Electronic Supplementary Material (ESI) for Faraday Discussions.

Uncovering the role of non-covalent interactions in solid-state photoswitches by non-spherical structure refinements with NoSpherA2

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Supplementary Information

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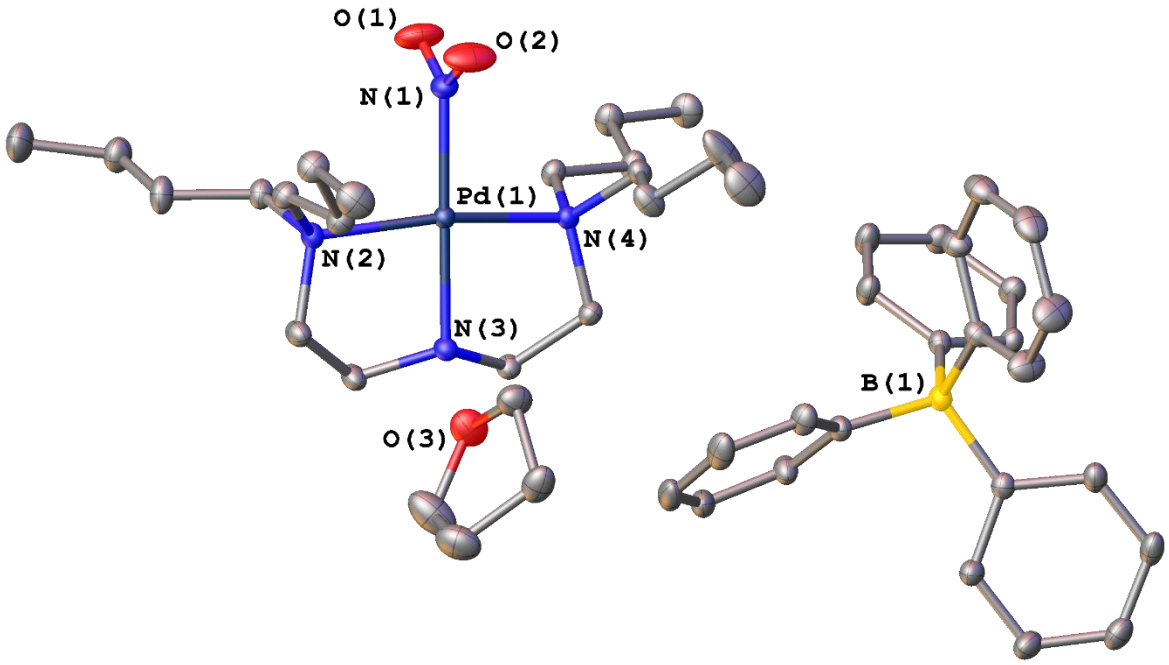
1. Complex 1: [Pd(Bu$_4$dien)(NO$_2$)]BPh$_4$.THF

(a)



(b)

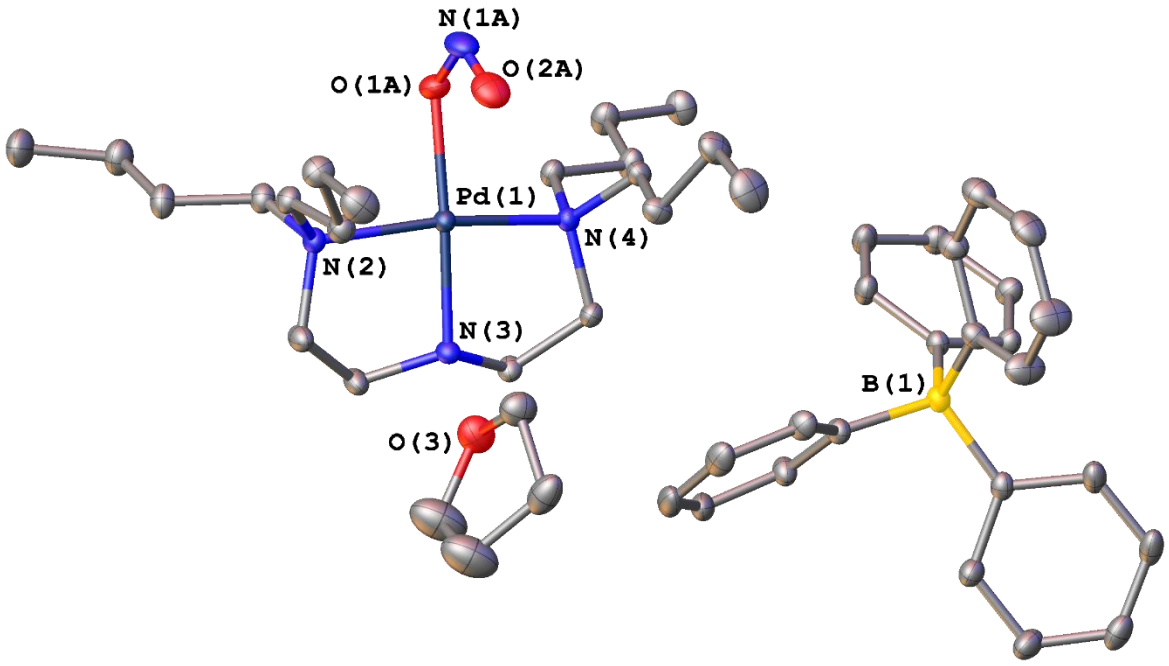


Figure S1.1 Single crystal X-ray structures showing the atomic connectivity in the asymmetric units of the ground state (a) and 100% photoexcited state (b) isomers of **1**,[1] with selected non-hydrogen atoms labelled. Ellipsoids are shown and 50% probability and hydrogen atoms are removed for clarity.

Table S1.1 Single-crystal X-ray structure data for **1** collected for HAR using NoSpherA2 in Olex2.[2]

	Ground state (GS)	**Excited state (ES)**
Photoexcitation level/%	0	100
Empirical formula	$C_{48}H_{73}BN_4O_3Pd$	$C_{48}H_{73}BN_4O_3Pd$
Formula weight	871.379	871.379
Temperature/K	100(1)	100(1)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
***a*/Å**	11.5486(1)	11.4841(1)
***b*/Å**	13.4064(2)	13.3657(1)
***c*/Å**	29.7815(3)	30.0180(3)
***α*/°**	90	90
***β*/°**	95.424(1)	94.602(1)
***γ*/°**	90	90
Volume/Å^3	4590.28(9)	4592.70(7)
Z	4	4
ρ_{calc}/gcm^{-3}	1.261	1.260
μ/mm^{-1}	0.448	0.448
***F*(000)**	1853.0	1853.0
Radiation	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	6.44 to 72.64	6.68 to 72.64
Completeness (resolution)	0.9978 (0.6 Å)	0.9977 (0.6 Å)
Reflections collected	116467	116537
Independent reflections	22256 [R_{int} = 0.0541, R_{sigma} = 0.0420]	22260 [R_{int} = 0.0542, R_{sigma} = 0.0425]
Data/restraints/parameters	22256/339/1159	22260/282/1111
Goodness-of-fit on F^2	1.059	1.047
Final *R* indexes [I>=2σ (I)]	R_1 = 0.0333, wR_2 = 0.0647	R_1 = 0.0350, wR_2 = 0.0715
Final *R* indexes [all data]	R_1 = 0.0477, wR_2 = 0.0707	R_1 = 0.0517, wR_2 = 0.0791
Largest diff. peak/hole / e Å^{-3}	1.11/-0.85	1.89/-1.14

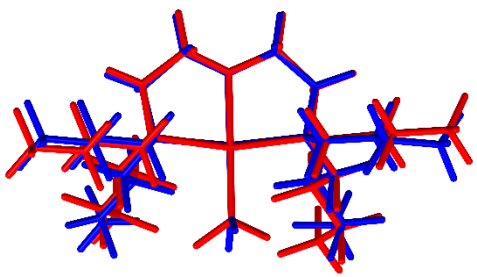
Table S1.2 Experimental bond lengths for non-hydrogen atoms determined by single-crystal X-ray diffraction for the ground state (GS) structure of **1** at 100 K. All bond lengths are all given in Å.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pd(1)	N(1)	2.0171(9)	C(46)	C(47)	1.532(2)
Pd(1)	N(2)	2.0922(9)	C(47)	C(48)	1.506(2)
Pd(1)	N(3)	2.0244(8)	C(21)	C(22)	1.4023(16)
Pd(1)	N(4)	2.0952(8)	C(21)	C(26)	1.4034(16)
O(1)	N(1)	1.2253(13)	C(21)	B(1)	1.6445(15)
O(2)	N(1)	1.2201(13)	C(22)	C(23)	1.3926(17)
N(2)	C(1)	1.5013(13)	C(23)	C(24)	1.387(2)
N(2)	C(5)	1.4943(13)	C(24)	C(25)	1.3946(19)
N(2)	C(9)	1.5081(13)	C(25)	C(26)	1.3947(16)
N(3)	C(2)	1.4800(13)	C(27)	C(28)	1.4001(14)
N(3)	C(3)	1.4796(13)	C(27)	C(32)	1.4036(15)
N(4)	C(4)	1.5042(13)	C(27)	B(1)	1.6427(15)
N(4)	C(13)	1.4920(13)	C(28)	C(29)	1.3925(16)
N(4)	C(17)	1.5066(12)	C(29)	C(30)	1.3890(19)
C(1)	C(2)	1.5149(15)	C(30)	C(31)	1.3930(18)
C(3)	C(4)	1.5140(14)	C(31)	C(32)	1.3943(15)
C(5)	C(6)	1.5172(15)	C(33)	C(34)	1.4070(14)
C(6)	C(7)	1.5266(15)	C(33)	C(38)	1.4032(14)
C(7)	C(8)	1.5210(16)	C(33)	B(1)	1.6470(15)
C(9)	C(10)	1.5198(15)	C(34)	C(35)	1.3944(15)
C(10)	C(11)	1.5215(16)	C(35)	C(36)	1.3898(16)
C(11)	C(12)	1.5180(18)	C(36)	C(37)	1.3940(15)
C(13)	C(14)	1.5155(14)	C(37)	C(38)	1.3929(14)
C(14)	C(15)	1.4920(17)	C(39)	C(40)	1.4022(15)
C(15)	C(16)	1.4849(19)	C(39)	C(44)	1.4077(14)
C(17)	C(18)	1.5257(14)	C(39)	B(1)	1.6467(15)
C(18)	C(19)	1.5261(15)	C(40)	C(41)	1.3992(15)
C(19)	C(20)	1.5206(16)	C(41)	C(42)	1.3920(17)
O(3)	C(45)	1.4278(15)	C(42)	C(43)	1.3879(17)
O(3)	C(48)	1.4351(18)	C(43)	C(44)	1.3928(16)
C(45)	C(46)	1.5091(18)			

