Electronic Supplementary Material (ESI) for Dalton Transactions.

Phosphine-ligated Dinitrosyl Iron Complexes for Redox-controlled NO Release

F. Wittkamp,[a] C. Nagel,[b] P. Lauterjung,[a] B. Mallick,[a] U. Schatzschneider,[b]* and U.-P. Apfel[a]*

[a] Lehrstuhl für Anorganische Chemie I, Ruhr-Universität Bochum, Universitätsstraße 150, D-44801 Bochum, Germany. E-mail: ulf.apfel@rub.de

[b] Institut für Anorganische Chemie, Julius-Maximilians-Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany. E-mail: ulrich.schatzschneider@uni-wuerzburg.de

Supporting Information

Myoglobin Assay. A 10 µM solution of horse skeletal muscle myoglobin (*Sigma Aldrich*) in 10 mL phosphate buffer (pH 7.4) was prepared and mixed with 0.5 mL of a 0.1 mM aqueous solution of sodium dithionite while purging with argon. After measuring the background with phosphate buffer (pH 7.4), one UV/Vis spectrum was recorded with 990 µL of the myoglobin solution. Subsequently, 10 µL of a 1 mM DNIC solution in DMSO were added. For photoactivation, the cuvette was either exposed to daylight or illuminated with a Xe lamp having a broad emission between 185-2000 nm for 8-9 min between the measurements.

Nitrosyl assay. To 2 mL of a 20 µM [Fe(tpp)] solution in DMSO, 8 µL of a 5 mM oxidized DNIC was added. The DNICs were oxidized by adding 100 µL 5 mM stock solution to 1 equivalent solid $(NH_4)_2[Ce(NO_3)_6]$.

SEC-UV. All measurements were carried out in a SEC-2F Spectroelectrochemical flow cell (*ALS*) with an Exemplar CCD Spectrometer (*B&W Tek*) and a BDS 100 Deuterium/Tungsten Light Soucre (*B&W Tek*). The components were connected via fiber optic patch cords. A platinum net, attached to a thin glass plate, was used as the working electrode, a $Ag/AgNO_3$ electrode as the reference, and a stainless steel pipe as the counter electrode. A 0.5 mM solution of compounds **1**-**4** in acetonitrile was used as the working solution. Solid tetrabutylammonium hexafluorophosphate was added as the electrolyte (c = 0.1 M). Before each measurement, a cyclic voltammogram was recorded in order to determine the $E_{1/2}$ value of each compound under these conditions.

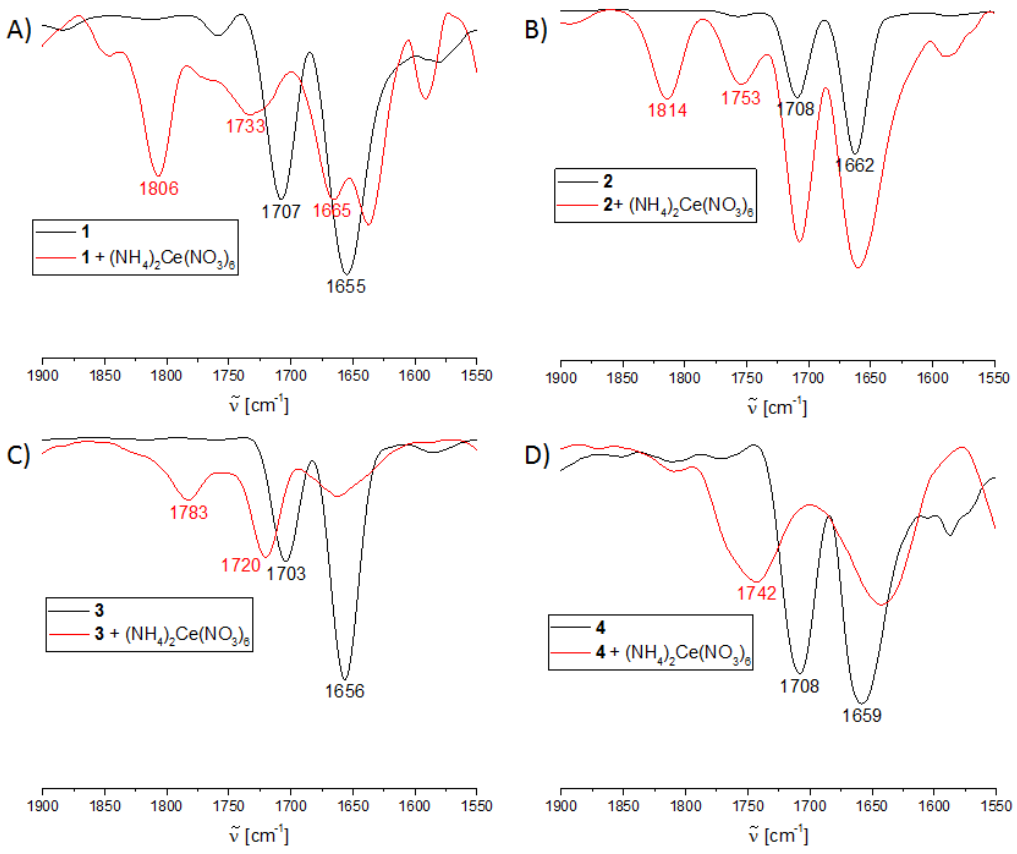

Fig. S1 Solution IR spectra of compounds **1**-**4** (approx. 1 mM in tetrahydrofuran), recorded from 1550 to 1900 cm^{-1} before (black) and directly after the addition of $(NH_4)_2[Ce(NO_3)_6]$ (red).

