Supporting Information to:

Isolation of a Stable Pyridine Radical Anion

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1. Experimental Section

General Considerations. All reactions were carried out under argon atmosphere using standard Schlenk techniques in flame dried glassware or in an argon filled glove box (water and oxygen content below 1 ppm). Tetrahydrofuran was dried over sodium wire, deuterated tetrahydrofuran over CaH_2. Solvents were stored over molecular sieves (Å3). 2,6-bis(diazaboryl)pyridine **1** was prepared according to the literature.[1] Naphthalene and benzophenone were sublimed *in vacuo* and Ph_2PCl was distilled prior to usage. All other compounds were used as received. UV-vis absorption spectra were recorded on a Varian Cary 50 spectrometer. Microanalyses were carried out at the Science Centre, London Metropolitan University.

Synthesis of K[1]$^\bullet$. A solution of **1** (277 mg, 0.723 mmol) in THF (10 ml) was added to KC_8 (131 mg, 0.971 mmol) at room temperature and the mixture was stirred for 4 hours. After filtration all volatile components were removed *in vacuo* and the residue was washed with pentane (2 ml). Yield: 0.19 g (68 %). Anal. calc. (%) for K[**1**]$^\bullet$ (M_r = 422.29): C, 59.73; H, 9.31; N, 16.58; Found: C, 59.63; H, 9.10; N, 16.23.

Reduction of Ph_2PCl with K[1]$^\bullet$. A solution of **1** (200 mg, 0.522 mmol) in THF (10 ml) was added to KC_8 (113 mg, 0.836 mmol) and stirred for 4 hours. The solution was then filtered directly into a stirred solution of Ph_2PCl (90 mg, 0.627 mmol, 1.2 eq.) in THF (10 ml). After stirring for 12 hours, a pale yellow solution was obtained. Characterization of the reaction mixture by multinuclear NMR spectroscopy[2] revealed Ph_4P_2 as the main product alongside a residual amount of unreacted Ph_2PCl and free **1**.

Reduction of Ph_3CCl with K[1]$^\bullet$. A solution of **1** (200 mg, 0.522 mmol) in THF (10 ml) was added to KC_8 (113 mg, 0.836 mmol) and stirred for 4 hours. The solution was then filtered directly into a stirred solution of Ph_3CCl (161 mg, 0.578 mmol, 1.1 eq.) in THF (10 ml) cooled to -78 °C. After warming to room temperature over a period of 12 hours gave a pale yellow solution. After removal of all volatile components *in vacuo*, analysis of the residue by multinuclear NMR spectroscopy identified the chinoidal Gomberg-Dimer[3] alongside unidentified byproducts and free **1**.

Reduction of benzophenone with K[1]$^\bullet$. A solution of **1** (200 mg, 0.522 mmol) in THF (10 ml) was added to KC_8 (113 mg, 0.836 mmol) and stirred for 4 hours. The solution was then filtered into an empty Schlenk flask. A solution prepared from freshly sublimed benzophenone (150 mg, 0.823 mmol) in THF (10 ml) was added. An immediate color change from yellow to the characteristic blue of the diphenylketyl radical anion was observed. NB: After washing a freshly prepared sample of K[**1**]$^{\bullet}$ with pentane, the pentane phase was colored yellow. Addition of solid benzophenone to the solution resulted in a color-change to blue. This further supports the observation that the pyridine radical anion forms a strong contact ion pair with [K]$^+$.

2. Crystallographic Section

Single crystals were picked at room temperature. The data for K[**1**]$^{\bullet}$ were collected from a shock-cooled crystal at 100 K mounted onto a 0.1 mm CryoLoop in perfluoroalkyl ether oil. The data were collected on a Bruker APEXII QUAZAR with an Incoatec microfocus source with mirror optics as monochromator. The diffractometer was equipped with an Oxford Cryosystems 800 low temperature device and used MoK$_\alpha$ radiation, λ = 0.71073 Å. All data were integrated with SAINT,[3] and an empirical absorption correction (SADABS) was applied.[4] All structures were solved by intrinsic phasing using SHELXT[5] and refined by full-matrix least-squares methods against F^2 with SHELXL.[6] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their U_{iso} values constrained to 1.5 times the U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms. Disordered moieties were refined using bond lengths restraints and displacement parameter restraints. The graphical representations were prepared with the Diamond 3.2k3 software.[7]

Crystallographic data (including structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. CCDC 1880032 contain the supplementary crystallographic data for this paper. This data can be obtained free of charge via http://www.ccdc.cam.ac.uk/structures/.

Table S1. Crystallographic data for compound K[**1**]$^{\bullet}$.

Parameter	K[**1**]$^{\bullet}$
Empirical formula	$C_{21}H_{39}B_2N_5K$
Formula weight	422.29
Temperature (K)	100(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	24.1981(16)
B (Å)	5.7782(4)
C (Å)	17.2288(11)
α (°)	90
β (°)	89.951(4)
γ (°)	90
Volume (Å^3)	2409.0(3)
Z	4
ρ calcd (g cm^{-3})	1.164
μ (mm^{-1})	0.237
F(000)	916.0
Crystal size (mm^3)	0.15 × 0.1 × 0.05
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data coll. (°)	1.682 to 55.786
Reflections collected	33738
Independent reflections	5730 [R_{int} = 0.0488, R_{sigma} = 0.0510]
Data/restraints/parameters	5730/411/307
Goodness-of-fit on F^2	1.030
R_1 [I > 2σ (I)][a]	0.0570
R_w (all data)[b]	0.1500
CCDC No.	1880032

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

The reader might wonder why the crystal structure of K[**1**]$^{\bullet}$ was not solved and refined in the orthorhombic space group *Pbcn*. The *β*-angle is in fact nearly 90 degree, but the disorder of the pyridine ring that describes the simultaneous occurrence of K[**1a**]$^{\bullet}$ and K[**1b**]$^{\bullet}$ in the crystal does not follow exactly the potential twofold axis through N1 and C3a/C3b. A disorder model in *Pbcn* was much worse than in *P*2_1/*c*

Table S2. Bond lengths for K[**1**]$^{\bullet}$.

Atom	Atom	Length (Å)		Atom	Atom	Length (Å)
K1A	N1[1]	2.751(4)		B2	C5	1.589(5)
K1A	N1	3.042(4)		B2	N5	1.428(5)
K1A	B1[1]	3.579(5)		N4	C7	1.451(4)
K1A	B2	3.508(5)		N4	C8	1.433(5)
K1A	C1[1]	3.077(4)		N3	C15	1.426(5)
K1A	C1	3.478(4)		N3	C16	1.479(5)
K1A	C4A[1]	3.283(18)		C1	C2A	1.489(10)
K1A	C5	3.144(4)		C1	C2B	1.509(10)
K1A	C5[1]	3.057(4)		C2A	C3A	1.332(12)
K1A	C13[1]	3.520(7)		C3A	C4A	1.485(12)
K1B	N1[1]	3.074(4)		C4A	C5	1.500(10)
K1B	N1	2.783(4)		C2B	C3B	1.486(12)
K1B	B1[1]	3.552(5)		C3B	C4B	1.348(12)
K1B	C1[1]	3.134(4)		C4B	C5	1.482(11)
K1B	C1	3.011(4)		N5	C6	1.469(4)
K1B	C2B	2.946(11)		N5	C11	1.428(5)
K1B	C4B[1]	3.532(19)		C6	C7	1.481(6)
K1B	C5	2.971(4)		C9	C8	1.499(5)
K1B	C5[1]	3.417(4)		C8	C10	1.496(6)
N1	C1	1.390(4)		C11	C12	1.478(7)
N1	C5	1.325(5)		C11	C13	1.535(5)
B1	N2	1.453(4)		C14	C15	1.556(6)
B1	N3	1.431(6)		C16	C17	1.546(6)
B1	C1	1.488(6)		C16	C18	1.492(5)
N2	C14	1.453(6)		C19	C20	1.555(5)
N2	C19	1.479(4)		C19	C21	1.550(5)
B2	N4	1.406(5)				

[1] = +X,1+Y,+Z

Table S3. Bond angles for K[**1**]$^{\bullet}$.

Atom	Atom	Atom	Angle [°]
N1^1	K1A	N1	171.8(2)
N1^1	K1A	B1^1	43.90(12)
N1	K1A	B1^1	128.09(16)
N1	K1A	B2	44.94(11)
N1^1	K1A	B2	142.82(17)
N1^1	K1A	C1	150.14(16)
N1	K1A	C1	23.41(8)
N1^1	K1A	C1^1	26.85(9)
N1	K1A	C1^1	146.74(16)
N1	K1A	C4A^1	138.4(2)
N1^1	K1A	C4A^1	47.0(2)
N1	K1A	C5^1	162.05(18)
N1^1	K1A	C5^1	25.68(11)
N1^1	K1A	C5	163.05(19)
N1	K1A	C5	24.67(10)
N1	K1A	C13^1	101.15(11)
N1^1	K1A	C13^1	82.53(11)
B2	K1A	B1^1	171.59(15)
B2	K1A	C13^1	70.46(11)
C1^1	K1A	B1^1	24.36(11)
C1	K1A	B1^1	107.67(12)
C1	K1A	B2	66.51(9)
C1^1	K1A	B2	164.05(16)
C1^1	K1A	C1	123.52(14)
C1^1	K1A	C4A^1	53.3(2)
C1^1	K1A	C5	155.06(10)
C1	K1A	C13^1	122.85(12)
C1^1	K1A	C13^1	107.80(11)
C4A^1	K1A	B1^1	77.5(2)
C4A^1	K1A	B2	110.8(2)
C4A^1	K1A	C1	131.6(2)
C4A^1	K1A	C13^1	97.7(2)
C5^1	K1A	B1^1	67.47(11)
C5	K1A	B1^1	148.76(12)
C5	K1A	B2	26.94(9)
C5^1	K1A	B2	120.31(14)
C5^1	K1A	C1^1	45.38(7)
C5	K1A	C1	41.49(6)
C5^1	K1A	C1	157.41(10)
C5	K1A	C4A^1	117.0(2)
C5^1	K1A	C4A^1	27.1(2)
C5^1	K1A	C5	137.45(19)
C5^1	K1A	C13^1	78.27(12)
C5	K1A	C13^1	95.92(12)
C13^1	K1A	B1^1	109.91(11)
N1	K1B	N1^1	161.12(10)
N1	K1B	B1^1	139.94(16)
N1^1	K1B	B1^1	43.36(11)
N1^1	K1B	C1^1	25.85(9)
N1	K1B	C1^1	164.40(18)
N1	K1B	C1	27.40(9)
N3	B1	K1B^2	117.0(2)
N3	B1	N2	104.7(4)
N3	B1	C1	129.7(3)
C1	B1	K1A^2	58.57(19)
C1	B1	K1B^2	61.7(2)
B1	N2	C19	127.4(4)
C14	N2	B1	112.6(3)
C14	N2	C19	119.1(3)
N4	B2	K1A	100.4(2)
N4	B2	C5	126.8(3)
N4	B2	N5	109.2(3)
C5	B2	K1A	63.65(18)
N5	B2	K1A	109.9(3)
N5	B2	C5	124.0(4)
B2	N4	C7	109.0(3)
B2	N4	C8	131.3(3)
C8	N4	C7	119.1(3)
B1	N3	C16	126.1(3)
C15	N3	B1	113.0(3)
C15	N3	C16	119.9(4)
K1A^2	C1	K1A	123.51(14)
K1A^2	C1	K1B^2	11.52(5)
N1	C1	K1A	60.4(2)
N1	C1	K1A^2	63.4(2)
N1	C1	K1B	67.2(2)
N1	C1	K1B^2	74.6(2)
N1	C1	B1	119.6(3)
N1	C1	C2A	113.0(6)
N1	C1	C2B	114.5(6)
B1	C1	K1A^2	97.1(2)
B1	C1	K1A	114.3(2)
B1	C1	K1B^2	93.5(2)
B1	C1	K1B	114.5(3)
B1	C1	C2A	127.3(6)
B1	C1	C2B	123.6(5)
C2A	C1	K1A^2	109.1(4)
C2A	C1	K1A	88.2(5)
C2A	C1	K1B^2	103.2(4)
C2B	C1	K1B	72.9(5)
C3A	C2A	C1	122.1(9)
C2A	C3A	C4A	118.7(10)
C3A	C4A	K1A^2	108.7(9)
C3A	C4A	C5	103.8(8)
C5	C4A	K1A^2	68.0(6)
C1	C2B	K1B	77.7(4)
C3B	C2B	K1B	113.0(7)
C3B	C2B	C1	103.9(8)
C4B	C3B	C2B	113.5(9)
C3B	C4B	C5	121.4(10)
C5	C4B	K1B^2	73.4(7)
K1A^2	C5	K1A	137.46(19)

