Eur. J. Inorg. Chem. **2014** · © WILEY-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, 2014 · ISSN 1099–0682

SUPPORTING INFORMATION

DOI: 10.1002/ejic.201301598
Title: A Catalyst with Two-Coordinate Nickel: Theoretical and Catalytic Studies
Author(s): Kartik Chandra Mondal, Prinson P. Samuel, Yan Li, Herbert W. Roesky,* Sudipta Roy, Lutz Ackermann,* Navdeep S. Sidhu, George M. Sheldrick, Elena Carl, Serhiy Demeshko, Susmita De, Pattiyil Parameswaran, Liviu Ungur, Liviu F. Chibotaru, Diego M. Andrada

Contents

(S1) Synthesis

All reactions and handling of reagents were performed under an atmosphere of dry nitrogen or argon using standard Schlenk techniques or a glove box where the O_2 and H_2O levels were usually kept below 1 ppm. Ligand cAAC was prepared according to literature methods.[S1a] $NiCl_2$ and lithium diisopropylamide (LDA) were purchased from Sigma Aldrich. Solvents were purified with the M-Braun solvent drying system. Solution NMR spectra were recorded on Bruker Avance 200, Bruker Avance 300, and Bruker Avance 500 MHz NMR spectrometers. Deuterated NMR solvent C_6D_6 was dried by stirring for 2 days over Na/K alloy followed by distillation in vacuum and degassed. EI-MS spectra were obtained with a Finnigan MAT 8230 or a Varian MAT CH5 instrument (70 eV) by EI-MS methods. Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen. Melting points were measured in sealed glass tubes on a Büchi B-540 melting point apparatus.

Synthesis of compound $(cAAC)_2NiCl_2$ (**1**): A 2:1 molar mixture of cAAC (2 mmol, 570 mg) and $NiCl_2$ (1 mmol, 130 mg) was placed in a 50 mL round bottom flask and THF (30 mL) was added at room temperature. The color of the solution slowly changes to an yellow-orange slurry on stirring for four hours. Then the resultant slurry was heated at 70 °C for 3-4 hours to obtain a more intense orange slurry which was cooled to room temperature and stirred for 64 h to produce a clear orange solution and a little cream colored insoluble precipitate. The clear orange filtrate was dried under vacuum and extracted with toluene (200 mL) and crystallized as red rod at room temperature from a concentrated solution via slow evaporation. The yield of the reaction is 85%. Compound **1** decomposes above 188 °C. Anal. found for $C_{40}H_{62}N_2NiCl_2$ (calcd): C 68.54 (68.58), H 8.95 (8.92), N 3.95 (3.99). Compound **1** is stable in air for several weeks and completely soluble in THF and moderately soluble in toluene and benzene.

Procedure 1; Synthesis of compound $(cAAC)_2Ni$ (**2**): A 1:2 molar mixture of $(cAAC)_2NiCl_2$ (**1**) (1 mmol, 700 mg) and $LiN\textit{i}Pr_2$ (LDA) (2 mmol, 214 mg) was placed in a 100 mL round bottom flask and THF (70 mL) was added at room temperature to obtain a dark purple solution. The color of the solution remains the same even after stirring for one hour. The time of reaction was further optimized to fifteen minutes. This solution was treated under vacuum and the residue extracted with toluene (40 mL). The solvent of this solution was treated under vacuum to remove all volatiles. The resultant solid was again extracted in 20 mL of toluene to obtain a dark purple solution which was reduced to 5 mL and stored at -32 °C in a refrigerator to obtain dark shiny plates of $(cAAC)_2Ni$·toluene (**2**·toluene). The yield is 55%. The dark black shiny crystals of **2**·toluene were quickly washed with acetone and filtered and dried under vacuum. C, H and N analysis (%) found (calcd) for $C_{40}H_{62}N_2Ni$ (**2**); C 76.38 (76.30), H 9.85 (9.93), N 4.50 (4.45). Compound **2** shows a dark purple color in solution and is dark black in the solid state. Anal. calcd for $C_{40}H_{62}NiN_2$ (found): Decomposition was observed above 161 °C, UV-visible bands at 533, 611 (strong) and 807 (weak) nm; ^{1}H NMR (500.133 MHz, C_6D_6, δ ppm): 7.054-6.99 (m, 3H, H_{ar}), 2.94 (m (broad), 2H, $CHMe_2$), 1.65-1.63 (m (broad), 8H, $NCMe_2$ and CH_2), 1.22-1.20 (d, 12H, $CHMe_2$), 0.91 (s, 6H, CMe_2); ^{13}C: 242.4, 144.9, 138.1, 129.2, 127.8, 1.25.6, 123.8, 75.4, 55.45, 52.3, 28.9, 27.9, 27.6, 22.6.

Fehler! Es ist nicht möglich, durch die Bearbeitung von Feldfunktionen Objekte zu erstellen.

Scheme S1. The proposed mechanism of reduction of **1** to **2** with LDA (Lithium diisopropylamide) in the presence of cAAC. During the reaction formation hydrogen gas was not observed.

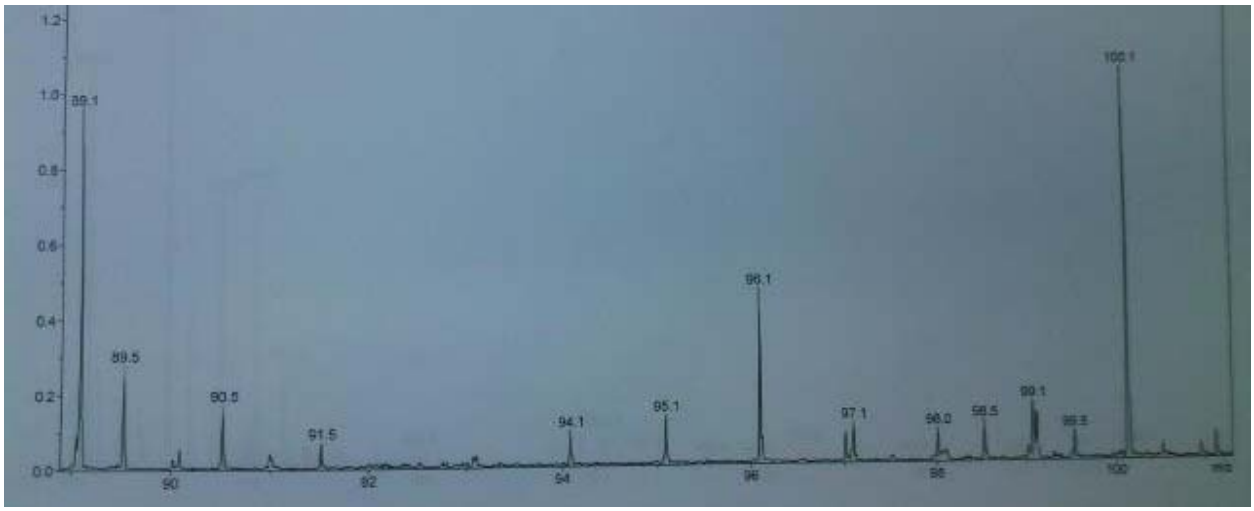


Figure S1. The ESI-MS spectrum of reaction shown in the scheme S1.

When the reaction of $NiCl_2$, cAAC and LDA is carried out in a molar ratio of 1:2:2 in THF a mixture of **2** and $Ni(N\textit{i}Pr_2)_2$ (**3**) is obtained. **3** looks similar to that of the known $Mg(N\textit{i}Pr_2)_2$ which is theoretically proposed to have a dimeric structure.[S1b] Thus the formation of compounds **2** and **3** is competing with each other. Compound **3** can be separately synthesized as a black crystalline solid when $NiCl_2$ is directly reacted with two equivalents of LDA in THF. A similar compound $Ni(N(SiMe_3)_2)_2$[S1c] related to **3** with two coordinate Ni is known in the literature which is a red liquid at room temperature.

Fehler! Es ist nicht möglich, durch die Bearbeitung von Feldfunktionen Objekte zu erstellen.*Scheme S2.* The synthesis of $Ni_2(N\textit{i}Pr_2)_4$ (**3**).

Procedure 3; Synthesis of compound $(cAAC)_2Ni$ (**2**): A 2:1 molar mixture of cAAC (570 mg, 2 mmol) and $NiCl_2$ (130 mg, 1 mmol) was placed in a 100 mL round bottom flask. Tetrahydrofuran (80 mL) was added at room temperature and stirred for 24 h to obtain an orange slurry. The resultant reaction mixture was then cooled to -20 °C and added to KC_8 (270 mg, 2 mmol) by means of a cannula. Then the reaction solution was slowly warmed to room temperature and stirred for 1.5 h. Graphite was separated by filtration to obtain a dark violet solution, which was dried under vacuum and extracted with toluene (30 mL). Finally the volume of toluene solution was decreased to 5 mL. Dark plates of **2**·toluene were formed in 43% yield after one day storing either at room temperature or at 0 °C in a refrigerator. Compound **2**·toluene was separated by filtration and dried under vacuum. The compound **2** is produced in 60% yield when preformed $(cAAC)_2NiCl_2$ (**1**) was reduced with two equivalents of KC_8 in THF.

Fehler! Es ist nicht möglich, durch die Bearbeitung von Feldfunktionen Objekte zu erstellen.

Scheme S3. Synthesis of compound $(cAAC)_2Ni$ (**2**).

Fehler! Es ist nicht möglich, durch die Bearbeitung von Feldfunktionen Objekte zu erstellen.

Scheme S4. The reaction between compound $(cAAC)_2Ni$ (**2**) and TEMPO radical to produce compound $(cAAC)Ni^{I}$-TEMPO which is characterized by EI-MS spectrometry given in Figure S2.

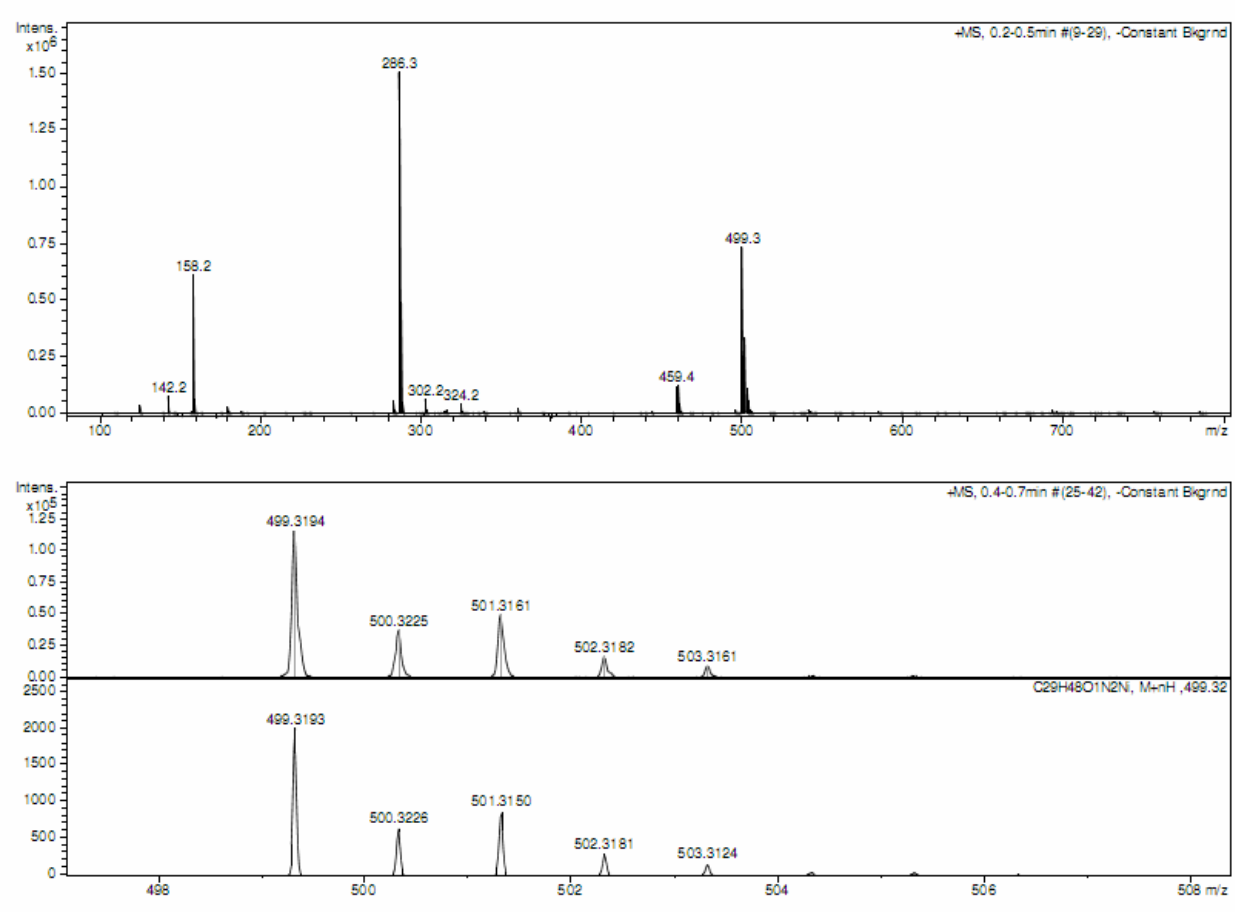


Figure S2. The EI-MS spectrum of reaction shown in the Scheme S4. The m/z; 499.3 corresponds to the compound $(cAAC)Ni^{I}$-TEMPO.

(S2). UV-visible spectroscopy of 2

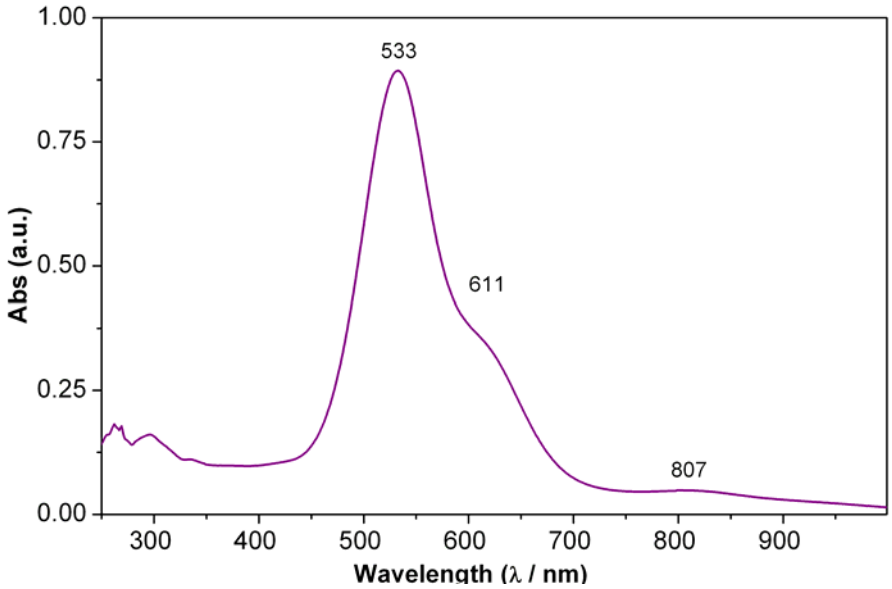


Figure S3. UV-visible spectrum of compound $(cAAC)_2Ni$ (**2**) in *n*-hexane.

We have additionally carried out calculations of **2** using PCM[TD-CAM-B3LYP/def2-SVP]//M06/def2-SVP[S1d] help in interpreting the band assignment of the UV-visible spectrum. The results are gathered in Tables S20 and S21. The calculations on the singlet state configuration yield four main excitations, namely, at 769.2 nm, 639.6 nm, 526.5 nm, and 405.5 nm with the oscillator strengths of 0.0031, 0.0130, 0.0129, and 0.4618, respectively. They mainly correspond to the electron promotion HOMO→LUMO, HOMO-2→LUMO, HOMO-3→LUMO (33%) and HOMO-3→LUMO (27%), in that order. This result is in reasonable agreement with the experimentally observed bands.

(S3). Magnetic property of 2

Magnetic susceptibility measurements. Temperature-dependent magnetic susceptibility measurements on compound **2**·toluene were carried out with a *Quantum-Design* MPMS-XL-5 SQUID magnetometer equipped with a 5 Tesla magnet in the range from 2.0 to 295 K at a magnetic field of 0.5 T. The powdered sample was placed in a teflon bucket and fixed in a non-magnetic sample holder. Each raw data file for the measured magnetic moment was corrected for the diamagnetic contribution of the teflon bucket. The molar susceptibility data were corrected for the diamagnetic contribution. The sample was prepared under an atmosphere of dry nitrogen using standard Schlenk techniques or a glove box where the O_2 and H_2O levels were usually kept below 1 ppm.

Temperature-independent paramagnetism ($TIP = 80 \cdot 10^{-6}$ cm^3mol^{-1}) and a Curie-behaved paramagnetic impurity ($PI = 0.9$ %) with spin $S = 1$ were included according to $\chi_{calc} = (1 - PI)\cdot\chi + PI\cdot\chi_{mono} + TIP$. [S2]

The χT vs T plot (Figure S4) in the temperature range of 300-2 K confirms the diamagnetic spin ground state (*S* = 0) of compound **2**.

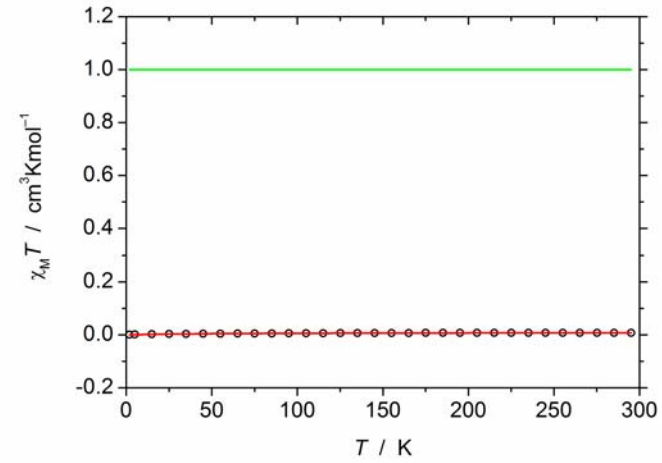


Figure S4. $\chi_M T$ *vs*. *T* plot of compound **2**·toluene. The open circles are the experimental values, red line represents fitting with above mentioned equation under consideration of *S* = 0 for **2**·toluene and the green line shows the expected curve for the hypothetical *S* = 1 case of Ni^{II}.

(S4). Crystal data of compound 1 and 2·toluene.

Crystal structure determination

The crystal structure of **2** was determined using single-crystal X-ray crystallography. The diffraction data were measured using the Cu Kα radiation from a rotating anode source on a SMART 6000 CCD area detector mounted on a Bruker three-circle diffractometer. Integration was done using SAINT,[S4] absorption correction and scaling was using SADABS[S5] and data reduction using XPREP.[S4] The structure was solved using direct methods as implemented in SHELXT; full-matrix least-squares refinement against F^2 was done using SHELXL-2013. [S6] Visualization and model building was done using SHELXLE. [S7]

Table S1. Crystal data and structure refinement for **2**·toluene.

Compound	$(cAAC)_2NiCl_2$ (**1**)	$(cAAC)_2Ni$·toluene (**2**·toluene)
Empirical formula	$C_{40}H_{62}N_2NiCl_2$	$2(C_{40}H_{62}N_2Ni)\cdot C_7H_8$
CCDC no.	956915	934645
Molecular weight	700.52	1351.35
Crystal size [mm]	0.2 x 0.1 x 0.09	0.65 × 0.20 × 0.18
Wavelength [pm]	0.71073	1.54178
Crystal system	Triclinic	Triclinic,
Space group	*P*-1	*P*-1
a [Å]	9.4340(10)	9.1361(18)
b [Å]	11.4930(10)	12.165(2)
c [Å]	18.0170(10)	18.538(4)

α [°]	101.53(2)	79.21(3)
β [°]	91.47(2)	76.32(3)
γ [°]	98.01(2)	89.36(3)
V [Å ^{3}]	1892.5(3)	1965.4(7)
Z	2	1
Temperature [K]	100(2)	100(2)
ρ [Mgm^{-3}]	1.229	1.142
μ [mm^{-1}]	0.683	0.92
F (000)	756	738
θ-area [°]	1.155 to 26.738	2.5 to 68.2
Total number reflect.	57070	62148
Unique reflections	8018	7063
R_{int}	0.0375	0.032
Number of restraints	0	45
Parameters	425	468
$R1$ [$I>2\sigma(I)$]	0.0277	0.0318
$wR2$ [$I>2\sigma(I)$]	0.0667	0.0833
$R1$ [all data]	0.0333	0.0320
$wR2$ [all data]	0.0695	0.0834
GooF	1.016	1.04
Extinction coefficient	n/a	n/a
Largest diff. peak / hole max. / min. [10^3·e·nm $^{-3}$]	0.439 and -0.281	0.295 and -0.266

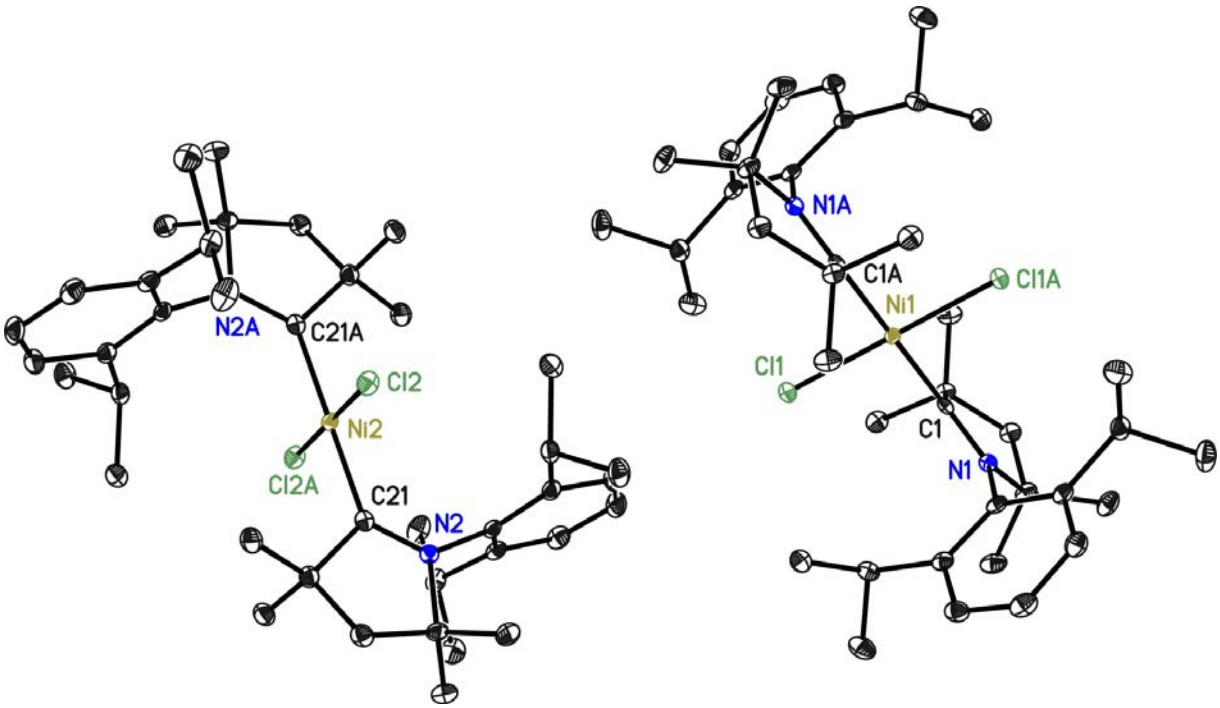


Figure S5. Molecular pictures of compound **1**. Two molecules are found in the unit cell.

Table S2. Bond lengths [Å] and angles [°] for **1**.

Ni(1)-C(1)	1.9150(14)
Ni(1)-C(1)#1	1.9150(14)

Ni(1)-Cl(1)	2.1720(5)
Ni(1)-Cl(1)#1	2.1720(5)
Ni(2)-C(21)	1.9296(15)
Ni(2)-C(21)#2	1.9297(15)
Ni(2)-Cl(2)#2	2.1808(5)
Ni(2)-Cl(2)	2.1808(5)
N(1)-C(1)	1.3154(18)
N(1)-C(9)	1.4714(18)
N(1)-C(2)	1.5367(17)
N(2)-C(21)	1.3150(18)
N(2)-C(29)	1.4693(18)
N(2)-C(22)	1.5402(18)
C(1)-C(4)	1.5336(19)
C(2)-C(6)	1.524(2)
C(2)-C(5)	1.525(2)
C(2)-C(3)	1.531(2)
C(3)-C(4)	1.535(2)
C(4)-C(8)	1.531(2)
C(4)-C(7)	1.5430(19)
C(9)-C(14)	1.414(2)
C(9)-C(10)	1.4173(19)
C(10)-C(11)	1.396(2)
C(10)-C(15)	1.524(2)
C(11)-C(12)	1.381(2)
C(12)-C(13)	1.381(2)
C(13)-C(14)	1.396(2)
C(14)-C(18)	1.5256(19)
C(15)-C(17)	1.537(2)
C(15)-C(16)	1.539(2)
C(18)-C(19)	1.537(2)
C(18)-C(20)	1.538(2)
C(21)-C(24)	1.5345(19)
C(22)-C(26)	1.525(2)
C(22)-C(25)	1.526(2)
C(22)-C(23)	1.531(2)
C(23)-C(24)	1.533(2)
C(24)-C(28)	1.530(2)
C(24)-C(27)	1.546(2)

C(29)-C(30)	1.411(2)
C(29)-C(34)	1.419(2)
C(30)-C(31)	1.396(2)
C(30)-C(35)	1.523(2)
C(31)-C(32)	1.378(2)
C(32)-C(33)	1.379(2)
C(33)-C(34)	1.396(2)
C(34)-C(38)	1.525(2)
C(35)-C(37)	1.5339(19)
C(35)-C(36)	1.535(2)
C(38)-C(39)	1.536(2)
C(38)-C(40)	1.539(2)

C(1)-Ni(1)-C(1)#1	180.0
C(1)-Ni(1)-Cl(1)	93.82(4)
C(1)#1-Ni(1)-Cl(1)	86.18(4)
C(1)-Ni(1)-Cl(1)#1	86.18(4)
C(1)#1-Ni(1)-Cl(1)#1	93.82(4)
Cl(1)-Ni(1)-Cl(1)#1	180.0
C(21)-Ni(2)-C(21)#2	180.0
C(21)-Ni(2)-Cl(2)#2	92.13(4)
C(21)#2-Ni(2)-Cl(2)#2	87.87(4)
C(21)-Ni(2)-Cl(2)	87.87(4)
C(21)#2-Ni(2)-Cl(2)	92.13(4)
Cl(2)#2-Ni(2)-Cl(2)	180.0
C(1)-N(1)-C(9)	126.62(12)
C(1)-N(1)-C(2)	115.04(11)
C(9)-N(1)-C(2)	118.09(11)
C(21)-N(2)-C(29)	128.05(12)
C(21)-N(2)-C(22)	115.36(12)
C(29)-N(2)-C(22)	116.57(11)
N(1)-C(1)-C(4)	108.56(12)
N(1)-C(1)-Ni(1)	134.40(10)
C(4)-C(1)-Ni(1)	116.85(10)
C(6)-C(2)-C(5)	108.46(12)
C(6)-C(2)-C(3)	111.00(12)
C(5)-C(2)-C(3)	113.72(12)
C(6)-C(2)-N(1)	112.48(12)

C(5)-C(2)-N(1)	110.60(11)
C(3)-C(2)-N(1)	100.50(11)
C(2)-C(3)-C(4)	106.46(11)
C(8)-C(4)-C(1)	113.66(11)
C(8)-C(4)-C(3)	111.47(12)
C(1)-C(4)-C(3)	103.41(11)
C(8)-C(4)-C(7)	107.95(12)
C(1)-C(4)-C(7)	108.40(11)
C(3)-C(4)-C(7)	111.94(12)
C(14)-C(9)-C(10)	120.63(13)
C(14)-C(9)-N(1)	118.89(12)
C(10)-C(9)-N(1)	120.27(12)
C(11)-C(10)-C(9)	118.21(13)
C(11)-C(10)-C(15)	116.29(13)
C(9)-C(10)-C(15)	125.34(13)
C(12)-C(11)-C(10)	121.68(14)
C(11)-C(12)-C(13)	119.41(14)
C(12)-C(13)-C(14)	121.95(14)
C(13)-C(14)-C(9)	118.01(13)
C(13)-C(14)-C(18)	116.09(13)
C(9)-C(14)-C(18)	125.78(13)
C(10)-C(15)-C(17)	109.20(12)
C(10)-C(15)-C(16)	113.06(13)
C(17)-C(15)-C(16)	107.73(13)
C(14)-C(18)-C(19)	109.67(12)
C(14)-C(18)-C(20)	112.62(12)
C(19)-C(18)-C(20)	107.98(12)
N(2)-C(21)-C(24)	107.83(12)
N(2)-C(21)-Ni(2)	133.69(11)
C(24)-C(21)-Ni(2)	118.37(10)
C(26)-C(22)-C(25)	108.32(12)
C(26)-C(22)-C(23)	111.17(12)
C(25)-C(22)-C(23)	114.04(12)
C(26)-C(22)-N(2)	111.05(12)
C(25)-C(22)-N(2)	111.61(12)
C(23)-C(22)-N(2)	100.55(11)
C(22)-C(23)-C(24)	106.51(12)
C(28)-C(24)-C(23)	111.66(12)

C(28)-C(24)-C(21)	114.46(12)
C(23)-C(24)-C(21)	103.62(11)
C(28)-C(24)-C(27)	108.61(12)
C(23)-C(24)-C(27)	110.89(12)
C(21)-C(24)-C(27)	107.48(12)
C(30)-C(29)-C(34)	120.76(13)
C(30)-C(29)-N(2)	119.87(12)
C(34)-C(29)-N(2)	119.01(12)
C(31)-C(30)-C(29)	118.27(14)
C(31)-C(30)-C(35)	116.78(13)
C(29)-C(30)-C(35)	124.77(13)
C(32)-C(31)-C(30)	121.63(14)
C(31)-C(32)-C(33)	119.43(14)
C(32)-C(33)-C(34)	122.16(14)
C(33)-C(34)-C(29)	117.55(13)
C(33)-C(34)-C(38)	116.51(13)
C(29)-C(34)-C(38)	125.77(13)
C(30)-C(35)-C(37)	113.74(12)
C(30)-C(35)-C(36)	108.18(12)
C(37)-C(35)-C(36)	108.36(12)
C(34)-C(38)-C(39)	109.35(13)
C(34)-C(38)-C(40)	113.46(12)
C(39)-C(38)-C(40)	108.16(13)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z+1 #2 -x+2,-y,-z

Table S3. Bond lengths [Å] and angles [°] for **2**·toluene.