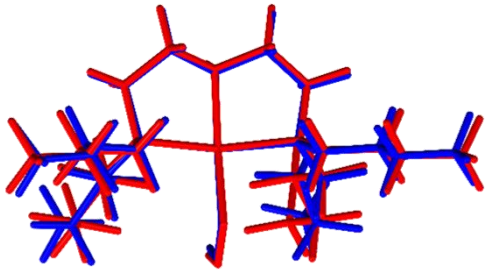
Table S1.3 Experimental bond lengths for non-hydrogen atoms determined by single-crystal X-ray diffraction for the excited state (ES) structure of **1** at 100 K. All bond lengths are all given in Å.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pd(1)	O(1A)	2.0418(9)	C(46)	C(47)	1.538(3)
Pd(1)	N(2)	2.0804(9)	C(47)	C(48)	1.478(3)
Pd(1)	N(3)	2.0137(9)	C(21)	C(22)	1.4046(17)
Pd(1)	N(4)	2.0901(9)	C(21)	C(26)	1.4021(17)
O(1A)	N(1A)	1.3010(15)	C(21)	B(1)	1.6430(17)
O(2A)	N(1A)	1.2070(17)	C(22)	C(23)	1.3919(19)
N(2)	C(1)	1.5033(15)	C(23)	C(24)	1.390(2)
N(2)	C(5)	1.4953(14)	C(24)	C(25)	1.388(2)
N(2)	C(9)	1.5028(15)	C(25)	C(26)	1.3960(17)
N(3)	C(2)	1.4854(14)	C(27)	C(28)	1.4019(15)
N(3)	C(3)	1.4790(14)	C(27)	C(32)	1.4044(16)
N(4)	C(4)	1.5046(14)	C(27)	B(1)	1.6385(16)
N(4)	C(13)	1.4921(14)	C(28)	C(29)	1.3958(17)
N(4)	C(17)	1.5022(14)	C(29)	C(30)	1.390(2)
C(1)	C(2)	1.5134(16)	C(30)	C(31)	1.392(2)
C(3)	C(4)	1.5141(15)	C(31)	C(32)	1.3921(16)
C(5)	C(6)	1.5178(16)	C(33)	C(34)	1.4087(15)
C(6)	C(7)	1.5257(17)	C(33)	C(38)	1.4036(14)
C(7)	C(8)	1.5202(19)	C(33)	B(1)	1.6450(16)
C(9)	C(10)	1.5258(16)	C(34)	C(35)	1.3926(16)
C(10)	C(11)	1.5198(18)	C(35)	C(36)	1.3921(17)
C(11)	C(12)	1.5217(19)	C(36)	C(37)	1.3911(16)
C(13)	C(14)	1.5163(16)	C(37)	C(38)	1.3940(15)
C(14)	C(15)	1.5225(17)	C(39)	C(40)	1.4021(17)
C(15)	C(16)	1.517(2)	C(39)	C(44)	1.4094(15)
C(17)	C(18)	1.5273(15)	C(39)	B(1)	1.6473(17)
C(18)	C(19)	1.5201(17)	C(40)	C(41)	1.3980(17)
C(19)	C(20)	1.5194(17)	C(41)	C(42)	1.3883(18)
O(3)	C(45)	1.4219(18)	C(42)	C(43)	1.392(2)
O(3)	C(48)	1.432(2)	C(43)	C(44)	1.3862(18)
C(45)	C(46)	1.518(2)			

(a)

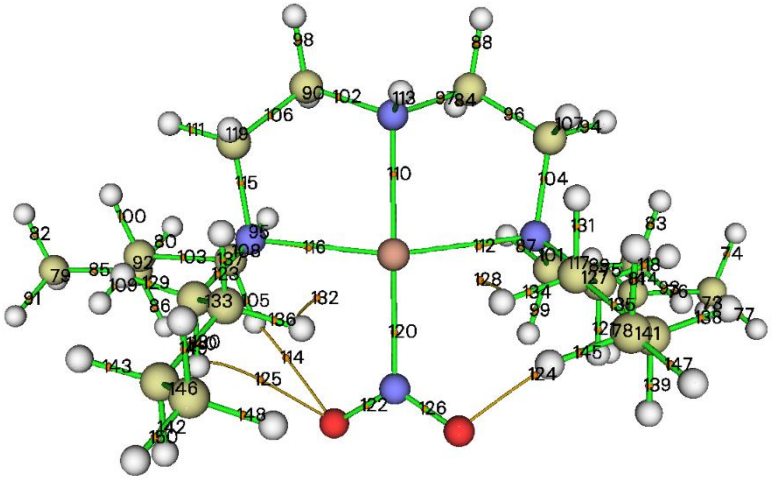


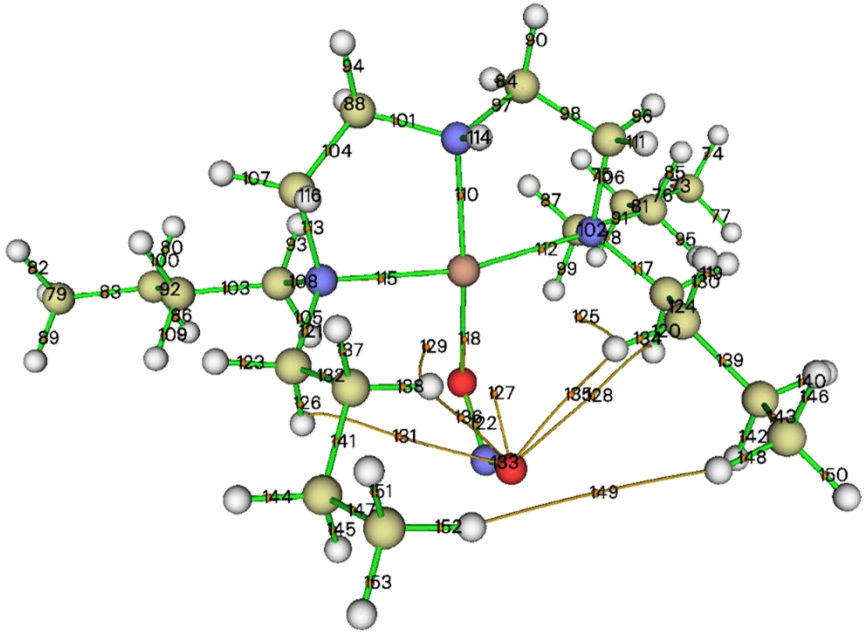
GS nitro-(η^1-NO_2): RMSD = 0.3861



ES nitrito-(η^1-ONO): RMSD = 0.1802

(b)





(c)

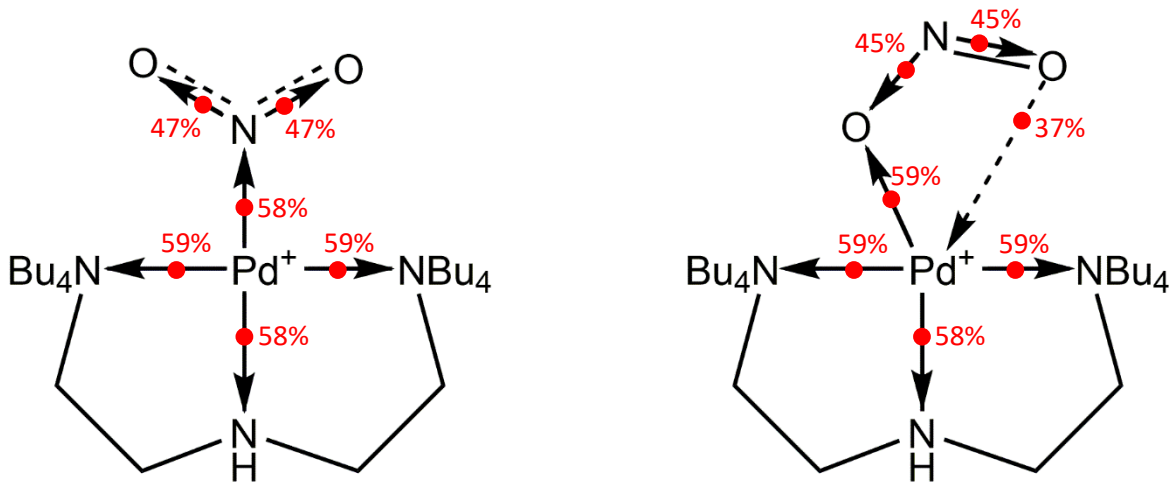


Figure S1.2 Theoretical analysis of the ground and photoexcited isomers of the photoactive $[Pd(Bu_4dien)(NO_2)]^+$ cation in **1**, from gas-phase molecular DFT calculations using Gaussian-09[3] [B3LYP/SDD for Pd and B3LYP/6-311+G(d) for C, H, N, and O]. **(a)** Molecular overlays between the geometry optimised structures (red) and experimental crystal structures (blue) of the cations in the GS and ES. **(b)** Diagrams showing the positions of (3,-1) bond critical points for the optimised GS and ES cations, generated from theoretical topology analysis in Multiwfn[4] (note: though CPs are found in each instance of interaction, the software does not generate the complete bond paths to Pd in the figures in some cases). **(c)** Graphical representations of the Pd^{II} square plane for the GS and ES cations, highlighting the positions of key (3,-1) bond critical points (red points) as a percentage along the relevant bond paths. % positions are always defined along the direction highlighted by the arrows (e.g. Pd→N is defined as the % along the path from Pd to N).