N1	K1B	C2B	50.3(2)		K1A	C5	K1B^2	136.58(15)
N1	K1B	C4B^1	147.4(2)		K1A^2	C5	K1B^2	9.08(6)
N1^1	K1B	C4B^1	41.4(2)		N1	C5	K1A	73.4(2)
N1	K1B	C5	26.36(11)		N1	C5	K1A^2	64.1(2)
N1^1	K1B	C5^1	22.77(9)		N1	C5	K1B	68.9(2)
N1	K1B	C5^1	152.45(16)		N1	C5	K1B^2	63.9(2)
C1	K1B	N1^1	163.51(17)		N1	C5	B2	121.0(3)
C1^1	K1B	B1^1	24.71(10)		N1	C5	C4A	120.6(6)
C1	K1B	B1^1	120.28(14)		N1	C5	C4B	115.3(6)
C1	K1B	C1^1	140.19(16)		B2	C5	K1A^2	110.1(2)
C1^1	K1B	C4B^1	47.3(2)		B2	C5	K1A	89.4(2)
C1	K1B	C4B^1	147.0(2)		B2	C5	K1B	100.6(2)
C1	K1B	C5^1	171.18(11)		B2	C5	K1B^2	118.5(2)
C1^1	K1B	C5^1	42.07(7)		C4A	C5	K1A^2	84.9(7)
C2B	K1B	C1	29.3(2)		C4A	C5	K1A	120.4(6)
C2B	K1B	C5	55.6(2)		C4A	C5	K1B^2	78.1(7)
C5	K1B	N1^1	149.37(16)		C4A	C5	B2	116.7(6)
C5^1	K1B	B1^1	64.32(10)		C4B	C5	K1B	103.0(6)
C5	K1B	B1^1	166.11(14)		C4B	C5	B2	123.5(6)
C5	K1B	C1	46.59(7)		B2	N5	C6	108.5(3)
C5	K1B	C1^1	168.38(14)		C11	N5	B2	131.8(3)
C5	K1B	C4B^1	121.3(2)		C11	N5	C6	118.6(3)
C5^1	K1B	C4B^1	24.55(19)		N5	C6	C7	105.5(3)
C5	K1B	C5^1	129.37(15)		N4	C7	C6	107.2(3)
K1A^2	N1	K1A	171.8(2)		N4	C8	C9	113.2(3)
K1A^2	N1	K1B^2	10.58(6)		N4	C8	C10	114.0(3)
K1A	N1	K1B^2	170.87(8)		C10	C8	C9	111.7(3)
C1	N1	K1A^2	89.8(2)		N5	C11	C12	113.2(3)
C1	N1	K1A	96.2(2)		N5	C11	C13	114.3(4)
C1	N1	K1B	85.4(2)		C12	C11	C13	110.6(4)
C1	N1	K1B^2	79.5(2)		C11	C13	K1A^2	82.5(3)
C5	N1	K1A^2	90.2(3)		N2	C14	C15	103.5(3)
C5	N1	K1A	82.0(2)		N3	C15	C14	105.6(4)
C5	N1	K1B	84.8(2)		N3	C16	C17	109.7(3)
C5	N1	K1B^2	93.3(2)		N3	C16	C18	111.1(3)
C5	N1	C1	121.26(16)		C18	C16	C17	109.1(4)
N2	B1	K1A^2	107.4(2)		N2	C19	C20	111.2(3)
N2	B1	K1B^2	97.7(2)		N2	C19	C21	109.9(3)
N2	B1	C1	125.5(4)		C21	C19	C20	107.6(3)
N3	B1	K1A^2	110.8(2)					

^{1} = +X,1+Y,+Z; ^{2} = +X,-1+Y,+Z

Representation of the crystal structure of K[1]$^{\bullet}$

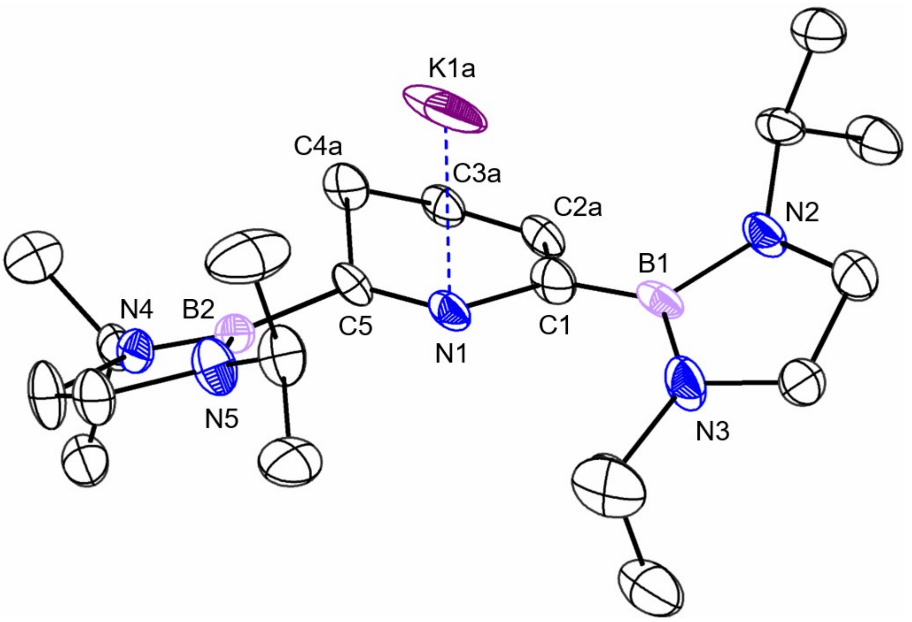


Figure S1. Crystal structure of K[**1a**]$^{\bullet}$. Thermal ellipsoids set at 50 % probability level, H-atoms omitted for clarity.

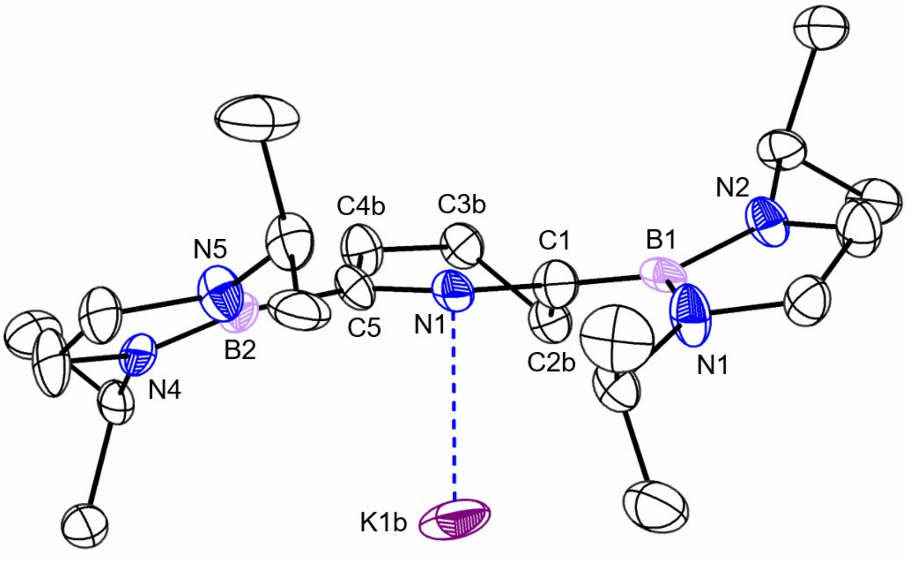


Figure S2. Crystal structure of K[**1b**]$^{\bullet}$. Thermal ellipsoids set at 50 % probability level, H-atoms omitted for clarity.