Ni1—C1_1	1.8419 (13)	C21—C22	1.472 (11)
Ni1—C1	1.8448 (14)	C22—C23	1.308 (15)
C1—N003	1.3381 (16)	C22—C27	1.395 (14)
C1—C2	1.5358 (17)	C23—C24	1.416 (12)
N002—C1_1	1.3420 (16)	C24—C25	1.383 (10)
N002—C5_1	1.4455 (15)	C25—C26	1.350 (13)
N002—C4_1	1.5116 (15)	C26—C27	1.459 (14)
C2—C11	1.5262 (19)	C1_1—C2_1	1.5376 (17)

C2—C12	1.5362 (18)	C2_1—C14_1	1.5305 (19)
C2—C3	1.5432 (17)	C2_1—C13_1	1.5356 (19)
N003—C5	1.4451 (16)	C2_1—C3_1	1.5453 (18)
N003—C4	1.5149 (16)	C3_1—C4_1	1.5335 (18)
C3—C4	1.5332 (18)	C4_1—C12_1	1.5271 (18)
C4—C13	1.5275 (18)	C4_1—C11_1	1.5292 (18)
C4—C14	1.5307 (19)	C5_1—C6_1	1.4039 (18)
C5—C10	1.4048 (19)	C5_1—C10_1	1.4096 (18)
C5—C6	1.4093 (19)	C6_1—C7_1	1.3960 (18)
C7—C8	1.380 (2)	C6_1—C15_1	1.5220 (18)
C7—C6	1.3952 (19)	C7_1—C8_1	1.379 (2)
C6—C18	1.5212 (19)	C8_1—C9_1	1.384 (2)
C8—C9	1.381 (2)	C9_1—C10_1	1.3936 (19)
C9—C10	1.398 (2)	C10_1—C18_1	1.5212 (19)
C10—C15	1.519 (2)	C15_1—C16_1	1.5320 (19)
C15—C17	1.5338 (19)	C15_1—C17_1	1.5342 (19)
C15—C16	1.534 (2)	C18_1—C20_1	1.5322 (19)
C18—C19	1.5336 (19)	C18_1—C19_1	1.5358 (19)
C18—C20	1.5350 (19)		
C1_1—Ni1—C1	166.42 (5)	C23—C22—C21	119.9 (8)
N003—C1—C2	106.49 (10)	C27—C22—C21	118.3 (9)
N003—C1—Ni1	130.16 (9)	C22—C23—C24	122.0 (9)
C2—C1—Ni1	123.05 (9)	C23—C24—C25	119.6 (8)
C1_1—N002—C5_1	122.32 (10)	C26—C25—C24	118.2 (8)
C1_1—N002—C4_1	117.07 (10)	C25—C26—C27	122.8 (8)
C5_1—N002—C4_1	120.60 (10)	C22—C27—C26	115.5 (11)
C11—C2—C1	110.49 (11)	N002—C1_1—C2_1	106.40 (10)
C11—C2—C12	109.00 (11)	N002—C1_1—Ni1	129.97 (9)
C1—C2—C12	108.50 (11)	C2_1—C1_1—Ni1	123.37 (9)
C11—C2—C3	111.63 (11)	C14_1—C2_1—C13_1	108.69 (11)
C1—C2—C3	104.88 (10)	C14_1—C2_1—C1_1	110.83 (11)
C12—C2—C3	112.24 (11)	C13_1—C2_1—C1_1	109.11 (11)
C1—N003—C5	121.67 (10)	C14_1—C2_1—C3_1	111.89 (11)
C1—N003—C4	117.25 (10)	C13_1—C2_1—C3_1	111.74 (11)
C5—N003—C4	121.03 (10)	C1_1—C2_1—C3_1	104.52 (10)
C4—C3—C2	106.87 (10)	C4_1—C3_1—C2_1	106.54 (10)
N003—C4—C13	111.96 (10)	N002—C4_1—C12_1	112.29 (10)
N003—C4—C14	111.34 (10)	N002—C4_1—C11_1	110.99 (10)

C13—C4—C14	108.12 (11)	C12_1—C4_1—C11_1	108.22 (11)
N003—C4—C3	100.30 (10)	N002—C4_1—C3_1	100.16 (9)
C13—C4—C3	112.12 (11)	C12_1—C4_1—C3_1	111.99 (11)
C14—C4—C3	112.94 (11)	C11_1—C4_1—C3_1	113.11 (11)
C10—C5—C6	121.33 (12)	C6_1—C5_1—C10_1	121.38 (11)
C10—C5—N003	120.27 (12)	C6_1—C5_1—N002	120.30 (11)
C6—C5—N003	118.39 (11)	C10_1—C5_1—N002	118.31 (11)
C8—C7—C6	121.30 (14)	C7_1—C6_1—C5_1	118.13 (12)
C7—C6—C5	118.01 (13)	C7_1—C6_1—C15_1	118.69 (12)
C7—C6—C18	119.02 (12)	C5_1—C6_1—C15_1	122.88 (11)
C5—C6—C18	122.73 (11)	C8_1—C7_1—C6_1	121.23 (13)
C7—C8—C9	119.86 (13)	C7_1—C8_1—C9_1	119.86 (12)
C8—C9—C10	121.42 (13)	C8_1—C9_1—C10_1	121.46 (13)
C9—C10—C5	117.86 (13)	C9_1—C10_1—C5_1	117.78 (12)
C9—C10—C15	119.22 (12)	C9_1—C10_1—C18_1	119.11 (12)
C5—C10—C15	122.71 (12)	C5_1—C10_1—C18_1	122.93 (11)
C10—C15—C17	109.74 (12)	C6_1—C15_1—C16_1	109.07 (11)
C10—C15—C16	112.96 (13)	C6_1—C15_1—C17_1	113.35 (11)
C17—C15—C16	110.07 (12)	C16_1—C15_1—C17_1	110.53 (11)
C6—C18—C19	113.53 (11)	C10_1—C18_1—C20_1	109.54 (11)
C6—C18—C20	109.19 (12)	C10_1—C18_1—C19_1	112.97 (11)
C19—C18—C20	109.99 (12)	C20_1—C18_1—C19_1	110.22 (12)
C23—C22—C27	121.7 (9)		

(S5). DFT calculations

Computational details

A. DFT calculations details

Theoretical calculations were performed with the GAUSSIAN 09 suite of programs.[S8] All geometry optimizations were computed using the functional M06[S9] with def2-SVP.[S10] The stationary points were located with the Berny algorithm[S11] using redundant internal coordinates. Analytical Hessians were computed to determine the nature of stationary points. [S12] The improvements in the electronic energies were carried out by computing single points on the M06/def2-SVP geometries at the M06/def2-TZVPP, B3LYP/def2-TZVPP, [S10,S13-14] PBE0/def2-TZVPP,[S10,S15-16] TPSS/def2-TZVPP[S10,S17] and BP86/def2-TZVPP levels of theory. [S18-19] The NBO[S20-24] and NRT[S25-27] analyses as well as the reported Wiberg[S28] bond indices were computed using the GENNBO 5.9 program. [S29] The energies associated with the donor-acceptor two-electron interactions have been computed according to the second-order perturbational theory. [S20]

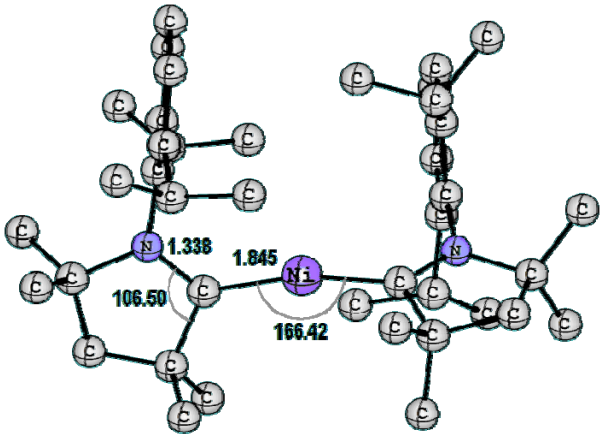
The CASSCF(2,2) calculations were performed using the MOLPRO 2012.1[S30] software program package. The biradical index[S31-S34] has been calculated, for an *ab initio* CI calculation with the canonical MOs, by the following equation:

Fehler! Es ist nicht möglich, durch die Bearbeitung von Feldfunktionen Objekte zu erstellen.

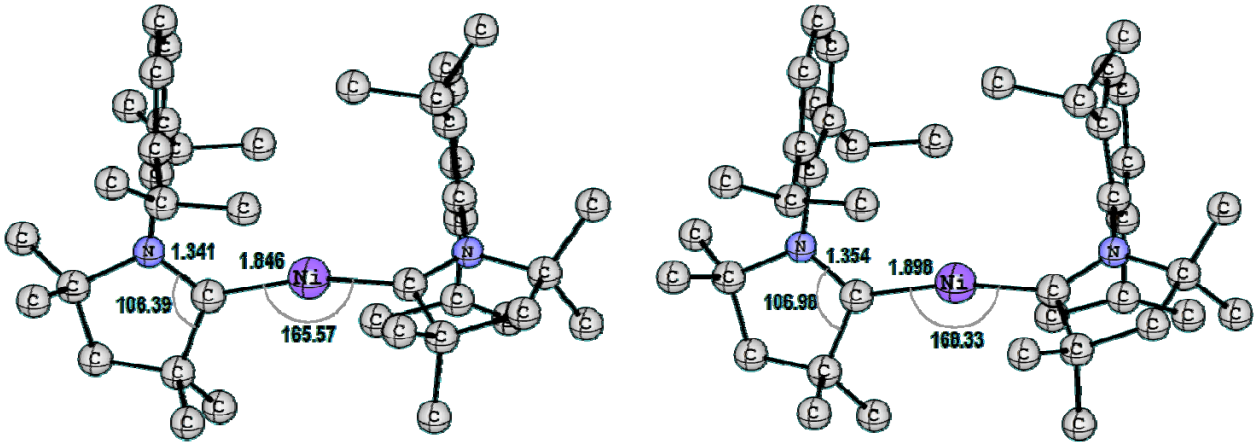
where c_o^2 is the weight of the closed-shell configuration in the CI wavefunction and c_d^2 is weight of the double excitation.

Nonspecific solvent effects were described by using the self-consistent reaction field (SCRF) approach in Tomasi's formalism.[S35-36] Single point PCM[TD-CAM-B3LYP/def2-SVP] [S37] calculations were performed to estimate the change in the UV-visible spectra profiles of compound **2** in the presence of *n*-hexane solvent.

B. Theoretical structures



(A)



(B) (C)

Figure S6. Comparison between the solid state (A) and the optimized theoretical structures (at the M06/def2-SVP level) in the singlet closed-shell state (B) and in the triplet state of compound **2** (C). Selected bond distances are shown in Å and angles in °. The hydrogen atoms are hidden for clarity.

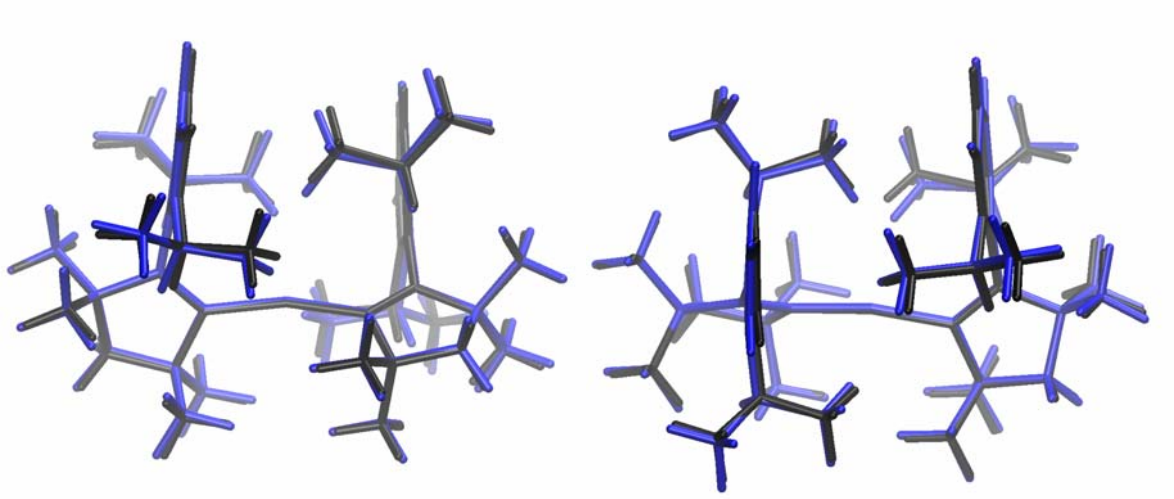


Figure S7. Superposition plot of the X-Ray (black) structure with the M06/def2-SVP optimized structure in singlet closed-shell electronic configuration (blue) for compound **2**.

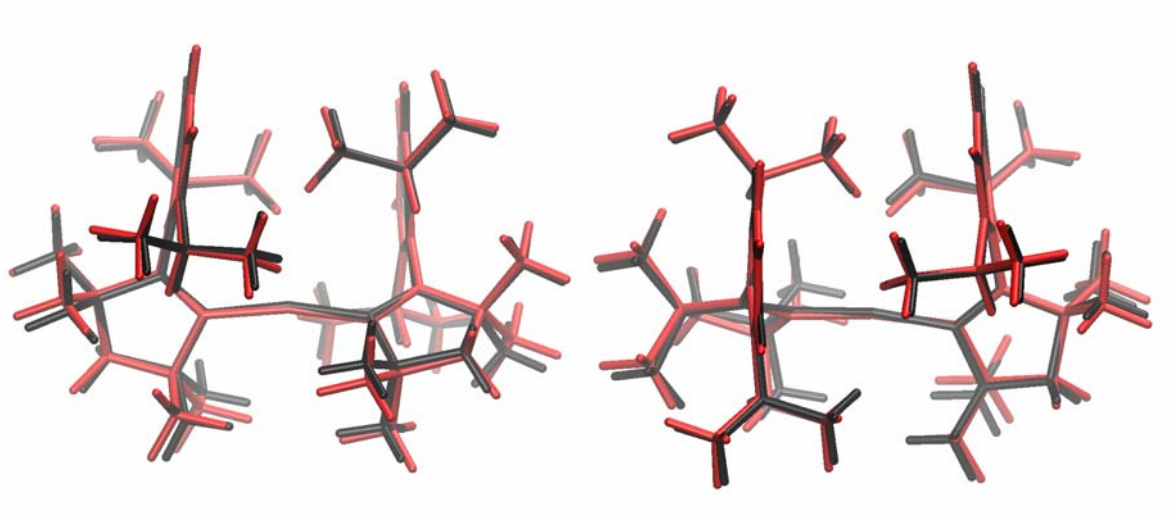


Figure S8. Superposition plot of the X-Ray (black) structure with the M06/def2-SVP optimized structure in triplet electronic configuration (red) for compound **2**.

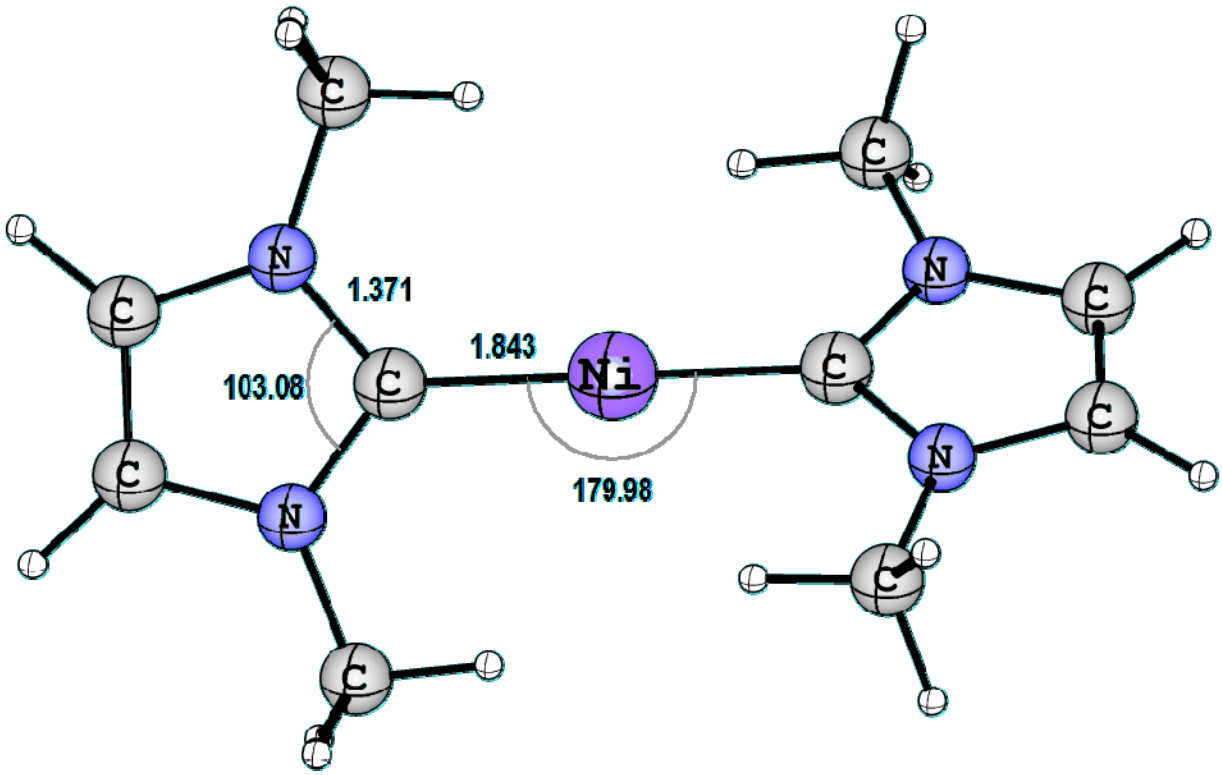


Figure S9. Optimized theoretical structure of compound $(NHC)_2Ni$ at the M06/def2-SVP level. Selected bond distances are shown in Å and angles in °. The hydrogen atoms are hidden for clarity.

Table S4. Coordinates for the optimized singlet state of Compound **2** at the M06/def2-SVP level of theory

E = -3176.6775598 Hartree

Ni	0.011591000000	-0.919127000000	-0.009581000000
C	-1.684869000000	-1.157938000000	-0.695836000000
N	2.820121000000	-0.425525000000	0.521106000000
C	-2.069809000000	-2.381987000000	-1.520616000000
N	-2.813549000000	-0.460109000000	-0.505234000000
C	-3.461504000000	-2.044036000000	-2.082815000000
H	-3.348973000000	-1.601316000000	-3.089549000000

H	-4.110680000000	-2.930520000000	-2.190909000000
C	-4.068820000000	-1.001801000000	-1.142725000000
C	-2.829728000000	0.792980000000	0.190200000000
C	-2.654260000000	3.194967000000	0.134512000000
H	-2.431385000000	4.119347000000	-0.408656000000
C	-2.537049000000	1.970590000000	-0.528381000000
C	-3.032453000000	3.258502000000	1.470078000000
H	-3.130084000000	4.228186000000	1.967559000000
C	-3.252388000000	2.085067000000	2.179845000000
H	-3.496141000000	2.137123000000	3.245996000000
C	-3.142321000000	0.835029000000	1.563257000000
C	-1.067185000000	-2.641317000000	-2.635065000000
H	-1.361150000000	-3.525190000000	-3.229523000000
H	-0.060806000000	-2.810219000000	-2.216480000000
H	-0.999095000000	-1.775422000000	-3.316747000000
C	-2.102602000000	-3.593253000000	-0.583775000000
H	-2.499847000000	-4.477808000000	-1.112801000000
H	-2.724539000000	-3.414938000000	0.308764000000
H	-1.088187000000	-3.831206000000	-0.225517000000
C	-4.837545000000	0.074232000000	-1.894889000000
H	-5.695186000000	-0.391936000000	-2.407649000000
H	-4.220388000000	0.567629000000	-2.660247000000
H	-5.234806000000	0.846110000000	-1.214602000000
C	-5.015265000000	-1.624719000000	-0.119266000000
H	-5.911128000000	-2.001271000000	-0.640390000000
H	-5.352751000000	-0.882081000000	0.622049000000
H	-4.562928000000	-2.473323000000	0.416071000000
C	-3.211561000000	-0.421260000000	2.405628000000
H	-3.369734000000	-1.274773000000	1.728481000000
C	-4.342257000000	-0.418344000000	3.423967000000
H	-4.415504000000	-1.400123000000	3.920303000000
H	-5.319358000000	-0.198440000000	2.961021000000
H	-4.179213000000	0.326924000000	4.221297000000
C	-2.000301000000	1.944172000000	-1.944925000000
H	-2.199102000000	0.943319000000	-2.367217000000
C	-1.857451000000	-0.646416000000	3.071540000000
H	-1.862189000000	-1.571489000000	3.674327000000
H	-1.595853000000	0.195051000000	3.738694000000
H	-1.067861000000	-0.737029000000	2.300955000000
C	-2.651312000000	2.978014000000	-2.854468000000
H	-2.322790000000	2.834205000000	-3.897105000000
H	-2.369577000000	4.007337000000	-2.573625000000
H	-3.752555000000	2.918774000000	-2.831697000000
C	-0.483542000000	2.111983000000	-1.917880000000
H	-0.011455000000	1.300509000000	-1.330774000000
H	-0.196721000000	3.076340000000	-1.460809000000
H	-0.065738000000	2.088094000000	-2.939059000000
C	1.702376000000	-1.143542000000	0.696894000000
C	2.096224000000	-2.354719000000	1.536233000000
C	3.473323000000	-1.988766000000	2.117833000000
H	3.337851000000	-1.548896000000	3.122881000000
H	4.138029000000	-2.862485000000	2.234776000000
C	4.074330000000	-0.934216000000	1.186594000000
C	2.819974000000	0.814875000000	-0.197033000000
C	3.141651000000	0.834473000000	-1.568385000000
C	3.219773000000	2.072359000000	-2.213702000000
H	3.467880000000	2.106242000000	-3.279700000000
C	2.964327000000	3.254881000000	-1.531225000000
H	3.037059000000	4.215402000000	-2.050250000000
C	2.582562000000	3.211520000000	-0.195656000000

H	2.332618000000	4.141900000000	0.325136000000
C	2.492749000000	1.999830000000	0.494002000000
C	5.057051000000	-1.535355000000	0.185494000000
H	4.636800000000	-2.398007000000	-0.352464000000
H	5.952588000000	-1.884800000000	0.725603000000
H	5.387791000000	-0.788471000000	-0.554680000000
C	4.798935000000	0.163595000000	1.951460000000
H	5.659744000000	-0.277520000000	2.480725000000
H	4.153700000000	0.640476000000	2.703995000000
H	5.186733000000	0.945436000000	1.277030000000
C	2.164264000000	-3.572666000000	0.609731000000
H	2.545612000000	-4.451629000000	1.159376000000
H	2.816731000000	-3.401935000000	-0.262406000000
H	1.163232000000	-3.816652000000	0.218846000000
C	1.081675000000	-2.623384000000	2.637496000000
H	1.380339000000	-3.499655000000	3.240741000000
H	0.083421000000	-2.808919000000	2.206786000000
H	0.992305000000	-1.755145000000	3.313582000000
C	3.257854000000	-0.439955000000	-2.377664000000
H	3.406435000000	-1.271576000000	-1.672277000000
C	1.931111000000	-0.705858000000	-3.081811000000
H	1.959692000000	-1.664232000000	-3.629529000000
H	1.700064000000	0.092889000000	-3.809180000000
H	1.112432000000	-0.755486000000	-2.338218000000
C	4.423081000000	-0.441354000000	-3.356065000000
H	4.519011000000	-1.427425000000	-3.840098000000
H	5.381554000000	-0.212112000000	-2.859760000000
H	4.283964000000	0.296633000000	-4.164623000000
C	1.944108000000	1.989412000000	1.906202000000
H	2.153571000000	0.999284000000	2.347387000000
C	2.570615000000	3.046879000000	2.805414000000
H	2.228834000000	2.917914000000	3.845791000000
H	2.281906000000	4.067920000000	2.502592000000
H	3.672573000000	2.998829000000	2.799238000000
C	0.425291000000	2.129914000000	1.862682000000
H	-0.022301000000	1.315854000000	1.260516000000
H	0.125004000000	3.093722000000	1.413352000000
H	-0.004302000000	2.081237000000	2.878566000000

Table S5. Coordinates for the optimized triplet state of Compound **2** at the M06/def2-SVP level of theory

E = -3176.6501055 Hartree

Ni	0.000305000000	-1.042949000000	-0.002046000000
C	-1.792965000000	-1.236012000000	-0.593016000000
N	2.854688000000	-0.401307000000	0.502104000000
C	-2.287016000000	-2.512726000000	-1.261787000000
N	-2.855398000000	-0.401404000000	-0.500591000000
C	-3.645008000000	-2.116083000000	-1.868396000000
H	-3.497888000000	-1.828907000000	-2.925395000000
H	-4.377673000000	-2.942158000000	-1.858362000000
C	-4.145428000000	-0.899664000000	-1.084130000000
C	-2.786097000000	0.840307000000	0.203781000000
C	-2.545301000000	3.242092000000	0.171667000000
H	-2.337450000000	4.168563000000	-0.374280000000
C	-2.503370000000	2.023076000000	-0.511543000000
C	-2.822261000000	3.294200000000	1.531374000000
H	-2.859828000000	4.257733000000	2.048644000000
C	-3.014261000000	2.114555000000	2.239769000000
H	-3.179451000000	2.157159000000	3.321839000000
C	-2.987843000000	0.870386000000	1.602576000000
C	-1.325720000000	-2.980159000000	-2.349706000000

