiltonian by the PHI program (equation S1).

X-Ray determination

Table S1. Crystal data and structure refinement for [CDP^{Ph}-Fe{N(SiMe$_3$)$_2$}$_2$]·toluene (**1**·toluene), [CDP^{Me}-Fe{N(SiMe$_3$)$_2$}$_2$]·0.5*n*-hexane (**2**·0.5*n*-hexane) and [CDP^{Me}-Fe{N(SiMe$_3$)$_2$}$_2$] (**2**).

Compound	**1**·C_7H_8	**2**·C_3H_7	**2**
CCDC	1965230	1965231	1966059
Internal code	Kuzu42_sq	Kuzu89	Kuzu89b
Empirical formula	$C_{56}H_{74}FeN_2P_2Si_4$	$C_{42}H_{69}FeN_2P_2Si_4$	$C_{39}H_{62}FeN_2P_2Si_4$
Formula weight	1005.32	832.14	789.05
Temperature/ K	100(2)	100(2)	180(2)
Crystal system	triclinic	triclinic	orthorhombic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_12_12_1$
a/ Å	14.358(1)	11.215(1)	12.3110(8)
b/ Å	15.795(1)	13.123(1)	16.4794(7)
c/ Å	16.772(2)	16.998(2)	21.9452(10)
α/ °	101.67(1)	88.64(1)	
β/ °	109.39(1)	83.80(1)	
γ/ °	112.53(1)	71.76(1)	
Volume/ Å^3	3068.0(5)	2361.9(3)	4452.2(4)
Z	2	2	4
ρ_{calc} g/ cm^3	1.088	1.170	1.177
μ/ mm^{-1}	0.409	0.518	0.546
F(000)	1072.0	894.0	1688
Crystal size/ mm^3	0.25 × 0.23 × 0.14	0.23 × 0.15 × 0.14	0.60 x 0.49 x 0.44
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
Θ range for data collection/ °	2.29 to 28.00	1.634 to 25.894	2.264 to 27.949
Index ranges	-18 ≤ h ≤ 17, -20 ≤ k ≤ 20, 0 ≤ l ≤ 22	-13 ≤ h ≤ 13, -16 ≤ k ≤ 16, -20 ≤ l ≤ 20	-16<=h<=16, -20<=k<=21, -26<=l<=28
Reflections collected	69139	18999	29404
Independent reflections	14592 [R_{int} = 0.0688, R_{sigma} = 0.0531]	9089 [R_{int} = 0.0291, R_{sigma} = 0.0291]	10570 [R_{int} = 0.0497, R_{sigma} = 0.0476
Flack-parameter	-	-	-0.006(11)
Data/restraints/parameters	14592/ 0/ 570	9089/ 0/ 475	10570/0/448
Goodness-of-fit on F^2	1.016	1.041	0.921
Final R indexes [I>=2σ (I)]	R_1 = 0.0435, wR_2 = 0.0957	R_1 = 0.0287, wR_2 = 0.0745	R_1 = 0.0268, wR_2 = 0.0535
Final R indexes [all data]	R_1 = 0.0732, wR_2 = 0.1057	R_1 = 0.0351, wR_2 = 0.0769	R_1 = 0.0339, wR_2 = 0.0550
Abs. structure parameter			–0.006(11)
Largest diff. peak/hole / e Å^{-3}	0.61/ –0.44	0.312/ –0.436	0.237/ –0.367

Table S2. The calculated NBO charge (q) and natural bond order (P) of the optimized structures of [(Me$_3$Si)$_2$N]$_2$Fe-C(PPh$_3$)$_2$ in the quintet state at the BP86/def2TZVPP level of theory.

q(Fe1)	q(C1)	q(P1Ph$_3$)	q(P2Ph$_3$)	q(N1((SiMe$_3$)$_2$)	q(N2((SiMe$_3$)$_2$)	P(Fe1-C1)
0.98	-1.47	0.84	0.85	-0.61	-0.59	0.38

Figure S9. Shape of the most important interacting MOs of fragments, plot of deformation densities Δρ of the pairwise orbital interactions and the associated interaction energies (ΔE_{orb}) between fragments. The direction of the charge flow is red to blue.