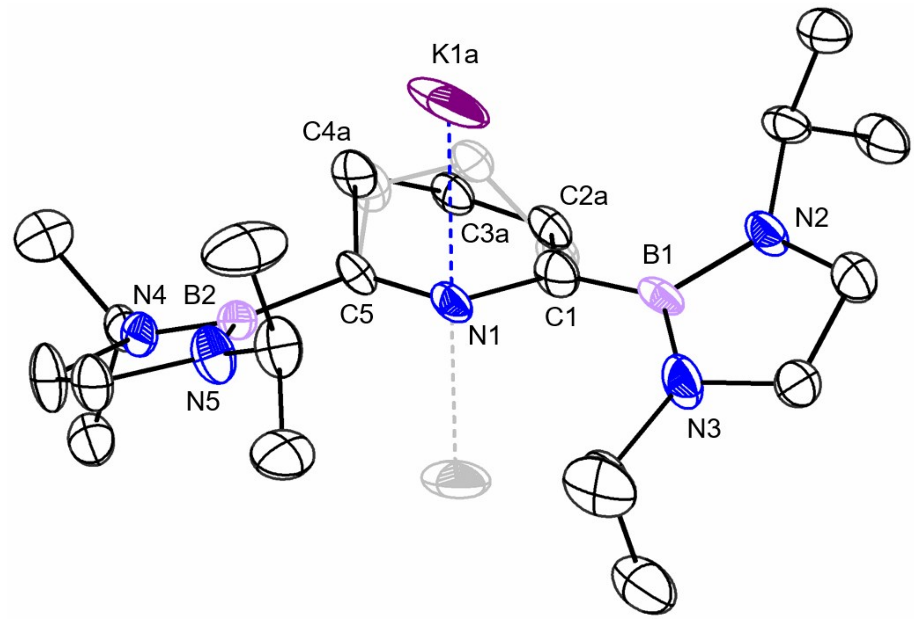


Figure S3. Crystal structure of K[**1**]$^{\cdot}$ with atoms and bonds of part a in black and part b greyed out. Thermal ellipsoids set at 50 % probability level, H-atoms omitted for clarity.

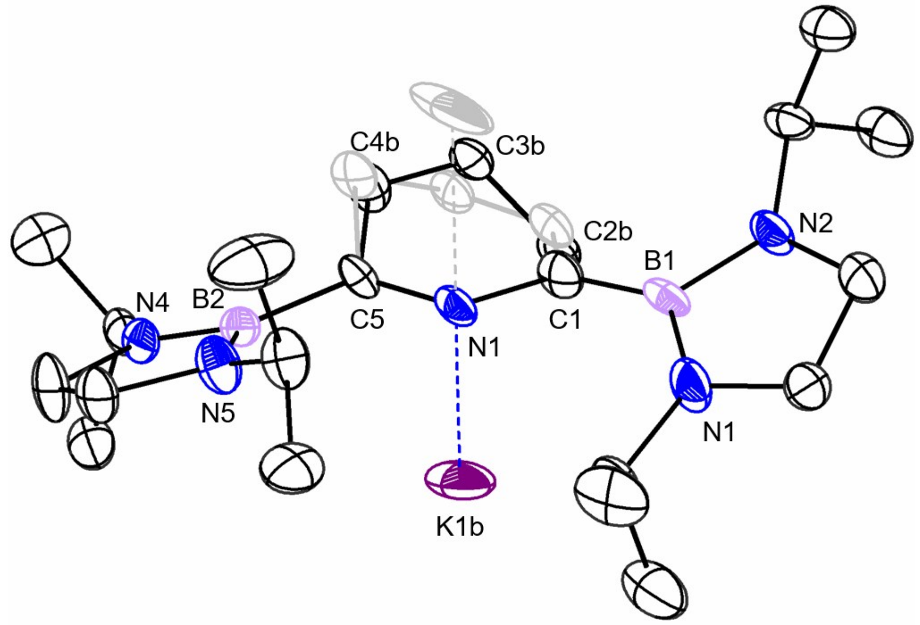


Figure S4. Crystal structure of K[**1**]$^{\cdot}$ with atoms and bonds of part b in black and part a greyed out. Thermal ellipsoids set at 50 % probability level, H-atoms omitted for clarity

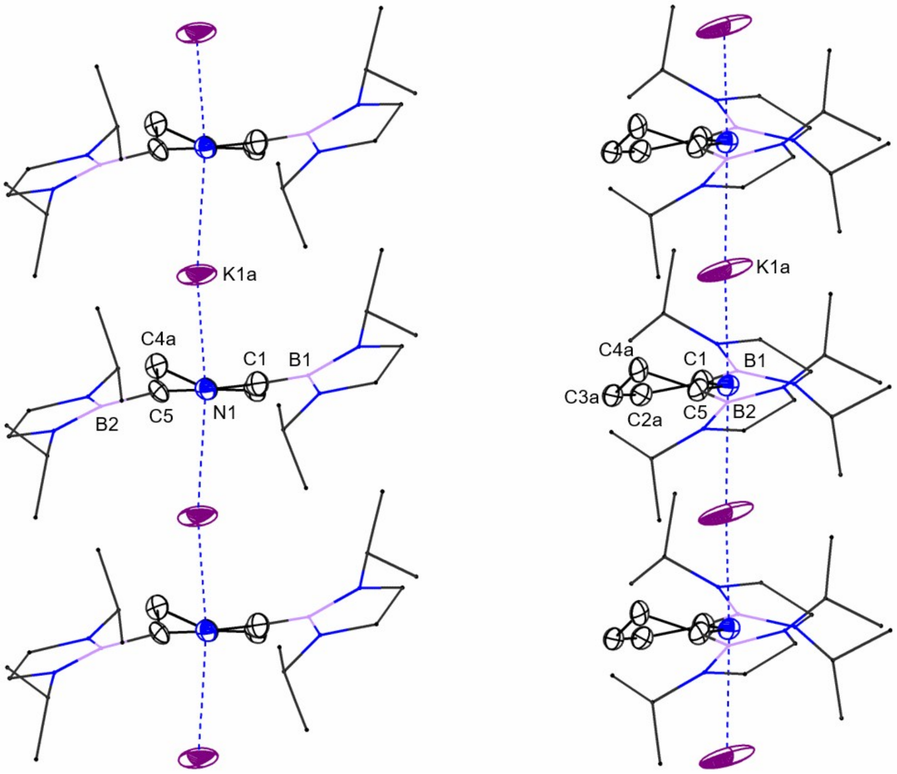


Figure S5. Crystal packing of K[**1a**]$^{\bullet}$. Left: Front view (N1 is in front of C3a). Right: Side view (thermal ellipsoids set at 50% probability level, H-atoms omitted for clarity, diazaboryl-groups are depicted in the wire model).

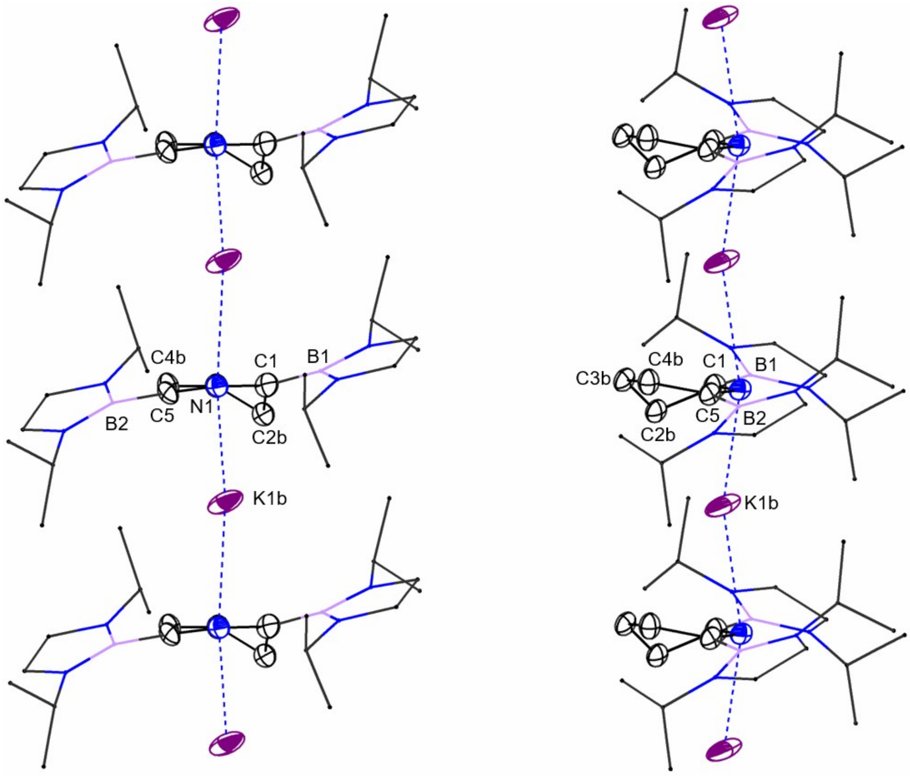


Figure 6. Crystal packing of K[**1b**]$^{\bullet}$. Left: Front view (N1 is in front of C3b). Right: Side view (thermal ellipsoids set at 50% probability level, H-atoms omitted for clarity, diazaboryl-groups are depicted in the wire model).

3. Computational Section

Calculations were performed with TURBOMOLE[8], DFT calculations were carried out with the BP86[9] and TPSS[10] density functionals. D3[11](BJ)[12] dispersion correction and the def2-TZVPP[13] basis set with corresponding RI-J[14] auxiliary bases were employed.

Solvation effects were treated with COSMO[15] using a dielectric constant of 7.58 for THF.

Calculations on K[1]$^{\bullet}$

Non-hydrogen atom coordinates were taken from the crystal structure. Hydrogen atoms coordinates were optimized on the TPSS-D3(BJ)/def2-TZVPP level of theory.