H	-1.726163000000	-3.867590000000	-2.873202000000
H	-0.340124000000	-3.244884000000	-1.928627000000
H	-1.157632000000	-2.183433000000	-3.094961000000
C	-2.424639000000	-3.618456000000	-0.211280000000
H	-2.826811000000	-4.542435000000	-0.665389000000
H	-3.092964000000	-3.326539000000	0.615698000000
H	-1.441828000000	-3.856402000000	0.230193000000
C	-4.804652000000	0.129302000000	-1.990829000000
H	-5.735605000000	-0.293052000000	-2.404265000000
H	-4.161016000000	0.406507000000	-2.839486000000
H	-5.070537000000	1.046270000000	-1.437936000000
C	-5.152856000000	-1.278945000000	-0.001702000000
H	-6.076615000000	-1.648767000000	-0.476610000000
H	-5.426170000000	-0.404253000000	0.611516000000
H	-4.782497000000	-2.070759000000	0.667046000000
C	-3.092524000000	-0.386188000000	2.445266000000
H	-3.179248000000	-1.242113000000	1.757954000000
C	-4.304219000000	-0.386569000000	3.369690000000
H	-4.402406000000	-1.360498000000	3.877891000000
H	-5.244468000000	-0.190929000000	2.828579000000
H	-4.213059000000	0.377856000000	4.160374000000
C	-2.044145000000	2.001923000000	-1.955439000000
H	-2.233076000000	0.991345000000	-2.357712000000
C	-1.809511000000	-0.605829000000	3.244164000000
H	-1.862303000000	-1.553418000000	3.808387000000
H	-1.640480000000	0.207267000000	3.972394000000
H	-0.935664000000	-0.663412000000	2.571420000000
C	-2.766321000000	3.015279000000	-2.834547000000
H	-2.481485000000	2.881994000000	-3.891440000000
H	-2.502191000000	4.052029000000	-2.562931000000
H	-3.862858000000	2.926312000000	-2.764653000000
C	-0.534752000000	2.218789000000	-2.011425000000
H	0.000863000000	1.443100000000	-1.435014000000
H	-0.250845000000	3.201316000000	-1.593228000000
H	-0.169741000000	2.180565000000	-3.052239000000
C	1.792085000000	-1.235834000000	0.593522000000
C	2.284765000000	-2.511842000000	1.264550000000
C	3.642480000000	-2.115319000000	1.871928000000
H	3.494833000000	-1.827350000000	2.928628000000
H	4.374751000000	-2.941751000000	1.862954000000
C	4.144085000000	-0.899796000000	1.087048000000
C	2.786643000000	0.839365000000	-0.204271000000
C	2.988413000000	0.867447000000	-1.603126000000
C	3.015442000000	2.110741000000	-2.242037000000
H	3.180755000000	2.151677000000	-3.324147000000
C	2.824111000000	3.291492000000	-1.535312000000
H	2.862162000000	4.254268000000	-2.053954000000
C	2.547360000000	3.241418000000	-0.175491000000
H	2.340199000000	4.168749000000	0.369247000000
C	2.504726000000	2.023370000000	0.509370000000
C	5.151770000000	-1.280703000000	0.005442000000
H	4.781038000000	-2.072910000000	-0.662641000000
H	6.075090000000	-1.650713000000	0.481046000000
H	5.425865000000	-0.406799000000	-0.608552000000
C	4.803331000000	0.129551000000	1.993236000000
H	5.734246000000	-0.292593000000	2.406975000000
H	4.159611000000	0.407049000000	2.841733000000
H	5.069321000000	1.046152000000	1.439808000000
C	2.422644000000	-3.619195000000	0.215791000000
H	2.823496000000	-4.542860000000	0.671703000000

H	3.092240000000	-3.329029000000	-0.610791000000
H	1.440149000000	-3.856904000000	-0.226523000000
C	1.322184000000	-2.977158000000	2.352303000000
H	1.721442000000	-3.864365000000	2.877078000000
H	0.336681000000	-3.241413000000	1.930754000000
H	1.154237000000	-2.179505000000	3.096600000000
C	3.093117000000	-0.390187000000	-2.444256000000
H	3.178611000000	-1.245362000000	-1.755819000000
C	1.811033000000	-0.609989000000	-3.244597000000
H	1.864127000000	-1.558180000000	-3.807778000000
H	1.643374000000	0.202427000000	-3.973911000000
H	0.936157000000	-0.666499000000	-2.573097000000
C	4.305861000000	-0.392182000000	-3.367353000000
H	4.404003000000	-1.366615000000	-3.874591000000
H	5.245635000000	-0.196590000000	-2.825414000000
H	4.215937000000	0.371661000000	-4.158733000000
C	2.045343000000	2.004613000000	1.953184000000
H	2.233691000000	0.994577000000	2.357012000000
C	2.767698000000	3.019035000000	2.830998000000
H	2.483843000000	2.886300000000	3.888224000000
H	2.502669000000	4.055436000000	2.558949000000
H	3.864218000000	2.930602000000	2.760250000000
C	0.536025000000	2.222184000000	2.008590000000
H	0.000216000000	1.445781000000	1.433371000000
H	0.252703000000	3.204113000000	1.588610000000
H	0.170986000000	2.185992000000	3.049470000000

Table S6. Coordinates for the optimized singlet state of $(NHC)_2Ni$ at the M06/def2-SVP level of theory

E = -2116.838063 Hartree

Ni	0.000004000000	0.000115000000	0.000368000000
N	2.696453000000	-0.979580000000	0.439842000000
N	2.696339000000	0.979688000000	-0.439991000000
N	-2.696561000000	0.979542000000	0.439798000000
N	-2.696232000000	-0.979784000000	-0.439917000000
C	1.843421000000	0.000110000000	0.000152000000
C	4.021450000000	-0.619173000000	0.277507000000
H	4.846468000000	-1.267189000000	0.568034000000
C	4.021385000000	0.619114000000	-0.278384000000
H	4.846318000000	1.267037000000	-0.569332000000
C	-1.843425000000	-0.000046000000	0.000114000000
C	-4.021524000000	0.618952000000	0.277549000000
H	-4.846618000000	1.266829000000	0.568150000000
C	-4.021304000000	-0.619365000000	-0.278276000000
H	-4.846197000000	-1.267395000000	-0.569124000000
C	-2.216026000000	2.226133000000	0.979193000000
H	-2.548940000000	3.084072000000	0.371790000000
H	-2.550178000000	2.372534000000	2.019395000000
H	-1.115143000000	2.161348000000	0.953911000000
C	-2.215347000000	-2.226260000000	-0.979225000000
H	-2.548085000000	-3.084284000000	-0.371853000000
H	-2.549354000000	-2.372747000000	-2.019469000000
H	-1.114480000000	-2.161233000000	-0.953988000000
C	2.215543000000	2.226292000000	-0.979123000000
H	2.549757000000	2.373016000000	-2.019259000000
H	1.114674000000	2.161204000000	-0.953966000000
H	2.548176000000	3.084175000000	-0.371483000000
C	2.215818000000	-2.226073000000	0.979337000000
H	2.549959000000	-2.372420000000	2.019554000000
H	1.114940000000	-2.161234000000	0.954117000000

H	2.548650000000	-3.084105000000	0.372019000000

C. Molecular Orbitals

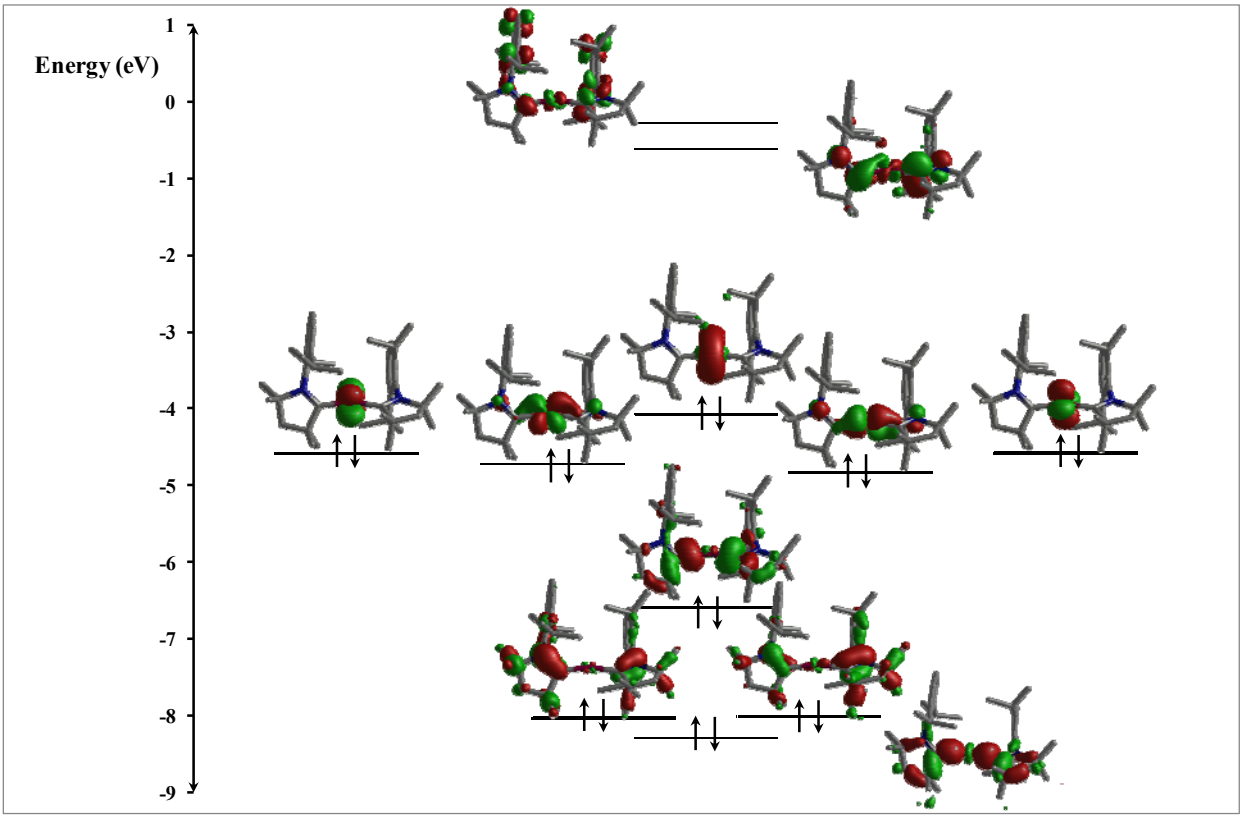


Figure S10. Frontier KS molecular orbitals (isocontour 0.045 au) of compounds **2** (M06/def2-TZVPP). Hydrogen atoms are omitted for clarity.

D. NBO Analysis

Table S7. Summary of Natural Population Analysis for compound **2** at the M06/def2-TZVPP level of theory.

Atom	Charge
Ni	0.34154
C_1	-0.03501
C_2	-0.03412
N_1	-0.51410
N_2	-0.51410

Table S8. Calculated bond distance and NRT and Wiberg bond order for compound **2** at the M06/def2-TZVPP level of theory.

Bond	Distance (Å)	Natural Bond Order			WBO
		Total	Covalent	Ionic	
Ni-$C_{carbene}$	1.846	0.4395	0.1164	0.3230	0.7391(0.7382)
$C_{carbene}$-N	1.341	1.5701	0.8982	0.6719	1.3186(1.3195)

Natural resonance theory (NRT) calculations

The NRT calculation involving 4 reference structures were performed. The calculation has produced a total of 1731 different resonance structures. Among them, 1614 structures have a very low weight (< 0.10%), the remaining 117 most important resonance structures have individual weights between 0.10% and 4.20%, resulting in a combined weight of 96.12 %.

Fehler! Es ist nicht möglich, durch die Bearbeitung von Feldfunktionen Objekte zu erstellen.

Scheme S5. Leading Resonance Structures describing the Ni-$C_{carbene}$ bonding situation.

Table S9. Comparison of the NBO representations for the different studied resonance structures.

Resonance structures	Total Lewis	%	Total non-Lewis	Residual Density %
Fehler! Es ist nicht möglich, durch die Bearbeitung von Feldfunktionen Objekte zu erstellen.	336.08865	97.7	7.91135	2.3
Fehler! Es ist nicht möglich, durch die Bearbeitung von Feldfunktionen Objekte zu erstellen.	336.20716	97.7	7.79284	2.3
Fehler! Es ist nicht möglich, durch die Bearbeitung von Feldfunktionen Objekte zu erstellen.	333.92324	97.1	10.07676	2.9
Fehler! Es ist nicht möglich, durch die Bearbeitung von Feldfunktionen Objekte zu erstellen.	336.41126	97.8	7.58874	2.2
Fehler! Es ist nicht möglich, durch die Bearbeitung von Feldfunktionen Objekte zu erstellen.	334.12474	97.1	9.87526	2.9

Fehler! Es ist nicht möglich, durch die Bearbeitung von Feldfunktionen Objekte zu erstellen.

Resonance structure **A**

Table S10. (Occupancy) Bond orbital/ Coefficients/ Hybrids for resonance structure **A**

---

1. (1.82670) BD (1)Ni 1- C 2
(84.01%) 0.9166*Ni 1 s(0.20%)p 0.16(0.03%)d99.99(99.77%) f 0.00(0.00%)
0.0000 0.0000 -0.0001 -0.0442 0.0049 0.0000 0.0020 -0.0007 0.0000 -0.0009 0.0173 0.0000 -0.0028 -0.0014 -0.0516
-
0.0003 0.7083 0.0014 -0.0004 -0.0003 -0.1882 -0.0006 0.6767 0.0019 0.0001 -0.0002 -0.0002 -0.0001 0.0002 0.0000 0.0007
(15.99%) 0.3999* C 2 s(0.01%)p 1.00(99.96%)d 0.00(0.03%) -0.0005 -0.0028 -0.0075 0.2115 -0.0236 0.4646 -0.0309 -0.8562 0.0673 0.0026 -0.0115 -0.0023 0.0046 -0.0110

3. (1.97616) BD (1) C 2- N 5
(33.33%) 0.5774* C 2 s(28.54%)p 2.50(71.27%)d 0.01(0.18%) 0.0001 0.5309 0.0597 -0.6595 -0.0557 0.5068 0.0653 0.1119 0.0323 -0.0291 -0.0036 0.0059 0.0208 -0.0223
(66.67%) 0.8165* N 5 s(37.21%)p 1.69(62.76%)d 0.00(0.03%) 0.0000 0.6099 0.0105 0.6803 -0.0199 -0.3807 0.0019 -0.1396 -0.0069 -0.0116 -0.0023 0.0049 0.0078 -0.0096

4. (1.97614) BD (1) N 3- C 55
(66.67%) 0.8165* N 3 s(37.21%)p 1.69(62.76%)d 0.00(0.03%) 0.0000 -0.6099 -0.0104 0.6742 -0.0198 0.3953 -0.0024 -0.1280 -0.0067 -0.0121 0.0018 0.0048 -0.0074 0.0096
(33.33%) 0.5774* C 55 s(28.53%)p 2.50(71.29%)d 0.01(0.18%) -0.0001 -0.5308 -0.0598 -0.6538 -0.0546 -0.5143 -0.0675 0.1115 0.0293 -0.0302 0.0020 0.0054 -0.0194 0.0222

5. (1.95115) BD (2) N 3- C 55
(78.85%) 0.8880* N 3 s(0.11%)p99.99(99.87%)d 0.18(0.02%) 0.0000 -0.0326 -0.0032 -0.1829 -0.0012 0.5296 0.0009 0.8275 0.0004 -0.0054 -0.0103 -0.0041 0.0057 0.0030
(21.15%) 0.4599* C 55 s(0.06%)p99.99(99.62%)d 5.27(0.32%) 0.0000 -0.0245 -0.0035 -0.2289 -0.0169 0.4979 0.0264 0.8325 0.0422 0.0203 0.0430 0.0193 -0.0242 -0.0041

166. (1.96766) LP (1)Ni 1 s(0.00%)p 0.00(0.00%)d 1.00(100.00%) f 0.00(0.00%)
0.0000 0.0000 0.0000 0.0028 -0.0006 0.0000 -0.0001 0.0007 0.0000 0.0000 -0.0002 0.0000 -0.0003 0.0063 0.1774 -0.0010 0.0376 -0.0001 -0.9811 0.0051 -0.0531 0.0003 -0.0409 0.0001 0.0000 0.0001 0.0000 0.0003 0.0000 -0.0001 0.0000

167. (1.96523) LP (2)Ni 1 s(0.13%)p 0.04(0.00%)d99.99(99.87%)

f 0.00(0.00%)
0.0000 0.0000 -0.0002 0.0350 -0.0059
0.0000 0.0000 -0.0003 0.0000 0.0002
-0.0070 0.0000 0.0000 0.0002 -0.0094
0.0002 0.4091 -0.0018 0.0759 -0.0004
-0.6707 0.0035 -0.6129 0.0020 0.0000
0.0000 -0.0001 0.0000 0.0000 0.0000
-0.0001

168. (1.93254) LP (3)Ni 1 s(15.06%)p 0.00(0.00%)d 5.64(84.94%)
f 0.00(0.00%)
0.0000 0.0000 0.0002 0.3879 -0.0100
 0.0000 0.0000 0.0001 0.0000 0.0000
-0.0046 0.0000 0.0000 -0.0004 -0.0126
-0.0001 -0.5213 -0.0028 -0.0020 0.0000
-0.6529 -0.0039 0.3887 0.0006 0.0000
0.0000 0.0000 0.0000 0.0001 0.0000
0.0002

169. (1.73202) LP (4)Ni 1 s(0.00%)p 1.00(0.04%)d99.99(99.96%)
f 0.00(0.00%)
0.0000 0.0000 -0.0001 0.0005 0.0005
0.0000 0.0025 0.0035 0.0000 0.0000
0.0010 0.0000 -0.0026 0.0189 0.9825
0.0029 0.0271 0.0000 0.1779 0.0006
-0.0157 -0.0001 0.0422 0.0000 0.0001
0.0007 0.0000 0.0002 0.0000 -0.0002
0.0000

170. (1.72375) LP (1) C 2 s(37.75%)p 1.65(62.23%)d 0.00(0.01%)
-0.0001 0.6137 -0.0307 0.7028 -0.0412
0.2105 -0.0113 0.2862 -0.0179 -0.0034
-0.0038 -0.0020 -0.0074 0.0050

171. (1.60894) LP (1) N 5 s(0.12%)p99.99(99.87%)d 0.12(0.01%)
0.0000 0.0338 0.0038 -0.1528 -0.0019
-0.5254 -0.0026 0.8362 0.0020 -0.0049
0.0088 -0.0030 -0.0044 -0.0031

172. (1.72361) LP (1) C 55 s(37.74%)p 1.65(62.25%)d 0.00(0.01%)
-0.0001 0.6135 -0.0307 -0.7031 0.0411
0.1989 -0.0112 -0.2942 0.0184 0.0028
-0.0045 0.0019 -0.0074 0.0046

173. (0.45176) LP (5)Ni 1 s(84.65%)p 0.00(0.00%)d 0.18(15.35%)
f 0.00(0.00%)
0.0000 0.0000 0.0000 0.9198 0.0200
 0.0000 0.0000 0.0002 0.0000 0.0000
0.0031 0.0000 0.0000 -0.0003 0.0021
0.0002 0.2380 0.0038 0.0008 0.0000
0.2918 0.0067 -0.1079 -0.0027 0.0000
0.0001 0.0002 0.0000 -0.0007 0.0000
-0.0014

829. (0.03021) BD*(1) N 3- C 55
(33.33%) 0.5774* N 3 s(37.21%)p 1.69(62.76%)d 0.00(0.03%)
0.0000 0.6099 0.0104 -0.6742 0.0198
-0.3953 0.0024 0.1280 0.0067 0.0121
-0.0018 -0.0048 0.0074 -0.0096
(66.67%) -0.8165* C 55 s(28.53%)p 2.50(71.29%)d 0.01(0.18%)
 0.0001 0.5308 0.0598 0.6538 0.0546
0.5143 0.0675 -0.1115 -0.0293 0.0302
-0.0020 -0.0054 0.0194 -0.0222

830. (0.33034) BD*(2) N 3- C 55
(21.15%) 0.4599* N 3 s(0.11%)p99.99(99.87%)d 0.18(0.02%)
0.0000 0.0326 0.0032 0.1829 0.0012
-0.5296 -0.0009 -0.8275 -0.0004 0.0054

0.0103 0.0041 -0.0057 -0.0030

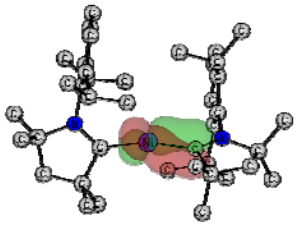
(78.85%) -0.8880* C 55
s(0.06%)p99.99(99.62%)d 5.27(0.32%)
0.0000 0.0245 0.0035 0.2289 0.0169
-0.4979 -0.0264 -0.8325 -0.0422 -0.0203
-0.0430 -0.0193 0.0242 0.0041

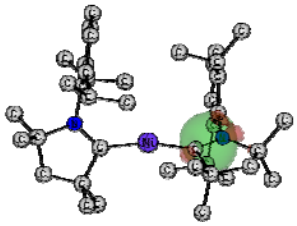
868. (0.45205) BD*(1)Ni 1- C 2
(15.99%)   0.3999*Ni 1
s(0.20%)p 0.16(0.03%)d99.99(99.77%)
f 0.00(0.00%)
0.0000 0.0000 0.0001 0.0442 -0.0049
0.0000 -0.0020 0.0007 0.0000 0.0009
-0.0173 0.0000 0.0028 0.0014 0.0516
0.0003 -0.7083 -0.0014 0.0004 0.0003
 0.1882 0.0006 -0.6767 -0.0019 -0.0001
 0.0002 0.0002 0.0001 -0.0002 0.0000
-0.0007

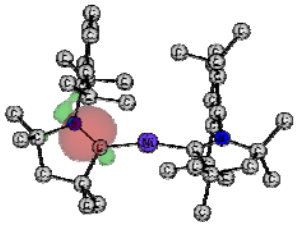
(84.01%) -0.9166* C 2
s(0.01%)p 1.00(99.96%)d 0.00(0.03%)
0.0005 0.0028 0.0075 -0.2115 0.0236
-0.4646 0.0309 0.8562 -0.0673 -0.0026
 0.0115 0.0023 -0.0046 0.0110

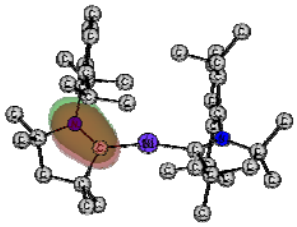
869. (0.03054) BD*(1) C 2- N 5
(66.67%)   0.8165* C 2
s(28.54%)p 2.50(71.27%)d 0.01(0.18%)
0.0001 0.5309 0.0597 -0.6595 -0.0557
0.5068 0.0653 0.1119 0.0323 -0.0291
-0.0036 0.0059 0.0208 -0.0223

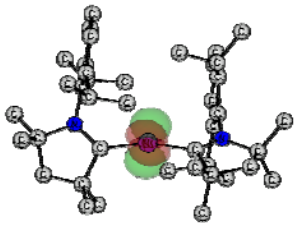
(33.33%) -0.5774* N 5
s(37.21%)p 1.69(62.76%)d 0.00(0.03%)
0.0000 0.6099 0.0105 0.6803 -0.0199
-0.3807 0.0019 -0.1396 -0.0069 -0.0116
-0.0023 0.0049 0.0078 -0.0096

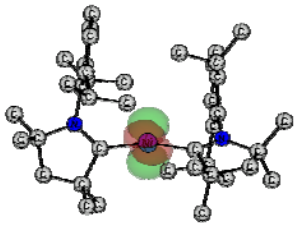

1

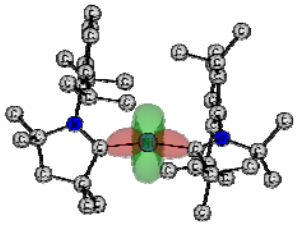

3

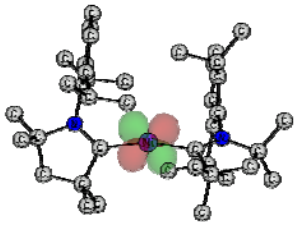

4

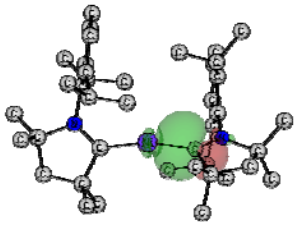

5


166


167


168


169


170

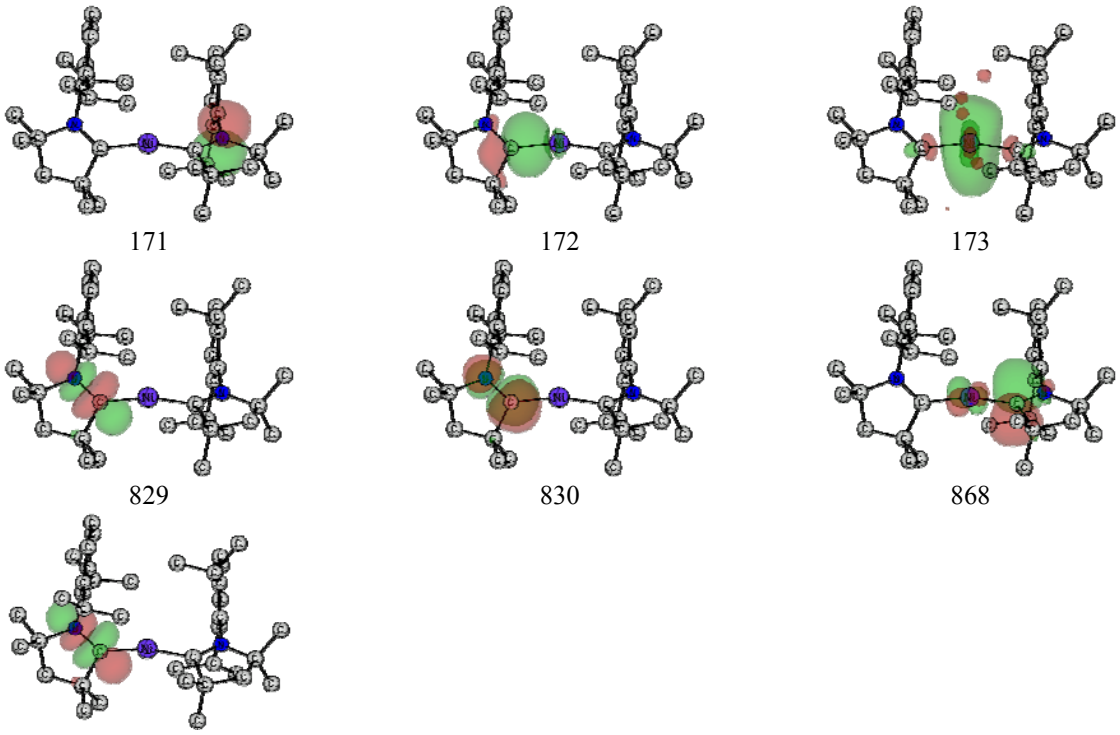


Figure S11. NBOs (isocontour 0.045 au) of compounds **2** (M06/def2-TZVPP) for resonance structure **A**. Hydrogen atoms are omitted for clarity.

Table S11. SECOND ORDER PERTURBATION THEORY ANALYSIS

Donor NBO (i)	Acceptor NBO (j)	E(2) kcal/mol	E(j)-E(i) a.u.	F(i,j) a.u.
1. BD (1)Ni 1- C 2	868. BD*(1)Ni 1- C 2	3.54	0.13	0.021
3. BD (1) C 2- N 5	173. LP (5)Ni 1	3.70	0.90	0.058
168. LP (3)Ni 1	869. BD*(1) C 2- N 5	0.53	0.69	0.017
168. LP (3)Ni 1	894. BD*(1) C19- H21	0.54	0.60	0.016
168. LP (3)Ni 1	915. BD*(1) C51- H52	2.48	0.62	0.035
168. LP (3)Ni 1	921. BD*(1) C43- H46	3.24	0.62	0.040
169. LP (4)Ni 1	868. BD*(1)Ni 1- C 2	10.69	0.10	0.031
169. LP (4)Ni 1	869. BD*(1) C 2- N 5	2.01	0.67	0.035
170. LP (1) C 2	173. LP (5)Ni 1	135.14	0.42	0.223
171. LP (1) N 5	868. BD*(1)Ni 1- C 2	96.85	0.21	0.131
173. LP (5)Ni 1	869. BD*(1) C 2- N 5	0.55	0.43	0.028
173. LP (5)Ni 1	871. BD*(1) N 5- C10	0.73	0.31	0.027
173. LP (5)Ni 1	894. BD*(1) C19- H21	1.20	0.34	0.037
173. LP (5)Ni 1	897. BD*(1) C23- H26	0.61	0.34	0.027
173. LP (5)Ni 1	915. BD*(1) C51- H52	3.93	0.36	0.069
173. LP (5)Ni 1	921. BD*(1) C43- H46	3.85	0.35	0.067
1. BD (1)Ni 1- C 2	829. BD*(1) N 3- C55	0.39	0.69	0.015
1. BD (1)Ni 1- C 2	830. BD*(2) N 3- C55	13.78	0.19	0.047
166. LP (1)Ni 1	829. BD*(1) N 3- C55	0.29	0.68	0.013
167. LP (2)Ni 1	829. BD*(1) N 3- C55	0.12	0.68	0.008
168. LP (3)Ni 1	829. BD*(1) N 3- C55	0.57	0.69	0.018
170. LP (1) C 2	829. BD*(1) N 3- C55	0.23	0.85	0.013
170. LP (1) C 2	830. BD*(2) N 3- C55	0.05	0.34	0.004
4. BD (1) N 3- C55	173. LP (5)Ni 1	3.72	0.90	0.058
172. LP (1) C55	173. LP (5)Ni 1	135.24	0.42	0.223

Fehler! Es ist nicht möglich, durch die Bearbeitung von Feldfunktionen Objekte zu erstellen.