Table S1.4 List of (3,-1) bond critical points (CPs) generated from theoretical topological analysis of the GS photoactive cation of **1**. Wavefunction calculated with Gaussian-09[3] [B3LYP/SDD for Pd and B3LYP/6-311+G(d) for C, H, N, and O] and CPs searched and visualised using Multiwfn.[4]

CP #	XYZ Coordinates (Bohr)			Type	Atom1 – Atom2
73	-10.6146	-8.3370905	-2.9121	(3,-1)	H(12C) – C(12)
74	-11.0199	-7.40527806	-1.02951	(3,-1)	H(12A) – C(12)
75	-7.03457	-7.21984872	-1.53897	(3,-1)	H(11A) – C(11)
76	-9.17633	-6.74246675	-2.1701	(3,-1)	C(12) – C(11)
77	-11.2972	-6.30939098	-2.84558	(3,-1)	C(12) – H(12B)
78	-7.31035	-6.13304809	-3.34308	(3,-1)	C(11) – H(11B)
79	11.23849	-7.89559283	-1.87616	(3,-1)	H(20B) – C(20)
80	7.616283	-6.88300501	-0.53364	(3,-1)	H(19A) – C(19)
81	-7.63524	-5.07107049	-1.39944	(3,-1)	C(11) – C(10)
82	11.61646	-6.60067287	-0.21657	(3,-1)	H(20A) – C(20)
83	-7.95197	-3.96210853	0.572071	(3,-1)	H(10A) – C(10)
84	-2.00107	-3.39056212	4.433096	(3,-1)	H(2A) – C(2)
85	9.672739	-6.33291781	-1.35439	(3,-1)	C(20) – C(19)
86	7.714017	-6.12279334	-2.51407	(3,-1)	C(19) – H(19B)
87	-3.95449	-3.90550023	-0.12746	(3,-1)	H(9B) – C(9)
88	-2.43921	-2.21405609	6.240763	(3,-1)	H(2B) – C(2)
89	-6.16269	-3.36747657	-0.62981	(3,-1)	C(10) – C(9)
90	2.551774	-2.92813313	4.692567	(3,-1)	H(3B) – C(3)
91	11.71313	-5.83595826	-2.21167	(3,-1)	C(20) – H(20C)
92	8.001229	-4.69731011	-0.81046	(3,-1)	C(19) – C(18)
93	-8.25111	-2.86714784	-1.22939	(3,-1)	C(10) – H(10B)
94	-5.60559	-1.63663058	3.82743	(3,-1)	H(1B) – C(1)
95	4.26109	-3.66895336	0.351241	(3,-1)	H(17A) – C(17)
96	-3.37284	-1.50296767	4.20765	(3,-1)	C(2) – C(1)
97	-1.3822	-1.56298378	4.673064	(3,-1)	C(2) – N(3)
98	2.742164	-1.51243968	6.360893	(3,-1)	H(3A) – C(3)
99	-4.31587	-2.72229696	-1.89102	(3,-1)	C(9) – H(9A)
100	8.261477	-3.22821572	0.915981	(3,-1)	H(18B) – C(18)
101	-4.4872	-1.98537644	-0.04427	(3,-1)	C(9) – N(2)
102	1.590538	-1.23724614	4.752079	(3,-1)	C(3) – N(3)
103	6.388641	-3.02202061	-0.29558	(3,-1)	C(18) – C(17)
104	-4.32814	-0.77240764	2.426717	(3,-1)	C(1) – N(2)
105	4.456796	-2.7360447	-1.59009	(3,-1)	C(17) – H(17B)
106	3.541836	-0.85428526	4.258472	(3,-1)	C(3) – C(4)
107	-4.68126	0.3033856	4.135576	(3,-1)	C(1) – H(1A)
108	4.614635	-1.72519225	0.127786	(3,-1)	C(17) – N(4)
109	8.410806	-2.45776088	-1.06151	(3,-1)	C(18) – H(18A)
110	0.018307	-0.35864791	2.630927	(3,-1)	Pd(1) – N(3)

111	5.770512	-0.58959519	3.87549	(3,-1)	H(4A) – C(4)
112	-2.43914	-0.30224592	0.544757	(3,-1)	Pd(1) – N(2)
113	-0.12999	0.68988262	4.893236	(3,-1)	N(3) – H(3)
114	3.213169	-1.70954513	-3.09913	(3,-1)	H(17B) … O(1)
115	4.359007	-0.17513343	2.400537	(3,-1)	C(4) – N(4)
116	2.437865	-0.11448571	0.544523	(3,-1)	Pd(1) – N(4)
117	-5.05214	0.76160971	0.254633	(3,-1)	N(2) – C(5)
118	-6.92605	1.41534019	0.329406	(3,-1)	H(5A) – C(5)
119	4.474816	1.15667089	3.951092	(3,-1)	C(4) – H(4B)
120	-0.01647	0.23004774	-1.85159	(3,-1)	Pd(1) – N(1)
121	-5.69124	1.51237323	-1.46385	(3,-1)	C(5) – H(5B)
122	0.799158	0.0695472	-4.07133	(3,-1)	O(1) – N(1)
123	4.94726	1.06948561	0.003754	(3,-1)	N(4) – C(13)
124	-3.93892	1.50035489	-2.78131	(3,-1)	H(5B) … O(2)
125	3.822251	0.60997591	-3.15315	(3,-1)	O(1) … H(13A)
126	-0.88006	0.96667765	-3.91275	(3,-1)	N(1) – O(2)
127	-5.17974	2.94895727	0.285973	(3,-1)	C(5) – C(6)
128	-2.30591	2.9685138	0.231197	(3,-1)	H(6B) … Pd(1)
129	6.769723	1.86422108	-0.08749	(3,-1)	C(13) – H(13B)
130	5.490564	1.59644156	-1.82588	(3,-1)	C(13) – H(13A)
131	-4.71724	4.36899359	1.944402	(3,-1)	H(6A) – C(6)
132	2.07756	3.07355619	-0.24149	(3,-1)	H(14A) … Pd(1)
133	4.915483	3.2505081	-0.29384	(3,-1)	C(13) – C(14)
134	-3.49404	4.3829634	0.199286	(3,-1)	C(6) – H(6B)
135	-5.60273	5.29373816	0.054107	(3,-1)	C(6) – H(6A)
136	3.129062	4.54891147	-0.51154	(3,-1)	H(14A) – C(14)
137	4.411841	4.87426652	1.15399	(3,-1)	H(14B) – C(14)
138	-7.66349	6.14328664	-0.085	(3,-1)	H(7B) – C(7)
139	-6.4286	6.1863319	-1.81898	(3,-1)	C(7) – H(7A)
140	5.16231	5.55394368	-0.89607	(3,-1)	C(14) – C(15)
141	-5.95442	7.65367797	-0.13137	(3,-1)	C(7) – C(8)
142	5.860878	6.20070667	-2.91714	(3,-1)	C(15) – H(15B)
143	7.150985	6.505207	-1.25224	(3,-1)	C(15) – H(15A)
144	-5.53044	9.14960822	1.521923	(3,-1)	H(8A) – C(8)
145	-4.28933	9.19222184	-0.21854	(3,-1)	C(8) – H(8B)
146	5.336764	7.87623474	-1.45242	(3,-1)	C(15) – C(16)
147	-6.30675	9.89420489	-0.32574	(3,-1)	C(8) – H(8C)
148	3.565181	9.27047705	-1.70214	(3,-1)	C(16) – C(16C)
149	4.859956	9.57560158	-0.0273	(3,-1)	C(16) – C(16A)
150	5.524207	10.07695928	-1.99726	(3,-1)	C(16) – C(16B)

Table S1.5 List of (3,-1) bond critical points (CPs) generated from theoretical topological analysis of the ES photoactive cation of **1**. Wavefunction calculated with Gaussian-09[3] [B3LYP/SDD for Pd and B3LYP/6-311+G(d) for C, H, N, and O] and CPs searched and visualised using Multiwfn.[4]

CP #	XYZ Coordinates (Bohr)			Type	Atoms
73	-10.7025	-8.26687	-2.70173	(3,-1)	H(12C) – C(12)
74	-11.2114	-7.07432	-0.9996	(3,-1)	H(12A) – C(12)
75	-7.19173	-7.1808	-1.14082	(3,-1)	H(11A) – C(11)
76	-9.23286	-6.67005	-2.02853	(3,-1)	C(12) – (C11)
77	-11.2502	-6.21351	-2.95758	(3,-1)	C(12) – H(12B)
78	-7.233	-6.31412	-3.07918	(3,-1)	C(11) – H(11B)
79	10.70243	-8.26692	-2.70174	(3,-1)	H(20B) – C(20)
80	7.191657	-7.18082	-1.14086	(3,-1)	H(19B) – C(19)
81	-7.65975	-5.002	-1.31685	(3,-1)	C(11) – C(10)
82	11.21136	-7.07443	-0.99956	(3,-1)	H(20A) – C(20)
83	9.23281	-6.6701	-2.02852	(3,-1)	C(20) – C(19)
84	-2.26888	-3.26614	4.59452	(3,-1)	H(2A) – C(2)
85	-8.07027	-3.64274	0.474946	(3,-1)	H(10A) – C(10)
86	7.232975	-6.31411	-3.07921	(3,-1)	C(19) – H(19A)
87	-4.02466	-3.90877	0.08521	(3,-1)	H(9B) – C(9)
88	2.268881	-3.26613	4.59453	(3,-1)	H(3B) – C(3)
89	11.2502	-6.21357	-2.95752	(3,-1)	C(20) – H(20C)
90	-2.63549	-1.9562	6.318058	(3,-1)	H(2B) – C(2)
91	-6.1544	-3.29464	-0.62456	(3,-1)	C(10) – C(9)
92	7.659716	-5.00203	-1.31684	(3,-1)	C(19) – C(18)
93	4.024643	-3.90877	0.085234	(3,-1)	H(17A) – C(17)
94	2.63548	-1.95619	6.318067	(3,-1)	H(3A) – C(3)
95	-8.15104	-2.767	-1.46435	(3,-1)	C(10) – H(10B)
96	-5.70963	-1.29	3.801037	(3,-1)	H(1B) – C(1)
97	-1.47679	-1.48143	4.738006	(3,-1)	C(2) – N(3)
98	-3.46929	-1.3041	4.236124	(3,-1)	C(2) – C(1)
99	-4.16914	-2.8421	-1.78276	(3,-1)	C(9) – H(9A)
100	8.070248	-3.6428	0.474969	(3,-1)	H(18B) – C(18)
101	1.476782	-1.48143	4.738012	(3,-1)	C(3) – N(3)
102	-4.4505	-1.97013	-0.0156	(3,-1)	C(9) – N(2)
103	6.154388	-3.29467	-0.62453	(3,-1)	C(18) – C(17)
104	3.469281	-1.3041	4.236136	(3,-1)	C(3) – C(4)
105	4.169128	-2.84211	-1.78274	(3,-1)	C(17) – H(17B)
106	-4.33829	-0.6023	2.409077	(3,-1)	C(1) – N(2)
107	5.709626	-1.28999	3.801055	(3,-1)	H(4A) – C(4)
108	4.450491	-1.97014	-0.01558	(3,-1)	C(17) – N(4)
109	8.151033	-2.76703	-1.46432	(3,-1)	C(18) – H(18A)
110	-1.2E-06	-0.44256	2.711972	(3,-1)	Pd(1) – N(3)
111	-4.65221	0.59677	4.027171	(3,-1)	C(1) – H(1A)
112	-2.39835	-0.32992	0.584261	(3,-1)	Pd(1) – N(2)
113	4.338283	-0.6023	2.40909	(3,-1)	C(4) – N(4)
114	-5.1E-06	0.622537	4.947088	(3,-1)	N(3) – H(3)
115	2.398349	-0.32993	0.584268	(3,-1)	Pd(1) – N(4)