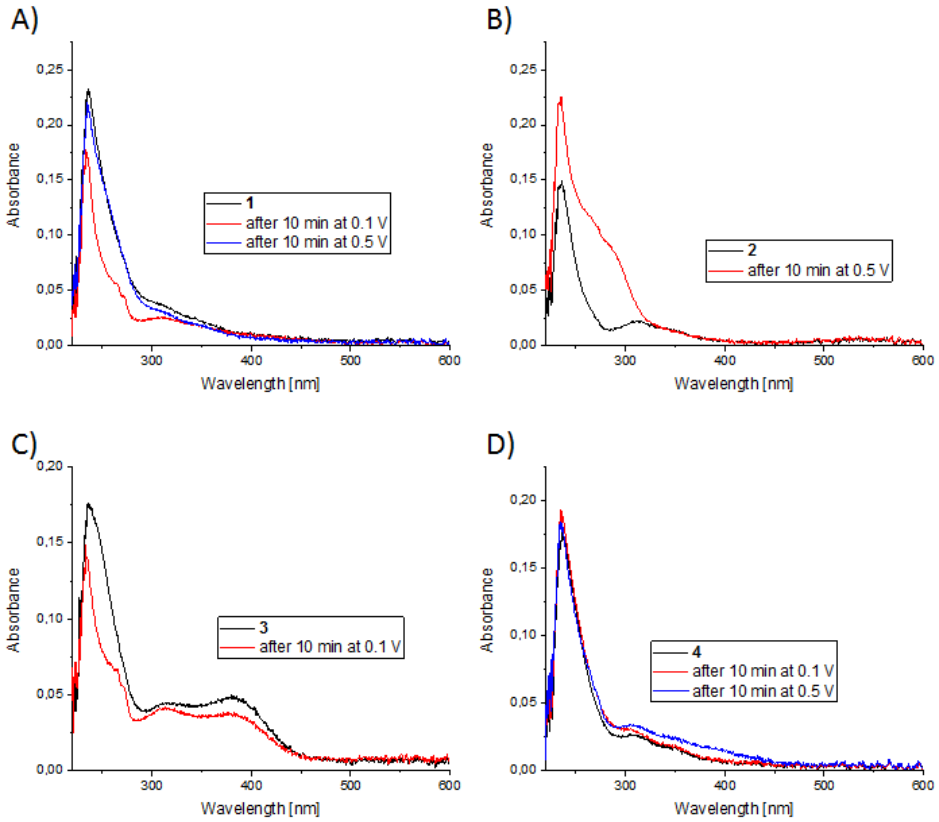

Fig. S2 SEC-UV/Vis spectra of A) $[Fe(NO)_2(triphos^{C})]$ **1**, B) $[Fe(NO)_2(diphos^{Si})]$ **2**, C) $[Fe(NO)_2(MePPh_2)_2]$ **3,** and D) $[Fe(NO)_2(triphos^{Si})]$ **4** in acetonitrile (500 µM). The potential was always kept slightly above the $E_{1/2}$ and E_{ox} values for 10 min, as determined by a previously recorded CV, and is reported *vs*. the Fc/Fc^{+} couple. The black trace shows the spectrum of the original compound while the red and blue traces were recorded after 10 min of electrolysis at 0.1 and 0.5 V, respectively.

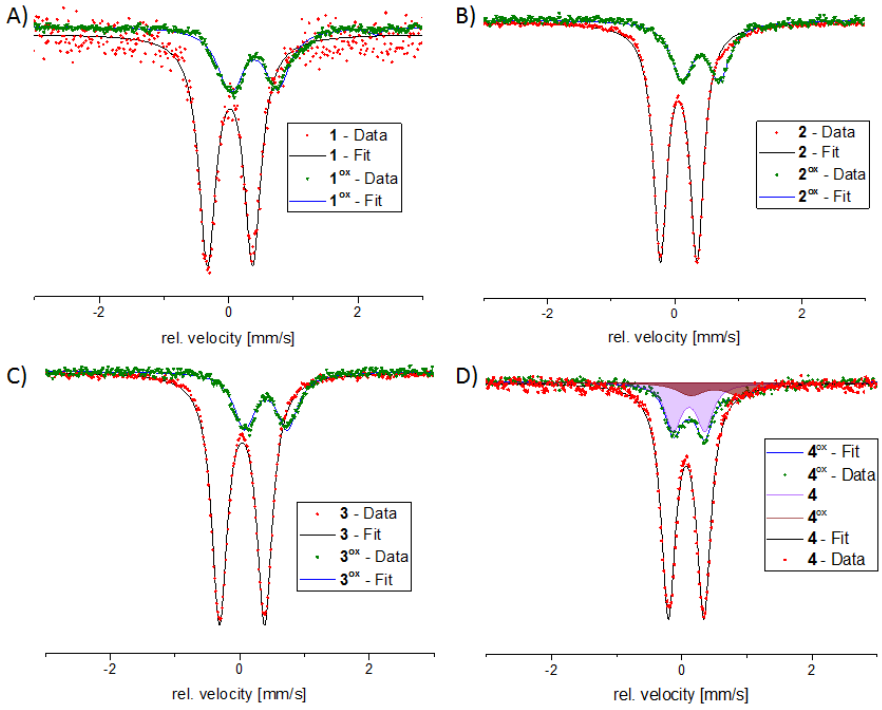

Fig. S3 Mössbauer spectra of frozen tetrahydrofuran solutions at 80 K A) $[Fe(NO)_2(triphos^{C})]$ **1**, B) $[Fe(NO)_2(diphos^{Si})]$ **2**, C) $[Fe(NO)_2(MePPh_2)_2]$ **3,** and D) $[Fe(NO)_2(triphos^{Si})]$ **4** before (red) and after oxidation with $(NH_4)_2Ce(NO_3)_6$ (green). Note: although measuring multiple samples of **4**, we always observed mixtures of oxidized and non-oxidized **4** under the conditions of sample preparation for Mössbauer spectroscopy.

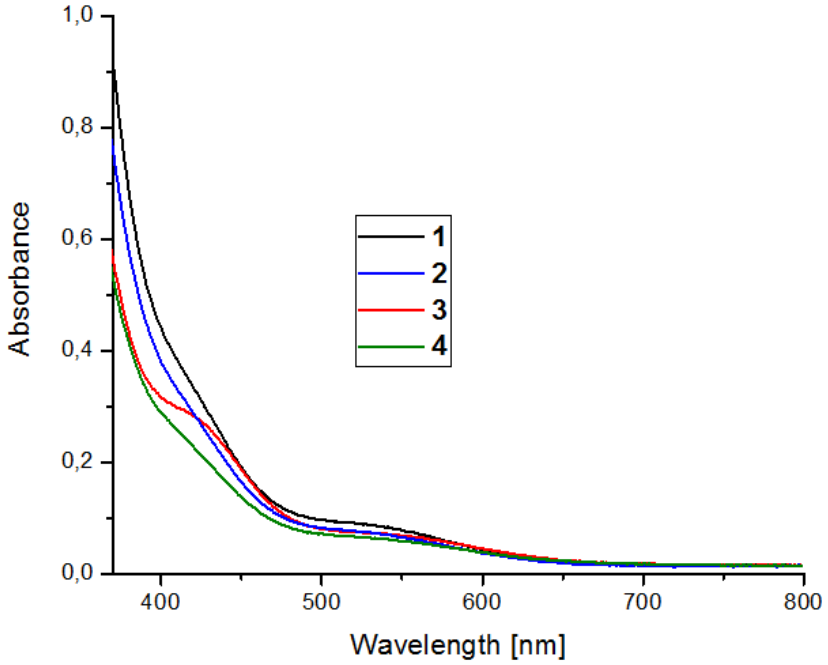

Fig. S4 UV/Vis spectra of compounds **1**-**4** (500 µM) in acetonitrile.