Resonance structure **B**

Table S12. (Occupancy) Bond orbital/ Coefficients/ Hybrids for resonance structure **B**

---

2. (1.97656) BD (1) C 2- N 5
(33.39%) 0.5778* C 2 s(26.10%)p 2.82(73.72%)d 0.01(0.18%)
0.0001 0.5072 0.0609 -0.6886 -0.0534
0.4928 0.0663 0.1096 0.0310 -0.0292
-0.0028 0.0058 0.0208 -0.0224
(66.61%) 0.8162* N 5 s(37.44%)p 1.67(62.53%)d 0.00(0.03%)
0.0000 0.6118 0.0108 0.6767 -0.0205
-0.3851 0.0022 -0.1365 -0.0068 -0.0118
-0.0024 0.0051 0.0073 -0.0096

3. (1.95124) BD (2) C 2- N 5
(21.13%) 0.4596* C 2 s(0.03%)p99.99(99.64%)d 9.89(0.32%)
0.0000 0.0177 0.0038 -0.2096 -0.0157
-0.4986 -0.0262 0.8374 0.0426 0.0213
-0.0437 0.0184 0.0223 0.0052
(78.87%) 0.8881* N 5 s(0.11%)p99.99(99.87%)d 0.17(0.02%)
0.0000 0.0334 0.0037 -0.1585 -0.0015
-0.5219 -0.0009 0.8374 0.0003 -0.0056
0.0104 -0.0037 -0.0054 -0.0033

4. (1.97644) BD (1) N 3- C 55
(66.62%) 0.8162* N 3 s(37.43%)p 1.67(62.54%)d 0.00(0.03%)
0.0000 -0.6117 -0.0107 0.6711 -0.0204
0.3975 -0.0027 -0.1284 -0.0066 -0.0122
0.0019 0.0050 -0.0070 0.0096
(33.38%) 0.5778* C 55 s(26.06%)p 2.83(73.76%)d 0.01(0.18%)
-0.0001 -0.5068 -0.0609 -0.6813 -0.0530
-0.5050 -0.0675 0.1007 0.0299 -0.0300
0.0018 0.0055 -0.0197 0.0224

5. (1.95116) BD (2) N 3- C 55
(78.85%) 0.8880* N 3 s(0.10%)p99.99(99.88%)d 0.19(0.02%)
0.0000 -0.0320 -0.0033 -0.1845 -0.0013
0.5293 0.0009 0.8274 0.0004 -0.0054
-0.0103 -0.0041 0.0058 0.0030
(21.15%) 0.4599* C 55 s(0.03%)p99.99(99.64%)d 9.26(0.32%)
0.0000 -0.0183 -0.0036 -0.2340 -0.0165
0.5006 0.0265 0.8297 0.0423 0.0204
0.0429 0.0193 -0.0242 -0.0041

166. (1.96766) LP (1)Ni 1 s(0.00%)p 0.00(0.00%)d 1.00(100.00%)
f 0.00(0.00%)
0.0000 0.0000 0.0000 0.0028 -0.0006
0.0000 -0.0001 0.0007 0.0000 0.0000
-0.0002 0.0000 -0.0003 0.0063 0.1774
-0.0010 0.0364 -0.0001 -0.9811 0.0051
-0.0527 0.0003 -0.0420 0.0001 0.0000
0.0001 0.0000 0.0003 0.0000 -0.0001
0.0000

167. (1.96523) LP (2)Ni 1 s(0.13%)p 0.04(0.00%)d99.99(99.87%)
f 0.00(0.00%)
0.0000 0.0000 -0.0002 0.0350 -0.0059
0.0000 0.0000 -0.0003 0.0000 0.0002
-0.0070 0.0000 0.0000 0.0002 -0.0095
0.0002 0.4099 -0.0018 0.0759 -0.0004
-0.6709 0.0035 -0.6122 0.0020 0.0000
0.0000 -0.0001 0.0000 0.0000 0.0000

-0.0001

168. (1.93254) LP (3)Ni 1
s(15.06%)p 0.00(0.00%)d 5.64(84.94%)
f 0.00(0.00%)
0.0000 0.0000 0.0002 0.3879 -0.0100
0.0000 0.0000 0.0001 0.0000 0.0000
-0.0046 0.0000 0.0000 -0.0004 -0.0126
-0.0001 -0.5213 -0.0028 -0.0020 0.0000
-0.6529 -0.0039 0.3887 0.0006 0.0000
0.0000 0.0000 0.0000 0.0001 0.0000
0.0002

169. (1.73226) LP (4)Ni 1
s(0.00%)p 1.00(0.04%)d99.99(99.96%)
f 0.00(0.00%)
0.0000 0.0000 -0.0001 0.0025 0.0003
0.0000 0.0024 0.0035 0.0000 0.0000
0.0002 0.0000 -0.0025 0.0190 0.9838
0.0029 -0.0045 -0.0001 0.1777 0.0006
-0.0073 -0.0001 0.0120 -0.0001 0.0001
0.0007 0.0000 0.0002 0.0000 -0.0002
0.0000

170. (1.60665) LP (5)Ni 1
s(0.17%)p 0.18(0.03%)d99.99(99.79%)
f 0.00(0.00%)
0.0000 0.0000 -0.0002 0.0415 -0.0046
0.0000 0.0001 0.0004 0.0000 0.0029
-0.0172 0.0000 0.0000 0.0003 0.0074
0.0001 -0.7092 -0.0013 -0.0059 0.0001
0.1872 0.0007 -0.6781 -0.0023 0.0000
0.0000 0.0002 0.0000 -0.0001 0.0000
-0.0006

171. (1.72155) LP (1) C 2
s(38.84%)p 1.57(61.15%)d 0.00(0.01%)
-0.0001 0.6225 -0.0289 0.6786 -0.0439
0.2418 -0.0089 0.3006 -0.0154 -0.0045
-0.0048 -0.0021 -0.0062 0.0042

172. (1.72131) LP (1) C 55
s(38.84%)p 1.57(61.15%)d 0.00(0.01%)
-0.0001 0.6226 -0.0289 -0.6773 0.0436
0.2274 -0.0084 -0.3143 0.0167 0.0041
-0.0052 0.0020 -0.0064 0.0039

173. (0.45175) LP (6)Ni 1
s(84.67%)p 0.00(0.00%)d 0.18(15.33%)
f 0.00(0.00%)
0.0000 0.0000 0.0000 0.9200 0.0200
0.0000 0.0000 0.0001 0.0000 0.0000
0.0030 0.0000 0.0000 -0.0003 0.0021
0.0002 0.2359 0.0038 0.0008 0.0000
0.2923 0.0067 -0.1099 -0.0027 0.0000
0.0001 0.0002 0.0000 -0.0007 0.0000
-0.0014

868. (0.03138) BD*(1) N 3- C 55
(33.38%) 0.5778* N 3
s(37.43%)p 1.67(62.54%)d 0.00(0.03%)
0.0000 0.6117 0.0107 -0.6711 0.0204
-0.3975 0.0027 0.1284 0.0066 0.0122
-0.0019 -0.0050 0.0070 -0.0096

(66.62%) -0.8162* C 55
s(26.06%)p 2.83(73.76%)d 0.01(0.18%)
0.0001 0.5068 0.0609 0.6813 0.0530
0.5050 0.0675 -0.1007 -0.0299 0.0300
-0.0018 -0.0055 0.0197 -0.0224

869. (0.33047) BD*(2) N 3- C 55
(21.15%) 0.4599* N 3
s(0.10%)p99.99(99.88%)d 0.19(0.02%)
0.0000 0.0320 0.0033 0.1845 0.0013
-0.5293 -0.0009 -0.8274 -0.0004 0.0054
0.0103 0.0041 -0.0058 -0.0030

(78.85%) -0.8880* C 55
s(0.03%)p99.99(99.64%)d 9.26(0.32%)

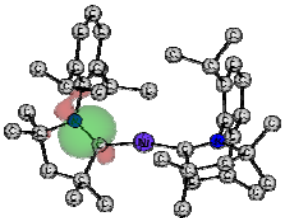
0.0000 0.0183 0.0036 0.2340 0.0165
-0.5006 -0.0265 -0.8297 -0.0423 -0.0204
-0.0429 -0.0193 0.0242 0.0041

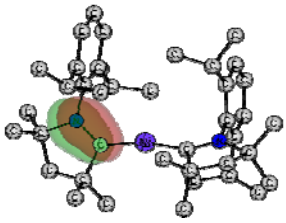
922. (0.03142) BD*(1) C 2- N 5
(66.61%) 0.8162* C 2 s(26.10%)p 2.82(73.72%)d 0.01(0.18%)
0.0001 0.5072 0.0609 -0.6886 -0.0534
0.4928 0.0663 0.1096 0.0310 -0.0292
-0.0028 0.0058 0.0208 -0.0224

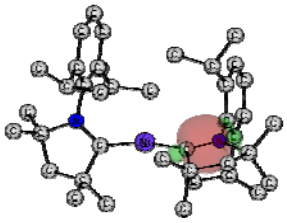
(33.39%) -0.5778* N 5 s(37.44%)p 1.67(62.53%)d 0.00(0.03%)
0.0000 0.6118 0.0108 0.6767 -0.0205
-0.3851 0.0022 -0.1365 -0.0068 -0.0118
-0.0024 0.0051 0.0073 -0.0096

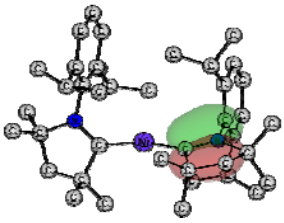
924. (0.33172) BD*(2) C 2- N 5
(78.87%) 0.8881* C 2 s(0.03%)p99.99(99.64%)d 9.89(0.32%)
0.0000 0.0177 0.0038 -0.2096 -0.0157
-0.4986 -0.0262 0.8374 0.0426 0.0213
-0.0437 0.0184 0.0223 0.0052

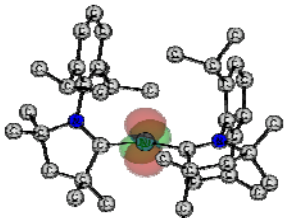
(21.13%) -0.4596* N 5 s(0.11%)p99.99(99.87%)d 0.17(0.02%)
0.0000 0.0334 0.0037 -0.1585 -0.0015
-0.5219 -0.0009 0.8374 0.0003 -0.0056
0.0104 -0.0037 -0.0054 -0.0033

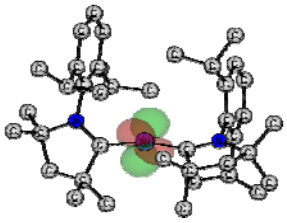

2

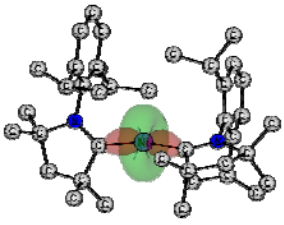

3

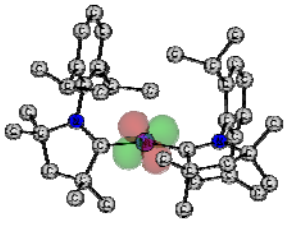

4

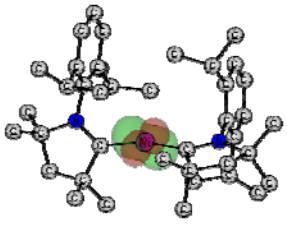

5

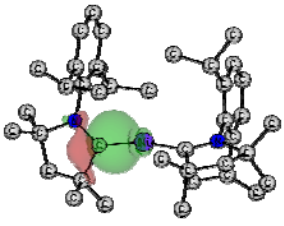

166

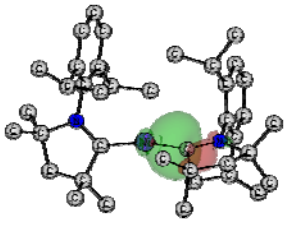

167

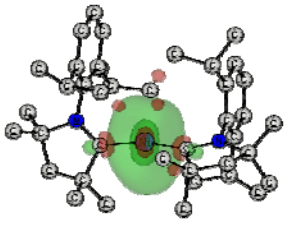

168

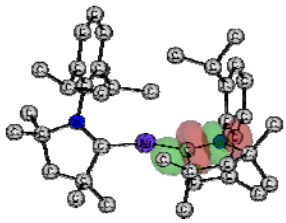

169


170

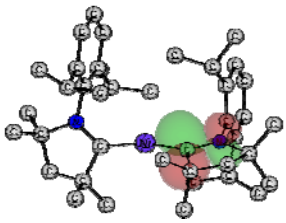

171


172

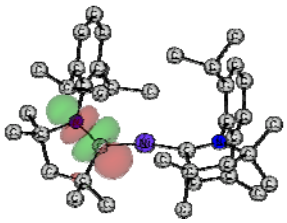

173



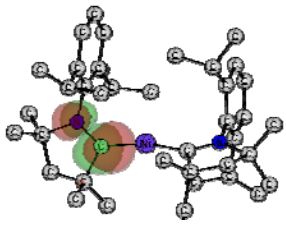
868



869



922



924

Figure S12. NBOs (isocontour 0.045 au) of compounds **2** (M06/def2-TZVPP) for resonance structure **B**. Hydrogen atoms are omitted for clarity.

Table S13. SECOND ORDER PERTURBATION THEORY ANALYSIS

Donor NBO (i)	Acceptor NBO (j)	E(2) kcal/mol	E(j)-E(i) a.u.	F(i,j) a.u.
166. LP (1)Ni 1	922. BD*(1) C 2- N 5	0.21	0.68	0.011
167. LP (2)Ni 1	922. BD*(1) C 2- N 5	0.21	0.68	0.011
169. LP (4)Ni 1	922. BD*(1) C 2- N 5	1.94	0.67	0.034
169. LP (4)Ni 1	924. BD*(2) C 2- N 5	9.92	0.16	0.036
170. LP (5)Ni 1	922. BD*(1) C 2- N 5	0.54	0.66	0.019
170. LP (5)Ni 1	924. BD*(2) C 2- N 5	24.21	0.15	0.055
173. LP (6)Ni 1	922. BD*(1) C 2- N 5	0.86	0.43	0.035
166. LP (1)Ni 1	868. BD*(1) N 3- C55	0.30	0.68	0.013
167. LP (2)Ni 1	868. BD*(1) N 3- C55	0.12	0.68	0.008
168. LP (3)Ni 1	868. BD*(1) N 3- C55	0.53	0.69	0.017
169. LP (4)Ni 1	868. BD*(1) N 3- C55	1.91	0.67	0.034
169. LP (4)Ni 1	869. BD*(2) N 3- C55	10.15	0.16	0.036
170. LP (5)Ni 1	868. BD*(1) N 3- C55	0.55	0.66	0.019
170. LP (5)Ni 1	869. BD*(2) N 3- C55	23.84	0.15	0.054
173. LP (6)Ni 1	868. BD*(1) N 3- C55	0.79	0.43	0.033
2. BD (1) C 2- N 5	173. LP (6)Ni 1	3.11	0.90	0.053
4. BD (1) N 3- C55	173. LP (6)Ni 1	3.12	0.90	0.053
171. LP (1) C 2	868. BD*(1) N 3- C55	0.22	0.85	0.013
172. LP (1) C55	173. LP (6)Ni 1	135.09	0.42	0.223
171. LP (1) C 2	173. LP (6)Ni 1	134.88	0.42	0.223

Fehler! Es ist nicht möglich, durch die Bearbeitung von Feldfunktionen Objekte zu erstellen.

Resonance structure **C**

Table S14. (Occupancy) Bond orbital/ Coefficients/ Hybrids for resonance structure **C**

---

1. (1.97932) 3C*(1)Ni 1- C 2- C 55	
(77.25%) 0.8789*Ni 1	s(0.05%)p 0.60(0.03%)d99.99(99.92%) f 0.00(0.00%) 0.0000 0.0000 0.0000 -0.0217 0.0049 0.0000 0.0000 -0.0003 0.0000 0.0002 0.0173 0.0000 0.0000 -0.0001 0.0019 -0.0001 0.7148 0.0015 0.0076 0.0000 -0.1816 -0.0005 0.6747 0.0017 0.0000 0.0000 -0.0002 0.0000 0.0002 0.0000 0.0007
(11.27%) -0.3358* C 2	s(0.03%)p99.99(99.92%)d 1.79(0.05%) -0.0001 -0.0144 0.0087 -0.2474 0.0281 -0.4828 0.0186 0.8353 -0.0781 0.0015 0.0158 0.0054 -0.0080 0.0127
(11.48%) -0.3388* C 55	s(0.08%)p99.99(99.87%)d 0.59(0.05%) -0.0001 -0.0277 0.0085 0.2836 -0.0272 -0.4892 0.0196 -0.8196 0.0778 -0.0013 0.0155 -0.0055 -0.0076 0.0129
3. (1.97627) BD (1) C 2- N 5	
(33.39%) 0.5778* C 2	s(26.10%)p 2.82(73.71%)d 0.01(0.19%) 0.0001 0.5073 0.0608 -0.6853 -0.0543 0.4995 0.0656 0.0980 0.0335 -0.0290 -0.0037 0.0059 0.0213 -0.0226
(66.61%) 0.8162* N 5	s(37.44%)p 1.67(62.53%)d 0.00(0.03%) 0.0000 0.6118 0.0108 0.6765 -0.0205 -0.3858 0.0022 -0.1354 -0.0068 -0.0118 -0.0024 0.0051 0.0073 -0.0096
4. (1.97620) BD (1) N 3- C 55	
(66.62%) 0.8162* N 3	s(37.43%)p 1.67(62.54%)d 0.00(0.03%) 0.0000 -0.6117 -0.0107 0.6709 -0.0204 0.3982 -0.0027 -0.1274 -0.0066 -0.0122 0.0019 0.0050 -0.0070 0.0096
(33.38%) 0.5778* C 55	s(26.08%)p 2.83(73.73%)d 0.01(0.19%) -0.0001 -0.5071 -0.0607 -0.6779 -0.0538 -0.5110 -0.0668 0.0907 0.0321 -0.0299 0.0026 0.0056 -0.0202 0.0227
165. (1.96766) LP (1)Ni 1	s(0.00%)p 0.00(0.00%)d 1.00(100.00%) f 0.00(0.00%) 0.0000 0.0000 0.0000 0.0028 -0.0006 0.0000 -0.0001 0.0007 0.0000 0.0000

-0.0002 0.0000 -0.0003 0.0063 0.1774
-0.0010 0.0364 -0.0001 -0.9811 0.0051
-0.0527 0.0003 -0.0420 0.0001 0.0000
0.0001 0.0000 0.0003 0.0000 -0.0001
0.0000

166. (1.96523) LP (2)Ni 1 s(0.13%)p 0.04(0.00%)d99.99(99.87%)
f 0.00(0.00%)
0.0000 0.0000 -0.0002 0.0350 -0.0059
0.0000 0.0000 -0.0003 0.0000 0.0002
-0.0070 0.0000 0.0000 0.0002 -0.0095
0.0002 0.4089 -0.0018 0.0759 -0.0004
-0.6706 0.0035 -0.6131 0.0020 0.0000
0.0000 -0.0001 0.0000 0.0000 0.0000
-0.0001

167. (1.93254) LP (3)Ni 1 s(15.06%)p 0.00(0.00%)d 5.64(84.94%)
f 0.00(0.00%)
0.0000 0.0000 0.0002 0.3879 -0.0100
0.0000 0.0000 0.0001 0.0000 0.0000
-0.0046 0.0000 0.0000 -0.0004 -0.0126
-0.0001 -0.5210 -0.0027 -0.0020 0.0000
-0.6530 -0.0039 0.3890 0.0006 0.0000
0.0000 0.0000 0.0000 0.0001 0.0000
0.0002

168. (1.73225) LP (4)Ni 1 s(0.00%)p 1.00(0.04%)d99.99(99.96%)
f 0.00(0.00%)
0.0000 0.0000 -0.0001 0.0028 0.0002
0.0000 0.0024 0.0035 0.0000 0.0000
0.0000 0.0000 -0.0025 0.0190 0.9838
0.0029 -0.0111 -0.0001 0.1777 0.0006
-0.0056 -0.0001 0.0056 -0.0001 0.0001
0.0007 0.0000 0.0002 0.0000 -0.0002
0.0000

169. (1.71853) LP (1) C 2 s(38.84%)p 1.57(61.15%)d 0.00(0.01%)
-0.0001 0.6226 -0.0286 0.6688 -0.0424
0.2207 -0.0078 0.3364 -0.0195 -0.0046
-0.0037 -0.0019 -0.0068 0.0048

170. (1.60842) LP (1) N 3 s(0.08%)p99.99(99.90%)d 0.17(0.01%)
-0.0001 0.0284 0.0034 0.1835 0.0018
-0.5299 -0.0025 -0.8273 -0.0022 0.0047
0.0088 0.0034 -0.0048 -0.0026

171. (1.60915) LP (1) N 5 s(0.09%)p99.99(99.90%)d 0.16(0.01%)
-0.0001 0.0292 0.0038 -0.1570 -0.0018
-0.5227 -0.0026 0.8373 0.0021 -0.0048
0.0088 -0.0030 -0.0044 -0.0030

172. (1.71584) LP (1) C 55 s(38.80%)p 1.58(61.19%)d 0.00(0.01%)
-0.0001 0.6223 -0.0284 -0.6610 0.0418
0.1960 -0.0070 -0.3664 0.0219 0.0041
-0.0040 0.0017 -0.0070 0.0047

173. (0.45228) LP (5)Ni 1 s(84.80%)p 0.00(0.00%)d 0.18(15.20%)
f 0.00(0.00%)
0.0000 0.0000 0.0000 0.9206 0.0199
0.0000 0.0000 0.0002 0.0000 0.0000
0.0027 0.0000 0.0000 -0.0003 0.0021
0.0002 0.2206 0.0037 0.0006 0.0000
0.2963 0.0067 -0.1245 -0.0028 0.0000
0.0001 0.0002 0.0000 -0.0007 0.0000
-0.0014

816. (0.63628) 3C*(1)Ni 1- C 2- C 55
(0.00%) 0.0000*Ni 1 s(0.00%)
0.0000 0.0000 0.0000 0.0000 0.0000

0.0000 0.0000 0.0000 0.0000 0.0000
0.0000 0.0000 0.0000 0.0000 0.0000
0.0000 -0.0008 0.0000 0.0000 0.0000
0.0002 0.0000 -0.0008 0.0000 0.0000
0.0000 0.0000 0.0000 0.0000 0.0000
0.0000

(50.24%) -0.7088* C 2 s(0.03%)p99.99(99.92%)d 1.79(0.05%)
0.0001 0.0144 -0.0087 0.2474 -0.0281
0.4828 -0.0186 -0.8353 0.0781 -0.0015
0.0158 -0.0054 0.0080 -0.0127

-

(49.76%) 0.7054* C 55 s(0.08%)p99.99(99.87%)d 0.59(0.05%)
0.0001 0.0277 -0.0085 -0.2836 0.0272
0.4892 -0.0196 0.8196 -0.0778 0.0013
-0.0155 0.0055 0.0076 -0.0129

817. (0.33899) 3C*(1)Ni 1- C 2- C 55
(22.75%) 0.4770*Ni 1 s(0.05%)p 0.60(0.03%)d99.99(99.92%)
f 0.00(0.00%)
0.0000 0.0000 0.0000 0.0217 -0.0049
0.0000 0.0000 0.0003 0.0000 -0.0002
-0.0173 0.0000 0.0000 0.0001 -0.0019
0.0001 -0.7148 -0.0015 -0.0076 0.0000
0.1816 0.0005 -0.6747 -0.0017 0.0000
0.0000 0.0002 0.0000 -0.0002 0.0000
-0.0007

(38.49%) -0.6204* C 2 s(0.03%)p99.99(99.92%)d 1.79(0.05%)
-0.0001 -0.0144 0.0087 -0.2474 0.0281
-0.4828 0.0186 0.8353 -0.0781 0.0015
0.0158 0.0054 -0.0080 0.0127

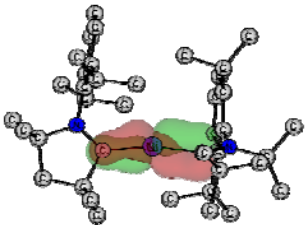
(38.76%) -0.6225* C 55 s(0.08%)p99.99(99.87%)d 0.59(0.05%)
-0.0001 -0.0277 0.0085 0.2836 -0.0272
-0.4892 0.0196 -0.8196 0.0778 -0.0013
0.0155 -0.0055 -0.0076 0.0129

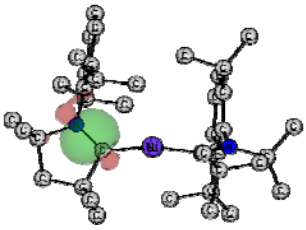
869. (0.03158) BD*(1) N 3- C 55
(33.38%) 0.5778* N 3 s(37.43%)p 1.67(62.54%)d 0.00(0.03%)
0.0000 0.6117 0.0107 -0.6709 0.0204
-0.3982 0.0027 0.1274 0.0066 0.0122
-0.0019 -0.0050 0.0070 -0.0096

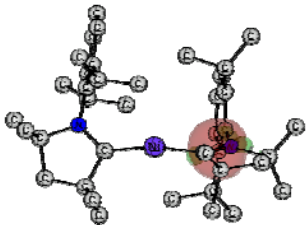
(66.62%) -0.8162* C 55 s(26.08%)p 2.83(73.73%)d 0.01(0.19%)
0.0001 0.5071 0.0607 0.6779 0.0538
0.5110 0.0668 -0.0907 -0.0321 0.0299
-0.0026 -0.0056 0.0202 -0.0227

920. (0.03169) BD*(1) C 2- N 5
(66.61%) 0.8162* C 2 s(26.10%)p 2.82(73.71%)d 0.01(0.19%)
0.0001 0.5073 0.0608 -0.6853 -0.0543
0.4995 0.0656 0.0980 0.0335 -0.0290
-0.0037 0.0059 0.0213 -0.0226

(33.39%) -0.5778* N 5 s(37.44%)p 1.67(62.53%)d 0.00(0.03%)
0.0000 0.6118 0.0108 0.6765 -0.0205
-0.3858 0.0022 -0.1354 -0.0068 -0.0118
-0.0024 0.0051 0.0073 -0.0096


1


3


4

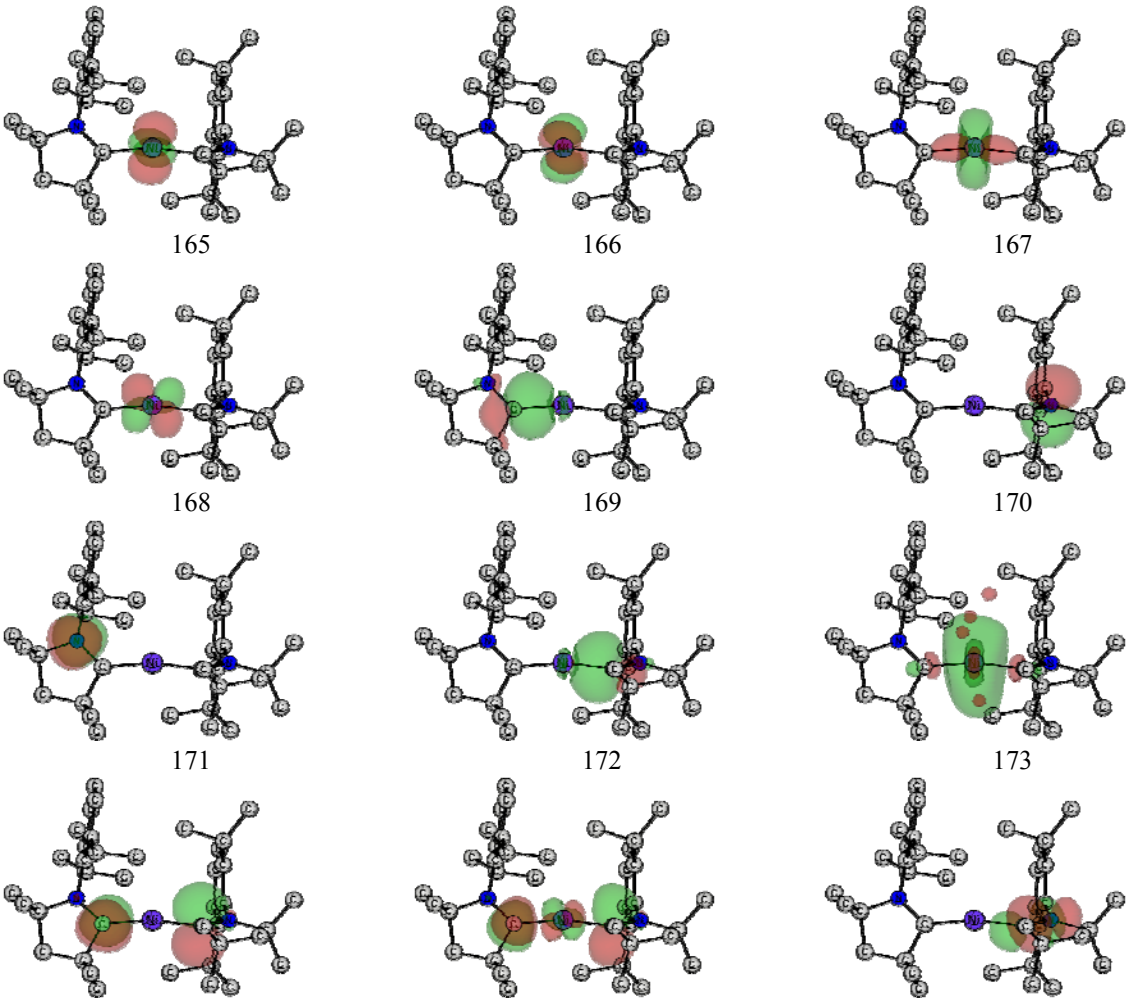


Figure S13. NBOs (isocontour 0.045 au) of compounds **2** (M06/def2-TZVPP) for resonance structure **C**. Hydrogen atoms are omitted for clarity.