116	4.652193	0.59678	4.027178	(3,-1)	C(4) – H(4B)
117	-4.9064	0.816916	0.079667	(3,-1)	N(2) – C(5)
118	5.53E-06	-0.19377	-1.83709	(3,-1)	Pd(1) – O(1A)
119	-6.77237	1.491894	-0.09378	(3,-1)	H(5A) – C(5)
120	-5.32945	1.521115	-1.71132	(3,-1)	C(5) – H(5B)
121	4.906405	0.8169	0.07967	(3,-1)	N(4) – C(13)
122	1.42E-06	0.764202	-4.16759	(3,-1)	O(1A) – N(1A)
123	6.772389	1.491866	-0.09379	(3,-1)	H(13B) – C(13)
124	-5.01568	3.024749	0.044152	(3,-1)	C(5) – C(6)
125	-2.17382	2.944062	0.268807	(3,-1)	Pd(1) … H(6B)
126	5.329459	1.52108	-1.71133	(3,-1)	C(13) – H(13A)
127	-1E-05	2.286559	-2.13512	(3,-1)	Pd(1) … O(2A)
128	-2.86043	2.495311	-2.75241	(3,-1)	H(5B) … O(2A)
129	2.173841	2.944055	0.268786	(3,-1)	Pd(1) … H(14A)
130	-4.85502	4.506161	1.692769	(3,-1)	H(6A) – C(6)
131	2.860424	2.495269	-2.75245	(3,-1)	H(13A) … O(2A)
132	5.015704	3.024732	0.044135	(3,-1)	C(13) – C(14)
133	-1.1E-05	2.553902	-4.31788	(3,-1)	N(1A) – O(2A)
134	-3.31015	4.422125	0.209293	(3,-1)	C(6) – H(6B)
135	-1.573	3.960236	-1.46794	(3,-1)	H(6B) … O(2A)
136	1.573	3.960233	-1.46796	(3,-1)	O(2A) … H(14A)
137	4.855042	4.50616	1.692738	(3,-1)	H(14B) – C(14)
138	3.310181	4.422114	0.209263	(3,-1)	C(14) – H(14A)
139	-5.33678	5.34725	-0.37517	(3,-1)	C(6) – C(7)
140	-7.31665	6.204588	-0.9622	(3,-1)	H(7B) – C(7)
141	5.336814	5.347227	-0.37521	(3,-1)	C(14) – C(15)
142	-5.75243	6.172321	-2.40723	(3,-1)	C(7) – H(7A)
143	-5.61049	7.701312	-0.71581	(3,-1)	C(7) – C(8)
144	7.31669	6.204545	-0.96225	(3,-1)	H(15A) – C(15)
145	5.752457	6.172286	-2.40727	(3,-1)	C(15) – H(15B)
146	-5.50336	9.255948	0.933	(3,-1)	H(8A) – C(8)
147	5.610539	7.701285	-0.71586	(3,-1)	C(15) – C(16)
148	-3.93945	9.220651	-0.52758	(3,-1)	C(8) – H(8B)
149	2.89E-05	9.191332	-0.59044	(3,-1)	H(8B) … H(16C)
150	-5.88538	9.932486	-1.05942	(3,-1)	C(8) – H(8C)
151	5.50347	9.255939	0.932936	(3,-1)	H(16A) – C(16)
152	3.939515	9.220631	-0.52759	(3,-1)	C(16) – H(16C)
153	5.885424	9.932454	-1.0595	(3,-1)	C(16) – H(16B)

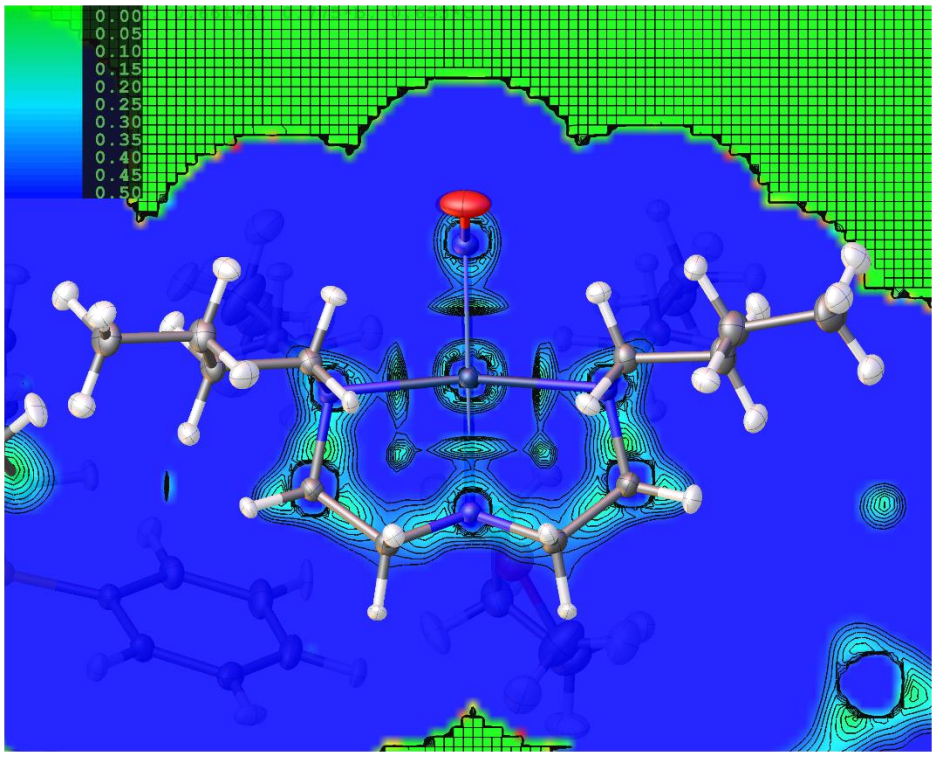
Table S1.6 Theoretical Natural Bond Orbital (NBO) analysis for the covalent bonds in the GS nitro-(η^1-NO_2) and ES nitrito-(η^1-ONO) ligands of **1**, calculated with Gaussian-09[3] [B3LYP/SDD for Pd and B3LYP/6-311+G(d) for C, H, N, and O)].

	Bond	Occupancy [electrons]	Localisation weights [atom type (%)]	Bond type
GS	N(1) – O(1)	(i) 1.98939	(i) N (48.62%), O (51.4%)	(i) σ(N-O)
		(ii) 1.98298	(ii) N (44.8%), O (55.9%)	(ii) π(N-O)
	N(1) – O(2)	1.98928	N (49.7%), O (50.3%)	σ(N-O)
ES	N(1A) – O(1A)	1.97594	N (39.6%), O (60.4%)	σ(N-O)
	N(1A) – O(2A)	(i) 1.99581	(i) N (35.4%), O (64.6%)	(i) π(N-O)
		(ii) 1.99027	(ii) N (44.2%), O (55.8%)	(ii) σ(N-O)

Table S1.7 Calculated Wiberg bond orders/indices from Natural Bond Orbital (NBO) analysis for selected bonds in the GS nitro-(η^1-NO_2) and ES nitrito-(η^1-ONO) isomers of **1**, calculated with Gaussian-09[3] [B3LYP/SDD for Pd and B3LYP/6-311+G(d) for C, H, N, and O)].