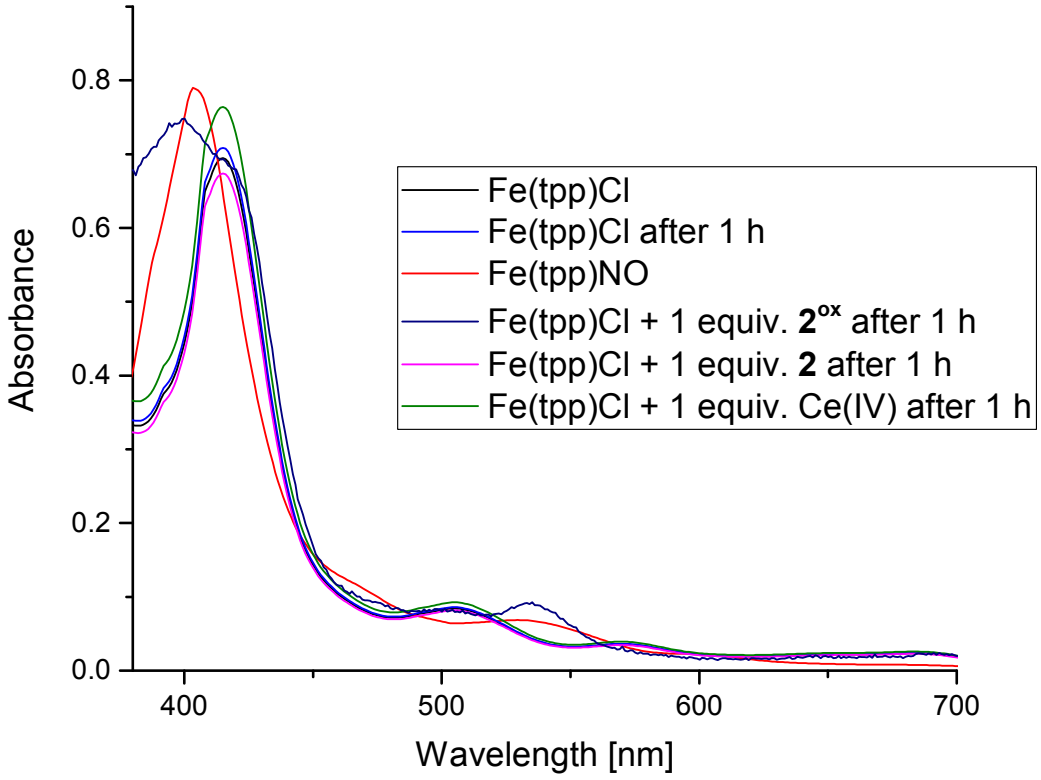

Fig. S5 UV/Vis spectroscopic changes of [FeCl(tpp)] upon a) no addition or addition of b) 1 eqiv. **2**; c) 1 equiv. Ce(IV) d) 1 equiv. $\mathbf{2}^{ox}$ after 1 hour reaction time.

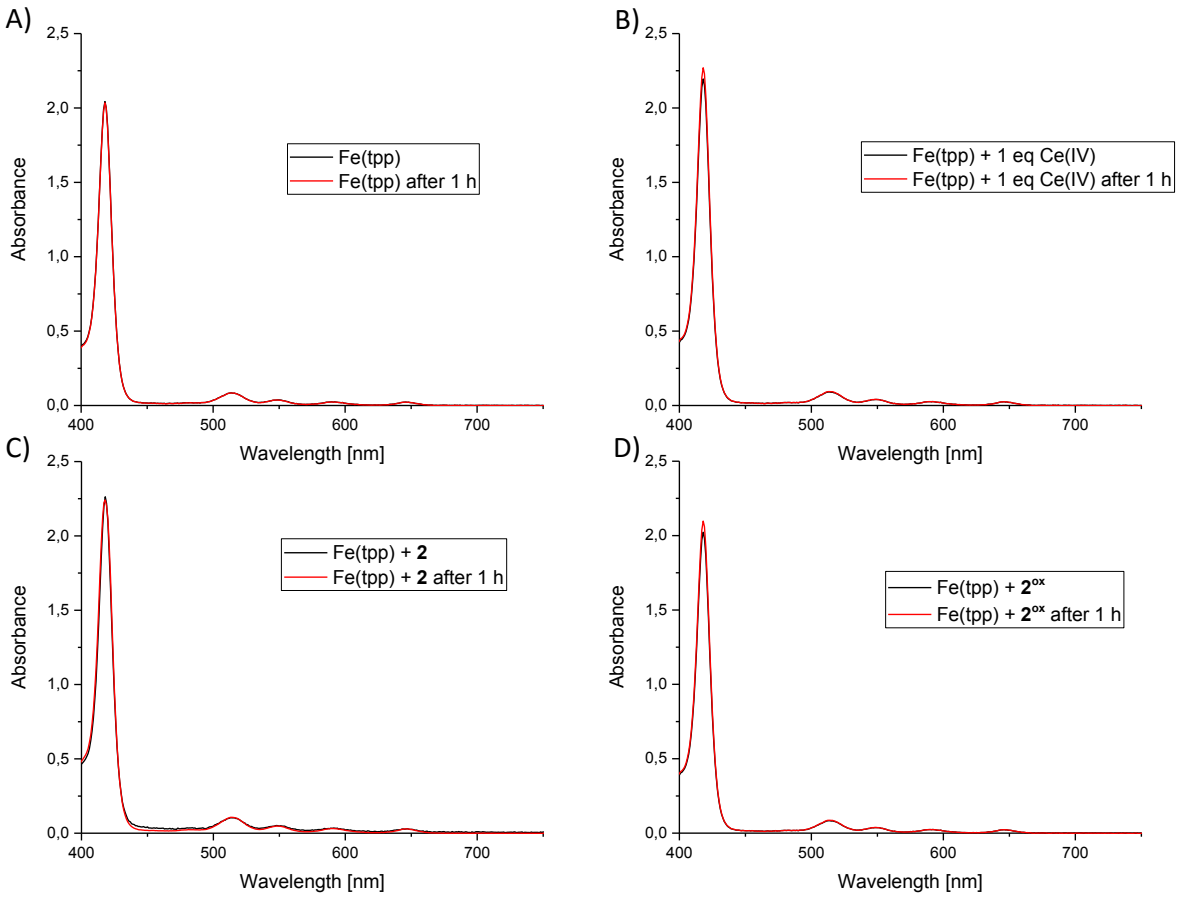

Fig. S6 UV/Vis spectroscopic changes of the Fe(tpp)-assay (20 µM in DMSO). A) Fe(tpp) (black) and Fe(tpp) after 1 h (red) (no substrate added); B) Fe(tpp) + 1 equiv. $(NH_4)_3[Ce(NO_3)_6]$ (black) and Fe(tpp) + 1 equiv. $(NH_4)_3[Ce(NO_3)_6]$ after 1 h (red); C) Fe(tpp) + 1 equiv. **2** (black) and Fe(tpp) + 1 equiv. **2** after 1 h (red); D) Fe(tpp) + 1 equiv. $\mathbf{2}^{ox}$ (black) and Fe(tpp) + 1 equiv. $\mathbf{2}^{ox}$ after 1 h (red).

Table S1 *Crystal data and refinement details for the crystal structure analysis of compounds* ***1*** *and* ***2****.*

	1	**2**
Empirical formula	$C_{41}H_{39}FeN_2O_2P_3$	$C_{38}H_{34}FeN_2O_2P_2Si$
Formula weight	740.5	696.6
Temperature/K	170(2)	170(2)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a/Å	8.4941(8)	13.2945(4)
b/Å	24.7850(20)	14.6620(4)
c/Å	18.1348(18)	18.8123(10)
α/°	90.00	90.00
β/°	108.378(8)	113.101(3)
γ/°	90.00	90.00
$Volume$/Å^3	3623.13(102)	3372.93(47)
Z	4	4
ρ_{calc}/g/cm^3	1.36	1.37
μ/mm^{-1}	0.587	0.615
F(000)	1543.8	1447.8
Crystal size/mm^3	0.12 x 0.08 x 0.06	0.4 x 0.4 x 0.02
Radiation/Å	MoK_α (λ = 0.71073)	MoK_α (λ = 0.71073)
2Θ range for data	4.8 to 50.0	6.0 to 50.0
Index ranges	-10 ≤ h ≤ 10, -29 ≤ k ≤ 29, -21 ≤ l ≤ 21	-15 ≤ h ≤ 15, -17 ≤ k ≤ 17, -22 ≤ l ≤ 22
Reflections collected	51019	47367
Independent reflections	6368 [R_{int} = 0.210]	5936 [R_{int} = 0.049]
Data/restraints/parameter	6368/0/443	5936/0/415
[a]Goodness-of-fit on F^2	0.974	1.057
[b,c]Final R indexes [I≥2σ(I)]	R_1 = 0.063, wR_2 = 0.093	R_1 = 0.033, wR_2 = 0.077
Final R indexes [all data]	R_1 = 0.146, wR_2 = 0.121	R_1 = 0.044, wR$_2$ = 0.083
Largest diff. peak/hole / e	0.339/-0.610	0.375/-0.267
CCDC reference	1449124	1449123

[a] $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{0.5}$; n = no. of reflections; p = no. of parameters. [b] $R_1 = \Sigma\,||F_o| - |F_c||/\Sigma\,|F_o|$.
[c] $wR_2 = \{\Sigma\,[w(F_o^2 - F_c^2)^2]/(\Sigma[w(F_o^2)^2]\}^{0.5}$.