Table S15. SECOND ORDER PERTURBATION THEORY ANALYSIS

Donor NBO (i)	Acceptor NBO (j)	E(2) kcal/mol	E(j)-E(i) a.u.	F(i,j) a.u.
1. 3C*(1)Ni 1- C 2- C55	817. 3C*(1)Ni 1- C 2- C55	2.27	0.18	0.019
168. LP (4)Ni 1	816. 3C*(1)Ni 1- C 2- C55	43.33	0.06	0.051
1. 3C*(1)Ni 1- C 2- C55	920. BD*(1) C 2- N 5	0.15	0.71	0.009
3. BD (1) C 2- N 5	173. LP (5)Ni 1	3.13	0.90	0.053
3. BD (1) C 2- N 5	816. 3C*(1)Ni 1- C 2- C55	0.12	0.72	0.010
171. LP (1) N 5	1. 3C*(1)Ni 1- C 2- C55	5.71	0.06	0.037
171. LP (1) N 5	816. 3C*(1)Ni 1- C 2- C55	59.62	0.17	0.097
171. LP (1) N 5	817. 3C*(1)Ni 1- C 2- C55	41.24	0.24	0.090
4. BD (1) N 3- C55	173. LP (5)Ni 1	3.14	0.90	0.053
4. BD (1) N 3- C55	816. 3C*(1)Ni 1- C 2- C55	0.08	0.72	0.008
170. LP (1) N 3	816. 3C*(1)Ni 1- C 2- C55	58.91	0.17	0.097
170. LP (1) N 3	817. 3C*(1)Ni 1- C 2- C55	41.40	0.24	0.090
169. LP (1) C 2	173. LP (5)Ni 1	135.17	0.42	0.223
172. LP (1) C55	173. LP (5)Ni 1	135.53	0.42	0.223

Fehler! Es ist nicht möglich, durch die Bearbeitung von Feldfunktionen Objekte zu erstellen.

Resonance structure **D**

Table S16. (Occupancy) Bond orbital/ Coefficients/ Hybrids for resonance structure **D**

---

2. (1.97664) BD (1) C 2- N 5	
(33.39%) 0.5778* C 2	s(26.12%)p 2.82(73.69%)d 0.01(0.18%) 0.0001 0.5075 0.0610 -0.6908 -0.0536 0.4872 0.0660 0.1187 0.0315 -0.0289 -0.0033 0.0060 0.0211 -0.0223
(66.61%) 0.8161* N 5	s(37.44%)p 1.67(62.53%)d 0.00(0.03%) 0.0000 0.6118 0.0108 0.6765 -0.0205 -0.3858 0.0022 -0.1354 -0.0068 -0.0118 -0.0024 0.0051 0.0073 -0.0096
3. (1.97652) BD (1) N 3- C 55	
(66.61%) 0.8162* N 3	s(37.43%)p 1.67(62.54%)d 0.00(0.03%) 0.0000 -0.6117 -0.0107 0.6709 -0.0204 0.3982 -0.0027 -0.1274 -0.0066 -0.0122 0.0019 0.0050 -0.0070 0.0096
(33.39%) 0.5778* C 55	s(26.08%)p 2.83(73.73%)d 0.01(0.18%) -0.0001 -0.5071 -0.0609 -0.6838 -0.0532 -0.4995 -0.0672 0.1097 0.0303 -0.0298 0.0023 0.0057 -0.0200 0.0223
164. (1.96766) LP (1)Ni 1	s(0.00%)p 0.00(0.00%)d 1.00(100.00%) f 0.00(0.00%) 0.0000 0.0000 0.0000 0.0028 -0.0006 0.0000 -0.0001 0.0007 0.0000 0.0000 -0.0002 0.0000 -0.0003 0.0063 0.1774 -0.0010 0.0364 -0.0001 -0.9811 0.0051 -0.0527 0.0003 -0.0420 0.0001 0.0000 0.0001 0.0000 0.0003 0.0000 -0.0001 0.0000
165. (1.96523) LP (2)Ni 1	s(0.13%)p 0.04(0.00%)d99.99(99.87%) f 0.00(0.00%) 0.0000 0.0000 -0.0002 0.0350 -0.0059 0.0000 0.0000 -0.0003 0.0000 0.0002 -0.0070 0.0000 0.0000 0.0002 -0.0095 0.0002 0.4099 -0.0018 0.0759 -0.0004 -0.6709 0.0035 -0.6122 0.0020 0.0000 0.0000 -0.0001 0.0000 0.0000 0.0000 -0.0001
166. (1.93254) LP (3)Ni 1	s(15.06%)p 0.00(0.00%)d 5.64(84.94%) f 0.00(0.00%) 0.0000 0.0000 0.0002 0.3879 -0.0100 0.0000 0.0000 0.0001 0.0000 0.0000 -0.0046 0.0000 0.0000 -0.0004 -0.0126 -0.0001 -0.5213 -0.0028 -0.0020 0.0000 -0.6529 -0.0039 0.3887 0.0006 0.0000 0.0000 0.0000 0.0000 0.0001 0.0000 0.0002
167. (1.73226) LP (4)Ni 1	s(0.00%)p 1.00(0.04%)d99.99(99.96%) f 0.00(0.00%) 0.0000 0.0000 -0.0001 0.0025 0.0003 0.0000 0.0024 0.0035 0.0000 0.0000 0.0002 0.0000 -0.0025 0.0190 0.9838

0.0029 -0.0045 -0.0001 0.1777 0.0006
-0.0073 -0.0001 0.0120 -0.0001 0.0001
0.0007 0.0000 0.0002 0.0000 -0.0002
0.0000

168. (1.60665) LP (5)Ni 1 s(0.17%)p 0.18(0.03%)d99.99(99.79%)
f 0.00(0.00%)
0.0000 0.0000 -0.0002 0.0415 -0.0046
0.0000 0.0001 0.0004 0.0000 0.0029
-0.0172 0.0000 0.0000 0.0003 0.0074
0.0001 -0.7092 -0.0013 -0.0059 0.0001
0.1872 0.0007 -0.6781 -0.0023 0.0000
0.0000 0.0002 0.0000 -0.0001 0.0000
-0.0006

169. (1.72169) LP (1) C 2 s(38.81%)p 1.58(61.18%)d 0.00(0.01%)
-0.0001 0.6223 -0.0290 0.6808 -0.0437
0.2474 -0.0087 0.2912 -0.0158 -0.0048
-0.0044 -0.0022 -0.0065 0.0041

170. (1.60842) LP (1) N 3 s(0.08%)p99.99(99.90%)d 0.17(0.01%)
-0.0001 0.0284 0.0034 0.1835 0.0018
-0.5299 -0.0025 -0.8273 -0.0022 0.0047
0.0088 0.0034 -0.0048 -0.0026

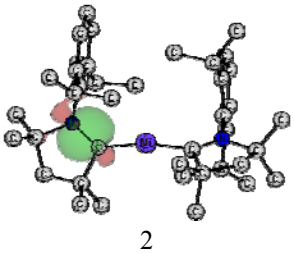
171. (1.60915) LP (1) N 5 s(0.09%)p99.99(99.90%)d 0.16(0.01%)
-0.0001 0.0292 0.0038 -0.1570 -0.0018
-0.5227 -0.0026 0.8373 0.0021 -0.0048
0.0088 -0.0030 -0.0044 -0.0030

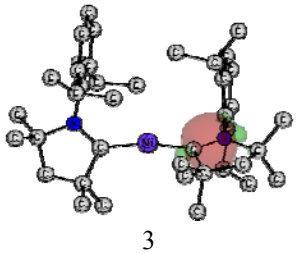
172. (1.72140) LP (1) C 55 s(38.82%)p 1.58(61.17%)d 0.00(0.01%)
-0.0001 0.6224 -0.0289 -0.6793 0.0435
0.2319 -0.0082 -0.3070 0.0170 0.0042
-0.0048 0.0022 -0.0066 0.0039

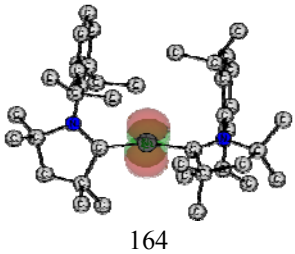
173. (0.45175) LP*(6)Ni 1 s(84.67%)p 0.00(0.00%)d 0.18(15.33%)
f 0.00(0.00%)
0.0000 0.0000 0.0000 0.9200 0.0200
0.0000 0.0000 0.0001 0.0000 0.0000
0.0030 0.0000 0.0000 -0.0003 0.0021
0.0002 0.2359 0.0038 0.0008 0.0000
0.2923 0.0067 -0.1099 -0.0027 0.0000
0.0001 0.0002 0.0000 -0.0007 0.0000
-0.0014

174. (0.67632) LP (2) C 2 s(0.07%)p99.99(99.87%)d 0.81(0.06%)
0.0000 0.0265 0.0053 -0.1957 0.0000
-0.5110 0.0084 0.8361 0.0052 0.0072
-0.0191 0.0068 0.0107 0.0043

175. (0.67577) LP (2) C 55 s(0.07%)p99.99(99.87%)d 0.89(0.06%)
0.0000 0.0254 0.0054 0.2218 0.0001
-0.5134 0.0079 -0.8281 -0.0050 -0.0068
-0.0187 -0.0074 0.0116 0.0038


2


3


164

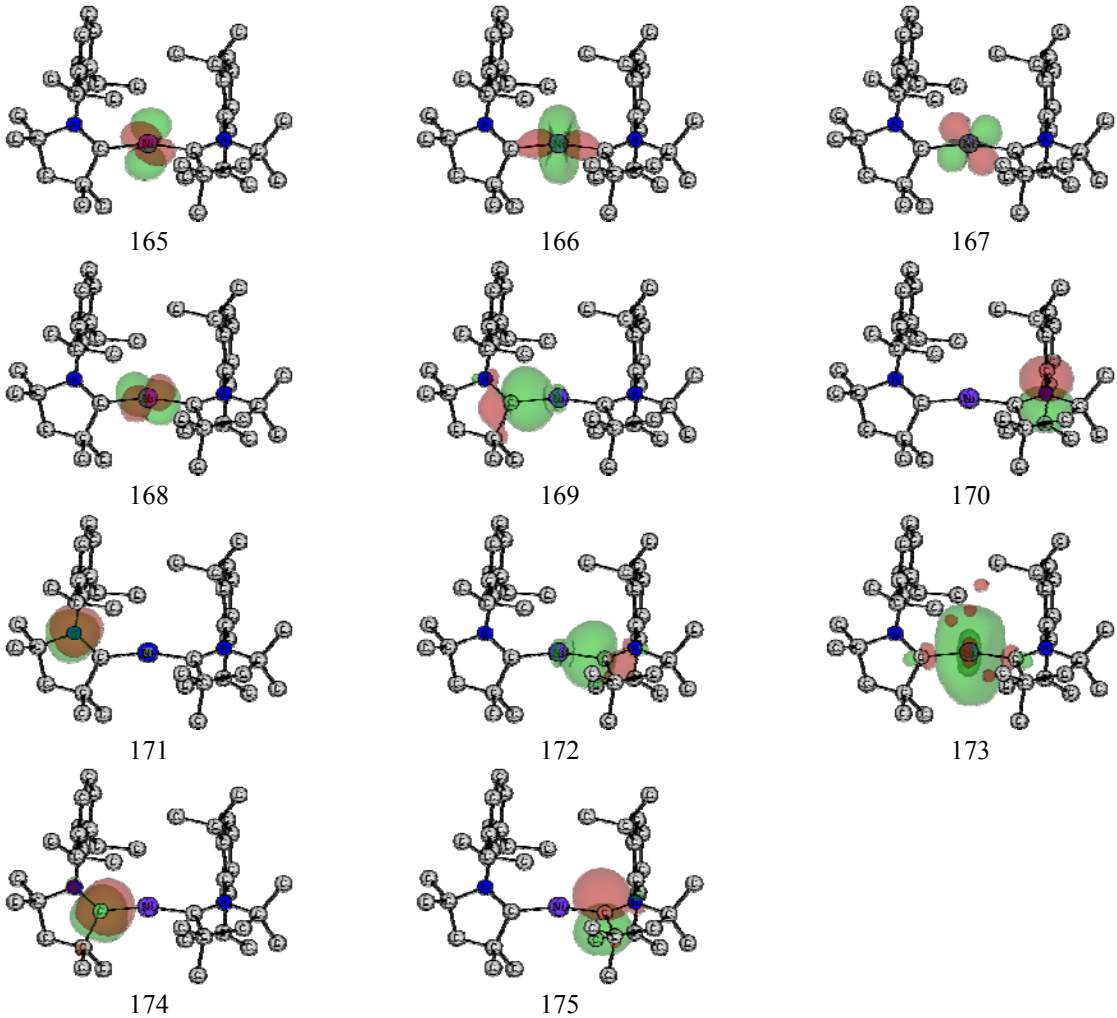


Figure S14. NBOs (isocontour 0.045 au) of compounds **2** (M06/def2-TZVPP) for resonance structure **D**. Hydrogen atoms are omitted for clarity.

Table S17. SECOND ORDER PERTURBATION THEORY ANALYSIS

Donor NBO (i)	Acceptor NBO (j)	E(2) kcal/mol	E(j)-E(i) a.u.	F(i,j) a.u.
165. LP (2)Ni 1	926. BD*(1) C 2- N 5	0.21	0.68	0.011
166. LP (3)Ni 1	926. BD*(1) C 2- N 5	0.49	0.69	0.017
165. LP (2)Ni 1	174. LP (2) C 2	0.11	0.08	0.003
167. LP (4)Ni 1	174. LP (2) C 2	22.36	0.07	0.039
168. LP (5)Ni 1	174. LP (2) C 2	59.84	0.06	0.057
164. LP (1)Ni 1	871. BD*(1) N 3- C55	0.30	0.68	0.013
165. LP (2)Ni 1	175. LP (2) C55	0.12	0.08	0.003
167. LP (4)Ni 1	175. LP (2) C55	22.82	0.07	0.039
168. LP (5)Ni 1	175. LP (2) C55	59.01	0.06	0.057
169. LP (1) C 2	173. LP*(6)Ni 1	134.80	0.42	0.223
174. LP (2) C 2	173. LP*(6)Ni 1	0.37	0.17	0.010
171. LP (1) N 5	174. LP (2) C 2	124.34	0.18	0.144
172. LP (1) C55	173. LP*(6)Ni 1	135.04	0.42	0.223
175. LP (2) C55	173. LP*(6)Ni 1	0.29	0.17	0.008
170. LP (1) N 3	175. LP (2) C55	124.52	0.18	0.144

Fehler! Es ist nicht möglich, durch die Bearbeitung von Feldfunktionen Objekte zu erstellen.

Resonance structure **E**

Table S18. (Occupancy) Bond orbital/ Coefficients/ Hybrids for resonance structure **E**

---

1. (1.94517) BD (1)Ni 1- C 2

(80.52%) 0.8973*Ni 1 s(2.78%)p 0.01(0.03%)d34.98(97.19%) f 0.00(0.00%)
0.0000 0.0000 0.0007 0.1665 0.0066 0.0000 -0.0002 0.0023 0.0001 -0.0008 -0.0100 0.0000 0.0005 0.0137 0.6983 0.0019 -0.4597 -0.0012 0.1205 0.0005 0.1694 0.0008 -0.4793 -0.0016 0.0001 0.0007 0.0002 0.0001 -0.0003 -0.0004 -0.0009

(19.48%) 0.4414* C 2 s(1.44%)p68.35(98.52%)d 0.02(0.03%)
0.0000 0.1201 0.0016 -0.0545 0.0189 -0.5155 0.0690 0.8421 -0.0482 -0.0140 0.0068 -0.0062 0.0009 0.0081

2. (1.92255) 3C (1)Ni 1- C 2- C 55

(23.34%) 0.4831*Ni 1 s(77.55%)p 0.00(0.02%)d 0.29(22.43%) f 0.00(0.00%)
-0.0001 0.0001 0.0054 0.8782 0.0652 0.0000 0.0000 0.0001 0.0009 -0.0002 0.0131 0.0000 0.0002 0.0000 0.0053 0.0001 0.3935 -0.0005 0.0028 0.0000 0.2618 0.0011 0.0293 -0.0009 -0.0001 0.0003 0.0001 0.0004 -0.0010 0.0001 -0.0018

(51.86%) 0.7201* C 2 s(37.01%)p 1.70(62.99%)d 0.00(0.01%)
-0.0001 0.6078 -0.0255 0.7088 -0.0571 0.3165 -0.0099 0.1546 -0.0071 -0.0038 -0.0063 -0.0022 -0.0049 0.0016

(24.80%) 0.4980* C 55 s(36.91%)p 1.71(63.09%)d 0.00(0.01%)
-0.0001 0.6070 -0.0256 -0.7118 0.0564 0.3079 -0.0105 -0.1613 0.0078 0.0031 -0.0067 0.0020 -0.0051 0.0013

3. (1.91258) 3C*(1)Ni 1- C 2- C 55

(0.60%) 0.0777*Ni 1 s(77.55%)p 0.00(0.02%)d 0.29(22.43%) f 0.00(0.00%)
-0.0001 0.0001 0.0054 0.8782 0.0652 0.0000 0.0000 0.0001 0.0009 -0.0002 0.0131 0.0000 0.0002 0.0000 0.0053 0.0001 0.3935 -0.0005 0.0028 0.0000 0.2618 0.0011 0.0293 -0.0009 -0.0001 0.0003 0.0001 0.0004 -0.0010 0.0001 -0.0018

(36.22%) -0.6018* C 2 s(37.01%)p 1.70(62.99%)d 0.00(0.01%)
-0.0001 0.6078 -0.0255 0.7088 -0.0571 0.3165 -0.0099 0.1546 -0.0071 -0.0038 -0.0063 -0.0022 -0.0049 0.0016

(63.18%) -0.7949* C 55 s(36.91%)p 1.71(63.09%)d 0.00(0.01%)
0.0001 -0.6070 0.0256 0.7118 -0.0564 -0.3079 0.0105 0.1613 -0.0078 -0.0031 0.0067 -0.0020 0.0051 -0.0013

4. (1.94421) BD (1)Ni 1- C 55

(80.47%) 0.8971*Ni 1 s(2.81%)p 0.01(0.03%)d34.60(97.16%) f 0.00(0.00%)
0.0000 0.0000 -0.0007 -0.1675 -0.0063 0.0000 -0.0002 0.0017 -0.0001 0.0008 0.0102 0.0000 0.0004 0.0134 0.6932 0.0017 0.4472 0.0011 0.1296 0.0004 -0.1799 -0.0009 0.4919 0.0015 0.0002

0.0006 -0.0002 0.0000 0.0003 -0.0004
0.0009

(19.53%) 0.4419* C 55 s(1.58%)p62.45(98.39%)d 0.02(0.03%)
0.0001 -0.1255 -0.0016 -0.0718 0.0195
0.5163 -0.0685 0.8395 -0.0486 -0.0139
-0.0065 -0.0061 -0.0004 -0.0082

6. (1.97560) BD (1) C 2- N 5
(33.35%) 0.5775* C 2 s(27.25%)p 2.66(72.56%)d 0.01(0.19%)
0.0001 0.5185 0.0610 -0.6886 -0.0534
0.4650 0.0697 0.1630 0.0291 -0.0297
-0.0030 0.0057 0.0211 -0.0219

(66.65%) 0.8164* N 5 s(37.44%)p 1.67(62.53%)d 0.00(0.03%)
0.0000 0.6118 0.0108 0.6765 -0.0205
-0.3858 0.0022 -0.1354 -0.0068 -0.0118
-0.0024 0.0051 0.0073 -0.0096

7. (1.97547) BD (1) N 3- C 55
(66.66%) 0.8165* N 3 s(37.43%)p 1.67(62.54%)d 0.00(0.03%)
0.0000 -0.6117 -0.0107 0.6709 -0.0204
0.3982 -0.0027 -0.1274 -0.0066 -0.0122
0.0019 0.0050 -0.0070 0.0096

(33.34%) 0.5774* C 55 s(27.18%)p 2.67(72.63%)d 0.01(0.19%)
-0.0001 -0.5178 -0.0610 -0.6832 -0.0528
-0.4767 -0.0710 0.1540 0.0279 -0.0306
0.0020 0.0053 -0.0201 0.0220

168. (1.96766) LP (1)Ni 1 s(0.00%)p 0.00(0.00%)d 1.00(100.00%)
f 0.00(0.00%)
0.0000 0.0000 0.0000 0.0029 -0.0001
0.0000 -0.0001 0.0007 0.0000 0.0000
-0.0001 0.0000 -0.0003 0.0063 0.1766
-0.0010 0.0365 -0.0002 -0.9813 0.0051
-0.0527 0.0002 -0.0420 0.0001 0.0000
0.0001 0.0000 0.0003 0.0000 -0.0001
0.0000

169. (1.96502) LP (2)Ni 1 s(0.13%)p 0.02(0.00%)d99.99(99.87%)
f 0.00(0.00%)
0.0000 0.0000 0.0002 0.0358 0.0043
0.0000 0.0000 -0.0003 0.0002 0.0001
-0.0056 0.0000 0.0001 0.0003 -0.0094
0.0002 0.4105 -0.0026 0.0759 -0.0004
-0.6701 0.0025 -0.6126 0.0023 0.0000
0.0000 -0.0001 0.0000 -0.0001 0.0000
-0.0002

170. (1.89526) LP (3)Ni 1 s(17.50%)p 0.00(0.02%)d 4.71(82.48%)
f 0.00(0.00%)
-0.0002 0.0002 0.0050 0.3988 0.1264
-0.0001 0.0000 -0.0002 0.0022 -0.0008
0.0133 0.0000 0.0004 -0.0002 -0.0124
-0.0003 -0.5118 -0.0140 -0.0020 -0.0001
-0.6434 -0.0175 0.3850 0.0043 -0.0001
0.0005 -0.0001 0.0006 -0.0004 0.0001
-0.0010

171. (1.60842) LP (1) N 3 s(0.08%)p99.99(99.90%)d 0.17(0.01%)
-0.0001 0.0284 0.0034 0.1835 0.0018
-0.5299 -0.0025 -0.8273 -0.0022 0.0047
0.0088 0.0034 -0.0048 -0.0026

172. (1.60915) LP (1) N 5 s(0.09%)p99.99(99.90%)d 0.16(0.01%)
-0.0001 0.0292 0.0038 -0.1570 -0.0018
-0.5227 -0.0026 0.8373 0.0021 -0.0048
0.0088 -0.0030 -0.0044 -0.0030

173. (0.05796) LP (4)Ni 1 s(95.73%)p 0.02(1.73%)d 0.03(2.52%)

f 0.00(0.01%)
-0.0028 0.0021 0.0687 -0.1124 0.9695
-0.0010 -0.0001 -0.0020 0.0320 -0.0119
0.1270 0.0006 0.0060 0.0020 0.0010
-0.0017 0.0437 -0.0803 -0.0003 -0.0004
 0.0671 -0.0980 -0.0450 0.0269 -0.0008
0.0036 -0.0012 0.0041 -0.0038 0.0004
0.0082

-

815. (0.05840) 3C*(1)Ni 1- C 2- C 55
(76.05%)   0.8721*Ni 1 s(77.55%)p 0.00(0.02%)d 0.29(22.43%)
f 0.00(0.00%)
-0.0001 0.0001 0.0054 0.8782 0.0652
 0.0000 0.0000 0.0001 0.0009 -0.0002
 0.0131 0.0000 0.0002 0.0000 0.0053
0.0001 0.3935 -0.0005 0.0028 0.0000
0.2618 0.0011 0.0293 -0.0009 -0.0001
0.0003 0.0001 0.0004 -0.0010 0.0001
-0.0018
(11.93%) -0.3454* C 2 s(37.01%)p 1.70(62.99%)d 0.00(0.01%)
 -0.0001 0.6078 -0.0255 0.7088 -0.0571
 0.3165 -0.0099 0.1546 -0.0071 -0.0038
-0.0063 -0.0022 -0.0049 0.0016
(12.02%)   0.3467* C 55 s(36.91%)p 1.71(63.09%)d 0.00(0.01%)
0.0001 -0.6070 0.0256 0.7118 -0.0564
 -0.3079 0.0105 0.1613 -0.0078 -0.0031
0.0067 -0.0020 0.0051 -0.0013

920. (0.39896) BD*(1)Ni 1- C 55
(19.53%)   0.4419*Ni 1 s(2.81%)p 0.01(0.03%)d34.60(97.16%)
f 0.00(0.00%)
0.0000 0.0000 0.0007 0.1675 0.0063
0.0000 0.0002 -0.0017 0.0001 -0.0008
-0.0102 0.0000 -0.0004 -0.0134 -0.6932
-0.0017 -0.4472 -0.0011 -0.1296 -0.0004
0.1799 0.0009 -0.4919 -0.0015 -0.0002
 -0.0006 0.0002 0.0000 -0.0003 0.0004
-0.0009
(80.47%) -0.8971* C 55 s(1.58%)p62.45(98.39%)d 0.02(0.03%)
-0.0001 0.1255 0.0016 0.0718 -0.0195
-0.5163 0.0685 -0.8395 0.0486 0.0139
 0.0065 0.0061 0.0004 0.0082

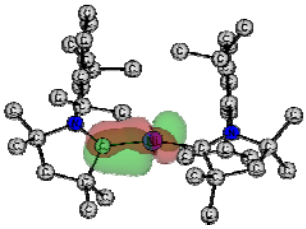
921. (0.03070) BD*(1) N 3- C 55
(33.34%)   0.5774* N 3 s(37.43%)p 1.67(62.54%)d 0.00(0.03%)
0.0000 0.6117 0.0107 -0.6709 0.0204
 -0.3982 0.0027 0.1274 0.0066 0.0122
-0.0019 -0.0050 0.0070 -0.0096
(66.66%) -0.8165* C 55 s(27.18%)p 2.67(72.63%)d 0.01(0.19%)
0.0001 0.5178 0.0610 0.6832 0.0528
0.4767 0.0710 -0.1540 -0.0279 0.0306
-0.0020 -0.0053 0.0201 -0.0220

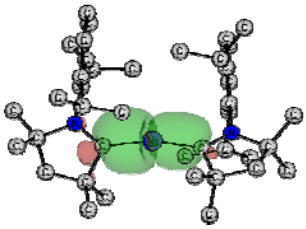
922. (0.39524) BD*(1)Ni 1- C 2
(19.48%)   0.4414*Ni 1 s(2.78%)p 0.01(0.03%)d34.98(97.19%)
f 0.00(0.00%)
0.0000 0.0000 -0.0007 -0.1665 -0.0066
 0.0000 0.0002 -0.0023 -0.0001 0.0008
 0.0100 0.0000 -0.0005 -0.0137 -0.6983
-0.0019 0.4597 0.0012 -0.1205 -0.0005
-0.1694 -0.0008 0.4793 0.0016 -0.0001
-0.0007 -0.0002 -0.0001 0.0003 0.0004
0.0009
(80.52%) -0.8973* C 2 s(1.44%)p68.35(98.52%)d 0.02(0.03%)

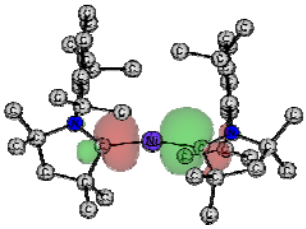
0.0000 -0.1201 -0.0016 0.0545 -0.0189
0.5155 -0.0690 -0.8421 0.0482 0.0140
-0.0068 0.0062 -0.0009 -0.0081

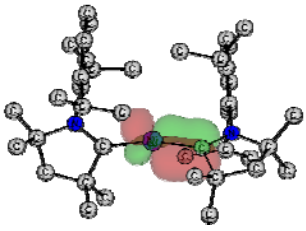
927. (0.03074) BD*(1) C 2- N 5
(66.65%) 0.8164* C 2
s(27.25%)p 2.66(72.56%)d 0.01(0.19%)
0.0001 0.5185 0.0610 -0.6886 -0.0534
0.4650 0.0697 0.1630 0.0291 -0.0297
-0.0030 0.0057 0.0211 -0.0219

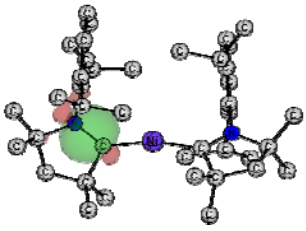
(33.35%) -0.5775* N 5
s(37.44%)p 1.67(62.53%)d 0.00(0.03%)
0.0000 0.6118 0.0108 0.6765 -0.0205
-0.3858 0.0022 -0.1354 -0.0068 -0.0118
-0.0024 0.0051 0.0073 -0.0096

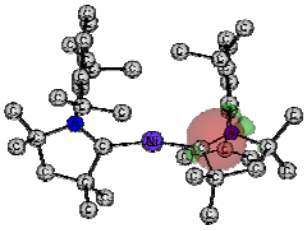

1

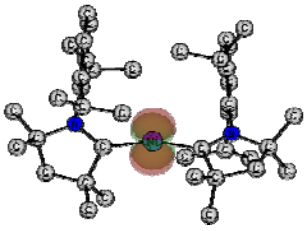

2

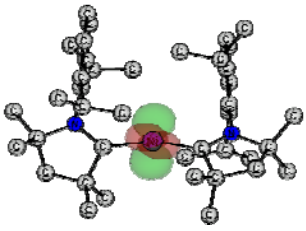

3

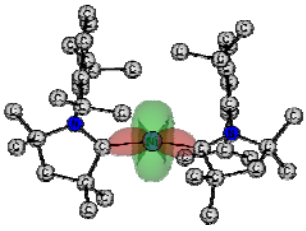

4

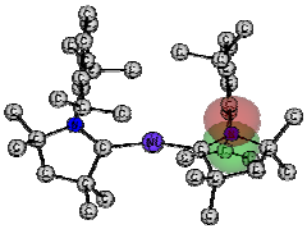

6

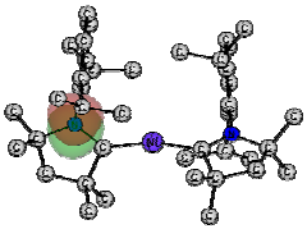

7

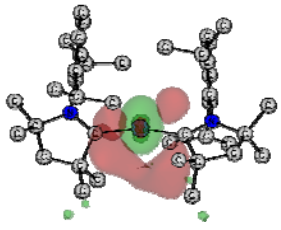

168

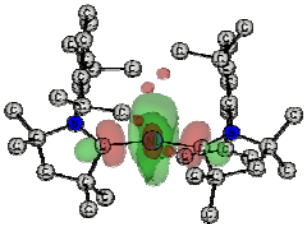

169

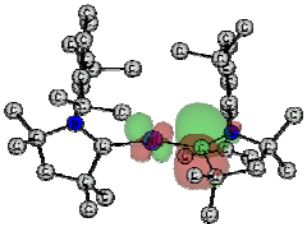

170

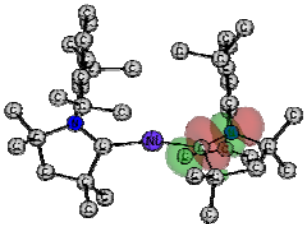

171

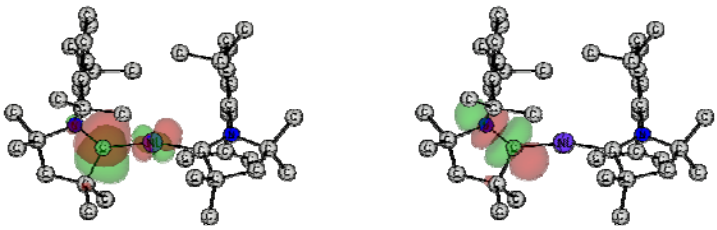

172


173


815


920


921



922 927

Figure S15. NBOs (isocontour 0.045 au) of compounds **2** (M06/def2-TZVPP) for resonance structure **E**. Hydrogen atoms are omitted for clarity.