GS		ES	
Bond	**Bond order**	**Bond**	**Bond order**
Pd(1) – N(1)	0.8783	Pd(1) – O(1A)	0.8282
Pd(1) – N(2)	0.3794	Pd(1) – N(2)	0.4387
Pd(1) – N(3)	0.6327	Pd(1) – N(3)	0.5879
Pd(1) – N(4)	0.3755	Pd(1) – N(4)	0.4387
N(1) – O(1)	1.4392	N(1A) – O(1A)	1.1751
N(1) – O(2)	1.4456	N(1A) – O(2A)	1.7825

(a)



(b)

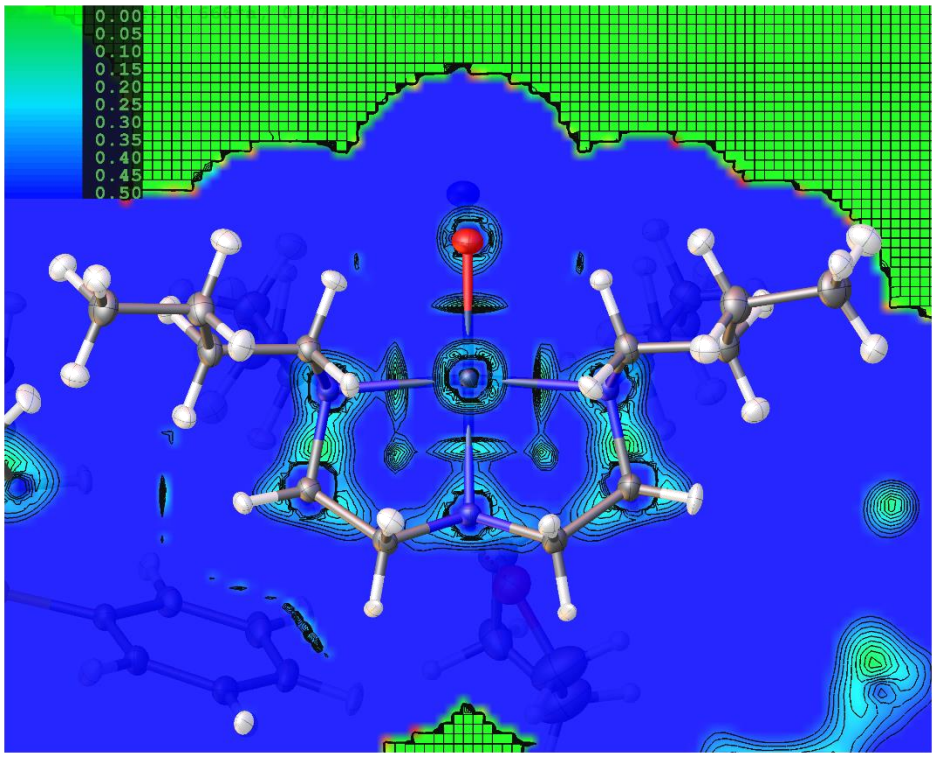


Figure S1.3 Reduced density gradient (RDG, *s*) 2D plots in the Pd(1), N(2), N(3), N(4) plane for the GS **(a)** and ES **(b)** of **1**, showing non-covalent interaction (NCI) features generated by HAR analysis in NoSpherA2.[2]

Supplementary Movies for Complex 1

SupplementaryMovie1.gif

Rotating 3D deformation density map for Complex **1** in the GS nitro-(η^1-NO_2) isomer.

https://doi.org/10.6084/m9.figshare.21586767

SupplementaryMovie2.gif

Rotating 3D deformation density map for Complex **1** in the ES nitrito-(η^1-ONO) isomer.

https://doi.org/10.6084/m9.figshare.21586773

SupplementaryMovie3.gif

Rotating 3D Laplacian map for Complex **1** in the GS nitro-(η^1-NO_2) isomer.

https://doi.org/10.6084/m9.figshare.21586782

SupplementaryMovie4.gif

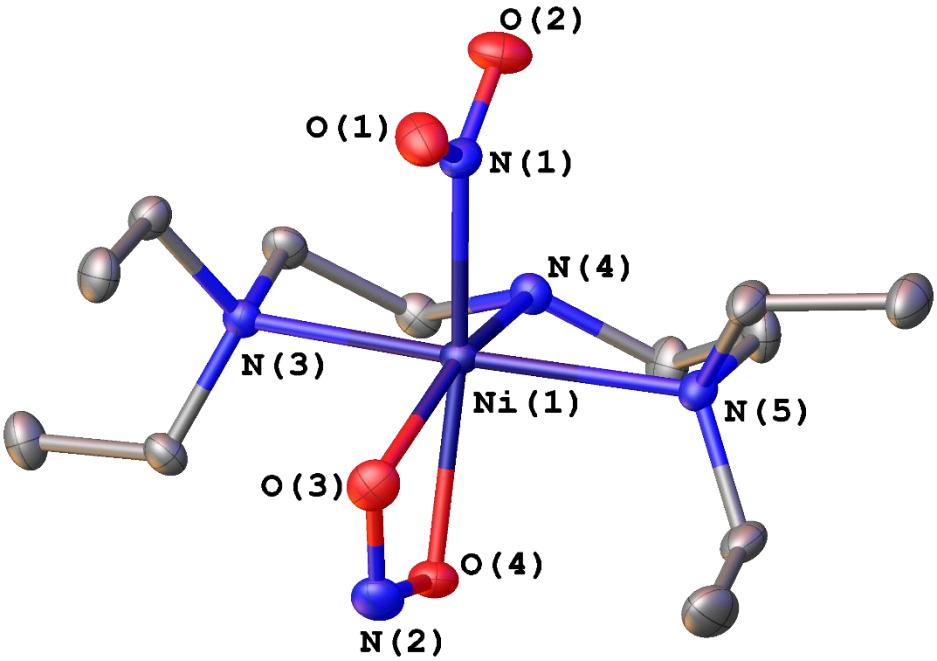
Rotating 3D Laplacian map for Complex **1** in the ES nitrito-(η^1-ONO) isomer.

https://doi.org/10.6084/m9.figshare.21586785

Supplementary movies can be accessed on FigShare via the links provided.

2. Complex 2: [Ni(Et$_4$dien)(NO$_2$)$_2$].

(a)



(b)

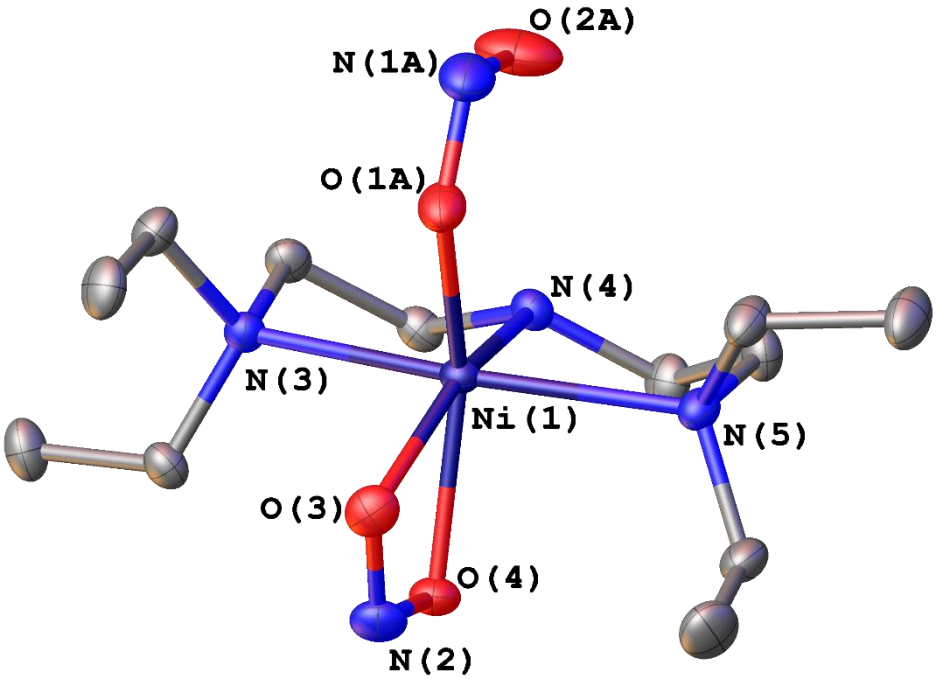


Figure S2.1 Single crystal X-ray structures showing the atomic connectivity in the asymmetric units of the ground state (a) and 100% photoexcited state (b) isomers of **2**,[5] with selected non-hydrogen atoms labelled. Ellipsoids are shown and 50% probability and hydrogen atoms are removed for clarity.

Table S2.1 Single-crystal X-ray structure data for **2** collected for HAR using NoSpherA2 in Olex2.[2]

	Ground state (GS)	**Excited state (ES)**
Photoexcitation level/%	0	100
Empirical formula	$C_{12}H_{29}N_5NiO_4$	$C_{12}H_{29}N_5NiO_4$
Formula weight	366.089	366.089
Temperature/K	100(1)	100(1)
Crystal system	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$
***a*/Å**	11.29901(16)	11.5006(2)
***b*/Å**	11.5909(2)	11.6540(2)
***c*/Å**	12.83109(18)	12.8103(2)
***α*/°**	90	90
***β*/°**	90	90
***γ*/°**	90	90
Volume/Å^3	1680.43(4)	1716.94(5)
Z	4	4
ρ_{calc}**/gcm^{-3}**	1.447	1.416
μ**/mm^{-1}**	1.179	1.154
***F*(000)**	786.0	786.0
Radiation	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	7.26 to 72.62	7.26 to 72.64
Completeness (resolution)	0.9960 (0.6 Å)	0.9955 (0.6 Å)
Reflections collected	12104	16753
Independent reflections	7857 [R_{int} = 0.0236, R_{sigma} = 0.0440]	8292 [R_{int} = 0.0270, R_{sigma} = 0.0410]
Data/restraints/parameters	7857/147/460	8292/147/460
Goodness-of-fit on F^2	1.064	1.030
Final *R* indexes [I>=2σ (I)]	R_1 = 0.0304, wR_2 = 0.0588	R_1 = 0.0303, wR_2 = 0.0595
Final *R* indexes [all data]	R_1 = 0.0367, wR_2 = 0.0625	R_1 = 0.0375, wR_2 = 0.0631
Largest diff. peak/hole / e Å^{-3}	0.46/-0.32	0.50/-0.25
Flack parameter	0.003(5)	-0.007(5)

