Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting information

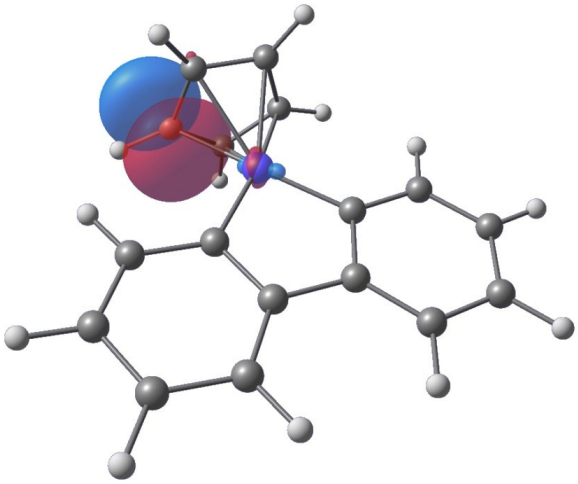

Figure S1. Highest occupied NBO of 9-nickelafluorenyl anion

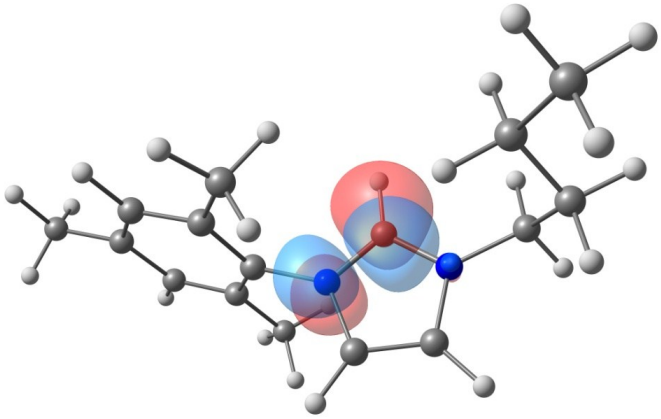

Figure S2. Lowest unoccupied NBO of imidazolium part of 4.

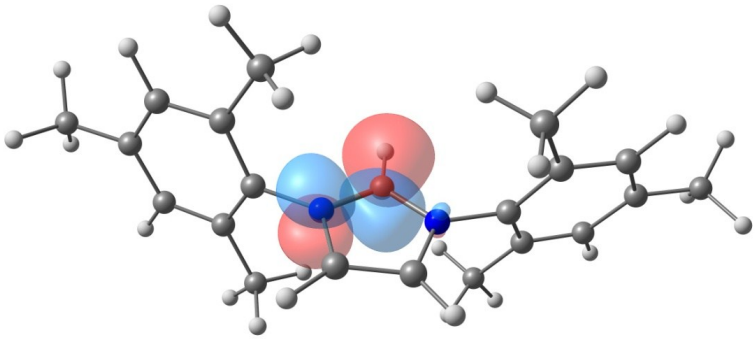

Figure S3. Lowest unoccupied NBO of imidazolium part of **3**.

Table S1 Crystal data and structure refinement.