Table S19. SECOND ORDER PERTURBATION THEORY ANALYSIS

Donor NBO (i)	Acceptor NBO (j)	E(2) kcal/mol	E(j)-E(i) a.u.	F(i,j) a.u.
1. BD (1)Ni 1- C 2	815. 3C*(1)Ni 1- C 2- C55	4.01	0.44	0.037
1. BD (1)Ni 1- C 2	921. BD*(1) N 3- C55	1.05	0.71	0.025
1. BD (1)Ni 1- C 2	922. BD*(1)Ni 1- C 2	5.13	0.15	0.027
2. 3C (1)Ni 1- C 2- C55	173. LP (4)Ni 1	1.73	1.05	0.038
2. 3C (1)Ni 1- C 2- C55	920. BD*(1)Ni 1- C55	2.61	0.45	0.033
2. 3C (1)Ni 1- C 2- C55	922. BD*(1)Ni 1- C 2	3.80	0.45	0.040
2. 3C (1)Ni 1- C 2- C55	927. BD*(1) C 2- N 5	1.44	1.01	0.034
3. 3C*(1)Ni 1- C 2- C55	922. BD*(1)Ni 1- C 2	0.96	0.29	0.016
3. 3C*(1)Ni 1- C 2- C55	920. BD*(1)Ni 1- C55	3.42	0.29	0.030
4. BD (1)Ni 1- C55	815. 3C*(1)Ni 1- C 2- C55	4.24	0.44	0.038
4. BD (1)Ni 1- C55	920. BD*(1)Ni 1- C55	5.29	0.15	0.028
4. BD (1)Ni 1- C55	922. BD*(1)Ni 1- C 2	1.07	0.15	0.012
6. BD (1) C 2- N 5	815. 3C*(1)Ni 1- C 2- C55	0.56	1.06	0.022
7. BD (1) N 3- C55	3. 3C*(1)Ni 1- C 2- C55	0.89	0.48	0.078
7. BD (1) N 3- C55	815. 3C*(1)Ni 1- C 2- C55	0.54	1.06	0.022
170. LP (3)Ni 1	815. 3C*(1)Ni 1- C 2- C55	2.38	0.41	0.028
170. LP (3)Ni 1	921. BD*(1) N 3- C55	0.71	0.68	0.020
170. LP (3)Ni 1	927. BD*(1) C 2- N 5	0.67	0.68	0.019
171. LP (1) N 3	920. BD*(1)Ni 1- C55	89.44	0.22	0.126
171. LP (1) N 3	921. BD*(1) N 3- C55	0.52	0.78	0.020
172. LP (1) N 5	922. BD*(1)Ni 1- C 2	89.73	0.22	0.126
172. LP (1) N 5	927. BD*(1) C 2- N 5	0.52	0.78	0.020

E. TD-DFT Results

Table S20. TD-CAM-B3LYP/def2-SVP results for compound **2** as a singlet closed-shell species in the gas and in the solvent (n-hexane).[a] Wavelength (λ), oscillator strength (f) and main assignment.[b]

	Gas phase (ε=1)			***n*-hexane (ε= 1.8819)**		
	λ(nm)	**f**	**Assignment**	**λ(nm)**	**f**	**Assignment**
1	772.5	0.0022	H→L(+60%) H-2→L(27%)	769.2	0.0031	H→L(+61%) H-2→L(26%)
2	640.3	0.0097	H-2→L(+52%) H→L(+29%)	639.6	0.0130	H-2→L(+52%) H→L(+28%)
3	527.4	0.0093	H-3→L(+30%) H-4→L+5(20%)	526.5	0.0129	H-3→L(+33%) H-4→L+5(22%)
4	399.8	0.3890	H-3→L(+25%)	405.5	0.4618	H-3→L(+27%)

[a] All the geometry was optimized at the M06/def2-SVP. [b] H means HOMO and L means LUMO.

Table S21. TD-UCAM-B3LYP/def2-SVP results for compound **2** as a triplet species the gas and in the solvent (n-hexane).[a] Wavelength (λ), oscillator strength (f), expectation values over the total spin operator (S^2) and main assignment.

	Gas phase (ε=1)			***n*-hexane (ε= 1.8819)**		
	λ(nm)	**f**	**Assignment**	**λ(nm)**	**F**	**Assignment**

1	642.2	0.0035	173→177A(0.954)	674.2	0.0143	173→175A(0.932) 173→177A(0.316)
2	579.3	0.0066	173→175A(0.934)	647.2	0.0004	173→176A(0.989)
3	565.4	0.0029	173→178A(0.865) 173→176A(-0.43)	604.4	0.0013	173→177A(0.935) 173→175A(-0.325)
4	505.1	0.0031	171→172B(0.705) 171→173B(0.479) 172→174A(0.301)	573.8	0.0048	173→178A(0.995)

[a] All the geometry was optimized at the M05-2X/def2-SVP.

(S6). Ab initio calculations

All ab initio calculations were performed with MOLCAS 7.8 program package, and were of CASSCF/CASPT2 level of theory.

Three structural models were employed: **A** (smallest), **B** (medium) and **C** (the entire molecule). The experimental geometry was used without optimization. Smaller models were obtained within the GaussView graphical program by deleting some distant ligand atoms. The broken bonds were saturated with hydrogen atoms, at standard distance imposed by the program. The geometry of the reduced structures was not optimized computationally. Figures S16 – S17 show the structures of the reduced models **A** and **B**.

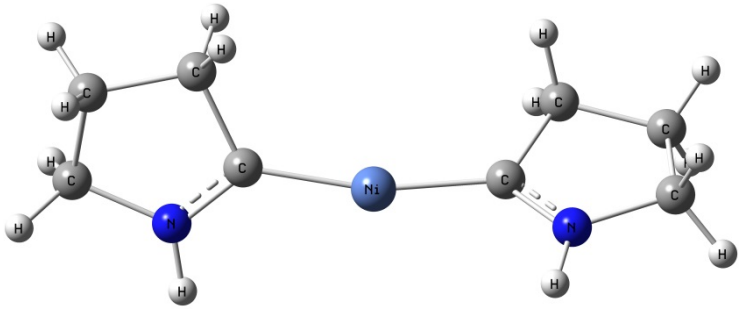


Figure S16. Structure of the model **A**.

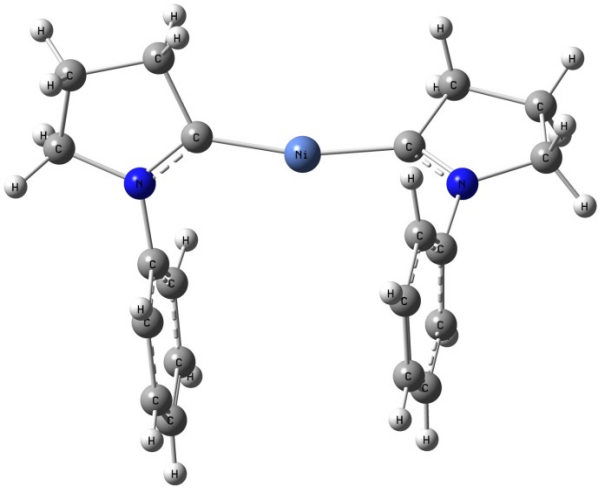


Figure S17. Structure of the model **B**.

All fragmented structural models were computed within three basis set approximations (Basis **1**, Basis **2** and Basis **3**). All basis sets were taken from the ANO-RCC basis set library, available in standard distribution of MOLCAS program package. Table S22 shows the contractions of the employed basis sets.

Table S22. The employed basis sets.

Basis 1	**Basis 2**	**Basis 3**
Ni.ANO-RCC...5s4p2d. N.ANO-RCC...3s2p.	Ni.ANO-RCC...6s5p3d2f1g. N.ANO-RCC...3s2p1d.	Ni.ANO-RCC...7s6p4d3f2g1h. N.ANO-RCC...4s3p2d1f.

C.ANO-RCC...3s2p. H.ANO-RCC...1s.	C.ANO-RCC...4s3p2d1f. (close) C.ANO-RCC...3s2p1d. (distant) H.ANO-RCC...2s.	C.ANO-RCC...5s4p3d2f1g. (close) C.ANO-RCC...4s3p2d1f. (distant) H.ANO-RCC...3s2p1d.

In order to ensure feasibility of the calculations, Cholesky decomposition of bielectronic integrals was employed. Threshold for Cholesky vectors was THRCholesky = 0.1d-7.

Active space of the CASSCF method included ten electrons spanning the five orbitals of the 3*d* shell of Ni^{2+} ion and two orbitals of the carbene radicals, CAS(10 in 7). At the CASPT2 level an imaginary shift of 0.05 Ha was employed in order to avoid intruder-state problems.

One singlet state, two triplet states and one quintet states were computed.

Enlarged RASSCF calculations were performed in order to check the obtained results. In this respect, five doubly occupied and five empty orbitals were added to the RAS1 and RAS3 spaces, respectively. Configurations which allow up to two holes in RAS1 and up to two electrons in RAS3 subspaces of the active space were allowed to mix in the multiconfigurational wave function. It was found that the most important configurations forming the wave function of the spin states (singlet, triplet and quintet) have the orbitals added to the RAS1 subspace doubly occupied. The orbitals added to the RAS3 subspace were empty in the final RASSCF wave functions of the spin states.

This proves the validity of our CASSCF/CASPT2 calculations.

Results of the *ab initio* calculations

Table S23. Energies of the calculated spin free states at CASSCF level of theory (cm^{-1}) in all computational models.

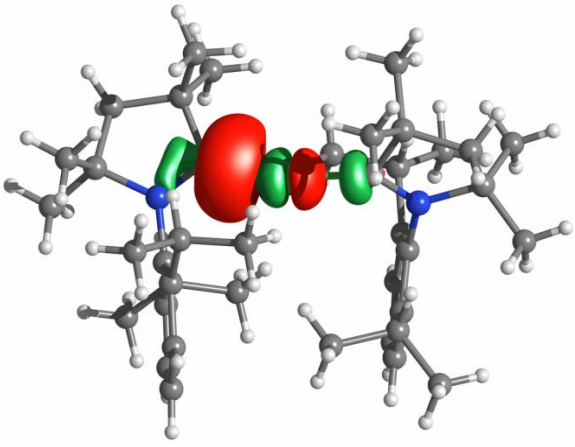
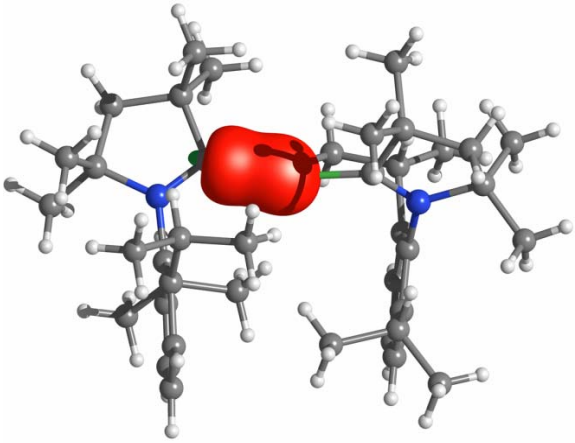
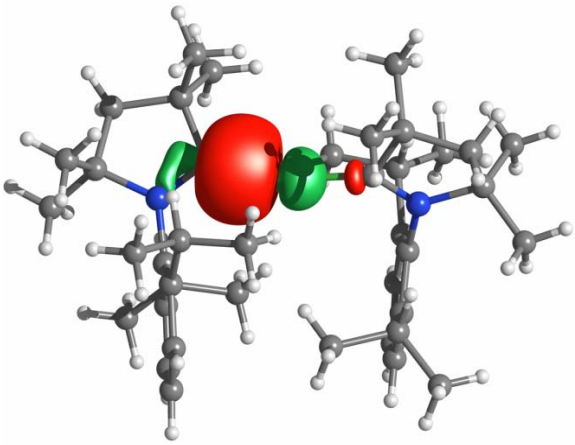
Spin	A1	A2	A3	B1	B2	B3	C1	C2	C2-RASSCF
0	0	0	0	0	0	0	0	0	0
1	5272 5709	5592 6447	5490 6323	4948 5454	5406 5866	5350 5811	5176 5686	5707 6546	9901 10392
2	8987	9401	9191	8590	8895	8818	8998	9751	25261

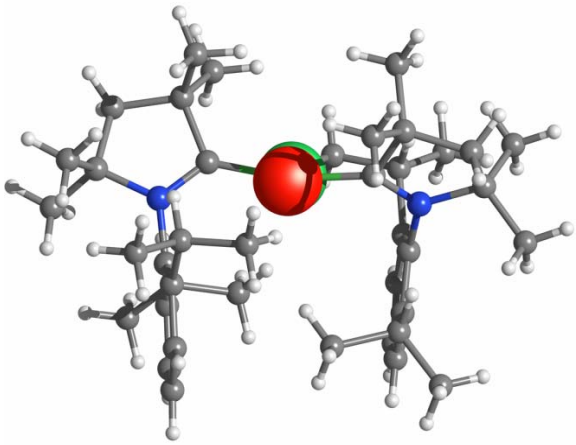
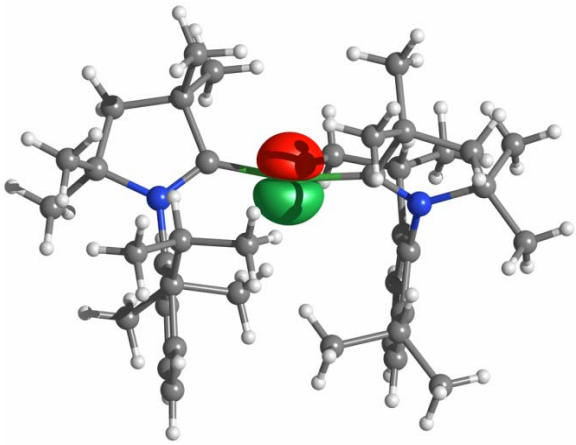
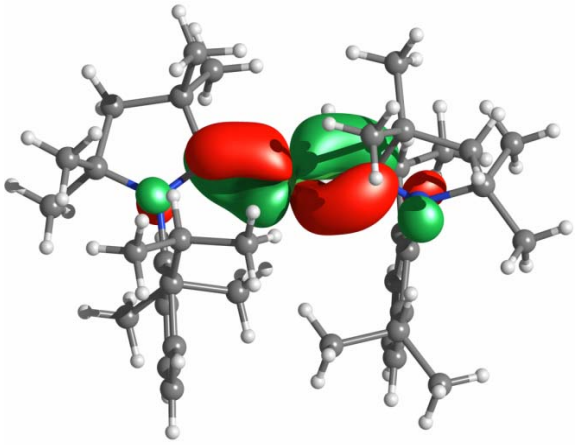
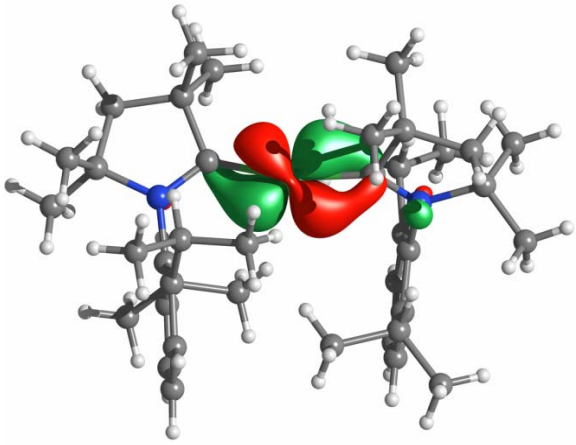
Table S24. Energies of the calculated spin free states at CASPT2 level of theory (cm^{-1}) in all computational models.

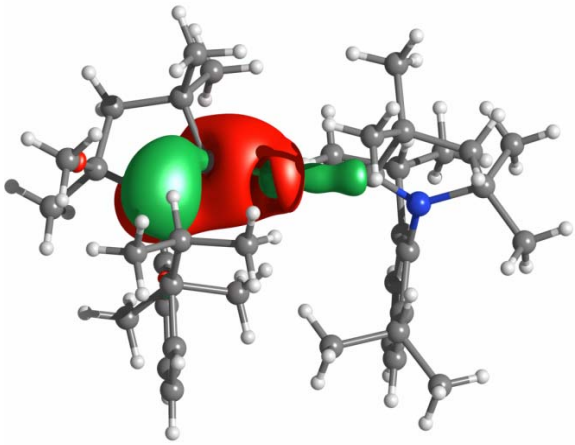
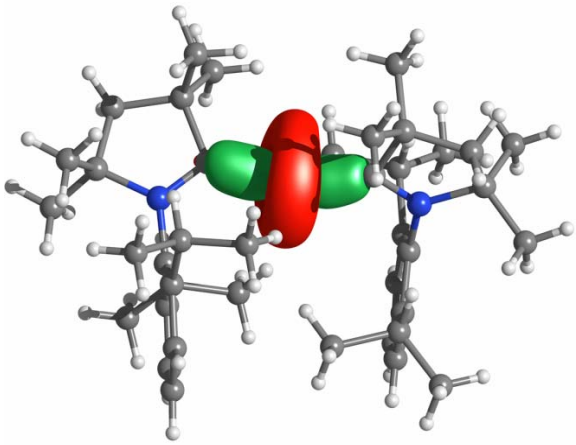
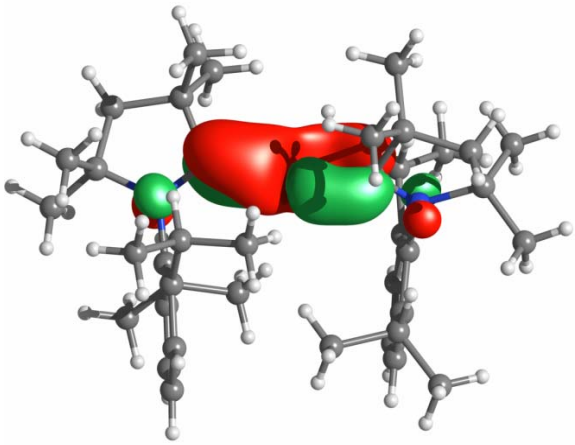
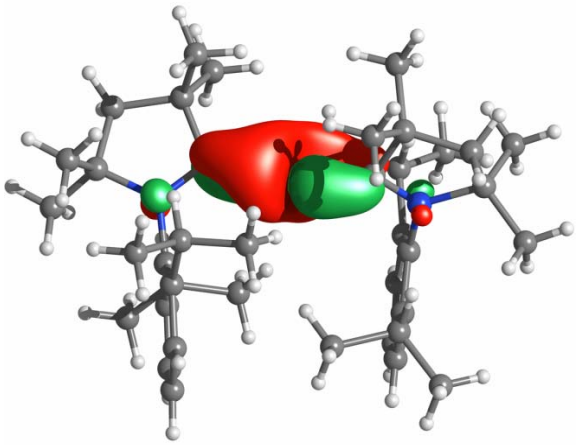
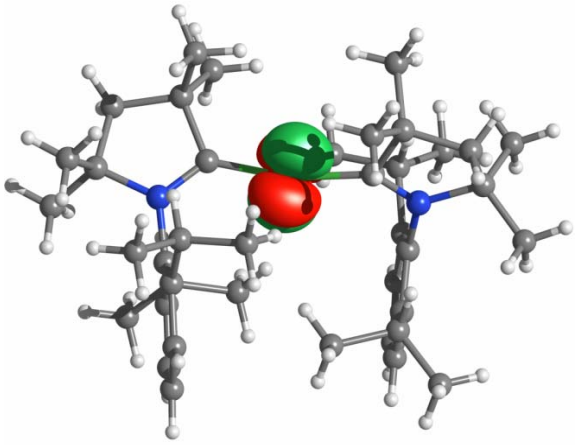
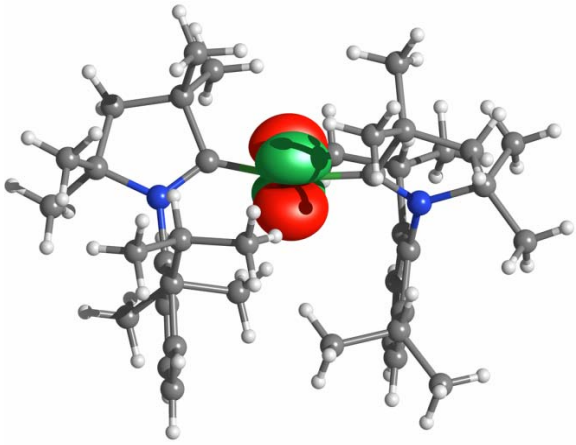
Spin	A1	A2	A3	B1	B2	B3	C1	C2
0	0	0	0	0	0	0	0	0
1	7765 7815	9201 9565	8850 9307	7244 7470	8175 8349	7884 8117	7816 8272	11646 12152
2	18104	20259	19451	17551	19079	18533	18696	23156

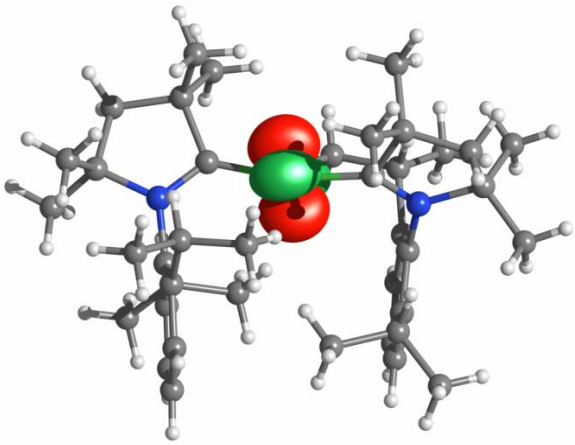
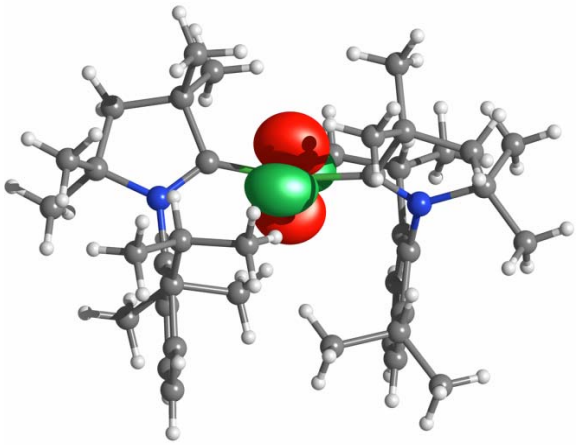
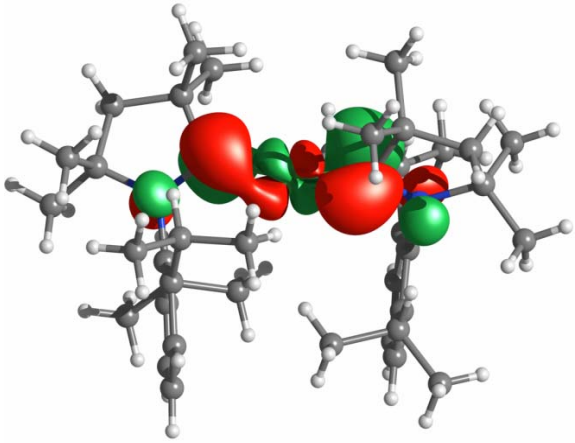
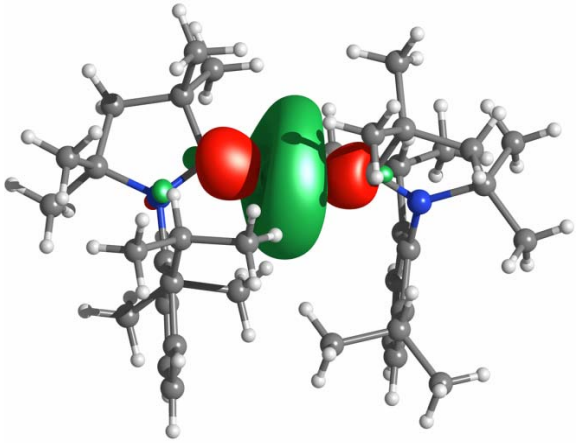
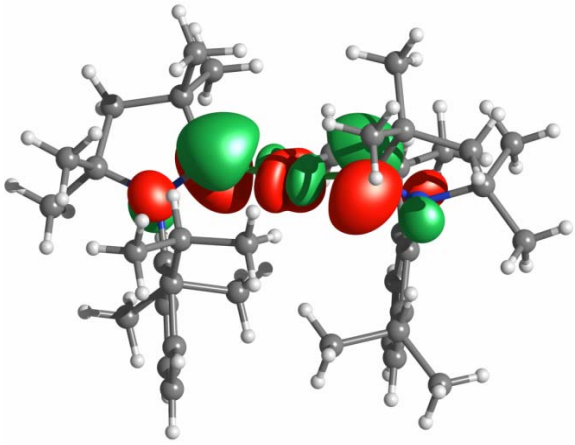
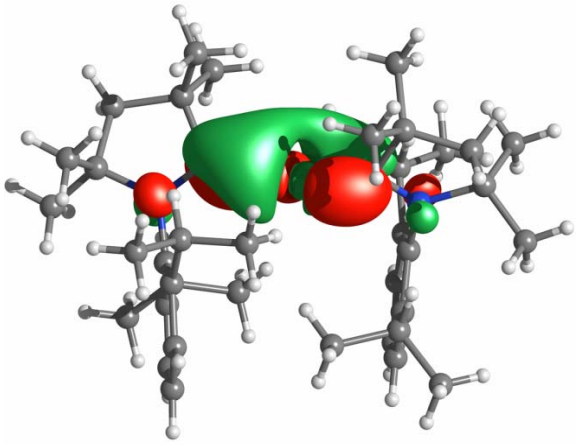
Analysis of the ground singlet state:

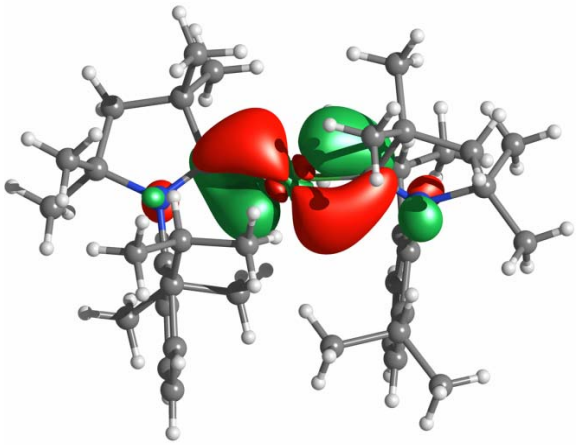
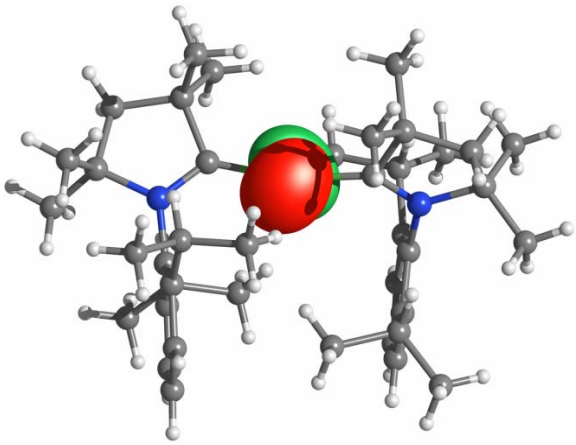
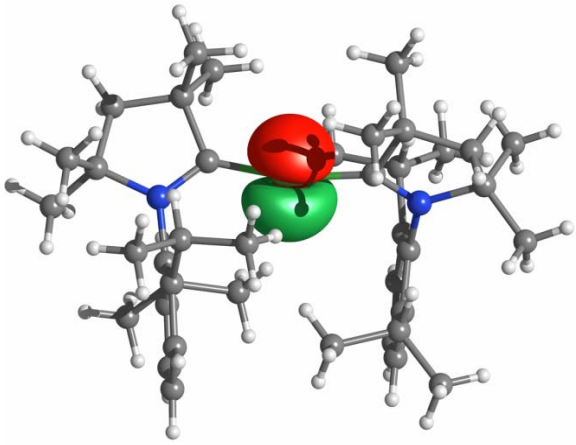
Table S25. Molecular orbitals of the ground state.