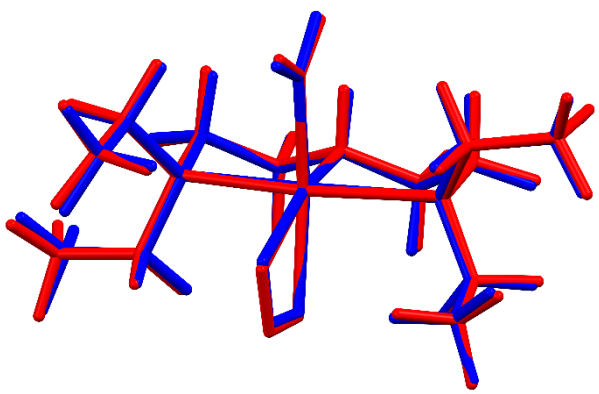
Table S2.2 Experimental bond lengths for non-hydrogen atoms determined by single-crystal X-ray diffraction of the photoactive [Ni(Et_4dien)(NO_2)$_2$] molecule (**2)**, in the ground state (GS) at 100 K. All bond lengths are all given in Å.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ni(1)	N(4)	2.0162(10)	N(5)	C(4)	1.4887(17)
Ni(1)	N(5)	2.2899(11)	N(3)	C(5)	1.4902(16)
Ni(1)	N(3)	2.2743(11)	N(3)	C(7)	1.4884(16)
Ni(1)	O(3)	2.1000(9)	N(3)	C(1)	1.4841(16)
Ni(1)	O(4)	2.1112(9)	N(2)	O(3)	1.2605(16)
Ni(1)	N(1)	2.0295(11)	N(2)	O(4)	1.2565(15)
O(2)	N(1)	1.2521(15)	C(5)	C(6)	1.5141(18)
C(3)	N(4)	1.4623(17)	C(7)	C(8)	1.524(2)
C(3)	C(4)	1.515(2)	C(9)	C(10)	1.529(2)
N(4)	C(2)	1.4682(18)	C(12)	C(11)	1.521(2)
N(5)	C(9)	1.4858(17)	O(1)	N(1)	1.2260(14)
N(5)	C(11)	1.4891(17)	C(2)	C(1)	1.5151(19)

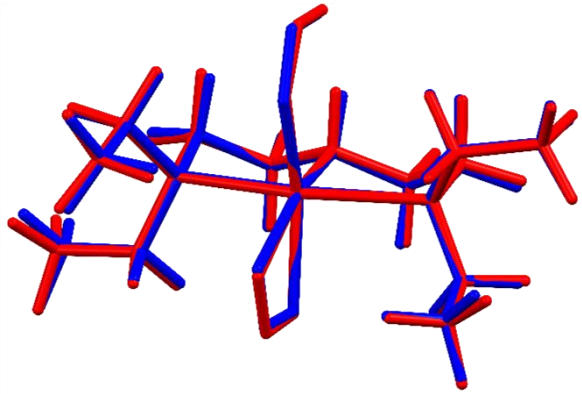
Table S2.3 Experimental bond lengths for non-hydrogen atoms determined by single-crystal X-ray diffraction of the photoactive [Ni(Et_4dien)(NO_2)$_2$] molecule (**2)**, in the excited state (ES) at 100 K. All bond lengths are all given in Å.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ni(1)	O(1A)	2.0074(9)	N(3)	C(7)	1.4904(16)
Ni(1)	O(3)	2.1080(9)	N(4)	C(2)	1.4688(16)
Ni(1)	O(4)	2.1221(9)	N(4)	C(3)	1.4628(16)
Ni(1)	N(3)	2.2792(10)	N(5)	C(4)	1.4864(16)
Ni(1)	N(4)	2.0223(10)	N(5)	C(9)	1.4853(16)
Ni(1)	N(5)	2.2997(10)	N(5)	C(11)	1.4912(17)
O(1A)	N(1A)	1.2674(16)	C(1)	C(2)	1.5099(18)
O(2A)	N(1A)	1.2070(17)	C(3)	C(4)	1.512(2)
O(3)	N(2)	1.2583(14)	C(5)	C(6)	1.5146(19)
O(4)	N(2)	1.2575(13)	C(7)	C(8)	1.525(2)
N(3)	C(1)	1.4887(15)	C(9)	C(10)	1.527(2)
N(3)	C(5)	1.4841(15)	C(11)	C(12)	1.519(2)

(a)

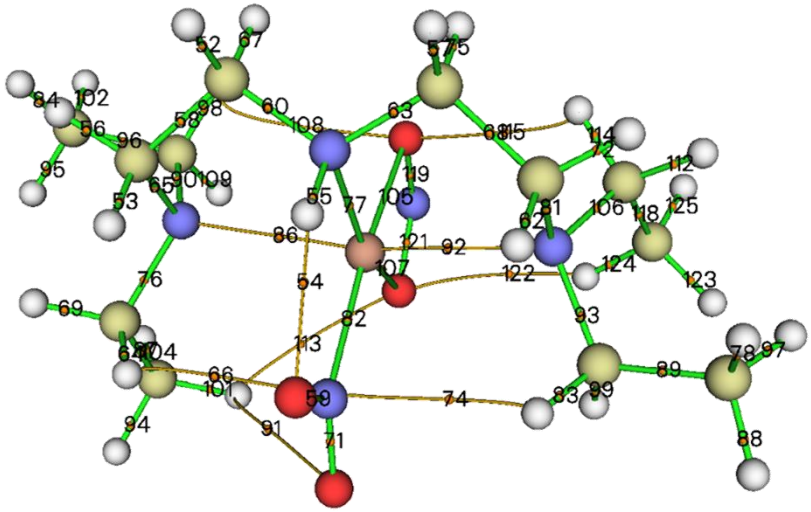


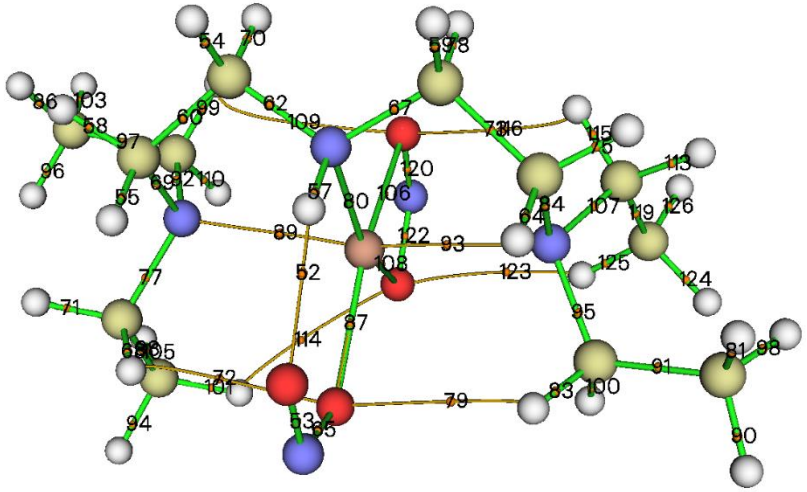
GS nitro-(η^1-<u>N</u>O$_2$): RMSD = 0.0926



ES nitrito-(η^1-<u>O</u>NO): RMSD = 0.1022

(b)





(C)

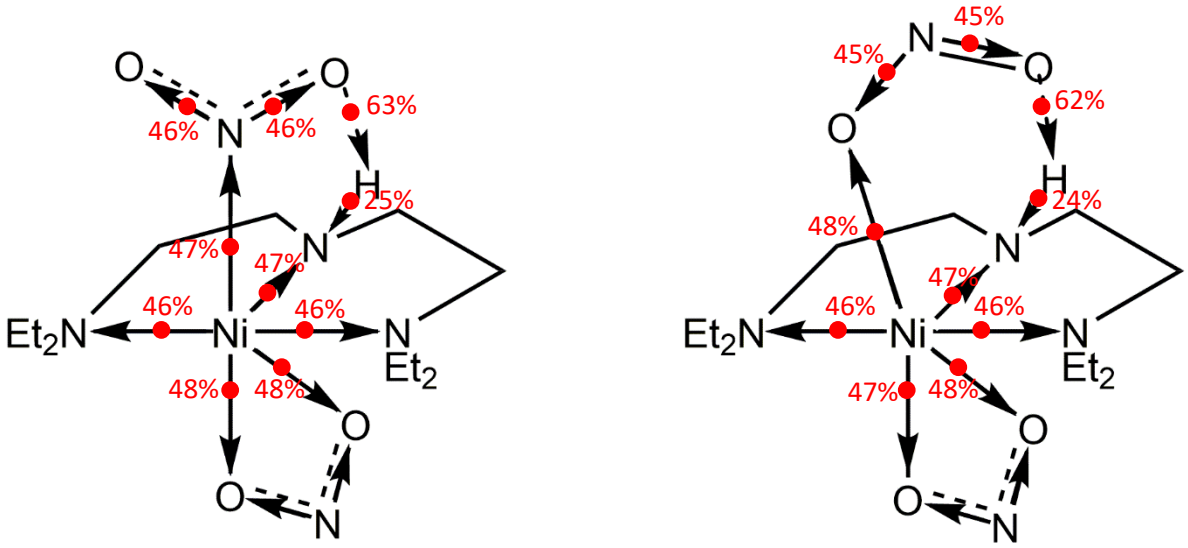


Figure S2.3 Theoretical analysis of the ground and photoexcited isomers of the [Ni(Et_4dien)(NO_2)$_2$] molecule in **2,** from gas-phase molecular DFT calculations using Gaussian-09[3] [B3LYP/SDD for Ni and B3LYP/6-311+G(d) for C, H, N, and O]. **(a)** Molecular overlays between the geometry optimised structures (red) and experimental crystal structures (blue) of the cations in the GS and ES. **(b)** Diagrams showing the positions of (3,-1) bond critical points for the optimised GS and ES cations, generated from theoretical topology analysis in Multiwfn[4]. **(c)** Graphical representations of the GS and ES molecules, highlighting the positions of key (3,-1) bond critical points (red points) as a percentage along the relevant bond paths. % positions are always defined along the direction highlighted by the arrows (e.g. Ni⟶N is defined as the % along the path from Ni to N).