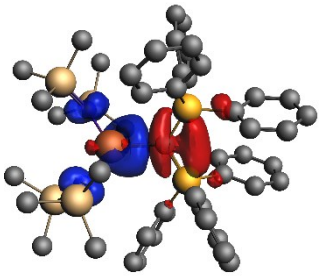
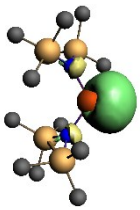
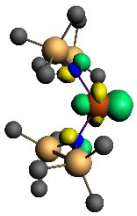
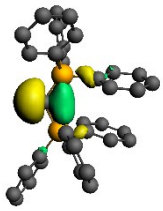
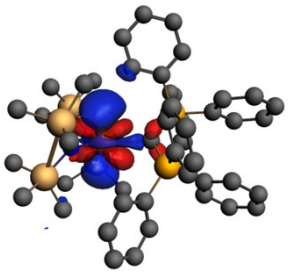
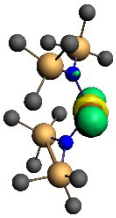
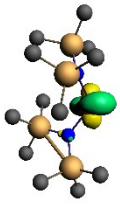
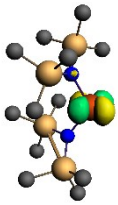
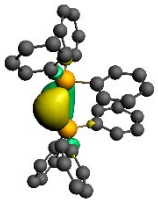
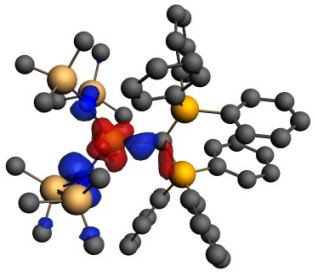
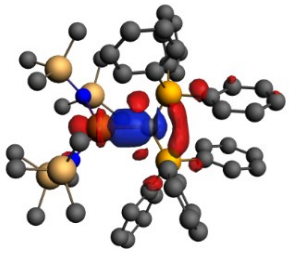
deformation densities Δρ	interacting MOs			
		+ 	← 	
v_1 = ±0.559	frag1-66A	frag1-64A	frag2-93A	
$\Delta E_{orb(1)}$ = -23.5 kcal/mol	(LUMO)	(SOMO-1)	(HOMO-1)	
	v = 0.164	v = 0.107	v = -0.243	
		+ 	← 	+ 
v_2 = ±0.991	frag1-62A	frag1-61A	frag1-63A	frag2-94A
$\Delta E_{orb(2)}$ = -12.1 kcal/mol	(SOMO-2)	(SOMO-3)	(HOMO)	(HOMO)
	v = 0.675	v = 0.153	v = -0.945	v = -0.020

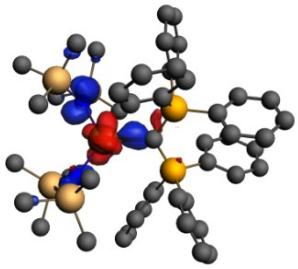
Figure S10. Plot of deformation densities $\Delta\rho_{3\text{-}7}$ of the pairwise orbital interactions between the quintet (Q) $[(Me_3Si)_2N]_2Fe$ and singlet (S) $C(PPh_3)_2$ fragments in $[(Me_3Si)_2N]_2Fe\text{-}C(PPh_3)_2$, associated interaction energies ΔE_{orb} (in kcal/mol) and eigenvalues ν. The eigenvalues ν indicate the size of the charge flow, and the direction of charge flow is red→blue.