Table S2 *Crystal data and refinement details for the crystal structure analysis of compounds* ***3*** *and* ***4****.*

	3	**4**
Empirical formula	$C_{26}H_{26}FeN_2O_2P_2$	$C_{40}H_{39}FeN_2O_2P_3Si$
Formula weight	516.3	756,6
Temperature/K	170(2)	112(2)
Crystal system	orthorhombic	triclinic
Space group	*Pbca*	*P1*
a/Å	15.8429(4)	9.2280(2)
b/Å	16.3266(5)	9.2901(2)
c/Å	38.8855(13)	12.6754(3)
α/°	90.00	91.268(2)
β/°	90.00	110.400(2)
γ/°	90.00	113.798(2)
Volume/Å^3	10058.15(5)	914.96(15)
Z	16	1
ρ_{calc}/g/cm^3	1.36	1.37
μ/mm^{-1}	0.752	5.157
F(000)	4287.3	393.9
Crystal size/mm^3	0.12 x 0.08 x 0.06	0.4 x 0.4 x 0.02
Radiation	MoK_α (λ = 0.71073)	CuK_α (λ = 1.54184)
2Θ range for data	5.8 to 50.0°	7.6 to 153.0
Index ranges	-18 ≤ *h* ≤ 18, -19 ≤ *k* ≤ 19, -46 ≤ *l* ≤ 46	-11 ≤ *h* ≤ 11, -11 ≤ *k* ≤ 11, -15 ≤ *l* ≤ 15
Reflections collected	136062	18276
Independent reflections	8840 [R_{int} = 0.075]	6738 [R_{int} = 0.021]
Data/restraints/parameter	8840/0/599	6738/3/443
[a]Goodness-of-fit on F^2	1.141	1.033
[b,c]Final *R* indexes [$I \geq 2\sigma(I)$]	R_1 = 0.043, wR_2 = 0.093	R_1 = 0.023, wR_2 = 0.061
Final *R* indexes [all data]	R_1 = 0.059, wR_2 = 0.100	R_1 = 0.024, wR_2 = 0.061
Largest diff. peak/hole / e	0.350/-0.358	0.625/-0.258
Flack parameter		-0.0038(19)
CCDC reference	1449122	1449125

[a] $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{0.5}$; *n* = no. of reflections; *p* = no. of parameters. [b] $R_1 = \Sigma\,||F_o| - |F_c||/\Sigma\,|F_o|$.
[c] $wR_2 = \{\Sigma\,[w(F_o^2 - F_c^2)^2]/(\Sigma[w(F_o^2)^2]\}^{0.5}$.

Table S3 *Energies (in nm), oscillator strength (f_{osc}), main orbital contributions, and type of transition involved in the most important singlet excitations for* ***1'*** *(RI-TPSS def2-tzvp def2/tzvp/j tightscf grid4 cosmo(THF)).*

state[a]	λ nm	f_{osc}	main transitions[b]	type of transition
5	433.4	0.0054	143a→150a (15%) 144a→150a (20%)	MLCT(Fe→NO)
8	392.9	0.0054	142a→145a (38%) 144a→146a (41%)	Fe/O→N
15	362.6	0.0170	144a→148a (44%) 144a→149a (38%)	MLCT(Fe(NO)$_2$→phenyl-π^*)
16	355.3	0.0056	143a→147a (79%)	MLCT(Fe(NO)$_2$→phenyl-π^*)
19	333.9	0.0253	144a→151a (55%)	MLCT(Fe(NO)$_2$→phenyl-π^*)
21[c]	314.1	0.0335	140a→145a (42%)	Fe/O→N
22[c]	321.7	0.0089	143a→150a (22%) 143a→151a (53%)	MLCT(Fe(NO)$_2$→phenyl-π^*)
24[c]	315.3	0.0404	144a→153a (53%)	MLCT(Fe(NO)$_2$→phenyl-π^*)
25[c]	316.4	0.0056	143a→152a (84%)	MLCT(Fe(NO)$_2$→phenyl-π^*)
32	299.6	0.0071	143a→153a (22%) 143a→154a (47%)	MLCT(Fe(NO)$_2$→phenyl-π^*)
40	254.0	0.0057	138a→145a (13%) 139a→145a (15%) 142a→153a (23%)	MLCT(Fe/O→phenyl-π^*/N)
45	249.7	0.0075	138a→146a (16%) 142a→153a (19%) 142a→155a (18%)	MLCT(Fe/O→phenyl-π^*/N) ILCT(phenyl-phenyl)

[a] Only strong transitions with an oscillator strength > 0.005 in the 250 to 600 nm range are reported. [b] Only contributions > 20% are listed. [c] The reversed order of states is due to differences in solvent shift since the numbering refers to the non-shifted states.

Table S4 *Energies (in nm), oscillator strength (f_{osc}), main orbital contributions, and type of transition involved in the most important singlet excitations for* ***2*** *(RI-TPSS def2-tzvp def2/tzvp/j tightscf grid4 cosmo(THF)).*

state[a]	λ nm	f_{osc}	main transitions[b]	type of transition
5	429.2	0.0041	180a→183a (14%) 180a→185a (17%)	MLCT(Fe→NO)
8	394.7	0.0042	178a→181a (40%) 180a→182a (30%)	MLCT(Fe→NO)
11	354.6	0.0057	178a→181a (20%) 180a→182a (14%)	MLCT(Fe→NO) ILCT(NO→NO)
13[c]	341.8	0.0065	177a→182a (14%) 179a→182a (11%)	MLCT(Fe→NO)
15[c]	360.7	0.0041	179a→182a (21%) 179a→183a (45%)	MLCT($Fe(NO)_2$→phenyl-π^*)
18[c]	344.1	0.0158	179a→185a (21%) 179a→186a (30%)	MLCT($Fe(NO)_2$→phenyl-π^*)
20[c]	313.6	0.0085	175a→181a (22%)	Fe/O→N
23[c]	320.2	0.0084	179a→185a (16%) 179a→188a (19%) 179a→189a (16%) 179a→191a (13%)	MLCT($Fe(NO)_2$→phenyl-π^*)
27	313.6	0.0062	179a→189a (27%)	MLCT($Fe(NO)_2$→phenyl-π^*)
28	313.5	0.0064	179a→188a (43%) 179a→191a (29%)	MLCT($Fe(NO)_2$→phenyl-π^*)
39[c]	290.8	0.0048	179a→193a (39%) 179a→194a (18%)	MLCT($Fe(NO)_2$→phenyl-π^*)
42[c]	291.0	0.0087	179a→195a (82%)	MLCT($Fe(NO)_2$→phenyl-π^*)
45	278.4	0.0046	178a→186a (32%) 178a→188a (28%)	MLCT($Fe(NO)_2$→phenyl-π^*)

[a] Only strong transitions with an oscillator strength > 0.04 in the 250 to 600 nm range are reported. [b] Only contributions > 20% are listed. [c] The reversed order of states is due to differences in solvent shift since the numbering refers to the non-shifted states.