K[**1a**]$^{\bullet}$_HOPT, *C*1

K	0.20219	-2.70398	-0.37105
N	0.00279	0.03942	-0.32035
B	-2.45741	-0.31368	-0.21915
N	-3.65051	-0.95768	-0.74295
B	2.50969	0.43652	-0.22295
N	3.64859	1.06702	-0.75305
N	-2.78041	0.00222	1.13865
C	-1.21341	-0.04218	-0.98845
C	-1.09761	0.24562	-2.44465
H	-1.98753	0.62590	-2.94733
C	0.07769	0.26392	-3.07145
H	0.14409	0.57394	-4.11459
C	1.25349	-0.34478	-2.39825
H	2.22374	-0.33987	-2.88441
C	1.14589	0.13872	-0.98275
N	2.75969	0.08472	1.13865
C	4.16129	0.39382	1.44975
H	4.72538	-0.53319	1.63977
H	4.24349	0.99626	2.36450
C	4.68069	1.11442	0.26525
H	4.91812	2.16000	0.51440
H	5.62048	0.67417	-0.10024
C	4.13079	3.23152	-1.79015
H	4.11617	3.75137	-2.75385
H	5.11620	3.41334	-1.34303
H	3.37687	3.69348	-1.14463
C	3.85169	1.77192	-1.98355
H	2.88113	1.71021	-2.49300
C	4.85359	1.13332	-2.89185
H	5.86560	1.15333	-2.46682
H	4.89562	1.65972	-3.85148
H	4.59656	0.08731	-3.08829
C	2.00279	-0.67928	2.07795
H	0.99591	-0.71509	1.63696
C	1.86749	-0.01808	3.39235
H	1.45671	0.99001	3.27996

H	2.82980	0.06944	3.91319
H	1.19854	-0.58223	4.05067
C	2.48229	-2.12768	2.24795
H	2.62796	-2.61607	1.27455
H	1.75911	-2.70634	2.83514
H	3.44311	-2.18463	2.77204
C	-4.71211	-1.05378	0.24485
H	-4.93039	-2.09932	0.50780
H	-5.65222	-0.60312	-0.10085
C	-4.13551	-0.29028	1.47125
H	-4.71897	0.62694	1.65232
H	-4.22645	-0.89987	2.38275
C	-1.94731	0.79182	2.07125
H	-0.95193	0.81989	1.62270
C	-1.89291	0.08802	3.44655
H	-1.52283	-0.93844	3.34791
H	-2.88642	0.05199	3.90533
H	-1.23117	0.62940	4.13025
C	-2.49431	2.16852	2.24725
H	-2.56150	2.69285	1.28806
H	-1.85633	2.76538	2.91053
H	-3.49553	2.15251	2.69388
C	-3.79191	-1.68208	-2.02485
H	-2.83447	-1.60309	-2.54427
C	-4.16191	-3.17368	-1.78875
H	-4.16737	-3.71987	-2.73788
H	-5.15778	-3.26299	-1.34596
H	-3.44506	-3.65891	-1.11448
C	-4.92491	-1.04488	-2.86915
H	-5.04319	-1.56291	-3.82758
H	-4.71074	0.00940	-3.06604
H	-5.87632	-1.10982	-2.33191

[**1a**]$^{\bullet-}$_HOPT, *C*1

N	0.00508	-0.00061	-0.32643
B	-2.45512	-0.35371	-0.22523
N	-3.64822	-0.99771	-0.74903
B	2.51198	0.39649	-0.22903
N	3.65088	1.02699	-0.75913
N	-2.77812	-0.03781	1.13257
C	-1.21112	-0.08221	-0.99453
C	-1.09532	0.20559	-2.45074
H	-1.98237	0.60210	-2.95290
C	0.07998	0.22389	-3.07753
H	0.14209	0.54482	-4.12123
C	1.25578	-0.38481	-2.40434
H	2.22683	-0.36389	-2.89681
C	1.14818	0.09869	-0.98883
N	2.76198	0.04469	1.13257
C	4.16358	0.35379	1.44367
H	4.73149	-0.57289	1.63444
H	4.25213	0.95748	2.36030
C	4.68298	1.07439	0.25917
H	4.92463	2.12128	0.51207

H	5.62743	0.63461	-0.10306
C	4.13308	3.19149	-1.79624
H	4.12561	3.71408	-2.76006
H	5.11535	3.37406	-1.33912
H	3.37330	3.65052	-1.15527
C	3.85398	1.73189	-1.98964
H	2.88209	1.66234	-2.49664
C	4.85588	1.09329	-2.89794
H	5.86734	1.10351	-2.46776
H	4.90557	1.62250	-3.85730
H	4.58715	0.05114	-3.09656
C	2.00508	-0.71931	2.07187
H	1.00622	-0.77351	1.61718
C	1.86978	-0.05811	3.38627
H	1.46143	0.95281	3.27720
H	2.83132	0.02694	3.91388
H	1.19590	-0.62258	4.04029
C	2.48458	-2.16771	2.24186
H	2.52970	-2.66870	1.27027
H	1.78949	-2.72074	2.88400
H	3.47892	-2.22157	2.70619
C	-4.70982	-1.09381	0.23877
H	-4.93000	-2.13980	0.50648
H	-5.65657	-0.64360	-0.10104
C	-4.13322	-0.33031	1.46517
H	-4.72541	0.58569	1.64853
H	-4.23002	-0.94252	2.37766
C	-1.94502	0.75179	2.06516
H	-0.95054	0.77282	1.60885
C	-1.89062	0.04799	3.44047
H	-1.51819	-0.97564	3.33460
H	-2.88647	0.00986	3.89777
H	-1.22910	0.58909	4.12661
C	-2.49202	2.12849	2.24116
H	-2.54941	2.65215	1.28054
H	-1.85983	2.72609	2.91180
H	-3.49935	2.11168	2.67759
C	-3.78962	-1.72211	-2.03093
H	-2.82887	-1.64225	-2.54296
C	-4.15962	-3.21371	-1.79483
H	-4.17320	-3.75787	-2.74665
H	-5.15407	-3.30198	-1.34475
H	-3.43154	-3.69204	-1.13194
C	-4.92262	-1.08491	-2.87524
H	-5.04782	-1.60687	-3.83253
H	-4.70194	-0.03251	-3.07771
H	-5.87383	-1.14153	-2.33406

K[**1b**]$^{\bullet}$_HOPT, *C*1

K	-0.17672	2.69989	-0.75401
N	0.01968	-0.04201	-0.31711
B	-2.44052	-0.39511	-0.21591
N	-3.63362	-1.03911	-0.73971
B	2.52658	0.35509	-0.21971

N	3.66548	0.98559	-0.74981
N	-2.76352	-0.07921	1.14189
C	-1.19652	-0.12361	-0.98521
C	-1.18532	0.45829	-2.37711
H	-2.15425	0.53015	-2.87261
C	-0.10442	-0.29041	-3.06891
H	-0.20347	-0.63869	-4.09528
C	1.08128	-0.23481	-2.42971
H	1.97870	-0.64602	-2.89690
C	1.16278	0.05729	-0.97951
N	2.77658	0.00329	1.14189
C	4.17818	0.31239	1.45299
H	4.73845	-0.61626	1.64055
H	4.26360	0.91326	2.36904
C	4.69758	1.03299	0.26849
H	4.93805	2.07918	0.51767
H	5.63710	0.59247	-0.09739
C	4.14768	3.15009	-1.78691
H	4.12978	3.67644	-2.74722
H	5.13213	3.33194	-1.33944
H	3.40065	3.61423	-1.13029
C	3.86858	1.69049	-1.98031
H	2.89782	1.61954	-2.49467
C	4.87048	1.05189	-2.88861
H	5.88144	1.07130	-2.46167
H	4.91431	1.57572	-3.84990
H	4.60955	0.00710	-3.08111
C	2.01968	-0.76071	2.08119
H	1.02011	-0.82318	1.63289
C	1.88438	-0.09951	3.39559
H	1.47727	0.91373	3.29317
H	2.84389	-0.01558	3.92346
H	1.21182	-0.66502	4.04842
C	2.49918	-2.20911	2.25119
H	2.55138	-2.71178	1.28099
H	1.80059	-2.76111	2.88840
H	3.48894	-2.26326	2.72168
C	-4.69522	-1.13521	0.24809
H	-4.91042	-2.17999	0.51077
H	-5.63474	-0.68452	-0.09896
C	-4.11862	-0.37171	1.47449
H	-4.70512	0.54407	1.65820
H	-4.20497	-0.98264	2.38452
C	-1.93042	0.71039	2.07449
H	-0.92954	0.71708	1.63419
C	-1.87602	0.00659	3.44979
H	-1.50885	-1.01730	3.34000
H	-2.87006	-0.02577	3.90738
H	-1.21095	0.54369	4.13383
C	-2.47742	2.08709	2.25049
H	-2.58333	2.60996	1.28844
H	-1.83623	2.69629	2.90097
H	-3.47263	2.07208	2.70772
C	-3.77502	-1.76351	-2.02161
H	-2.81688	-1.68819	-2.53742
C	-4.14502	-3.25511	-1.78551
H	-4.15014	-3.79557	-2.73778

H	-5.14345	-3.34342	-1.34693
H	-3.42420	-3.73668	-1.11742
C	-4.90802	-1.12631	-2.86591
H	-5.02580	-1.64780	-3.82230
H	-4.69605	-0.07164	-3.06779
H	-5.86010	-1.19060	-2.32956

[**1b**]$^{\bullet-}$_HOPT, *C*1

N	0.01734	-0.00194	-0.32800
B	-2.44286	-0.35504	-0.22680
N	-3.63596	-0.99904	-0.75060
B	2.52424	0.39516	-0.23060
N	3.66314	1.02566	-0.76070
N	-2.76586	-0.03914	1.13100
C	-1.19886	-0.08354	-0.99610
C	-1.18766	0.49836	-2.38800
H	-2.15432	0.59736	-2.88974
C	-0.10676	-0.25034	-3.07980
H	-0.19585	-0.60144	-4.10987
C	1.07894	-0.19474	-2.44060
H	1.97332	-0.62368	-2.90591
C	1.16044	0.09736	-0.99040
N	2.77424	0.04336	1.13100
C	4.17584	0.35246	1.44210
H	4.74316	-0.57526	1.63155
H	4.26648	0.95550	2.35906
C	4.69524	1.07306	0.25760
H	4.93759	2.11974	0.51089
H	5.64043	0.63289	-0.10368
C	4.14534	3.19016	-1.79780
H	4.13820	3.71304	-2.76143
H	5.12748	3.37143	-1.34037
H	3.38493	3.64877	-1.15734
C	3.86624	1.73056	-1.99120
H	2.89292	1.66093	-2.49789
C	4.86814	1.09196	-2.89950
H	5.88022	1.10370	-2.47044
H	4.91658	1.61992	-3.85973
H	4.60046	0.04938	-3.09722
C	2.01734	-0.72064	2.07030
H	1.01844	-0.77699	1.61446
C	1.88204	-0.05944	3.38470
H	1.47309	0.95131	3.27576
H	2.84379	0.02684	3.91178
H	1.20912	-0.62419	4.03968
C	2.49684	-2.16904	2.24030
H	2.54246	-2.66942	1.26833
H	1.80171	-2.72303	2.88166
H	3.49130	-2.22345	2.70459
C	-4.69756	-1.09514	0.23720
H	-4.91765	-2.14108	0.50474

H	-5.64301	-0.64501	-0.10453
C	-4.12096	-0.33164	1.46360
H	-4.71277	0.58371	1.64815
H	-4.21546	-0.94445	2.37566
C	-1.93276	0.75046	2.06360
H	-0.93834	0.76902	1.60877
C	-1.87836	0.04666	3.43890
H	-1.50817	-0.97775	3.33266
H	-2.87351	0.01132	3.89795
H	-1.21422	0.58658	4.12319
C	-2.47976	2.12716	2.23960
H	-2.53537	2.65187	1.27954
H	-1.84809	2.72336	2.91178
H	-3.48737	2.10990	2.67502
C	-3.77736	-1.72344	-2.03250
H	-2.81692	-1.64044	-2.54435
C	-4.14736	-3.21504	-1.79640
H	-4.16129	-3.75856	-2.74856
H	-5.14191	-3.30341	-1.34649
H	-3.41967	-3.69427	-1.13364
C	-4.91036	-1.08624	-2.87680
H	-5.03623	-1.60980	-3.83307
H	-4.68723	-0.03478	-3.08061
H	-5.86133	-1.14146	-2.33514

Calculations on 1

Non-hydrogen atom coordinates were taken from the crystal structure. Hydrogen atoms coordinates were optimized on the TPSS-D3(BJ)/def2-TZVPP level of theory.