Table S2.4 List of (3,-1) bond critical points (CPs) generated from theoretical topological analysis of the GS molecule of **2**. Wavefunction calculated with Gaussian-09[3] [B3LYP/SDD for Ni and B3LYP/6-311+G(d) for C, H, N, and O] and CPs searched and visualised using Multiwfn.[4]

CP #	XYZ Coordinates (Bohr)			Type	Atoms
52	-2.53093	-2.87384	5.210817	(3,-1)	H(2A) – C(2)
53	-4.33424	-3.53372	1.726293	(3,-1)	H(1B) – C(1)
54	0.253341	-4.23859	0.728009	(3,-1)	O(2) … H(4)
55	0.148758	-3.38821	2.310049	(3,-1)	H(4) – N(4)
56	-5.69803	-2.35854	2.899407	(3,-1)	H(1A) – C(1)
57	2.446156	-2.43864	5.444634	(3,-1)	H(3B) – C(3)
58	-3.46917	-2.13233	3.260304	(3,-1)	C(1) – C(2)
59	0.299691	-3.92998	-2.07032	(3,-1)	O(2) – N(1)
60	-1.42837	-2.02344	3.743065	(3,-1)	C(2) – N(4)
62	4.614263	-2.96263	2.16532	(3,-1)	H(4B) – C(4)
63	1.371031	-1.79772	3.856921	(3,-1)	N(4) – C(3)
64	-4.92864	-2.58418	-2.37788	(3,-1)	H(5A) – C(5)
65	-4.49153	-1.53051	1.449098	(3,-1)	C(1) – N(3)
66	-2.53373	-2.81636	-2.43892	(3,-1)	H(5A) … N(1)
67	-2.50876	-0.74994	4.831922	(3,-1)	C(2) – H(2B)
68	3.438557	-1.63869	3.54768	(3,-1)	C(3) – C(4)
69	-6.859	-1.8704	-1.7901	(3,-1)	H(5B) – C(5)
71	0.263288	-2.84907	-3.59145	(3,-1)	N(1) – O(1)
72	5.697982	-1.55579	3.387227	(3,-1)	C(4) – H(4A)
74	2.934756	-2.58449	-2.24963	(3,-1)	N(1) … H(9A)
75	2.167902	-0.34914	4.973205	(3,-1)	C(3) – H(3A)
76	-5.15125	-1.04429	-1.12319	(3,-1)	C(5) – N(3)
77	-0.01134	-0.87799	1.301336	(3,-1)	N(4) – Ni(1)
78	8.940855	-2.22897	-0.42102	(3,-1)	H(10C) – C(10)
81	4.534622	-0.96553	1.795995	(3,-1)	C(4) – N(5)
82	0.096929	-1.28221	-1.28689	(3,-1)	N(1) – Ni(1)
83	5.247024	-2.08151	-2.01155	(3,-1)	H(9A) – C(9)
84	-8.91659	1.035383	2.382587	(3,-1)	H(8B) – C(8)
86	-2.04373	-0.11847	0.057703	(3,-1)	N(3) – Ni(1)
87	-5.61845	-0.55613	-3.22295	(3,-1)	C(5) – C(6)
88	9.159984	-1.83686	-2.50228	(3,-1)	H(10A) – C(10)
89	7.256941	-1.12885	-1.5084	(3,-1)	C(10) – C(9)
90	-5.19561	0.987451	0.733244	(3,-1)	N(3) – C(7)
91	-2.16339	-0.76363	-4.66325	(3,-1)	O(1) … H(6C)
92	2.0118	0.102642	0.200243	(3,-1)	Ni(1) – N(5)
93	5.290524	-0.51374	-0.76429	(3,-1)	C(9) – N(5)
94	-6.07407	-0.37463	-5.39393	(3,-1)	H(6A) – C(6)
95	-9.21129	1.646599	0.358841	(3,-1)	H(8A) – C(8)
96	-7.122	1.920773	1.260787	(3,-1)	C(8) – C(7)
97	9.330833	-0.2423	-1.0981	(3,-1)	C(10) – H(10B)
98	-5.07949	2.382864	2.177644	(3,-1)	C(7) – H(7A)
99	5.602186	-0.08851	-2.70759	(3,-1)	C(9) – H(9B)
101	-4.39638	0.729914	-4.62459	(3,-1)	C(6) – H(6C)

102	-8.93775	3.102755	1.890764	(3,-1)	C(8) – H(8C)
104	-6.41369	1.331077	-4.16569	(3,-1)	C(6) – H(6B)
105	-0.16046	1.950131	0.575312	(3,-1)	Ni(1) – O(4)
106	5.056985	1.557666	1.039033	(3,-1)	N(5) – C(11)
107	-0.19567	1.812241	-1.22261	(3,-1)	Ni(1) – O(3)
108	-2.9103	3.053842	1.774468	(3,-1)	H(7A) … O(4)
109	-5.39569	2.904435	0.137965	(3,-1)	C(7) – H(7B)
112	6.610717	2.390647	2.011762	(3,-1)	H(11B) – C(11)
113	-2.44947	2.017477	-3.62156	(3,-1)	H(6C) … O(3)
114	4.594733	3.067936	2.291954	(3,-1)	C(11) – H(11A)
115	2.327879	3.460958	2.025198	(3,-1)	H(11A) … O(4)
118	5.635055	3.569112	0.303952	(3,-1)	C(11) – C(12)
119	-0.40723	4.437441	0.352377	(3,-1)	O(4) – N(2)
121	-0.42554	4.286265	-1.42114	(3,-1)	O(3) – N(2)
122	2.301282	4.287022	-1.92421	(3,-1)	O(3) … H(12A)
123	6.855954	4.250926	-1.46918	(3,-1)	C(12) – H(12C)
124	4.751793	4.661507	-1.47796	(3,-1)	C(12) – H(12A)
125	6.057793	5.71533	-0.14549	(3,-1)	C(12) – H(12B)

Table S2.5 List of (3,-1) bond critical points (CPs) generated from theoretical topological analysis of the ES molecule of **2**. Wavefunction calculated with Gaussian-09[3] [B3LYP/SDD for Ni and B3LYP/6-311+G(d) for C, H, N, and O] and CPs searched and visualised using Multiwfn.[4]

CP #	XYZ Coordinates (Bohr)			Type	Atoms
52	0.306823	-4.3973	0.871913	(3,-1)	O(2A) ... H(4)
53	0.429853	-5.14547	-2.16974	(3,-1)	O(2A) – N(1A)
54	-2.52241	-2.73518	5.163717	(3,-1)	H(2A) – C(2)
55	-4.32556	-3.45044	1.687351	(3,-1)	H(1B) – C(1)
57	0.16178	-3.30391	2.27956	(3,-1)	H(4) – N(4)
58	-5.69168	-2.2633	2.844855	(3,-1)	H(1A) – C(1)
59	2.454553	-2.27989	5.386912	(3,-1)	H(3B) – C(3)
60	-3.46266	-2.02662	3.202333	(3,-1)	C(1) – C(2)
62	-1.42125	-1.90851	3.680529	(3,-1)	C(2) – N(4)
64	4.618679	-2.8326	2.106634	(3,-1)	H(4A) – C(4)
65	0.299612	-3.59194	-3.09968	(3,-1)	N(1A) – O(1A)
67	1.373682	-1.67061	3.789919	(3,-1)	N(4) – C(3)
68	-4.86699	-2.54568	-2.43894	(3,-1)	H(5A) – C(5)
69	-4.4868	-1.45157	1.383978	(3,-1)	C(1) – N(3)
70	-2.5036	-0.6173	4.74896	(3,-1)	C(2) – H(2B)
71	-6.81635	-1.8513	-1.87949	(3,-1)	H(5B) – C(5)
72	-2.54547	-2.55301	-2.75672	(3,-1)	H(5A) … O(1A)
73	3.439556	-1.49982	3.478012	(3,-1)	C(3) – C(4)
75	5.699038	-1.40714	3.311036	(3,-1)	(C4) – H(4B)
77	-5.12566	-1.00061	-1.20111	(3,-1)	C(5) – N(3)
78	2.161264	-0.19882	4.885157	(3,-1)	C(3) – H(3A)
79	2.910391	-2.2527	-2.58716	(3,-1)	O(1A) … H(9A)
80	-0.00999	-0.78333	1.241593	(3,-1)	N(4) – Ni(1)
81	8.89745	-2.14667	-0.53181	(3,-1)	H(10C) – C(10)
83	5.185791	-1.97452	-2.0988	(3,-1)	H(9A) – C(9)
84	4.527718	-0.8391	1.718153	(3,-1)	C(4) – N(5)
86	-8.95378	1.075562	2.228895	(3,-1)	H(8A) – C(8)
87	0.081479	-0.99263	-1.63121	(3,-1)	O(1A) – Ni(1)
88	-5.57108	-0.53913	-3.30682	(3,-1)	C(5) – C(6)
89	-2.04224	-0.04045	-0.01019	(3,-1)	N(3) – Ni(1)
90	9.103055	-1.76747	-2.61637	(3,-1)	H(10A) – C(10)
91	7.211682	-1.04016	-1.61195	(3,-1)	C(10) – C(9)
92	-5.20998	1.04875	0.632895	(3,-1)	N(3) – C(7)
93	2.002864	0.207679	0.128372	(3,-1)	Ni(1) – N(4)
94	-5.9997	-0.37816	-5.48712	(3,-1)	H(6A) – C(6)
95	5.257854	-0.40819	-0.8551	(3,-1)	C(9) – N(5)
96	-9.22553	1.668861	0.197053	(3,-1)	H(8C) – C(8)
97	-7.15137	1.969342	1.12581	(3,-1)	C(8) – C(7)
98	9.295911	-0.16669	-1.22317	(3,-1)	C(10) – H(10B)
99	-5.12697	2.455823	2.068453	(3,-1)	C(7) – H(7A)
100	5.55672	0.008895	-2.79952	(3,-1)	C(9) – C(9B)
101	-4.34128	0.744479	-4.7011	(3,-1)	C(6) – H(6C)
103	-8.98747	3.139007	1.721393	(3,-1)	C(8) – H(8B)

105	-6.36823	1.335323	-4.28043	(3,-1)	C(6) – H(6B)
106	-0.17206	2.001866	0.536634	(3,-1)	Ni(1) – O(4)
107	5.045494	1.675445	0.934125	(3,-1)	N(5) – C(11)
108	-0.21095	1.913155	-1.25261	(3,-1)	Ni(1) – O(3)
109	-2.9427	3.109395	1.74688	(3,-1)	H(7A) ... O(4)
110	-5.41862	2.959882	0.020194	(3,-1)	C(7) – H(7B)
113	6.610967	2.514013	1.883946	(3,-1)	H(11B) – C(11)
114	-2.42974	2.08194	-3.6517	(3,-1)	H(6C) … O(3)
115	4.598953	3.194952	2.182208	(3,-1)	C(11) – H(11A)
116	2.321579	3.549487	1.979804	(3,-1)	H(11A) … O(4)
119	5.618262	3.681788	0.180076	(3,-1)	C(11) – C(12)
120	-0.43256	4.494361	0.38577	(3,-1)	O(4) – N(2)
122	-0.45423	4.392712	-1.39174	(3,-1)	O(3) – N(2)
123	2.278513	4.375142	-2.01687	(3,-1)	O(3) … H(12A)
124	6.821046	4.350758	-1.61081	(3,-1)	C(12) – H(12C)
125	4.716977	4.765286	-1.59947	(3,-1)	C(12) – H(12A)
126	6.040169	5.824848	-0.28855	(3,-1)	C(12) – H(12B)