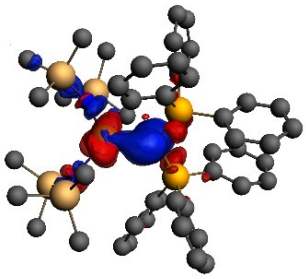
ν3= ±0.193
ΔEorb(3) = -5.2 kcal/mol



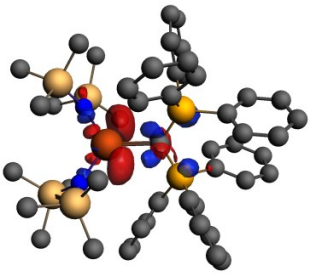
ν4 = ±0.141
ΔEorb(4) = -4.7 kcal/mol



ν5 = ±0.175
ΔEorb(5) = -4.7 kcal/mol



ν6 = ±0.217
ΔEorb(6) = -3.7 kcal/mol



ν7 = ±0.090
ΔEorb(7) = -1.0 kcal/mol

Table S3. Cartesian coordinates and SCF energy of calculated molecular structure of **$[(Me_3Si)_2N]_2Fe\text{-}C(PPh_3)_2$** at the BP86/def2-TZVPP level.

$[(Me_3Si)_2N]_2Fe\text{-}C(PPh_3)_2$

SCF Energy = -5122.3891173

C	-0.0543130	3.2601700	-5.1734129
C	0.7323028	2.1042756	-5.1844222
C	-0.7171880	3.6327804	-4.0039197
C	0.8537846	1.3280139	-4.0316168
C	-2.2510447	-1.9647513	-3.3392088
C	-1.4837174	-0.8429945	-3.0146262
C	-4.2251458	1.7342969	-2.9416235
C	-0.5910558	2.8590069	-2.8471184
C	0.1953874	1.7035936	-2.8448499
C	-2.4272982	-2.9918146	-2.4107570
C	4.4642445	-1.3257124	-2.0692351
C	4.3147950	0.0636891	-2.0644453
C	3.3519182	-2.1366773	-1.8400556
C	3.0632575	0.6333901	-1.8302703
C	-3.9543493	4.4572589	-1.6299057
C	-0.8875227	-0.7273323	-1.7493679
C	2.0970926	-1.5669638	-1.6080486
C	1.9356159	-0.1731241	-1.5925819
C	-6.3086894	2.7146131	-0.9798770
C	-0.2426405	5.7155616	-1.0050344
C	-1.8518275	-2.8800754	-1.1427808
C	-1.0972036	-1.7532695	-0.8147388
C	-4.8595602	-0.7710895	-0.3088663
C	3.6679738	4.3777457	-0.1573115
C	2.6486827	3.4385645	0.0285414
C	0.0151989	1.4517639	0.1614589
C	-2.1794358	7.3707494	0.5315917
C	4.6866852	4.4955709	0.7887834
C	2.6328799	2.6122345	1.1559590
C	3.4328831	-0.4145211	1.5908486
C	2.0448985	-0.2214904	1.6487657
C	3.9883567	-1.6721211	1.8417988
C	0.4634532	6.5224541	1.7906797
C	1.2288655	-1.3274964	1.9479064
C	-4.6097957	5.1191225	2.1478329
C	3.1695350	-2.7563909	2.1600439
C	-5.6635586	0.9941869	1.9893863
C	1.7842325	-2.5806107	2.2084250
C	4.6742106	3.6836213	1.9285615
C	-2.9020081	-0.2705073	1.9695494
C	3.6502711	2.7553484	2.1172273
C	0.6941574	1.8839503	3.0820629
C	0.7840885	3.2304023	3.4740751
C	-3.0102658	3.1148656	3.7655448
C	-2.3264437	6.0173537	3.9330332
C	0.3430511	0.9288859	4.0505509
C	0.5728801	3.6018594	4.8024087
C	0.1150024	1.3056002	5.3757978
C	0.2462873	2.6408967	5.7608178