1_HOPT, *C*1

N	-0.04050	-0.41721	0.09328
B	-1.01446	-0.25021	2.35504
C	-0.58284	-1.12733	1.11067
N	2.35233	0.17873	-2.32415
B	0.98676	-0.15750	-2.15211
C	-0.72540	-2.50741	1.03710
H	-1.16716	-3.04786	1.87088
N	0.22568	0.46757	-3.16601
C	-0.27967	-3.18929	-0.08011
H	-0.37082	-4.27000	-0.14875
C	0.28670	-2.45702	-1.11211
H	0.65082	-2.96037	-2.00500
N	-0.20985	0.12169	3.46950
C	0.39156	-1.07568	-1.01428
N	-2.30252	0.31882	2.50803
C	3.86792	1.29668	-0.72555
H	4.33808	1.97442	-1.44686
H	4.59712	1.10676	0.06895
H	3.00601	1.80561	-0.28523
C	3.44802	-0.00931	-1.38457
H	3.05398	-0.67445	-0.60710

C	1.11575	1.12476	-4.12013
H	0.76455	2.12526	-4.39472
H	1.20306	0.53712	-5.04745
C	2.45927	1.18519	-3.38163
H	3.30027	0.98874	-4.05699
H	2.61132	2.18484	-2.94817
C	4.62935	-0.69635	-2.05350
H	4.32392	-1.65194	-2.48968
H	5.43283	-0.88407	-1.33278
H	5.04451	-0.07335	-2.85409
C	-1.19304	0.29583	-3.46512
H	-1.62442	-0.14996	-2.56151
C	-1.43749	-0.64906	-4.63008
H	-1.01764	-0.24994	-5.56054
H	-2.51101	-0.79747	-4.79003
H	-0.98028	-1.62577	-4.44245
C	-1.86840	1.64206	-3.70053
H	-1.49811	2.11865	-4.61511
H	-1.68457	2.31758	-2.86010
H	-2.95014	1.51444	-3.81357
C	-0.93034	1.12927	4.24325
H	-0.57686	2.14206	3.98878
H	-0.78418	0.98809	5.32129
C	-2.39572	0.95682	3.82955
H	-2.92847	0.30841	4.54273
H	-2.92338	1.91513	3.78891
C	1.25096	0.09957	3.61961
H	1.45105	0.38689	4.66180
C	1.80687	-1.29523	3.40777
H	1.67957	-1.61624	2.36996
H	1.30214	-2.02009	4.05348
H	2.87836	-1.31297	3.63437
C	1.92595	1.10399	2.69483
H	1.72499	0.83818	1.65289
H	3.01027	1.12165	2.85401
H	1.54519	2.11705	2.86308
C	-3.51468	-0.08407	1.79914
H	-3.17870	-0.38893	0.80088
C	-4.18398	-1.26784	2.46417
H	-5.06748	-1.58974	1.90098
H	-4.51525	-1.01735	3.47846
H	-3.49650	-2.11626	2.53281
C	-4.48421	1.07884	1.64399
H	-3.99042	1.93854	1.18112
H	-4.88570	1.39319	2.61388
H	-5.33254	0.78726	1.01646

Calculated Mulliken spin densities

Table S4. Mulliken spin densities (TPSS-D3(BJ)/def2-TZVPP) for selected atoms for K[**1a**]$^{\bullet}$_HOPT.

No.	Atom	Mulliken Spin Population
1	K	0.173079
2	N	-0.000324
3	B	0.030278
4	N	0.026394
5	B	0.018118
6	N	0.004213
7	N	0.027493
8	C	0.253177
9	C	0.03409
11	C	0.021525
13	C	0.437921
15	C	-0.018826
16	N	0.004325
17	C	-0.000263
20	C	-0.000494
23	C	-0.00031
27	C	0.002502
29	C	0.000242
33	C	0.002773
35	C	-0.000182
39	C	0.000963
43	C	-0.002261
46	C	-0.00159
49	C	-0.002162
51	C	0.002243
55	C	0.001104
59	C	-0.000848
61	C	0.000892
65	C	0.000632

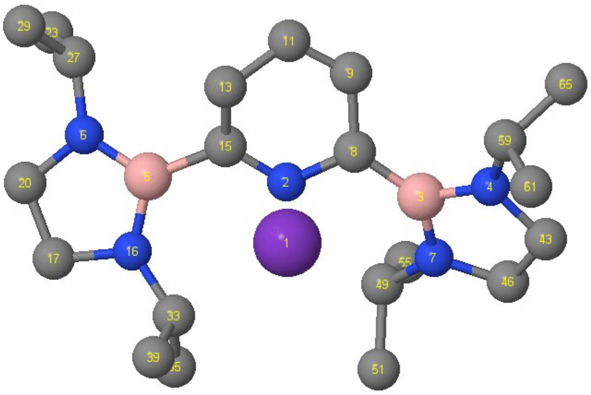
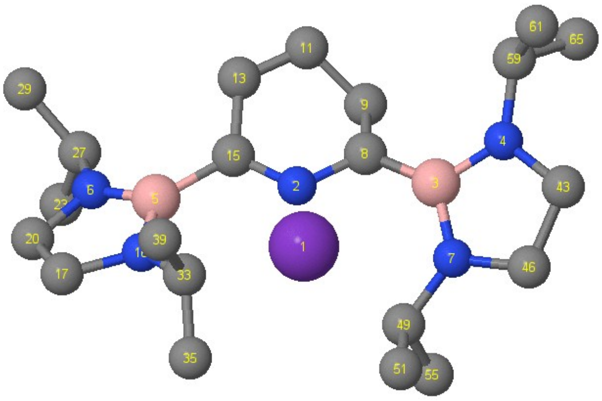


Table S5. Mulliken spin densities (TPSS-D3(BJ)/def2-TZVPP) for selected atoms for K[**1b**]$^{\cdot}$_HOPT.

No.	Atom	Mulliken Spin Population
1	K	0.148548
2	N	-0.01888
3	B	0.049011
4	N	0.015827
5	B	0.00585
6	N	0.013373
7	N	0.012236
8	C	0.045636
9	C	0.469242
11	C	0.041682
13	C	0.00987
15	C	0.198894
16	N	0.017033
17	C	-0.00075
20	C	-0.001465
23	C	0.000517
27	C	0.000976
29	C	0.000184
33	C	-0.000283
35	C	0.001526
39	C	0.000899
43	C	-0.001238
46	C	-0.000994
49	C	0.002461
51	C	0.000353
55	C	0.000219
59	C	-0.000115
61	C	0.000196
65	C	0.000225



Natural Population Analysis

TPSS-D3(BJ)/def2-TZVPP level of theory.

Table S6. Distribution of Natural Charges of K[**1a**]$^{\bullet}$_HOPT and K[**1b**]$^{\bullet}$_HOPT.

K[**1a**]$^{\bullet}$_HOPT				K[**1b**]$^{\bullet}$_HOPT		
No.	**Atom**	**Natural Charge**		**No.**	**Atom**	**Natural Charge**
1	K	0.82652		1	K	0.85182
2	N	-0.52015		2	N	-0.49448
3	B	0.76856		3	B	0.79976
4	N	-0.60835		4	N	-0.59894
5	B	0.81495		5	B	0.78788
6	N	-0.60152		6	N	-0.60906
7	N	-0.60797		7	N	-0.60244
8	C	-0.2597		8	C	-0.19573
9	C	-0.26638		9	C	-0.45265
10	H	0.19348		10	H	0.18313
11	C	-0.21598		11	C	-0.20690
12	H	0.19208		12	H	0.19597
13	C	-0.41666		13	C	-0.29130
14	H	0.18657		14	H	0.19097
15	C	-0.11223		15	C	-0.19571
16	N	-0.60134		16	N	-0.59792
17	C	-0.20138		17	C	-0.20257
18	H	0.1612		18	H	0.16850
19	H	0.17583		19	H	0.17196
20	C	-0.20042		20	C	-0.19955
21	H	0.16986		21	H	0.16244
22	H	0.17175		22	H	0.17295
23	C	-0.58246		23	C	-0.58039
24	H	0.20116		24	H	0.20149
25	H	0.1851		25	H	0.19352
26	H	0.20481		26	H	0.18257
27	C	-0.04212		27	C	-0.04044
28	H	0.20943		28	H	0.20273
29	C	-0.57882		29	C	-0.57890
30	H	0.18596		30	H	0.18748
31	H	0.19887		31	H	0.19704
32	H	0.19971		32	H	0.20649
33	C	-0.05287		33	C	-0.05883
34	H	0.21581		34	H	0.23457
35	C	-0.58032		35	C	-0.57566
36	H	0.20998		36	H	0.19091
37	H	0.18708		37	H	0.18388
38	H	0.19946		38	H	0.20130
39	C	-0.5938		39	C	-0.58350
40	H	0.17324		40	H	0.20359
41	H	0.19377		41	H	0.19626
42	H	0.20109		42	H	0.18106
43	C	-0.19061		43	C	-0.18996
44	H	0.1593		44	H	0.16696
45	H	0.1692		45	H	0.16793
46	C	-0.18757		46	C	-0.18805

47	H	0.16153		47	H	0.15488
48	H	0.16417		48	H	0.16945
49	C	-0.04715		49	C	-0.04988
50	H	0.2356		50	H	0.22515
51	C	-0.58394		51	C	-0.58495
52	H	0.18728		52	H	0.20666
53	H	0.18825		53	H	0.18820
54	H	0.19672		54	H	0.19548
55	C	-0.58543		55	C	-0.58659
56	H	0.20491		56	H	0.17381
57	H	0.19508		57	H	0.19459
58	H	0.18437		58	H	0.19952
59	C	-0.02145		59	C	-0.01919
60	H	0.20803		60	H	0.20925
61	C	-0.59106		61	C	-0.59250
62	H	0.19855		62	H	0.19758
63	H	0.194		63	H	0.18691
64	H	0.18056		64	H	0.20190
65	C	-0.58647		65	C	-0.58659
66	H	0.19207		66	H	0.19320
67	H	0.20269		67	H	0.19645
68	H	0.18757		68	H	0.18651

Table S7. Distribution of Natural Charges of **1**_HOPT.