Table S5 *Energies (in nm), oscillator strength (f_{osc}), main orbital contributions, and type of transition involved in the most important singlet excitations for* ***3*** *(RI-TPSS def2-tzvp def2/tzvp/j tightscf grid4 cosmo(THF)).*

state[a]	λ nm	f_{osc}	main transitions[b]	type of transition
1	514.3	0.0070	133a→134a (28%) 133a→135a (43%)	MLCT(Fe→NO)
5	429.9	0.0057	133a→136a (48%) 133a→143a (18%)	MLCT(Fe→NO)
8	399.3	0.0086	131a→134a (31%) 132a→135a(30%)	Fe/O→N
20[c]	313.5	0.0242	127a→134a (15%) 127a→135a (16%) 129a→134a (14%) 128a→135a (16%)	Fe/O→N
21[c]	326.2	0.0100	133a→143a (42%)	MLCT($Fe(NO)_2$→phenyl-π·)
22[c]	328.9	0.0090	133a→140a (92%)	MLCT($Fe(NO)_2$→phenyl-π·)
23[c]	320.3	0.0291	132a→143a (19%) 133a→142a (39%)	MLCT($Fe(NO)_2$→phenyl-π·)
25[c]	309.9	0.0115	132a→143a (30%) 133a→142a (22%)	MLCT($Fe(NO)_2$→phenyl-π·)
26[c]	316.1	0.0128	132a→141a (19%) 132a→142a (53%)	MLCT($Fe(NO)_2$→phenyl-π·)
42	261.1	0.0137	127a→134a (37%) 129a→134a (49%)	LMCT(phenyl-π→$Fe(NO)_2$)
43[c]	248.9	0.0328	128a→134a (18%) 128a→135a (42%)	MLCT(Fe→NO)
44[c]	253.4	0.0101	127a→135a (36%) 129a→135a (48%)	LMCT(phenyl-π→$Fe(NO)_2$)
49	244.9	0.0184	128a→136a (27%) 128a→137a (36%)	LLCT(phenyl-π/P→NO)
50	244.4	0.0201	128a→136a (48%) 128a→137a (25%)	LLCT(phenyl-π/P→NO)

[a] Only strong transitions with an oscillator strength > 0.01 in the 250 to 400 nm and > 0.005 in the 400 to 600 nm range are reported. [b] Only contributions > 20% are listed. [c] The reversed order of states is due to differences in solvent shift since the numbering refers to the non-shifted states.

Table S6 *DFT-optimized geometry of* ***1'*** *(RI-TPSS def2-tzvp def2/tzvp/j tightscf grid4 cosmo(THF)).The CH_2PPh_2 group of* ***1*** *was replaced by a methyl moiety to facilitate calculations.*

C	7.47011244670615	10.19081948364876	12.25461539732632
C	8.66947082874766	10.82487145432438	11.91222554571646
C	9.32039451218351	10.45218545763243	10.72522760809308
C	8.77273568545665	9.47499780061973	9.89514063423460
C	7.57070815560250	8.85155396797251	10.24318732974778
C	6.92184553357205	9.20932530725747	11.42539535839599
P	9.39717541667991	12.10652430856604	13.02587753136151
Fe	8.42531843246838	12.54671928891029	14.97470579577264
N	9.64806876707227	13.23317117448500	15.84079867923084
O	10.53523752475385	13.70278826882548	16.47607143931119
C	9.69340734106469	13.56779989063306	11.92032456947104
C	8.50462653569045	14.52045677739433	11.62028674491669
C	8.02409046831655	15.27539660827079	12.88795704682537
P	7.24680194905302	14.29825271910177	14.26723809616282
C	7.09211907492414	15.58763951058316	15.58188566738481
C	5.91520721971173	15.71054000920649	16.33732158309498
C	5.83490535761181	16.62393268495617	17.39003899299314
C	6.92886806457238	17.43083865624131	17.70679566998245
C	8.10881037577121	17.31008344144701	16.96913645315797
C	8.19283453807086	16.39235798140897	15.92190263273218
C	9.04652221535637	15.59845265504184	10.65302676112888
C	7.34885584231074	13.78257293215214	10.92460914160714
C	11.10215444397710	11.43231738514800	13.25431674846847
C	11.26262497566785	10.41551518315911	14.20996910993574
C	12.51044110000552	9.83657150557126	14.43263238689230
C	13.62554607932967	10.27724459545572	13.71395079810241
C	13.48025886685840	11.29402099662479	12.77015380956200
C	12.22602824293995	11.86603519186915	12.53676695862761
N	7.49914272624878	11.29809978158264	15.52632931217775
O	6.89719873729109	10.38978247472696	16.01463100015286
C	5.49488066673032	14.07686668371363	13.74198684264249
C	4.87419757738145	12.82990941575252	13.87925923094005
C	3.54319808361229	12.64922572776012	13.49518998377178
C	2.81809471712411	13.71754197592924	12.96706594656006
C	3.42564205344253	14.96943332035104	12.83222331863514
C	4.75263369571327	15.14930684949532	13.21955132407224
H	10.26430949133708	10.91502211028763	10.44820831508440
H	5.05344909497925	15.09183298192933	16.10505237386272
H	14.60132394388535	9.83404185362343	13.89353152971554
H	10.48806544150276	14.14510184443477	12.41112601260395
H	10.09629679306108	13.20989486093490	10.96446903831434
H	12.61487682908842	9.04918615624782	15.17443179527446
H	3.07637931644523	11.67469151988777	13.60955861477123
H	5.43847805747119	11.99998786204864	14.29152604976166
H	7.32185311542047	16.06234925477160	12.58728516103871
H	8.88691860275100	15.78086157517015	13.33796368598918
H	10.40253338125916	10.08729599608846	14.78901801049044
H	8.96989168737482	17.92741793924014	17.21099368797289
H	1.78359273043093	13.57926281938140	12.66458788863709
H	2.86449113295475	15.80750499068040	12.42753940831048
H	12.14101924684118	12.65259273800487	11.79349772443635
H	5.99036164392118	8.72492691225952	11.70583782250355
H	6.96736665574293	10.47045690746093	13.17468740895314
H	14.34264588400874	11.64676418601755	12.21049696727975
H	5.20320444269013	16.13322305492803	13.12091279540156
H	6.86521339549647	18.14409059886341	18.52397999880214
H	4.91329570447114	16.70402188444463	17.96059203181078
H	9.28681207704104	9.19615420119187	8.97909603870278
H	9.12973970245738	16.30300586692243	15.37975221551772
H	7.14671070089275	8.08767188138051	9.59702744809635
H	7.70349305715633	13.30265176218750	10.00559264579682
H	6.55344695843506	14.48764962809742	10.65902304504244
H	6.91216088864617	13.00793335297946	11.56184564351353
H	8.25533586430941	16.31092170288428	10.39261731480128
H	9.87471505116568	16.15429197942116	11.10768774360850
H	9.40910385674373	15.13428311241130	9.72853013471740

Table S7 *DFT-optimized geometry of* ***2*** *(RI-TPSS def2-tzvp def2/tzvp/j tightscf grid4 cosmo(THF)).*