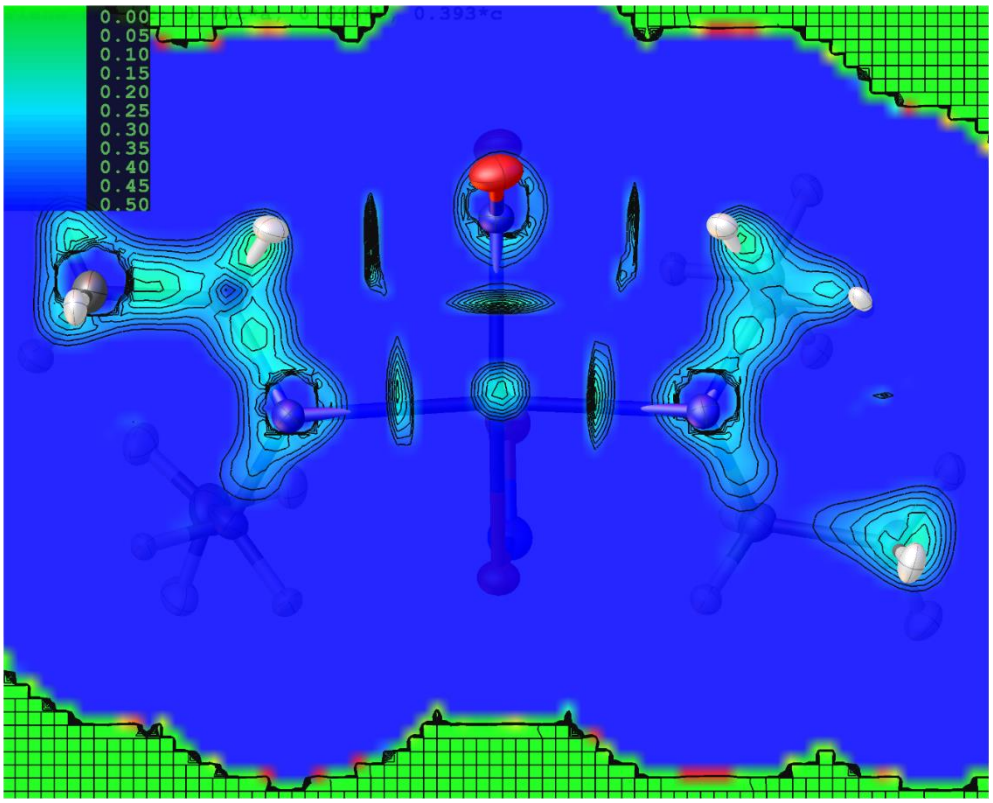
Table S2.6 Theoretical Natural Bond Orbital (NBO) analysis for the covalent bonds in the GS nitro-(η^1-$\underline{N}O_2$) and ES nitrito-(η^1-$\underline{O}NO$) ligands of **2**, calculated with Gaussian-09[3] [B3LYP/SDD for Ni and B3LYP/6-311+G(d) for C, H, N, and O)].

	Bond	Spin	Occupancy [electrons]	Localisation weights [atom type (%)]	Bond type
GS	N(1) – O(1)	α	0.99657	N (45.0%), O (55.0%)	σ(N-O)
	N(1) – O(2)	α	0.99585	N (45.5%), O (54.5%)	σ(N-O)
	N(1) – O(1)	β	(i) 0.99270	(i) N (44.1%), O (55.9%)	(i) σ(N-O)
		β	(ii) 0.99526	(ii) N (30.8%), O (69.2%)	(ii) π(N-O)
		β	(iii) 0.94078	(iii) N (58.3%), O (41.7%)	(ii) π(N-O)
	N(1) – O(2)	β	0.97874	N (52.0%), O (48.0%)	σ(N-O)
ES	N(1A) – O(1A)	α	0.99514	N (43.0%), O (57.0%)	σ(N-O)
	N(1A) – O(2A)	α	0.99631	N (43.4%), O (56.6%)	σ(N-O)
	N(1A) – O(1A)	β	0.98813	N (48.2%), O (51.8%)	σ(N-O)
	N(1A) – O(2A)	β	(i) 0.99625	(i) N (25.6%), O (73.4%)	(i) π(N-O)
		β	(ii) 0.98829	(ii) N (44.0%), O (56.0%)	(ii) σ(N-O)
		β	(iii) 0.98185	(iii) N (42.7%), O (57.3%)	(iii) π(N-O)

Table S2.7 Calculated Wiberg bond orders/indices from Natural Bond Orbital (NBO) analysis for selected bonds in the GS nitro-(η^1-$\underline{N}O_2$) and ES nitrito-(η^1-$\underline{O}NO$) isomers of **2**, calculated with Gaussian-09[3] [B3LYP/SDD for Ni and B3LYP/6-311+G(d) for C, H, N, and O)].

GS		ES	
Bond	**Bond order**	**Bond**	**Bond order**
Ni(1) – N(1)	0.2177	Ni(1) – O(1A)	0.2266
Ni(1) – N(3)	0.1393	Ni(1) – N(3)	0.1331
Ni(1) – N(4)	0.2040	Ni(1) – N(4)	0.1992
Ni(1) – N(5)	0.1360	Ni(1) – N(5)	0.1316
Ni(1) – O(3)	0.2377	Ni(1) – O(3)	0.2295
Ni(1) – O(4)	0.2247	Ni(1) – O(4)	0.2193
N(1) – O(1)	1.3014	N(1A) – O(1A)	1.1641
N(1) – O(2)	1.2126	N(1A) – O(2A)	1.3378
N(2) – O(3)	1.5120	N(2) – O(3)	1.5167
N(2) – O(4)	1.4864	N(2) – O(4)	1.4841

(a)



(b)

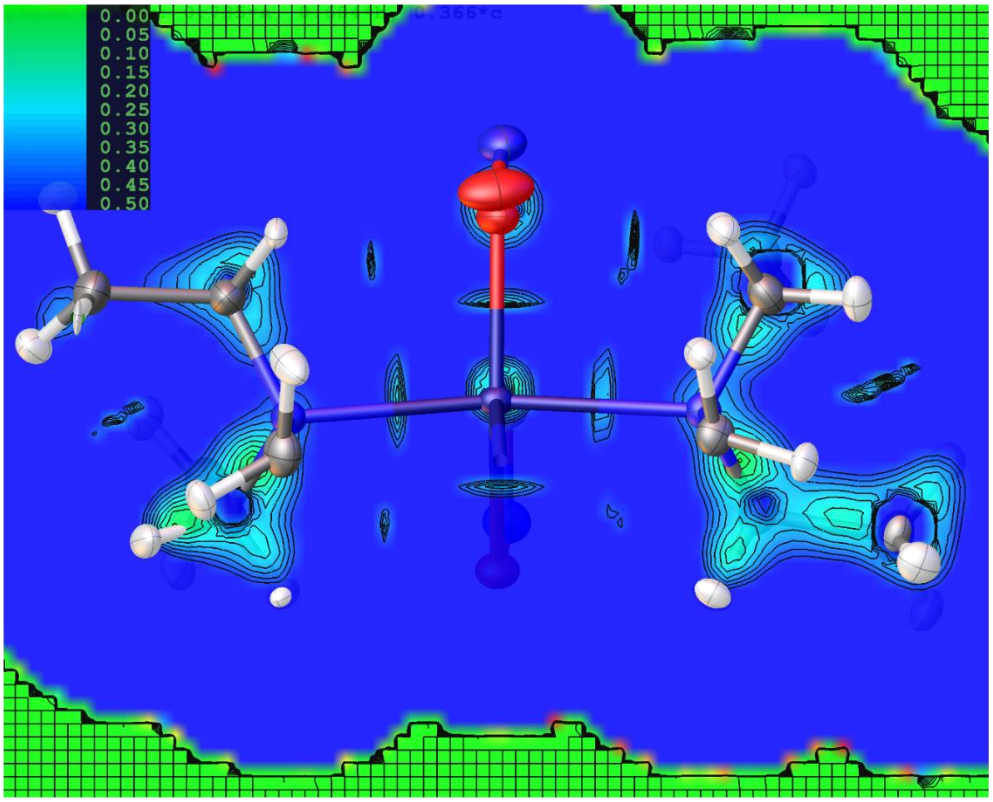


Figure S2.3 Reduced density gradient (RDG, *s*) 2D plots in the Ni(1), N(1), N(3), N(5) plane for the GS **(a)** and the Ni(1), O(1A), N(3), N(5) plane for the ES **(b)** of **2**, showing non-covalent interaction (NCI) features generated by HAR analysis in NoSpherA2.[2]

Supplementary Movies for Complex 2

SupplementaryMovie5.gif

Rotating 3D deformation density map for Complex **1** in the GS nitro-(η^1-NO_2) isomer.

https://doi.org/10.6084/m9.figshare.21586788

SupplementaryMovie6.gif

Rotating 3D deformation density map for Complex **1** in the ES nitrito-(η^1-ONO) isomer.

https://doi.org/10.6084/m9.figshare.21586794

SupplementaryMovie7.gif

Rotating 3D Laplacian map for Complex **1** in the GS nitro-(η^1-NO_2) isomer.

https://doi.org/10.6084/m9.figshare.21586797

SupplementaryMovie8.gif

Rotating 3D Laplacian map for Complex **1** in the ES nitrito-(η^1-ONO) isomer.

https://doi.org/10.6084/m9.figshare.21586800

Supplementary movies can be accessed on FigShare via the links provided.

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