Compound	**1**	**2**	**3**	**4**	**5**	**7**
Empirical formula	$C_{46}H_{56}N_2NiO_2$	$C_{44}H_{52}N_2NiO$	$C_{42}H_{46}N_2NiO$	$C_{33}H_{36}N_2Ni$	$C_{38}H_{40}N_2Ni$	$C_{69}H_{93}Cl_{17}N_6Ni$
Formula weight	727.63	683.59	653.52	519.35	583.43	1667.85
Temperature/K	100.00(10)	100(2)	100(2)	100(2)	100.00(10)	100.0(2)
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic	trigonal
Space group	$Pca2_1$	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_1/n$	R3c
***a*/Å**	9.0713(2)	17.1430(5)	13.0464(6)	10.6985(1)	13.4758(2)	15.3884(4)
***b*/Å**	24.610(2)	13.1907(2)	17.1568(8)	15.4023(1)	13.6096(2)	15.3884(4)
***c*/Å**	16.8975(5)	17.5420(4)	15.5211(6)	16.7954(1)	17.1452(3)	61.781(2)
***α*/°**	90	90.00	90.00	90.00	90	90
***β*/°**	90	114.528(3)	101.257(2)	96.035(1)	105.054(2)	90
***γ*/°**	90	90.00	90.00	90.00	90	120
Volume/Å^3	3772.2(3)	3608.8(1)	3407.3(3)	2752.23(4)	3036.52(9)	12669.9(8)
Z	4	4	4	4	4	6
ρ_{calc} mg/mm^3	1.281	1.258	1.274	1.253	1.276	1.312
μ/mm^{-1}	0.555	0.574	0.605	0.728	0.668	0.808
***F*(000)**	1560.0	1464.0	1392.0	1104.0	1240.0	5196.0
Crystal size/mm^3	0.412 × 0.131 × 0.043	0.519 × 0.182 × 0.076	0.35 × 0.15 × 0.1	0.57 × 0.41 × 0.23	0.63 × 0.42 × 0.29	0.25 × 0.25 × 0.05
Radiation	Mo*K*α (λ = 0.71073)	Mo*K*α (λ = 0.71073)	Mo*K*α (λ = 0.71073)	Mo*K*α (λ = 0.71073)	Mo*K*α (λ = 0.71073)	Mo*K*α (λ = 0.71073)
2*Θ* range for data collection	5.85 to 59.026°	5.96 to 62.68°	5.12 to 46.5°	6.44 to 69.9°	6.474 to 66.864°	5.652 to 53.462°
Index ranges	$-10 \le h \le 12$, $-31 \le k \le 33$, $-23 \le l \le 21$	$-23 \le h \le 24$, $-19 \le k \le 18$, $-25 \le l \le 21$	$-14 \le h \le 14$, $-19 \le k \le 19$, $-17 \le l \le 17$	$-16 \le h \le 17$, $-24 \le k \le 24$, $-26 \le l \le 23$	$-20 \le h \le 12$, $-20 \le k \le 15$, $-26 \le l \le 26$	$-19 \le h \le 16$, $-19 \le k \le 19$, $-78 \le l \le 78$
Reflections collected	14432	41020	22387	43738	24629	51307
Independent reflections	8281 [R_{int} = 0.0679, R_{sigma} = 0.1078]	10889 [R_{int} = 0.0359, R_{sigma} = 0.0849]	4859 [R_{int} = 0.094, R_{sigma} = 0.1326]	11418 [R_{int} = 0.0201, R_{sigma} = 0.0493]	10953 [R_{int} = 0.0256, R_{sigma} = 0.0338]	5990 [R_{int} = 0.0777, R_{sigma} = 0.0309]
Data/restraints/parameters	8281/7/466	10889/0/437	4859/0/421	11418/0/329	10953/0/376	5990/1/297
Goodness-of-fit on F^2	1.025	1.041	1.080	1.061	1.021	1.067
Final *R* indexes [*I*>=2*σ* (*I*)]	R_1 = 0.0756, wR_2 = 0.1611	R_1 = 0.0371, wR_2 = 0.0831	R_1 = 0.0730, wR_2 = 0.1240	R_1 = 0.0322, wR_2 = 0.0820	R_1 = 0.0340, wR_2 = 0.0860	R_1 = 0.0618, wR_2 = 0.1636
Final *R* indexes [all data]	R_1 = 0.1023, wR_2 = 0.1803	R_1 = 0.0497, wR_2 = 0.0890	R_1 = 0.1220, wR_2 = 0.1400	R_1 = 0.0413, wR_2 = 0.0877	R_1 = 0.0422, wR_2 = 0.0911	R_1 = 0.0691, wR_2 = 0.1693
Largest diff. peak/hole / e Å^{-3}	1.41/-0.84	0.46/-0.41	0.40/-0.37	0.51/-0.40	0.47/-0.32	0.65/-0.45

Table S2: Exact energies (Hartree/particle), zero-point corrections (Hartree/particle), number of imaginary frequencies, sum of electronic and thermal Free Energies (Hartree/particle) and frontier orbital energies (Hartree).

Compound	Number of imaginary frequencies	Energy	Zero-point correction	Sum of electronic and thermal free energies	Frontier orbital energy	Solvent	Temperature
9-nickelafluorenyl anion	0	-2164.00477952	0.240784	-2163.806439	HO NBO -0.10342	THF	298.15 K
1^{+}	0	-925.799700206	0.433427	-925.421814	LU NBO -0.19496	THF	298.15 K
2^{+}	0	-1004.40634788	0.494026	-1003.969709	LU NBO -0.19958	THF	298.15 K
3^{+}	0	-924.596950906	0.409945	-924.242930	LU NBO -0.11345	THF	298.15 K
4^{+}	0	-732.863787531	0.360553	-732.553397	LU NBO -0.11288	THF	298.15 K
5	0	-3089.865128	0.676751	-3089.260086	-	THF	298.15 K
9-nickelafluorenyl anion	0	-2163.98047085	0.240496	-2163.798230	-	1,4-dioxane	374.2 K
1^{+}	0	-925.779389352	0.433495	-925.423723	-	1,4-dioxane	374.2 K
5	0	-3089.86060321	0.677100	-3089.285612	-	1,4-dioxane	374.2 K