Fe	-0.02629463992289	3.72981505159548	1.85534047341617
P	-1.37306689665944	3.60952693048181	3.64056877640601
P	-1.60075110670745	4.30121998940726	0.39117727234566
Si	-3.89265799941111	2.66769717089049	1.90431068091268
C	-7.72375522749170	4.34295778890061	2.40270443780427
H	-8.22590854092981	4.98807665393266	3.11930165644698
N	1.00092847509688	4.99276522494191	2.11396802637868
C	-5.70182019991667	3.17043323882187	1.68757316667828
C	-1.01012143356530	4.41144849658666	-1.35850208682863
C	-3.18756920077724	3.70093471051541	3.33566667064096
H	-3.37798370296939	4.74606241455940	3.05141897822554
H	-3.75611237815688	3.50731989386637	4.25328506629835
C	0.52691237021019	6.07060211827364	6.32427581055299
H	1.53662325026456	6.15083667513564	6.71826567560335
N	0.42031296236990	2.21816881892323	1.37431288208174
C	-2.08898883118023	1.81376604333200	5.73094734729615
H	-2.97493892486925	2.42546693357066	5.87672719498330
C	-1.07099944222529	4.95671336248491	4.86821817455140
C	-2.45425618716994	5.91807326946796	0.60046027526244
C	-1.16498870810974	2.12345749456670	4.72039925354621
C	-2.05925488309235	5.85034338462913	5.30052202294187
H	-3.07352039735319	5.78005262085346	4.92052542151998
C	-3.83618320243935	0.81213840230742	2.24136378840761
C	-1.88158075347965	4.75001394277779	-2.40643558388324
H	-2.92554055093451	4.97474092230249	-2.20169644507804
C	-0.46580121244540	6.95892689277965	6.74912125876399
H	-0.23214686808189	7.73276526407671	7.47534939650881
C	-0.02351193830480	1.32462164840679	4.58116008473955
H	0.69824730277974	1.56157946843654	3.80557588803022
C	-4.92464951724555	0.17914449841050	2.87180589183855
H	-5.80409729503613	0.76012921188109	3.14178308489485
O	0.79983331763866	1.14980885155658	1.00524644462253
C	-4.90710791641767	-1.18843177275027	3.15066571407146
H	-5.76193364296659	-1.65377300919329	3.63524776110100
C	-8.41673811034186	3.85724533044693	1.29299919584939
H	-9.45984445585183	4.12221886349786	1.14097387761475
C	-7.76286925022007	3.02769787114243	0.37805703079324
H	-8.29638693719855	2.64388097515486	-0.48790057246473
O	1.77931284284148	5.87590350065965	2.28997858557694
C	-3.82670138830236	6.09754179207678	0.37164936286412
H	-4.45395600437577	5.25981051801394	0.08260999377996
C	-2.94953730189794	3.05047168641890	0.28644383674045
H	-2.44069594106758	2.13656973906316	-0.04434528826296
H	-3.66396881368548	3.30961916032243	-0.50532022710588
C	-6.38231670250652	4.00200736519627	2.59437873386759
H	-5.86515062800526	4.39569936089590	3.46622191688390
C	-2.70452451153180	-1.35197287692084	2.17501572170057
H	-1.83517572709580	-1.94402135339888	1.90054443440643
C	0.22803722492969	5.08312457141859	5.38829057732541
H	1.00961594664782	4.40456760691218	5.05578469376243
C	-6.42396601663927	2.68961654148025	0.57710749461607
H	-5.93723921280224	2.03693636646019	-0.14602334877549
C	-4.41211101655639	7.35761351515392	0.51967327117185
H	-5.47786679833592	7.47804711515936	0.34433423436285
C	-1.75653418436310	6.84703358816733	6.23311304879529
H	-2.53546526524978	7.53322224112119	6.55536043858254
C	-3.79552611221550	-1.95807559462812	2.80075273489858
H	-3.78070368405955	-3.02421469588989	3.01234438942818
C	-2.72761620778666	0.01625156095352	1.89987443962164
H	-1.86228323635809	0.46158674857043	1.41573465083831
C	-1.87985177423660	0.72101344086819	6.57087654462761
H	-2.60719112891244	0.49060533628535	7.34500689145534
C	0.19020978657321	0.23434680837920	5.42737465791120
H	1.08128704633128	-0.37577202606406	5.30474295389240
C	-0.73908252285321	-0.07227245764158	6.42126222003968
H	-0.57762151623078	-0.92340397561097	7.07752943990368
C	-1.68201695590569	7.02791409213121	0.98153841555164
H	-0.62109320962698	6.90296028220111	1.17698594966841
C	-3.63320037125725	8.45475030217582	0.88809739484946
H	-4.08934233018100	9.43447436999792	1.00136200873605
C	-1.41716272908420	4.81035756582963	-3.71973581691574
H	-2.10133647742010	5.07303334082279	-4.52235297986269
C	-2.26471588172802	8.28664127618639	1.11695652849693
H	-1.65169862755021	9.13471922692437	1.40986696276753
C	0.33288815981626	4.14369204185749	-1.65091514355776
H	1.00970647509679	3.88832811438458	-0.83936631495996
C	0.79877053615515	4.20587379306177	-2.96695994521833
H	1.84369930997501	3.99591639778251	-3.17953638371869
C	-0.07506640484752	4.53750723151192	-4.00276803497479
H	0.28552702741417	4.58661073473875	-5.02676103664509

Table S8 *DFT-optimized geometry of* ***3*** *(RI-TPSS def2-tzvp def2/tzvp/j tightscf grid4 cosmo(THF)).*

Fe	4.70481589638141	8.13725058665318	10.94797387264143
P	3.86886240423443	6.39790943015916	9.83804624886980
P	2.86650739463375	9.06431497487717	11.79911922782779
C	2.53672495435431	6.72046324191630	8.61512314438936
N	5.53467689470464	7.48402271820129	12.21478543261725
N	5.24242146280305	9.20674901894547	9.81270149071697
O	5.65041753977638	9.98176355335147	9.00439437094527
C	1.84530311100799	7.84470711232078	6.57199335112675
H	2.09205850312546	8.46798403719328	5.71670819684304
C	2.83100818976577	7.53214402100965	7.50529287824849
H	3.83795324774310	7.91914711391903	7.37057772832017
C	3.20607452812539	5.02728322241976	10.87284412013230
H	2.38600947981228	5.39044132753109	11.49756655207372
H	2.86555924425757	4.18787111856858	10.25894329427245
H	4.01504476362821	4.69052527501390	11.52690049170157
C	1.74938486830553	7.99517624693175	12.79042143488533
C	1.74819584072419	9.88644704432819	10.59025740624924
H	1.38708888663853	9.16034444657355	9.85742907842012
H	0.90129314197314	10.36824182592905	11.08804032182936
H	2.33542819967925	10.64452316526624	10.06506435980925
C	1.46364643584949	6.56377169142614	14.73618665626656
H	1.86727515076266	6.13034636018284	15.64728193477752
C	1.22845990998741	6.23928993856814	8.77061058520651
H	0.96992617179065	5.61065241761572	9.61706857167618
C	4.78043134211349	12.03595166653185	13.93259681699555
H	5.79238534095327	12.42570782968394	14.00594021406572
C	0.43889969550873	7.68879166179857	12.39597797772831
H	0.02121516583715	8.11976046228417	11.49128833089786
C	2.18651918854222	11.01993468263492	13.74373306842575
H	1.17496035734418	10.62514712314613	13.68435265878676
C	5.12084438388423	5.50704268537942	8.81173404196506
O	6.15642305951727	7.02075436419475	13.12017161985257
C	4.51017409137573	10.96274036454131	13.07952412756017
H	5.30676043602948	10.51340417256202	12.49139556244445
C	3.21258894558378	10.44720584365738	12.97462052514697
C	2.45630538038616	12.08988885184486	14.59631259170159
H	1.65491149382008	12.52382923210378	15.18852042337126
C	5.69740991886922	3.81735305720271	7.16461903738497
H	5.38839729666414	3.04878436856370	6.46095523807630
C	2.25335643483286	7.41714392305114	13.96912922457375
H	3.26895681759056	7.63766137066429	14.28795990951627
C	0.15844339356917	6.26253521598266	14.33333314232036
H	-0.45609023782393	5.59334986181659	14.92962650486050
C	-0.34959384991858	6.82562702643699	13.16283267025865
H	-1.36372270846141	6.59959639170896	12.84372216543658
C	4.73654343887775	4.50923819371382	7.90111780882158
H	3.68390022152517	4.27693938402582	7.75854541566567
C	3.75463004929186	12.60065098161289	14.69159758123976
H	3.96407559982685	13.43277038592209	15.35850369591800
C	0.23851308050417	6.56038011443224	7.83708587229346
H	-0.76998015331748	6.17788893024477	7.97141871921455
C	6.48153335257646	5.79975491595250	8.96588117402091
H	6.77907592058072	6.57904949211030	9.66337576761511
C	0.54325602857770	7.36103034658401	6.73634024050287
H	-0.22647761982205	7.60769779887326	6.01009114242143
C	7.05425836438270	4.11346420577286	7.32852663482216
H	7.80182056245924	3.57485939715296	6.75228915837798
C	7.44450964236329	5.10502827970255	8.22950671821792
H	8.49715834589128	5.34223852920800	8.35847746965272