Orbital	CASSCF (10,7)	RASSCF (20,17)
163		 57.9% (Ni) + 42.1% (Ligand)
164		 87.3% (Ni) + 12.7% (Ligand)
165		 59.8% (Ni) + 40.2% (Ligand)

166		 99.8% (Ni) + 0.2% (Ligand)
167		 99.8% (Ni) + 0.2% (Ligand)
168	 58.6% (Ni) + 41.4% (Ligand)	 88.9% (Ni) + 11.1% (Ligand)

169		
	13.5% (Ni) + 86.5% (Ligand)	90.4% (Ni) + 9.6% (Ligand)
170		
	61.2% (Ni) + 38.8% (Ligand)	80.8% (Ni) + 19.2% (Ligand)
171		
	99.6% (Ni) + 0.4% (Ligand)	98.7% (Ni) + 1.3% (Ligand)

172		
	99.7% (Ni) + 0.3% (Ligand)	98.9% (Ni) + 1.1% (Ligand)
173		
	36.0% (Ni) + 64.0% (Ligand)	82.8% (Ni) + 17.2% (Ligand)
174		
	35.0% (Ni) + 65.0% (Ligand)	64.0% (Ni) + 36.0% (Ligand)

175	 69.2% (Ni) + 30.8% (Ligand)
176	 85.9% (Ni) + 14.1% (Ligand)
177	 83.2% (Ni) + 16.8% (Ligand)

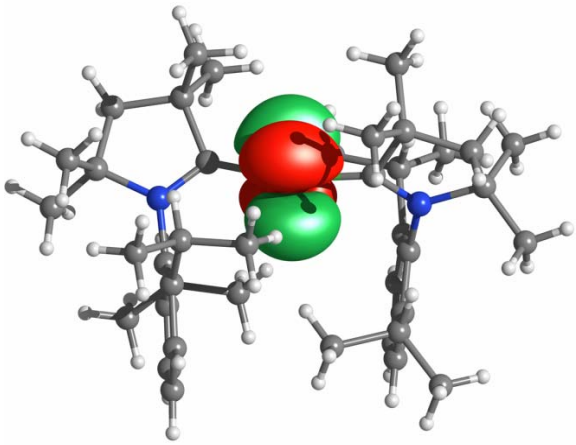
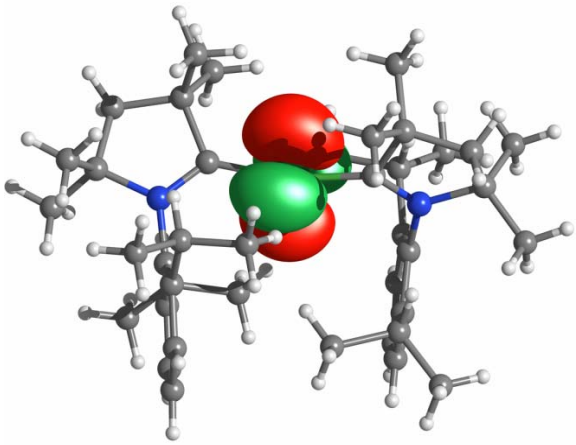
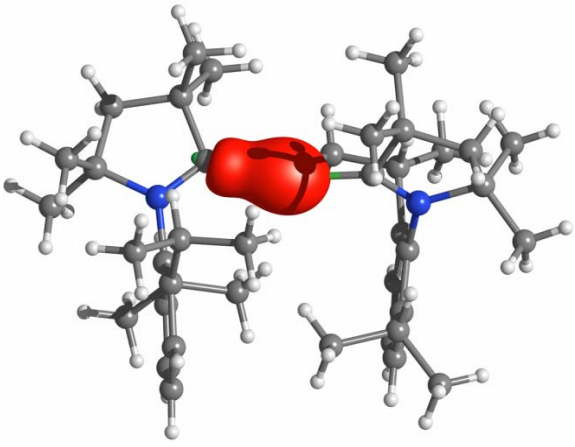
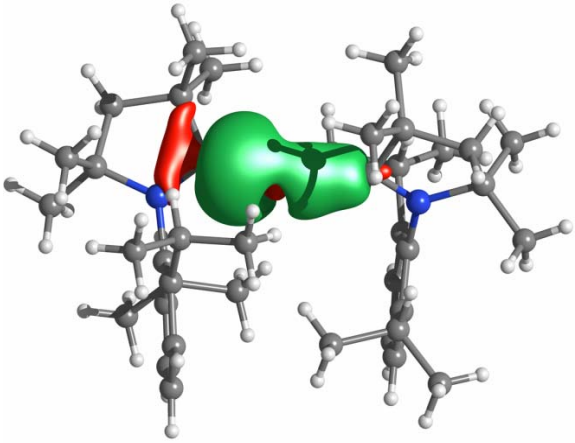
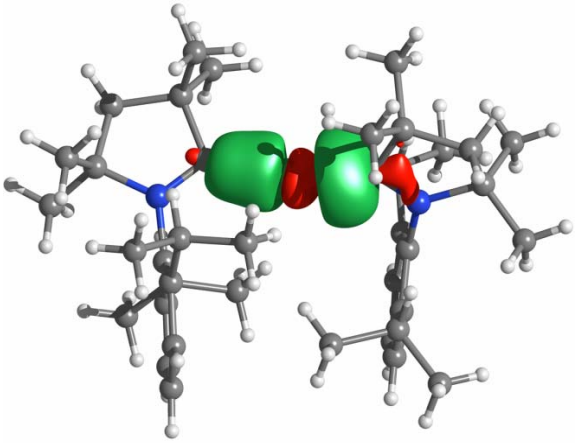
178	 97.3% (Ni) + 2.7% (Ligand)
179	 97.7% (Ni) + 2.3% (Ligand)

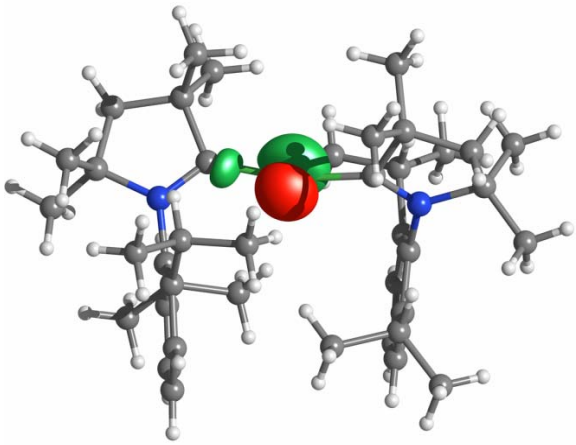
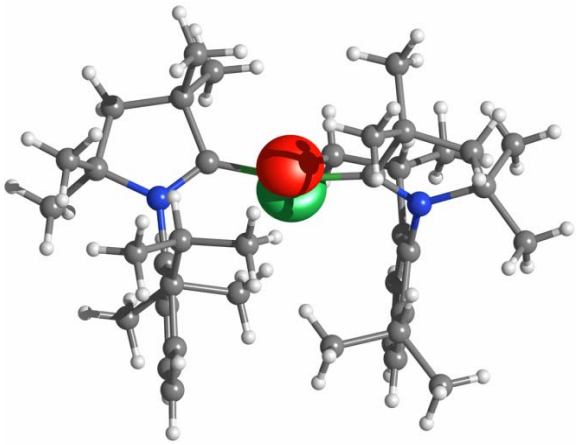
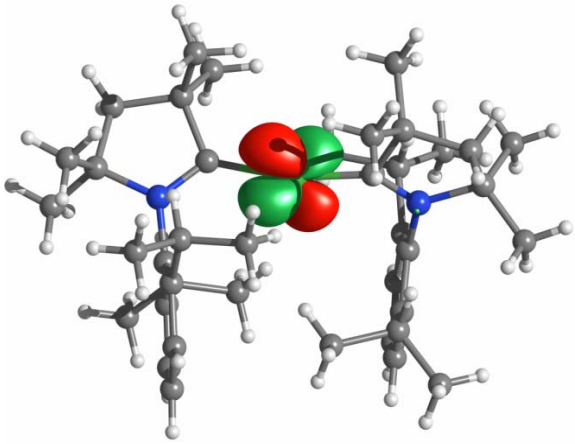
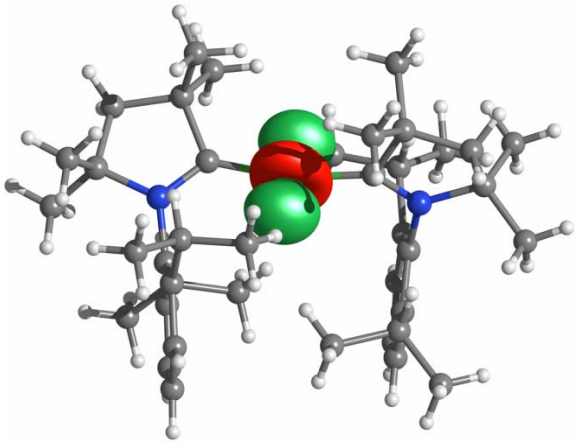
Table S26. Main configurations of the ground state.

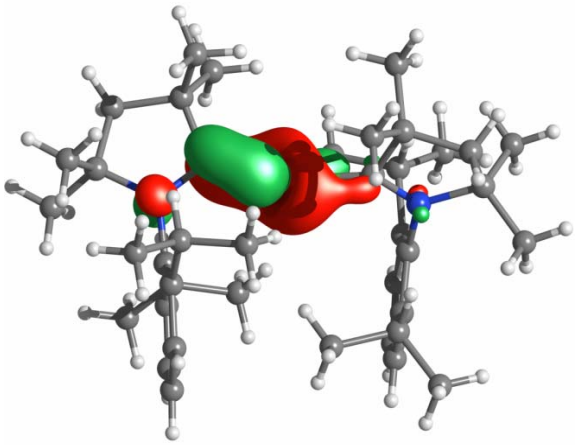
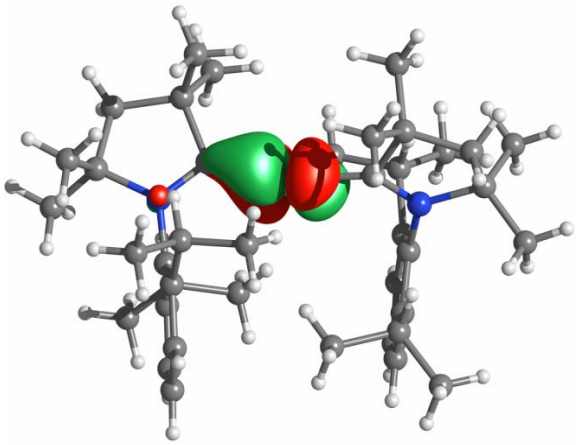
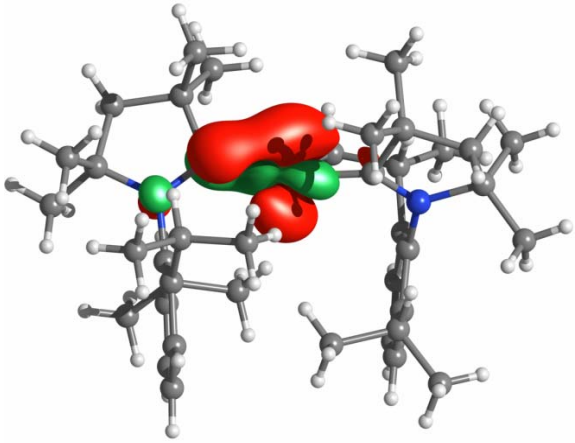
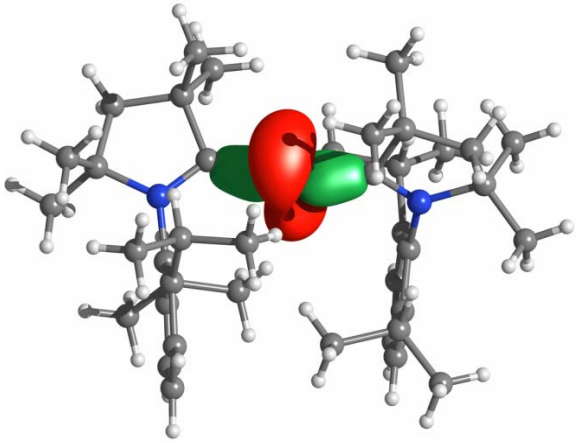
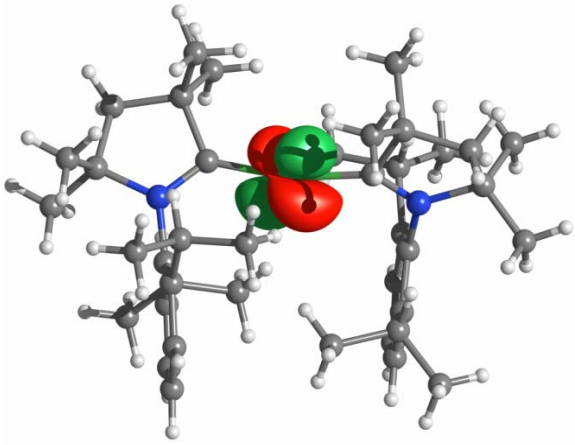
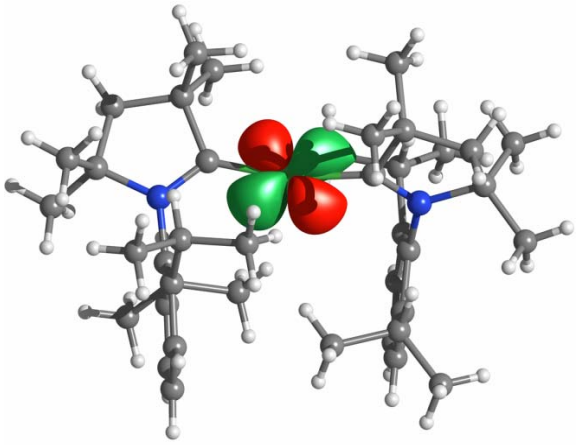
	CASSCF (10,7)	Coeff.	RASSCF(20,17)	Coeff.
1	2222200	0.81425	22222222220000000	0.96118
2	u2d22ud	0.33343	22222220220200000	-0.08159
3	222220	-0.3171	222222uu22dd00000	-0.07733
4	2202202	-0.25649	222222ud22ud00000	0.06733
5	202222	0.17748	22222202222000000	-0.06637
6	222uudd	0.08232	22222uu222d0d0000	-0.05921
7	2202220	-0.07626	22222u2d220ud0000	0.0583
8	222202	-0.06546	22222u2u220dd0000	0.05316
9			22222ud222u0d0000	-0.05168

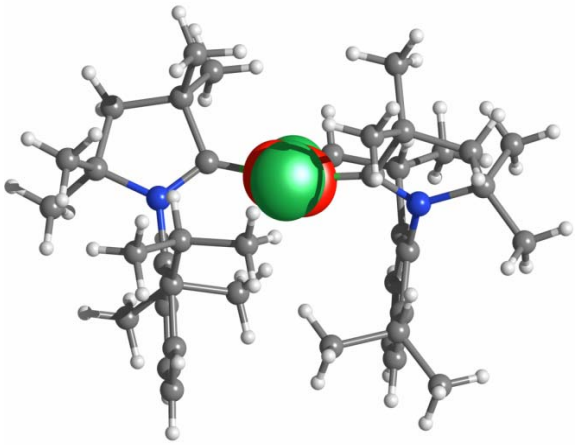
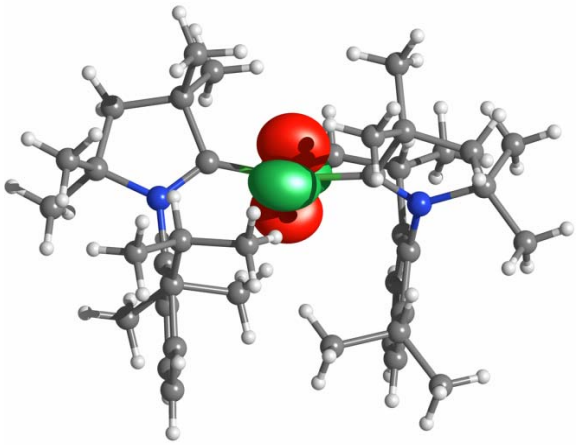
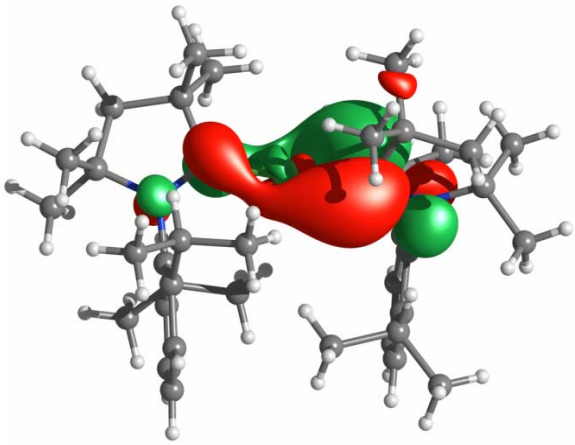
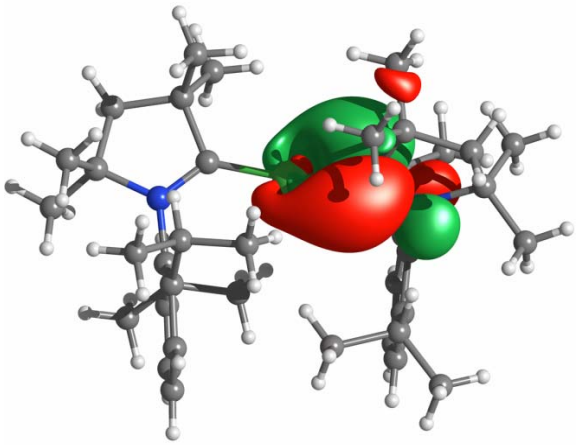
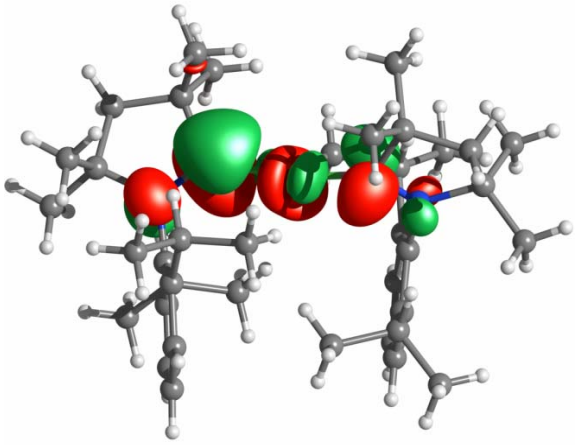
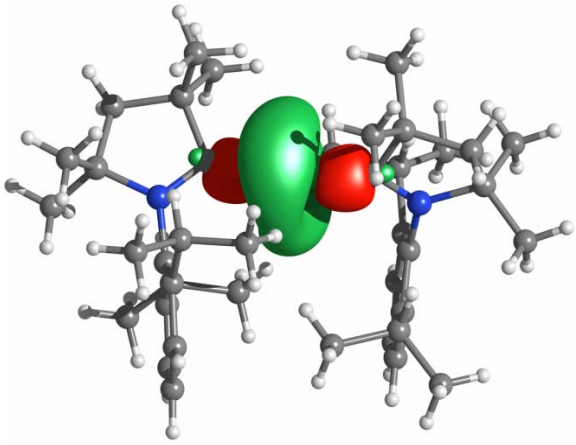
Analysis of the triplet states:

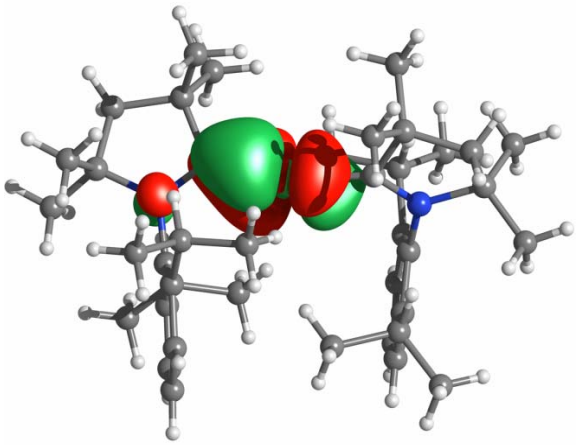
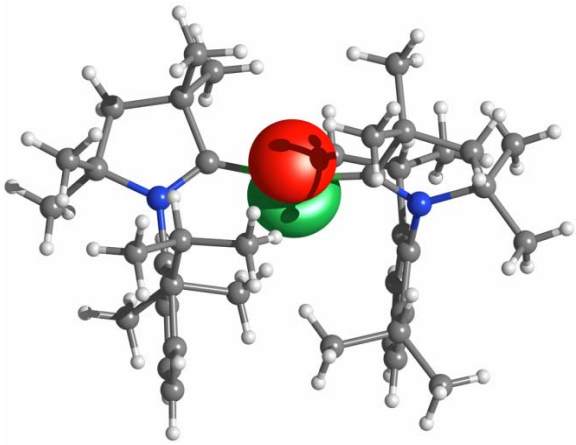
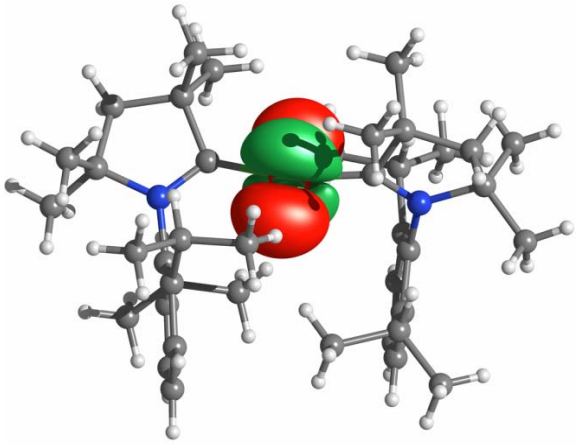
Table S27. Average molecular orbitals of the spin triplet states.

Orbital	CASSCF (10,7)	RASSCF (20,17)
163		 95.4% (Ni) + 4.6% (Ligand)
164		 50.3% (Ni) + 49.7% (Ligand)
165		 73.6% (Ni) + 26.4% (Ligand)

166		97.7% (Ni) + 2.3% (Ligand)
167		99.8% (Ni) + 0.2% (Ligand)
168		
	95.7% (Ni) + 4.3% (Ligand)	99.2% (Ni) + 0.8% (Ligand)

169		
	77.6% (Ni) + 22.4% (Ligand)	95.6% (Ni) + 4.4% (Ligand)
170		
	82.0% (Ni) + 18.0% (Ligand)	95.4% (Ni) + 4.6% (Ligand)
171		
	97.8% (Ni) + 2.2% (Ligand)	97.6% (Ni) + 2.4% (Ligand)

172		
	96.2% (Ni) + 3.8% (Ligand)	99.8% (Ni) + 0.2% (Ligand)
173		
	9.1% (Ni) + 90.9% (Ligand)	6.9% (Ni) + 93.1% (Ligand)
174		
	32.4% (Ni) + 67.6% (Ligand)	89.5% (Ni) + 10.5% (Ligand)

175	 84.6% (Ni) + 15.4% (Ligand)
176	 85.1% (Ni) + 14.9% (Ligand)
177	 97.3% (Ni) + 2.7% (Ligand)

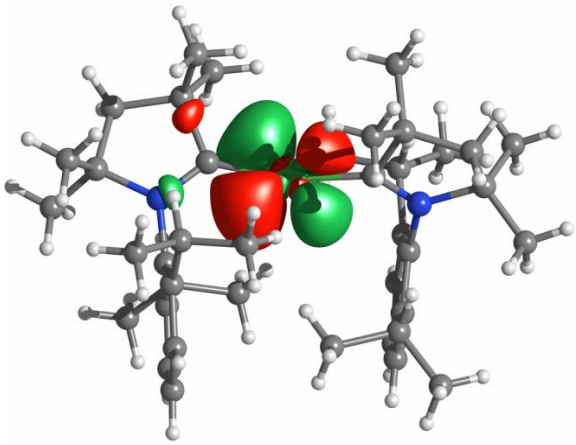
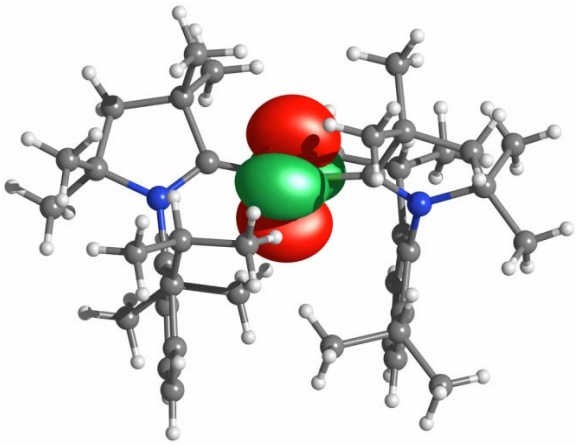
178	 89.4% (Ni) + 10.6% (Ligand)
179	 97.4% (Ni) + 2.6% (Ligand)

Table S28. Main configurations of the spin triplet state.