No.	Atom	Natural Charge		No.	Atom	Natural Charge
1	N	-0.41045		35	H	0.18874
2	B	0.86605		36	H	0.19822
3	C	-0.08322		37	H	0.19947
4	N	-0.61137		38	C	-0.58342
5	B	0.84842		39	H	0.18698
6	C	-0.22767		40	H	0.20639
7	H	0.20243		41	H	0.19834
8	N	-0.60987		42	C	-0.18908
9	C	-0.17301		43	H	0.16212
10	H	0.20298		44	H	0.17888
11	C	-0.22666		45	C	-0.19955
12	H	0.20263		46	H	0.16266
13	N	-0.61554		47	H	0.18405
14	C	-0.07788		48	C	-0.02244
15	N	-0.61503		49	H	0.17313
16	C	-0.59079		50	C	-0.57629
17	H	0.18836		51	H	0.20232
18	H	0.20038		52	H	0.20034
19	H	0.20874		53	H	0.19624
20	C	-0.025		54	C	-0.59189
21	H	0.19645		55	H	0.21508
22	C	-0.19568		56	H	0.19249
23	H	0.1817		57	H	0.19368
24	H	0.16274		58	C	-0.02776
25	C	-0.19662		59	H	0.1972
26	H	0.17926		60	C	-0.58436

27	H	0.16694		61	H	0.19772
28	C	-0.5795		62	H	0.18888
29	H	0.20085		63	H	0.19842
30	H	0.19623		64	C	-0.58218
31	H	0.18732		65	H	0.20517
32	C	-0.02375		66	H	0.18864
33	H	0.19805		67	H	0.19968
34	C	-0.58534				

Structural and electronical data for a geometry optimized structure K[1]$^{\bullet}$_geoopt.

Selected structural and electronical data for the fully optimized structure of K[**1**]$^{\bullet}$_geoopt on the BP86-D3(BJ)/def2-TZVPP/COSMO(THF) level of theory. The calculated structure resembles the semiquinoidal structure proposed for K[**1a**]$^{\bullet}$ (see manuscript, Figure 2).

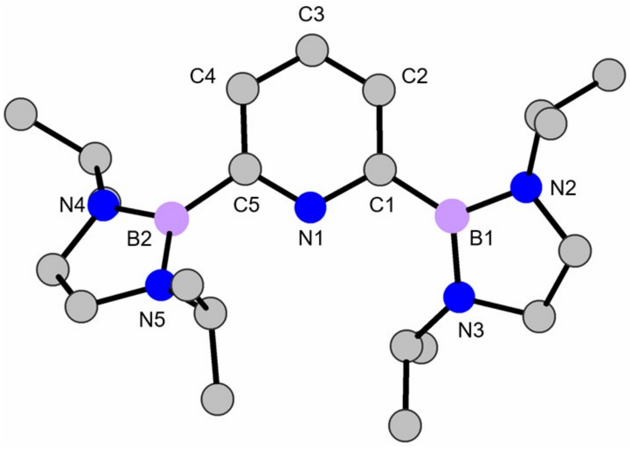


Figure S7. Optimized geometry of K[**1**]$^{\bullet}$_geoopt. Hydrogen and potassium atoms omitted for clarity. Selected bond lengths [pm]: B1–C1 154, B2–C5 158, C1–C2 145, C2–C3 139, C3–C4 144, C4–C5 143, N–K: 289.

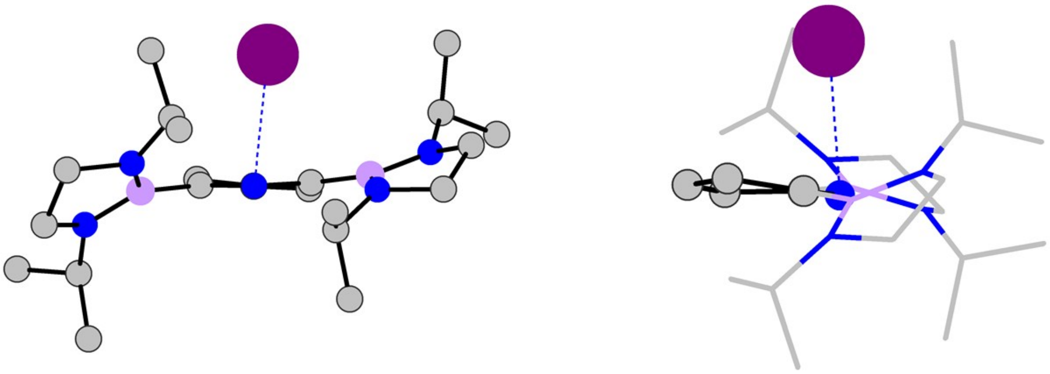


Figure S8. Representation of the distortion of the pyridine ring. Left: View along the hypothetical N1–C3 bond. Right: View along the hypothetical C5–C1 bond.

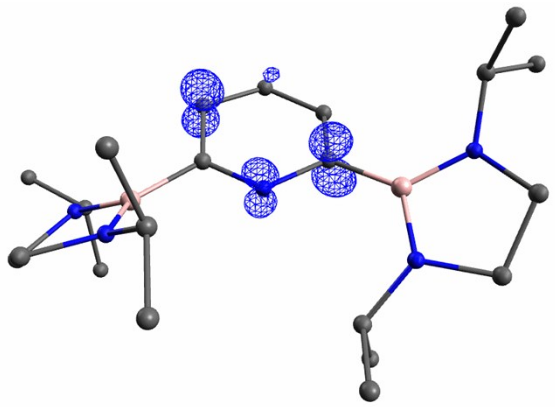


Figure 9. Visualization of the spin density distribution by Mulliken spin population analysis on the BP86-D3(BJ)/def2-TZVPP level of theory (isosurface level = 0.015 a.u.). The calculated electron spin density is mainly distributed on atoms of the pyridine ring with only minor contributions of the two boron atoms (Table S8).

Calculated atomic coordinates for K[**1**]$^{\bullet}$_geoopt, *C*1

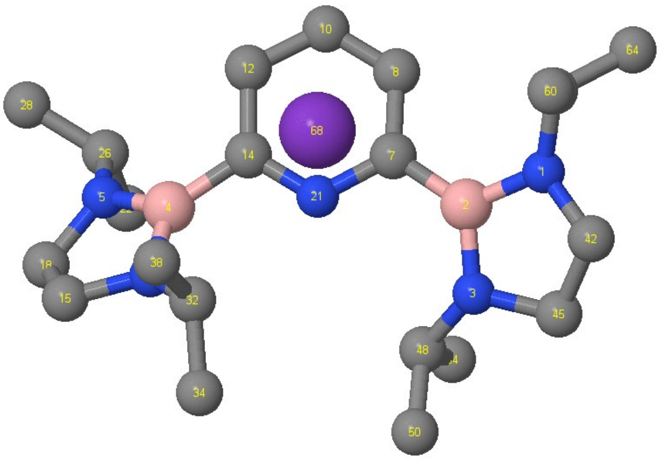
N	-3.73922	-0.82269	-0.66231
B	-2.45168	-0.24898	-0.25365
N	-2.59842	0.16973	1.13785
B	2.51297	0.25760	-0.26071
N	3.68590	0.99298	-0.66192
N	2.73284	-0.24027	1.07381
C	-1.18031	-0.11155	-1.11945
C	-1.16410	-0.09234	-2.57335
H	-2.11386	0.00716	-3.12957
C	0.03100	-0.16645	-3.27252
H	0.03413	-0.14786	-4.37814
C	1.27368	-0.21596	-2.54293
H	2.24027	-0.29764	-3.06559
C	1.21834	0.01787	-1.13106
C	4.13609	-0.02352	1.43530
H	4.74908	-0.94305	1.25262
H	4.26898	0.25288	2.50515
C	4.58027	1.11527	0.49675
H	4.44690	2.10422	1.00232
H	5.65535	1.02729	0.22250
N	0.05499	0.04780	-0.45108
C	3.52160	3.41517	-1.26762
H	3.46580	4.10780	-2.13648
H	4.33340	3.78223	-0.60005
H	2.55971	3.47601	-0.71211
C	3.77504	1.97156	-1.74565
H	2.95310	1.70814	-2.44462
C	5.10264	1.85562	-2.51352
H	5.97162	2.13358	-1.87488
H	5.10655	2.53267	-3.39626
H	5.25645	0.81348	-2.87036
C	1.91180	-1.19902	1.80056
H	0.90533	-1.08663	1.33994
C	1.76595	-0.83284	3.28588
H	1.40377	0.21228	3.38882
H	2.73103	-0.92676	3.83360
H	1.03122	-1.50425	3.78204
C	2.40553	-2.65239	1.63246

H	2.56864	-2.89985	0.55769
H	1.68228	-3.37904	2.06959
H	3.37901	-2.81505	2.14725
C	-4.60207	-0.90815	0.51737
H	-4.54534	-1.92303	0.99152
H	-5.67670	-0.71450	0.29139
C	-4.02014	0.13887	1.47903
H	-4.50937	1.13377	1.30471
H	-4.21123	-0.13430	2.54257
C	-1.71977	1.11929	1.82223
H	-0.71336	0.91812	1.39446
C	-1.67221	0.86114	3.33627
H	-1.41703	-0.20232	3.54014
H	-2.64543	1.08417	3.83178
H	-0.89985	1.50045	3.81856
C	-2.06603	2.58799	1.50727
H	-2.06257	2.74993	0.40668
H	-1.31559	3.27534	1.95940
H	-3.06703	2.88003	1.90089
C	-3.95496	-1.77627	-1.74729
H	-3.06201	-1.69951	-2.40226
C	-4.03521	-3.24311	-1.27029
H	-3.99269	-3.93898	-2.13696
H	-4.97768	-3.45321	-0.71753
H	-3.19077	-3.48808	-0.58518
C	-5.18418	-1.40777	-2.59740
H	-5.30380	-2.10525	-3.45666
H	-5.08166	-0.37406	-2.99386
H	-6.11877	-1.45253	-1.99329
K	-0.15823	-2.82320	-0.64384

Calculated Mulliken spin densities

Table S8. Mulliken spin densities (BP86-D3(BJ)def2-TZVPP) for selected atoms for K[**1a**]$^{\bullet}$_geoopt.