Table S9 *DFT-optimized geometry of [**1'**]$^+$ (UKS RI-TPSS def2-tzvp def2/tzvp/j tightscf grid4 cosmo(THF)). The CH_2PPh_2 group of **1** was replaced by a methyl moiety to facilitate calculations.*

C	7.49366916390615	10.10229025060704	12.48874743613670
C	8.58192076397954	10.79242388646949	11.93831780681327
C	8.98270463479986	10.51695705547894	10.61985956631297
C	8.29116893842395	9.57153832313761	9.86595211734596
C	7.20169997490065	8.89143239510532	10.41855616466121
C	6.80576379323966	9.15388146813976	11.73024539505000
P	9.49783019699333	12.00474966113575	12.94106149560495
Fe	8.61836090201046	12.71832284742616	15.02180778150528
N	10.13448071089623	13.70077053455877	15.83412853104002
O	10.87776730276370	14.58613621505410	15.46412666168166
C	9.77475893209758	13.53216167234918	11.92625108986816
C	8.59894382473120	14.50822743043364	11.62716683818788
C	8.12155850103433	15.31101732953841	12.87317880496348
P	7.21445880388150	14.46294109414364	14.25025710973508
C	7.02450912151606	15.71448326136019	15.56577816678029
C	5.85553633441439	15.70599433784927	16.34754188143036
C	5.71235188322241	16.60377099026279	17.40347760221150
C	6.73177573934203	17.51261018964081	17.69583733972199
C	7.89976735975003	17.51785005222301	16.93040279486379
C	8.05387286328432	16.61961108670378	15.87544247569286
C	9.18786035083096	15.56888576519329	10.66269267586773
C	7.43340691574681	13.80366477945548	10.91499857833281
C	11.15071780717806	11.27293038705117	13.19669813676838
C	11.27772882852167	9.87275697348789	13.22708367930405
C	12.51464691724468	9.28702127399679	13.48887652322385
C	13.63387201443273	10.08702571896523	13.72964720497830
C	13.51133967320449	11.47802303946792	13.71288791613453
C	12.27668002507523	12.07260214439359	13.45707923058612
N	7.83436081913334	11.49661305559218	15.94634214195162
O	7.25088238122687	10.65358988237724	16.50894653493742
C	5.52266744499382	14.08683042577064	13.69300071611609
C	4.96418818284029	12.82558852244516	13.94008206056813
C	3.65806655954120	12.54352958759889	13.53693576760226
C	2.90465857615269	13.51982813670713	12.88479398624945
C	3.45364882954997	14.78250848062470	12.64174872375817
C	4.75577260079862	15.06986033497533	13.04475206398839
H	9.83464556007701	11.02928454279353	10.18192186029610
H	5.05396772733974	15.00764241490916	16.12695562376799
H	14.59713222987087	9.62827429993925	13.93288841500283
H	10.57105894688059	14.08118302161208	12.44277176308293
H	10.19703575876176	13.19543508121539	10.97156590082398
H	12.60221409395226	8.20452417920878	13.50165519953660
H	3.23266954319690	11.56412260522585	13.73447918858121
H	5.54433026611359	12.06420935864268	14.45246154871241
H	7.47203191046910	16.12649890823235	12.53227958211344
H	8.99045708135835	15.78262463658621	13.34745764889392
H	10.41601513145756	9.24014359817209	13.03693047652591
H	8.69727864176392	18.22005848575414	17.15471515542350
H	1.88885061697471	13.30084975606693	12.56869595115844
H	2.86599128618827	15.54605336348622	12.14054482386640
H	12.20376061676454	13.15517782441410	13.46541435899987
H	5.96490710718482	8.62225547630394	12.16564660204938
H	7.18561986833657	10.29874786023512	13.51116789171022
H	14.37721811678762	12.10546081519729	13.90263333520228
H	5.16533915483013	16.05898924625449	12.86036236647831
H	6.61782623039435	18.21183894008820	18.51907383911376
H	4.80167009025454	16.59328283035708	17.99523151486684
H	8.60503079460695	9.36323692512777	8.84729433251104
H	8.97721073650552	16.63282956099170	15.30571580395917
H	6.66586592914631	8.15500160056532	9.82669511565169
H	7.78815131567344	13.32240306560480	9.99788343063517
H	6.66405515626208	14.53246463695942	10.64032009326716
H	6.96207721265026	13.03598183787059	11.53582401658440
H	8.41994115714196	16.30059594720137	10.39084240518169
H	10.02626857822962	16.10170120719488	11.12447125095592
H	9.54522446916758	15.08894238406896	9.74566150507245

Table S10 *DFT-optimized geometry of [**2**]$^+$ (UKS RI-TPSS def2-tzvp def2/tzvp/j tightscf grid4 cosmo(THF)).*