H	-0.1497385	3.8665658	-6.0745322
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H	-2.7148472	-2.0298261	-4.3235548
H	-1.3364575	4.5293137	-3.9865520
H	1.4627235	0.4255970	-4.0596855
H	-4.8404082	2.2061786	-3.7233589
H	-1.3546749	-0.0573728	-3.7557432
H	-3.1819804	1.7520580	-3.2852195
H	-4.5326216	0.6830566	-2.8609667
H	-4.5771401	4.8519513	-2.4474763
H	-3.0236896	-3.8674763	-2.6673406
H	5.1722989	0.7100135	-2.2534409
H	5.4406130	-1.7724371	-2.2587474
H	-6.7926788	3.2304425	-1.8236671
H	-1.1092279	3.1515008	-1.9290798
H	3.4532859	-3.2221170	-1.8490118
H	-2.9043110	4.5733336	-1.9267705
H	2.9642403	1.7166415	-1.8538858
H	-1.0183648	5.6475019	-1.7784334
H	1.2401174	-2.2189956	-1.4523671
H	0.3560985	6.6133886	-1.2232946
H	0.4164512	4.8459342	-1.1074286
H	-6.7650504	1.7184708	-0.9033287
H	3.6550687	5.0234409	-1.0354497
H	-4.1158480	5.0848082	-0.7447575
H	-4.0938331	-1.1257744	-1.0101299
H	-5.7131999	-0.4103077	-0.8997116
H	1.8356452	3.3530059	-0.6936860
H	-6.5591977	3.2705741	-0.0660820
H	-1.9982932	-3.6665337	-0.4022399
H	-2.9881657	7.1309030	-0.1729264
H	-1.6278164	8.2303395	0.1199053
H	-5.2108085	-1.6366930	0.2741052
H	-0.6548543	-1.6745658	0.1753941
H	5.4818985	5.2283250	0.6494950
H	-2.6423448	7.6991224	1.4708117
H	-5.0313533	4.3358877	1.5035992
H	4.0	0.4135458	1.3348849
H	0.7793102	7.5167606	1.4383466
H	-6.5652598	1.2323939	1.4101915
H	-4.6408535	6.0668176	1.5929946
H	5.0694042	-1.8009927	1.7833979
H	1.3399414	5.8629104	1.7076523
H	-3.2833573	-1.2458838	2.3091439
H	0.1462485	-1.2045341	1.9827695
H	3.6062711	-3.7345809	2.3623297
H	1.1318636	-3.4199993	2.4507991
H	-1.9673517	-0.4326819	1.4184018
H	-5.4645640	1.8435070	2.6550872
H	-5.8991656	0.1244987	2.6227908
H	-5.2695232	5.2239486	3.0228554
H	0.2051087	6.6160650	2.8531885
H	5.4581780	3.7834118	2.6797918
H	1.0330233	3.9970127	2.7452565
H	-2.6635196	0.3247951	2.8606021
H	3.6350040	2.1521346	3.0251724
H	-3.4504419	2.2772020	3.2150625
H	-2.2245203	7.0184645	3.4954344
H	0.2692863	-0.1236565	3.7922690
H	-2.0410425	2.7885503	4.1616617

H	-1.3783584	5.7684808	4.4288319
H	-3.6682252	3.3278656	4.6225042
H	-3.0972204	6.0810517	4.7169116
H	0.6677429	4.6500042	5.0850550
H	-0.1527393	0.5452239	6.1095773
H	0.0876621	2.9317255	6.7993837
N	-3.5163511	1.9332198	0.0042278
N	-1.7437633	4.4570313	1.3520659
Si	-4.4343109	2.6585086	-1.2963177
Si	-0.9878379	5.8997917	0.7255506
Si	-4.1934081	0.5692836	0.8610785
Si	-2.8541064	4.6639480	2.6981954
P	0.2876075	0.6404844	-1.3363886
P	1.2300887	1.4194972	1.3727470
Fe	-1.7628479	2.6649179	0.5115902