No.	Atom	Mulliken Spin Population
1	N	-0.135359
2	B	0.000186
3	N	-0.15172
4	B	0.056707
5	N	-0.114294
6	N	-0.101271
7	C	-0.154283
8	C	-0.161451
10	C	-0.132531
12	C	-0.333118
14	C	0.057982
15	C	-0.10208
18	C	-0.093047
21	N	-0.287749
22	C	-0.33393
26	C	0.06441
28	C	-0.308163
32	C	0.100199
34	C	-0.335075



38	C	-0.371329
42	C	-0.094479
45	C	-0.090332
48	C	0.123069
50	C	-0.33787
54	C	-0.343802
58	C	0.063299
60	C	-0.329271
64	C	-0.305506
68	K	0.511102

4. UV-vis Spectroscopy

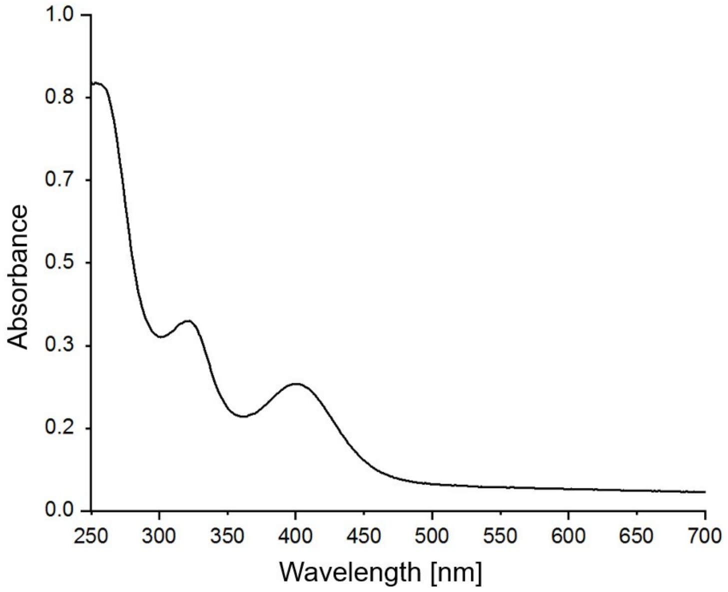


Figure S10. UV-vis spectrum of K[**1**]$^{\bullet}$ measured in THF.

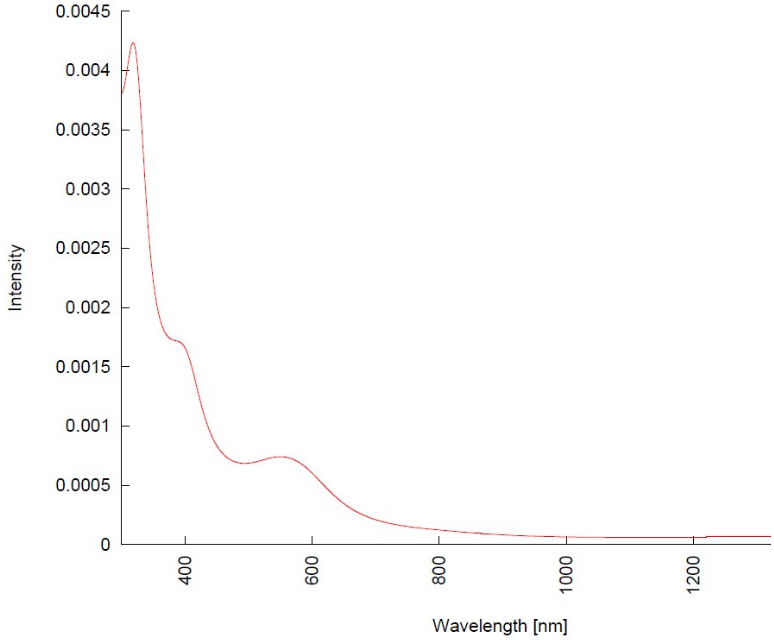


Figure S11. Calculated absorption spectrum of K[**1a**]$^{\bullet}$. Calculated absorptions (from Table S10) were broadened by Lorentz lines with 5000 cm^{-1} half width.

Table S9. Assignment of visual absorption maximum.

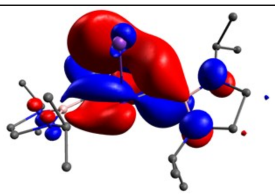
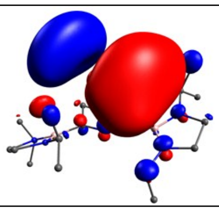
Wave-length [nm]	**assignment**	**MOs**	
587 (calculated) 400 (measured)	HOMO(α) (SOMO) → LUMO(α)+2		

Table S10. Calculated electronic excitation spectrum of K[**1a**]$^{\cdot}$ (TD-DFT, URPA formalism, TPSS-D3(BJ)/def2-TZVPP)

Wavelength [nm]	**Intensity [a.u.]**		**Wavelength [nm]**	**Intensity [a.u.]**
1.39E+03	5.55E-02		2.45E+02	1.52E-03
7.93E+02	9.42E-03		2.43E+02	7.56E-03
5.87E+02	5.39E-02		2.42E+02	2.15E-05
5.76E+02	5.30E-03		2.42E+02	6.54E-03
5.49E+02	3.26E-02		2.42E+02	2.37E-03
5.22E+02	1.23E-02		2.41E+02	1.16E-02
5.09E+02	1.28E-03		2.40E+02	2.15E-04
4.92E+02	5.49E-03		2.39E+02	3.12E-03
4.85E+02	2.15E-03		2.39E+02	9.75E-04
4.66E+02	4.55E-03		2.38E+02	3.72E-03
4.55E+02	6.80E-04		2.38E+02	1.57E-03
4.51E+02	2.02E-03		2.38E+02	1.12E-03
4.40E+02	1.66E-03		2.37E+02	1.90E-02
4.32E+02	2.55E-03		2.36E+02	2.69E-03
4.20E+02	2.78E-03		2.35E+02	1.99E-03
4.06E+02	1.80E-02		2.35E+02	2.98E-04
4.05E+02	1.23E-02		2.35E+02	1.13E-03
4.00E+02	3.46E-02		2.34E+02	9.43E-05
3.91E+02	8.69E-03		2.33E+02	8.04E-03
3.81E+02	4.22E-03		2.33E+02	5.83E-03
3.79E+02	6.17E-03		2.32E+02	2.32E-04
3.72E+02	4.76E-03		2.32E+02	3.51E-04
3.71E+02	2.53E-03		2.31E+02	9.23E-04
3.66E+02	2.82E-03		2.31E+02	6.22E-03
3.59E+02	7.05E-03		2.30E+02	2.08E-03
3.47E+02	5.54E-03		2.30E+02	2.25E-04
3.45E+02	1.75E-03		2.29E+02	2.36E-03
3.38E+02	1.86E-03		2.29E+02	6.54E-04
3.33E+02	3.23E-03		2.29E+02	2.71E-03
3.25E+02	4.96E-02		2.29E+02	2.99E-03
3.25E+02	3.97E-04		2.28E+02	2.39E-03
3.23E+02	1.59E-02		2.28E+02	2.18E-03

3.23E+02	3.80E-02		2.27E+02	4.14E-03
3.20E+02	1.26E-03		2.27E+02	2.10E-03
3.17E+02	1.64E-02		2.26E+02	6.51E-03
3.16E+02	1.66E-03		2.26E+02	2.71E-03
3.14E+02	3.01E-02		2.25E+02	8.16E-04
3.11E+02	2.29E-03		2.24E+02	1.89E-02
3.09E+02	2.02E-03		2.24E+02	2.22E-03
3.06E+02	1.88E-04		2.23E+02	9.73E-03
3.05E+02	5.04E-03		2.22E+02	4.97E-02
3.01E+02	7.01E-04		2.22E+02	1.63E-02
2.98E+02	3.85E-03		2.21E+02	1.12E-02
2.98E+02	5.80E-05		2.21E+02	1.27E-03
2.96E+02	6.58E-04		2.20E+02	1.14E-02
2.95E+02	2.60E-05		2.20E+02	4.11E-04
2.94E+02	1.88E-04		2.20E+02	6.41E-04
2.94E+02	9.80E-03		2.20E+02	3.78E-03
2.91E+02	6.69E-04		2.19E+02	1.59E-04
2.90E+02	1.18E-02		2.19E+02	4.48E-04
2.90E+02	7.54E-04		2.19E+02	1.25E-03
2.88E+02	1.15E-03		2.19E+02	1.19E-03
2.87E+02	1.29E-04		2.18E+02	9.53E-03
2.86E+02	1.45E-04		2.18E+02	6.28E-03
2.85E+02	1.15E-03		2.17E+02	4.29E-04
2.83E+02	2.75E-03		2.17E+02	1.00E-03
2.80E+02	5.38E-04		2.17E+02	7.96E-03
2.79E+02	5.80E-03		2.16E+02	1.98E-04
2.78E+02	9.62E-04		2.16E+02	4.14E-03
2.76E+02	1.95E-03		2.16E+02	1.92E-03
2.76E+02	3.51E-03		2.16E+02	3.82E-04
2.75E+02	3.38E-04		2.16E+02	1.77E-03
2.74E+02	8.31E-04		2.15E+02	5.16E-03
2.73E+02	1.68E-02		2.15E+02	3.91E-03
2.72E+02	3.96E-04		2.15E+02	2.37E-03
2.69E+02	5.69E-04		2.14E+02	3.54E-03
2.68E+02	1.74E-03		2.14E+02	2.92E-04
2.68E+02	1.21E-04		2.14E+02	9.03E-04
2.67E+02	1.44E-04		2.14E+02	1.39E-03
2.67E+02	1.35E-03		2.13E+02	1.63E-03
2.67E+02	1.24E-03		2.13E+02	2.20E-03
2.66E+02	1.16E-03		2.12E+02	4.02E-03
2.65E+02	1.55E-02		2.12E+02	3.68E-02
2.63E+02	6.27E-04		2.12E+02	1.18E-03
2.63E+02	3.76E-02		2.12E+02	1.87E-03
2.60E+02	3.24E-03		2.11E+02	2.94E-03
2.60E+02	7.32E-02		2.11E+02	2.15E-03
2.58E+02	5.19E-03		2.11E+02	1.75E-03