Fe	-0.04352351672247	4.01648160800706	1.82642684112211
P	-1.30149987081110	3.65004536007594	3.84795711024897
P	-1.76442790051762	4.39376791324290	0.22257691677996
Si	-3.82615528896191	2.66780152436831	2.00266863021333
C	-7.54285413073164	4.57684890205152	2.45276832894615
H	-8.00170766891919	5.28513951044177	3.13746762413351
N	0.91411162815580	5.41672352420708	2.11559551912676
C	-5.59699033956196	3.26269797326148	1.78295903627973
C	-1.07445823970302	4.40968867106917	-1.46498885387077
C	-3.08702282329869	3.70770064163913	3.43075449493741
H	-3.28495241539601	4.75982464655429	3.18265810003328
H	-3.65629896389871	3.49716736621480	4.34579760640318
C	-0.10199418069706	5.72008315686076	7.19977566625422
H	0.46342447906899	5.50888115814649	8.10280923114795
N	0.83881649981843	2.38961753547453	1.14061605669176
C	-1.87383337092403	1.44247848180433	5.50518472817730
H	-2.86913405932298	1.85583302718722	5.63465174589157
C	-1.05701920803946	4.95607379823943	5.10553683317314
C	-2.76819381948288	5.90085803287741	0.38877132524791
C	-0.93248455508230	2.07834061411145	4.68013636479958
C	-1.55658967731687	6.24951377122675	4.87741308684928
H	-2.12182480602271	6.47614791370883	3.97722111873619
C	-3.82375311895739	0.82792488774066	2.38633329805249
C	-0.96814914452706	5.61417124137084	-2.17983634256370
H	-1.34881313780596	6.53895633682555	-1.75735218544108
C	-0.61142054575168	6.99937759141948	6.97337843897911
H	-0.44263003685389	7.78968852130706	7.69901168690165
C	0.35001988185381	1.52692237702264	4.53553638246259
H	1.08489463704930	2.01138742227479	3.89790296301062
C	-4.92463847830527	0.26871368203012	3.06464427504843
H	-5.77179040682593	0.89681644453131	3.33141231365749
O	0.51870276591552	1.25314827738413	0.86111477176215
C	-4.95790013687043	-1.08681839812412	3.39399244272949
H	-5.81950781215672	-1.49627236284692	3.91470945707683
C	-8.27355644389539	4.06736696998009	1.37870738174177
H	-9.30323832531252	4.37774439398997	1.22302328963393
C	-7.67761264502803	3.15337329396776	0.50571524431145
H	-8.24234888128769	2.74939732917365	-0.33027469976539
O	1.43970629103099	6.42048121349668	2.39888925350731
C	-4.08423812091225	5.95047220862823	-0.09990004118056
H	-4.53671432725650	5.07894590220341	-0.56177968833336
C	-2.86720229267708	2.93969646023389	0.36076163904244
H	-2.22364838297734	2.06790462511450	0.18816161784703
H	-3.59108060530812	2.95294511494018	-0.46440784463060
C	-6.21888503142857	4.17809275433905	2.65018647304324
H	-5.67444646724560	4.59226567055752	3.49521251840083
C	-2.78929967645719	-1.38349468393650	2.37205742573536
H	-1.95530077838305	-2.02375392797163	2.09758629281918
C	-0.31945724934971	4.70086264698373	6.27156964057874
H	0.07759515790031	3.70890242198312	6.46261465110042
C	-6.35666424082204	2.75530957893510	0.70958203828265
H	-5.91700500575960	2.03437701659014	0.02222897407341
C	-4.82065129747011	7.12974744983160	0.00099773596253
H	-5.83795037331633	7.16025811599947	-0.37772627063102
C	-1.33914436781598	7.26180593454835	5.81004193751605
H	-1.73837652876462	8.25535904733609	5.62758831460809
C	-3.88951139551586	-1.91616335088141	3.04645637385093
H	-3.91565993529528	-2.97330931824393	3.29681685420891
C	-2.75882401774340	-0.02678654306953	2.04731772712784
H	-1.88498780783723	0.35740785299359	1.52625719759592
C	-1.53108112581952	0.26800885742420	6.17169249231466
H	-2.26376622660837	-0.22159124664475	6.80640250974879
C	0.68818968152375	0.35407395026228	5.21008696325513
H	1.68271810988966	-0.06619880442802	5.09360683170527
C	-0.25233714316881	-0.27615021414560	6.02598120715105
H	0.00913241012811	-1.19211273208230	6.54807374610659
C	-2.20400555496278	7.04721404152734	0.97170434600953
H	-1.18386123293682	7.02543259118581	1.34366426634925
C	-4.25366837975883	8.26625050018819	0.58247677438390
H	-4.83204236595195	9.18246645862924	0.65821140298947
C	-0.38486399723190	5.62449838889012	-3.44607705257060
H	-0.31610201194563	6.55849371143113	-3.99617652311479
C	-2.94438451123949	8.22583783425144	1.06497561040557
H	-2.49786151201863	9.10837959309136	1.51330685376182
C	-0.57111549278037	3.22313135399214	-2.02677206653992
H	-0.62993219422667	2.28324953001460	-1.48629764896855
C	0.00746206215840	3.24266169155284	-3.29451600533041
H	0.38594482663116	2.32003897937111	-3.72461173568053
C	0.10276872676649	4.44132480373458	-4.00543697281289
H	0.55671944208350	4.45314938232487	-4.99207204860906

Table S11 *DFT-optimized geometry of [**3**]$^{+}$ (UKS RI-TPSS def2-tzvp def2/tzvp/j tightscf grid4 cosmo(THF)).*

Fe	4.41974935707372	8.10915784029435	10.88273146713569
P	3.79772815297341	6.12647683573516	9.69422972558385
P	2.64335233844777	9.32510489146786	11.91819439385267
C	2.47151791801762	6.46079518015661	8.49745271362307
N	5.36859245391670	7.54931025898720	12.21555276583566
N	5.22681180501113	9.34131696100582	9.57497750961238
O	4.90631763867520	10.00512867575330	8.61530139003066
C	1.74827192434048	7.59774552529785	6.47989419150409
H	1.97648327110556	8.22679070986108	5.62457016539835
C	2.75300118857802	7.28376121049190	7.39126832904515
H	3.75636094419851	7.67129167983613	7.23720499028919
C	3.19505010762670	4.79631867179878	10.80004407007235
H	2.36338493794534	5.15488338122705	11.41245527101916
H	2.87901481160186	3.92831965863277	10.21436284623660
H	4.01859001403174	4.50704243771130	11.45806257153019
C	1.56867581456763	8.18368475858614	12.83796764952111
C	1.58931742128944	10.21071655642193	10.71074619149852
H	1.20508135832208	9.51749399580400	9.95773741483354
H	0.75893299945839	10.70606433721081	11.22210626109201
H	2.20868628594598	10.96130369065908	10.21267529082108
C	1.28431597924095	6.65928633128946	14.70496951697184
H	1.67186690164234	6.20380678296756	15.61143544479088
C	1.16773730382770	5.97375407077626	8.68245712620991
H	0.92800456959306	5.33611790598881	9.52740037293446
C	4.97877116956933	12.13008373511748	13.76528458480059
H	5.96495199762234	12.55829424747980	13.61235202571666
C	0.28759324798870	7.84352274288167	12.37426642426852
H	-0.11692903422809	8.30021219626858	11.47662460585432
C	2.44008896308390	11.01716924328435	14.16040527609767
H	1.45622525308460	10.58633117746202	14.32279916218291
C	5.19255677184194	5.41783189166923	8.76236801183996
O	5.81972469993025	7.06982607461855	13.18444302111142
C	4.51421206557593	11.13759596351539	12.90236521757159
H	5.14258331649352	10.80353036501164	12.07968304819806
C	3.24162260468765	10.57790209907361	13.09473176675135
C	2.91236468109664	12.00731556612749	15.02075915063832
H	2.29055325601947	12.34317789150997	15.84550947825038
C	6.04797368367622	4.00422836776477	6.99213975595328
H	5.86951337728159	3.35787069086611	6.13773733787390
C	2.06490612490092	7.57711888389172	14.00713648221753
H	3.05251228977599	7.83296820424188	14.38140047498996
C	0.00804521088557	6.32753787785421	14.24051768012142
H	-0.59865813315352	5.61051665580274	14.78581454580076
C	-0.48719588168867	6.92015340112063	13.07781718520552
H	-1.48096339388412	6.67053731072353	12.71779450974940
C	4.96763710080472	4.58480972734199	7.65423752739591
H	3.95619824994499	4.39083944943716	7.30891297859563
C	4.17930502182516	12.56354837899917	14.82454124263014
H	4.54376206129928	13.33240703206901	15.49973710533013
C	0.16550120014518	6.29606393230367	7.76624819432862
H	-0.83818697997578	5.90737214206283	7.91164808347508
C	6.50552162300232	5.66942488178371	9.18849827172208
H	6.69217866867978	6.32007305529120	10.03890637091817
C	0.45288855623910	7.10609041725944	6.66653567851585
H	-0.32950321193533	7.35366922284255	5.95505974701378
C	7.35376485665465	4.25220074022169	7.42482716753494
H	8.19233262999349	3.79940654522839	6.90367223358125
C	7.58213692115990	5.08470403577111	8.52159195836196
H	8.59569453417113	5.28456450514134	8.85627002596050