2.57E+02	7.42E-03		2.11E+02	4.05E-04
2.57E+02	3.62E-02		2.10E+02	8.02E-03
2.56E+02	1.50E-03		2.10E+02	2.74E-02
2.56E+02	1.30E-02		2.09E+02	2.95E-03
2.56E+02	1.58E-02		2.09E+02	1.93E-02
2.55E+02	3.05E-03		2.09E+02	6.02E-03
2.53E+02	3.91E-04		2.09E+02	3.10E-02
2.53E+02	2.90E-03		2.08E+02	1.80E-03
2.52E+02	2.06E-03		2.08E+02	5.24E-04
2.52E+02	1.97E-03		2.08E+02	4.19E-03
2.51E+02	6.35E-03		2.08E+02	5.14E-05
2.50E+02	1.35E-03		2.07E+02	1.16E-04
2.50E+02	3.72E-03		2.07E+02	6.04E-03
2.50E+02	3.51E-03		2.07E+02	3.26E-03
2.48E+02	2.73E-04		2.07E+02	2.75E-03
2.48E+02	7.80E-05		2.06E+02	8.45E-04
2.47E+02	6.28E-04		2.06E+02	2.87E-04
2.47E+02	3.81E-03		2.06E+02	6.25E-03
2.46E+02	1.31E-02		2.06E+02	3.79E-04
2.46E+02	8.43E-04		2.05E+02	3.00E-03
2.45E+02	1.16E-03		2.05E+02	2.08E-03
2.45E+02	4.79E-03		2.05E+02	1.89E-03

5. EPR Spectroscopical Section

For the EPR measurements, solid K[**1**]$^{\bullet}$ was filled into a quartz EPR tube (outer diameter 3.8 mm) in the glove box. The tube was sealed with Critoseal® before taking it out of the glove box for flame sealing using a hydrogen torch.

The continuous wave (cw) EPR spectrum of solid K[**1**]$^{\bullet}$ at X-Band (9.75 GHz) was recorded at room temperature (295 K) on a Bruker ELEXSYS E580 spectrometer equipped with a Bruker EN 4118X-MD4 resonator. The modulation frequency was set to 100 kHz and the modulation amplitude to 0.5 mT at a microwave power of 0.4 mW (26 dB). After data acquisition, the spectrum was baseline-corrected using the spectrum of an empty EPR quartz-tube as a reference, to compensate for resonator background signals. After frequency correction to a value of 9.75 GHz, field-correction of the spectrum was performed using Li:LiF as a field standard (g = 2.002293).[16] The g-value of the sample was then calculated from the center of the experimental spectrum according to $g = (h\cdot\nu)/(\beta_e B_0)$ and determined as 2.0029.

6. Cyclic voltammetry

Cyclic voltammetry measurements (CV) were conducted with a VMP3 potentiostat from Bio-Logic Science Instruments. The CV measurements of **1** (0.1 mol L^{-1}) were performed in THF (in analogy to the chemical reduction with K or KC_8) with 0.75 mol L^{-1} [nBu$_4$N][PF$_6$] (supplied in battery grade from Sigma-Aldrich, dried at 100 °C at 1 mbar for 1 day) as supporting electrolyte. The working electrode was a self-manufactured platinum disc electrode with a diameter d = 1 mm, the counter electrode was a Pt-wire and the reference electrode was a Pt-wire as quasi-reference electrode (q-Pt) (Pt wire 99.9 % supplied by MaTeck GmbH). Before each measurement, the working electrode was polished with MetaDi® diamond polishing compounds from Buehler with the smallest grid size of 0.25 µm. The sweep rate typically was 0.1 or 0.05 V s^{-1}. Addition of ferrocene (0.1 mol L^{-1}) and repeating the measurement supplied potential values relatively to the Fc/Fc$^+$ redox couple. In some cases, naphthalene (0.1 mol L^{-1}) was added for reasons of comparison. Neither the addition of ferrocene nor of naphthalene changed the signal of **1** (see Figures S12-S14).

Table S11. Data extracted from CV measurements. Potentials are given in V vs. q-Pt if not otherwise stated, currents in mA.

	E_{pc}	E_{pa}	$E_{pc/2}$	$E_{pa/2}$	i_{pc}	i_{pa}	$E_{1/2}$	$E_{1/2}$ vs. Fc
1	−2.989	--	−2.710	--	−0.337	--	−2.805	−3.502
Naphthalene	−2.351	−2.149	−2.247	−2.224	−0.130	0.068	−2.244	−2.941
Ferrocene	0.580	0.810	0.659	0.718	−0.132	0.121	0.697	0

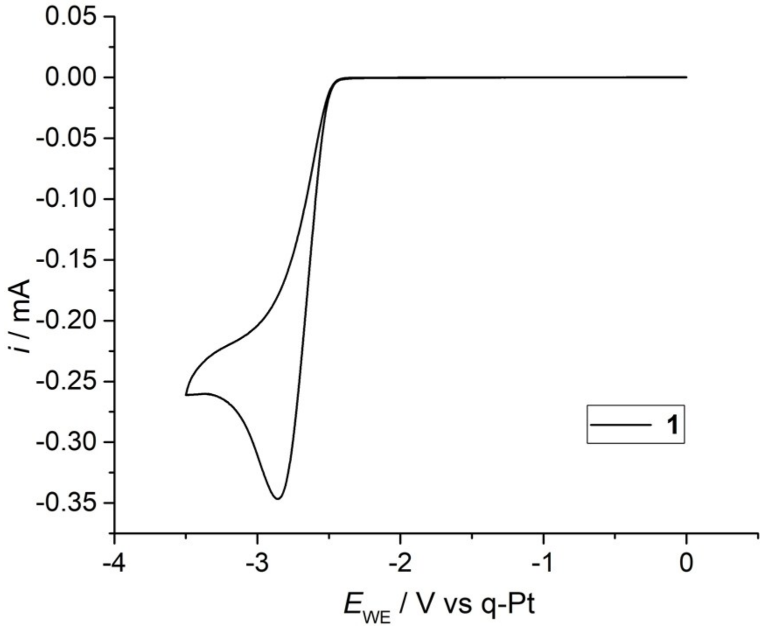


Figure S12. Cyclic voltammogram of **1** in THF at a Pt disc electrode (d = 1 mm). The solution contained **1** (0.1 mol L^{-1}) and Bu$_4$N PF$_6$ (0.75 mol L^{-1}) as supporting electrolyte. Sweep rate was v = 50 mV s^{-1}.

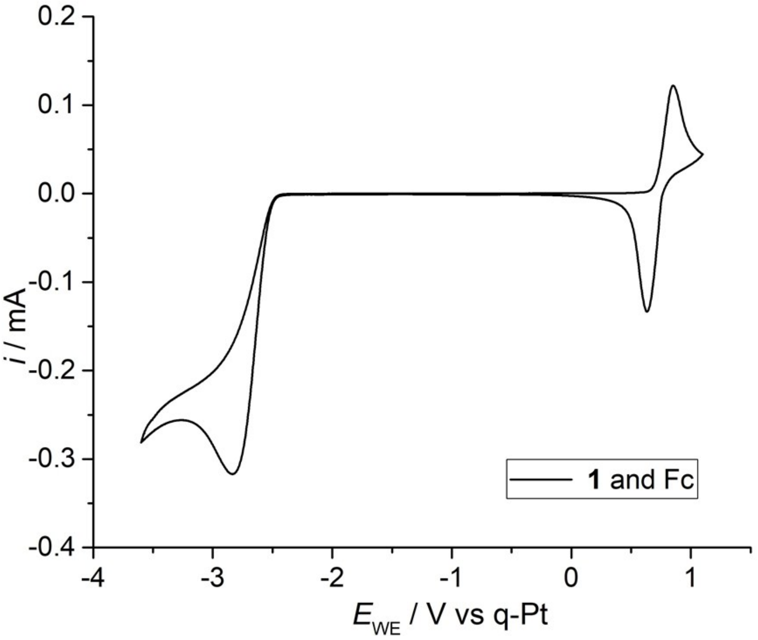


Figure S13. Cyclic voltammogram of **1** in THF at a Pt disc electrode (d = 1 mm). The solution contained **1** and ferrocen (each 0.1 mol L^{-1}) and Bu_4N PF_6 (0.75 mol L^{-1}) as supporting electrolyte. Sweep rate was v = 50 mV s^{-1}.

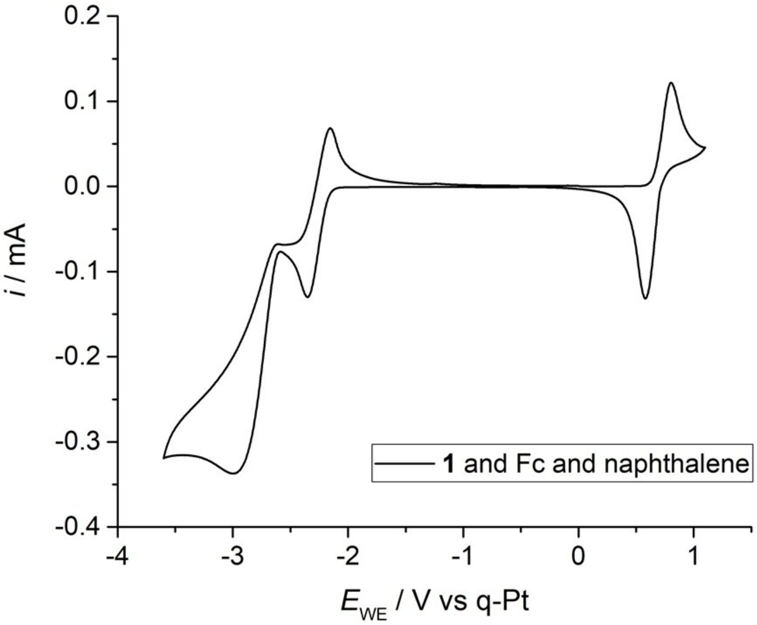


Figure S14. Cyclic voltammogram of **1** in THF at a Pt disc electrode (d = 1 mm). The solution contained **1**, ferrocen and naphthalene (each 0.1 mol L^{-1}) and Bu_4N PF_6 (0.75 mol L^{-1}) as supporting electrolyte. Sweep rate was v = 50 mV s^{-1}.

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