	CASSCF (10,7)	Coeff.	RASSCF(20,17)	Coeff.
			root 1	
1	22u22u0	-0.64774	22222u2222u000000	0.96778
2	2u222u0	0.44287	222222222uu000000	-0.13327
3	2uu22du	0.28174	22222u2022u200000	0.05972
4	20u22u2	0.2548		
5	2u022u2	0.20937		
6	u2222u0	0.1979		
7	22022uu	0.15202		
8	22u220u	-0.1075		
9	20222uu	-0.10509		
10	2uu2220	0.0915		
			root 2	
1	u2222u0	0.73709	222222222uu000000	0.96802
2	u2u22du	0.26808	22222u2222u00000	0.13332

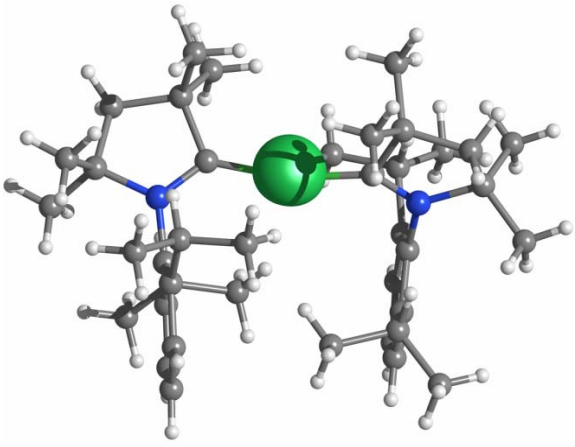
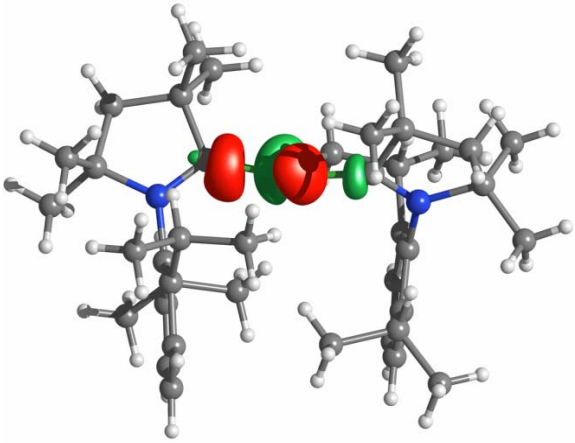
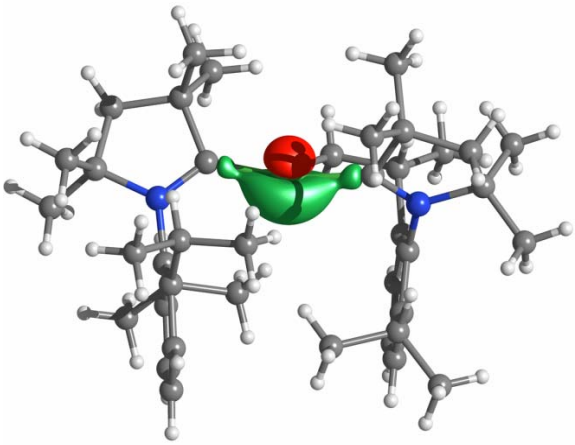
			0	
3	uu222du	0.25188	222222202uu20000	-0.05953
4	uud22u2	0.18727		
5	2u222u0	-0.1757		
6	u0222u2	0.17267		
7	22u220u	-0.16648		
8	u2022u2	0.15636		
9	2uu22du	-0.13267		
10	2u2220u	-0.12123		

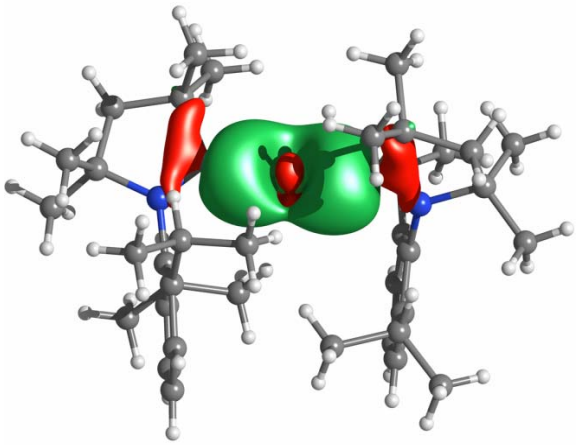
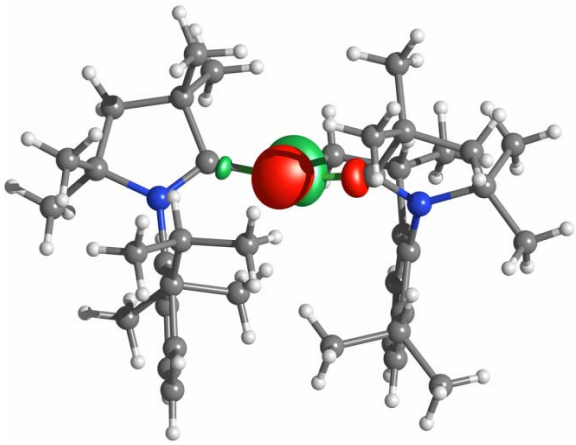
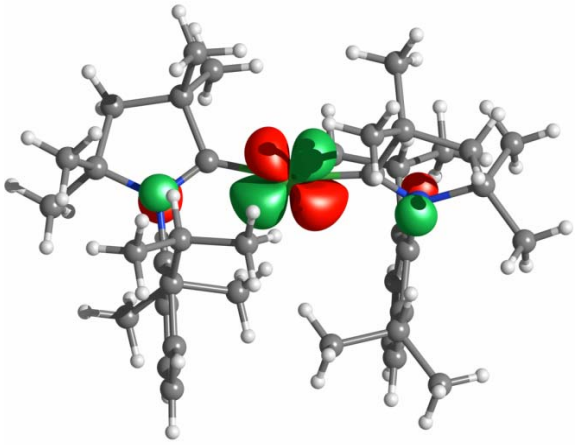
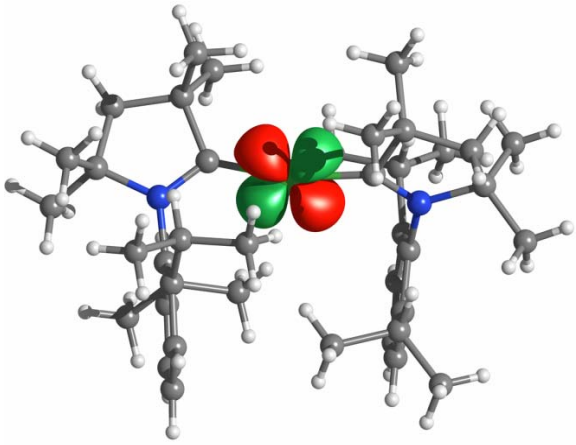
Table S29. Spin density of the spin triplet states.

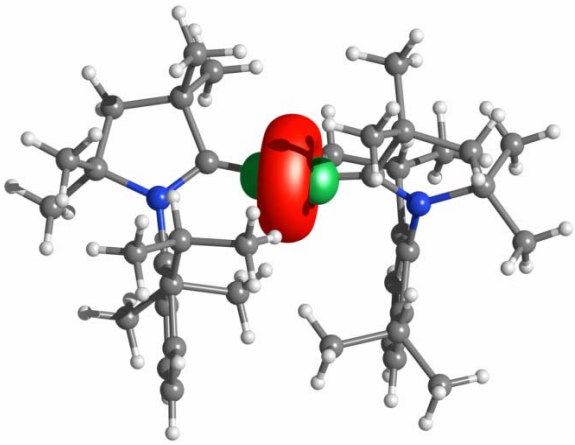
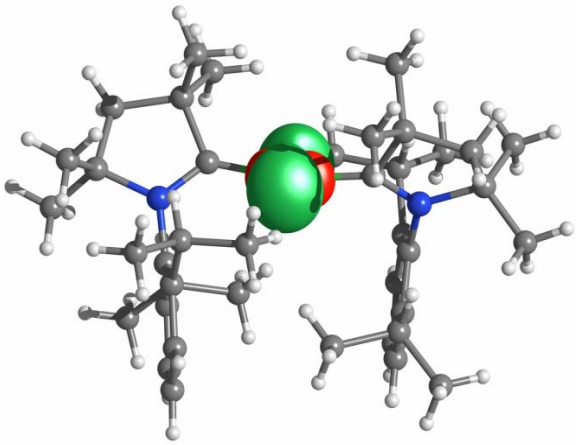
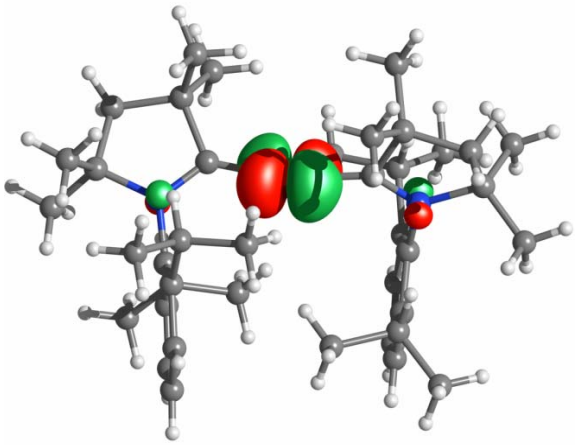
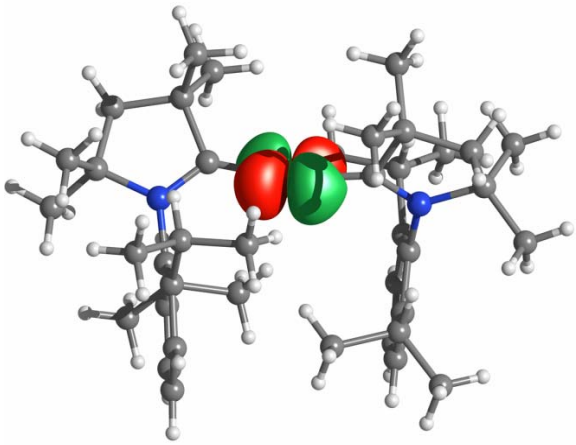
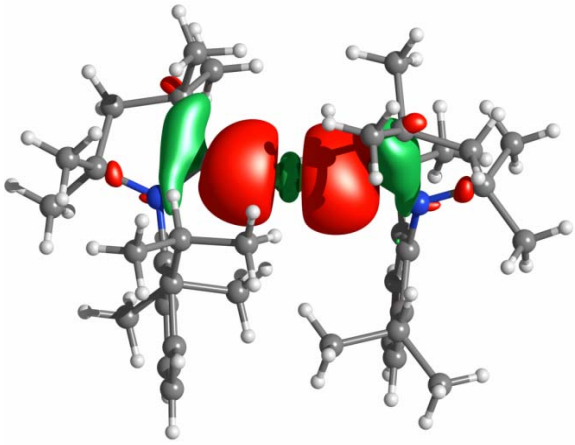
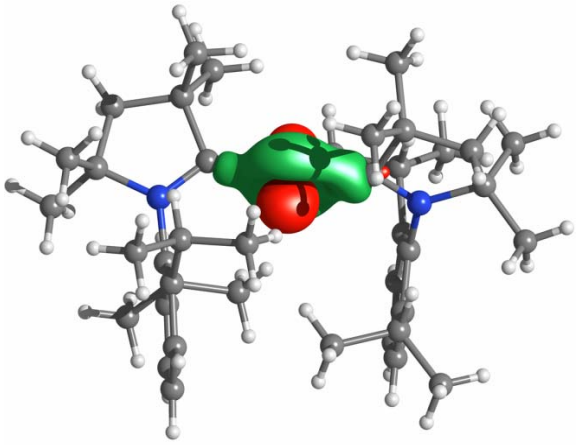
Ni	N1	N2	C1	C1_1
		root 1		
1.1483	0.1083	0.0013	0.0077	0.6732
		root 2		
1.1518	0.1081	0.0016	0.006	0.6706

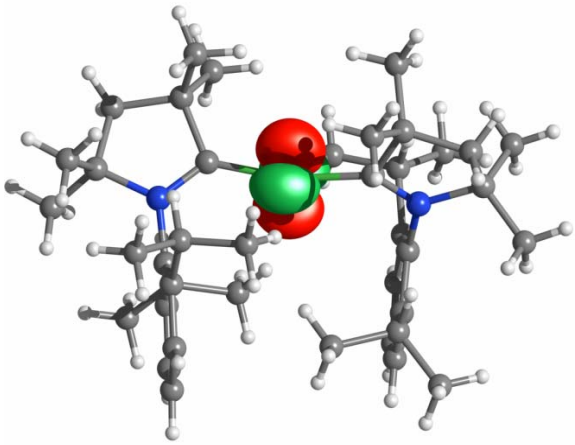
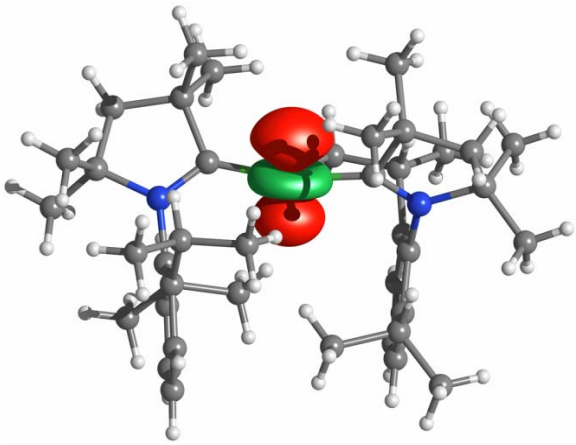
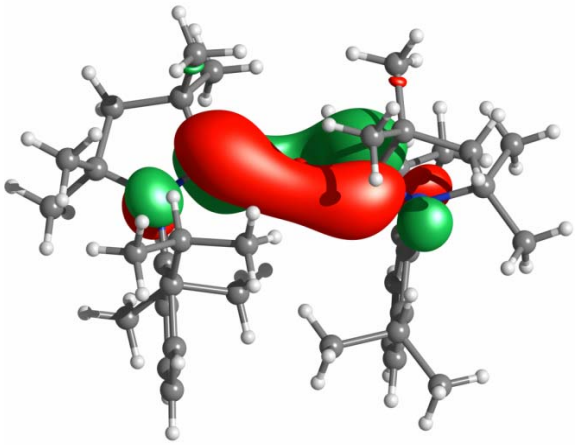
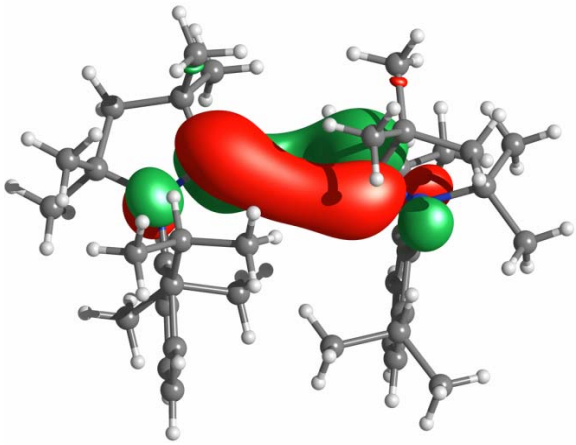
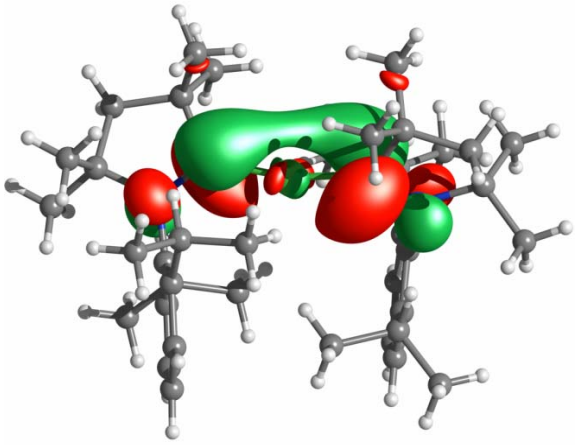
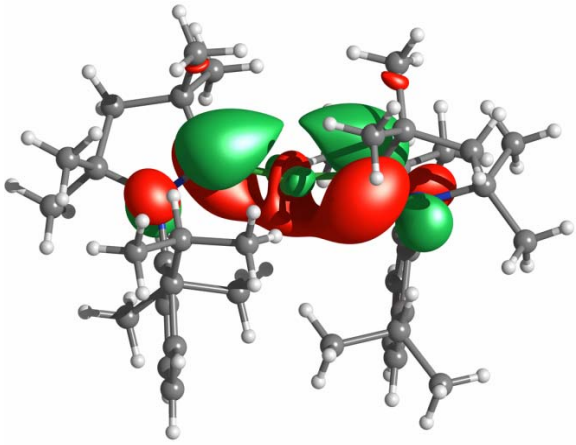
Analysis of the lowest spin quintet state:

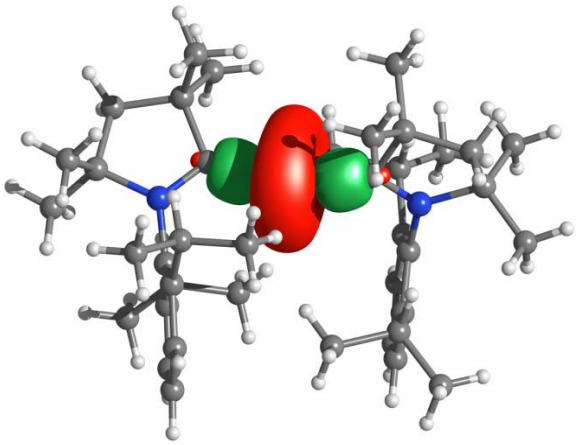
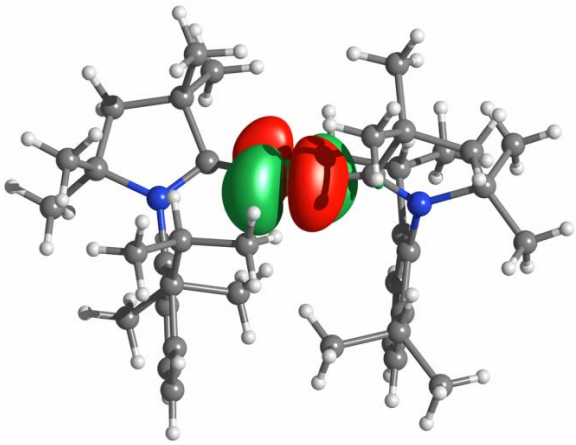
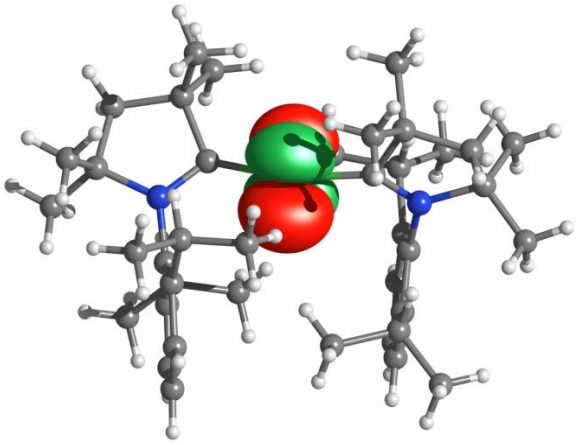
Table S30. Average molecular orbitals of the spin triplet states.

Orbital	CASSCF (10,7)	RASSCF (20,17)
163		 99.7% (Ni) + 0.3% (Ligand)
164		 91.1% (Ni) + 8.9% (Ligand)
165		 97.9% (Ni) + 2.1% (Ligand)

166		39.1% (Ni) + 60.9% (Ligand)
167		96.5% (Ni) + 3.5% (Ligand)
168	 90.2% (Ni) + 9.8% (Ligand)	 98.8% (Ni) + 1.2% (Ligand)

169		
	92.7% (Ni) + 7.3% (Ligand)	94.0% (Ni) + 6.0% (Ligand)
170		
	95.8% (Ni) + 4.2% (Ligand)	98.8% (Ni) + 1.2% (Ligand)
171		
	18.6% (Ni) + 81.4% (Ligand)	95.3% (Ni) + 4.7% (Ligand)

172		
	99.8% (Ni) + 0.2% (Ligand)	95.7% (Ni) + 4.3% (Ligand)
173		
	7.1% (Ni) + 92.9% (Ligand)	8.3% (Ni) + 91.7% (Ligand)
174		
	6.8% (Ni) + 93.2% (Ligand)	8.7% (Ni) + 91.3% (Ligand)

175	 75.1% (Ni) + 24.9% (Ligand)
176	 88.8% (Ni) + 11.2% (Ligand)
177	 98.0% (Ni) + 2.0% (Ligand)

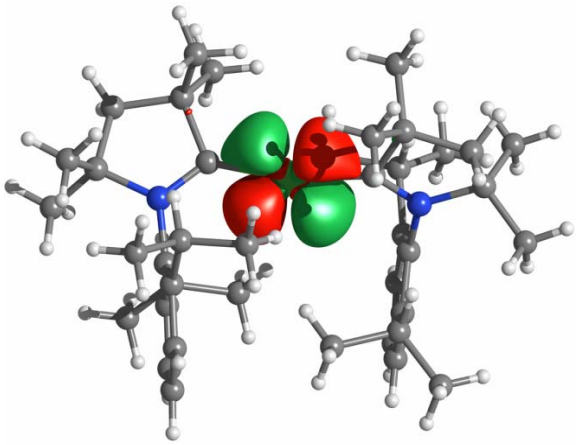
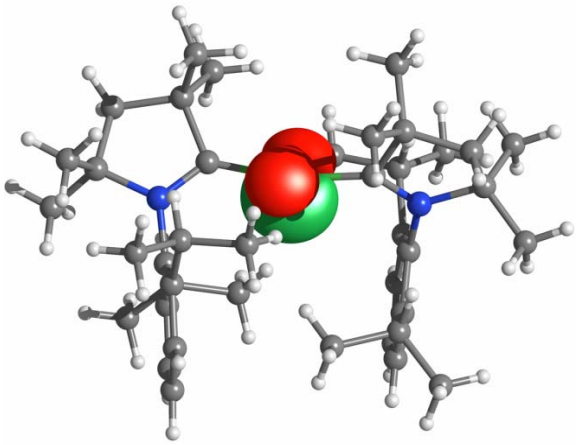
178	 82.2% (Ni) + 17.8% (Ligand)
179	 83.3% (Ni) + 16.7% (Ligand)

Table S31. Main configurations of the spin quintet state

	CASSCF (10,7)	Coeff.	RASSCF(20,17)	Coeff.
1	2u22uuu	0.99917	222222u22uuu0000 0	-0.98565

Table S32. Spin density in the spin quintet state

Ni	N1	N2	C1	C1_1
2.2013	0.1232	0.1235	0.7114	0.7118

(S7). Theoretical calculation at different level

An improvement of the electronic energies of each species has been performed at the M06/def2-TZVPP,[S9,S10] TSPP/def2-TZVPP,[S10,S17] BP86/def2-TZVPP,[S10,S18,S19] PBE0/def2-TZVPP,[S10,S15,S16] and B3LYP/def2-TZVPP[S10,S13,S14] levels of theory. All these methods predict that the singlet closed-shell state lies below the triplet state by 27.0 kcal mol^{-1} (M06), 34.9 kcal mol^{-1} (BP86), 32.2 kcal mol^{-1} (TPSS), 24.2 kcal mol^{-1} (B3LYP), and 18.7 kcal mol^{-1} (PBE0).

(S8). Theoretical calculation of oxidation state of nickel atom in 2

Table S33. Energies of the calculated spin states (2) employing the experimental structure (cm^{-1}).

Spin	CASSCF (10,7)	CASPT2 (10,7)	RASSCF (20,17)
0	0	0	0
1	5707 6546	11646 12152	9901 10392
2	9751	23156	25261

_ENREF_22 _ENREF_21 _ENREF_22In order to acquire better understanding of the electronic structure of the ground and low-lying excited spin states, we have performed high-level multiconfigurational ab initio calculations of CASSCF/CASPT2 level of theory on the experimental structure using MOLCAS program package.[S38] Several structural and computational models were employed in order to ensure reliability of the reported data. Active space of the CASSCF method included five orbitals of the last shell of Ni atom and two orbitals of both carbenes. In order to check the obtained results, we have further enlarged the active space within a RASSCF calculation by including five doubly occupied orbitals and five empty orbitals to the initial active space. Table 1 shows the energies of the obtained spin states within the largest computational model.

All *ab initio* calculations predict the spin singlet to be the lowest in energy. The main configuration of the ground singlet is the one where the orbitals of the last shell are doubly occupied, a picture quite close to the orbital energy scheme shown in Figure S10. Within the CASSCF calculation, in view of hybridization of the Ni and carbene frontier orbitals it is not easy to estimate the exact oxidation state of the central metal atom. However, the RASSCF calculation shows a much smaller hybridization (Table S25), while the main configuration has all five 3d orbitals of the Ni doubly occupied (Table S26).

According to our values the biradicaloid character is about 86.3% which has been computed within CASSCF(2,2) with Molpro. The biradical index does not mean that the compound is 86.3 % of biradical and 13.7 % of closed-shell species. The 86.3 % is just giving an idea of a strong contribution of the triple state into the singlet closed shell ground state of **2**. The CASSCF calculations give the possibility to consider the compound as a "mix" of states. The occupation numbers for HOMO and LUMO are 1.50 and 0.50 electrons, respectively. NBA analysis shows the formation of a double bond with this carbon atom in contrast to a single bond formed with the other carbon atom (Tables S27-S29). We can assume a Ni^{I} electronic configuration for lowest and first excited spin triplet states. Further increase of the spin state leads to a configuration where Ni has two unpaired electrons (S = 1), while each of the close carbon atoms holds one unpaired electron (S = 1/2 on each C), with some small tail on the nitrogen atoms. This picture is quite similar to usual Ni^{II} compounds (Table S30-S32).

(S9). Catalytic studies of compound 2

In this report, we investigated the catalytic activity of the complex **2** for the homo-coupling reaction of various aryl chlorides/fluorides. We initiated the optimization studies using *p*-chlorotoluene (**3c**) as the model substrate (Table S34).

Table S34. Optimization of $(cAAC)_2Ni$ (**2**) catalyzed homo-coupling reaction.

Fehler! Es ist nicht möglich, durch die Bearbeitung von Feldfunktionen Objekte zu erstellen.

General procedure for catalytic studies of compound 2

In an oven-dried schlenk flask, compound $(cAAC)_2Ni$ (**2**) and LDA were dissolved in THF (3-4 mL) under N_2 atmosphere and then the aryl chloride (**3**) (2 mmol) was added drop wise via a syringe and allowed to stir for 4-6 h until **3** disappeared, monitored via thin layer chromatography (TLC). The reaction mixture was concentrated; the residue was dissolved in ethylacetate and extracted. The organic layer was dried, concentrated and purified on silica to afford the desired product **4 (**SiO_2, hexane/ethyl acetate, 200:1 to 100:1). The analytical data of all the biaryl products (**4**) were in accordance with those reported in the literature.[S39] The representative ^1H NMR spectra ($CDCl_3$, 300 MHz, 298 K) of bi-aryl compounds were shown in Figure S18-S20.

Fehler! Es ist nicht möglich, durch die Bearbeitung von Feldfunktionen Objekte zu erstellen.

Figure S18. ^1H NMR spectrum of biphenyl.
HR-MS (154.0783)

Fehler! Es ist nicht möglich, durch die Bearbeitung von Feldfunktionen Objekte zu erstellen.

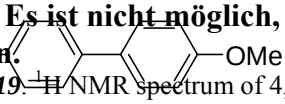


Figure S19. ^{1}H NMR spectrum of 4,4´-dimethoxybiphenyl.
HR-MS (214.0994)

Fehler! Es ist nicht möglich, durch die Bearbeitung von Feldfunktionen Objekte zu erstellen.

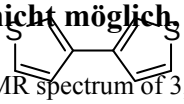


Figure S20. ^{1}H NMR spectrum of 3,3´-bithiophene.
HR-MS (165.9911)

The EI-MS of 4,4´-dimethylbiphenyl (Scheme 2; entry 3) is found to be 182.1.

(S10) Theoretical investigation of mechanistic pathways

All geometries were optimized at the DFT level of theory using the exchange functional of Becke in conjunction with the correlation functional of Perdew (BP86).[S18-19,S40] The basis sets used is def2-SVP. The calculations were carried out with the Gaussian 09 program package.[S41] The energies were obtained by single point calculation on the optimized geometries at M06/def2-TZVPP level of theory. The zero point energy correction was done by adding the zero point energy at the BP86/def2-SVP level of theory.

Fehler! Es ist nicht möglich, durch die Bearbeitung von Feldfunktionen Objekte zu erstellen.

Scheme S6: Schematic representation of the alternative catalytic pathways for the reaction of L_2Ni with PhX to give Ph-Ph (L = :C(Me)$_2$(CH$_2$)(Me)$_2$N-Me and X = Cl, F). The reaction energy of each step is given in Table S35.

Table S35: Reaction energy at the M06/def2-TZVPP//BP86/def2-SVP level of theory incorporating the zero point energy correction from the BP86/def2-SVP level for each step in the alternative catalytic pathways for the reaction of L_2Ni with PhX to give Ph-Ph (L = :C(Me)$_2$(CH$_2$)(Me)$_2$N-Me and X = Cl, F; Scheme S6)

L	X	ΔE_1	ΔE_2	ΔE_3	ΔE_4	ΔE_5	$\Delta E_{overall}$
L	Cl	-50.8	+50.5	-92.6	-42.1	+6.4	-86.5
L	F	-31.8	+44.7	-65.5	-20.8	-17.5	-70.1

Table S36: Optimized Cartesian coordinates (BP86/def2-SVP level of theory) and total energies E (in a.u) at the M06/def2-TZVPP//BP86/def2-SVP level of theory including zero point energy correction from the BP86/def2-SVP level of theory using G09 program package.

Fehler! Es ist nicht möglich, durch die Bearbeitung von Feldfunktionen Objekte zu erstellen.

$(cAAC)_2Ni$

E = -3177.79346

Ni	0.004538000	-0.908614000	-0.097851000
N	-2.855940000	-0.543563000	0.384516000
C	-1.715068000	-1.267669000	0.527825000
C	-4.148392000	-1.173115000	0.908585000
C	-3.669813000	-2.624323000	1.129738000
H	-3.950856000	-3.237444000	0.247115000
H	-4.153378000	-3.088085000	2.014491000
C	-2.118921000	-2.576695000	1.248513000
C	-4.622341000	-0.491220000	2.211400000
H	-3.883841000	-0.580831000	3.030450000
H	-5.563531000	-0.969352000	2.553202000
H	-4.833773000	0.584899000	2.046289000
C	-5.304944000	-1.092492000	-0.104599000
H	-5.077886000	-1.632925000	-1.043220000
H	-5.560357000	-0.042263000	-0.353678000
H	-6.207253000	-1.561522000	0.339950000
C	-1.656863000	-2.513136000	2.725634000
H	-1.973093000	-3.431645000	3.266670000
H	-2.077142000	-1.639589000	3.263648000
H	-0.553822000	-2.436360000	2.783042000
C	-1.481297000	-3.814786000	0.591123000
H	-0.378297000	-3.783465000	0.696592000
H	-1.716573000	-3.864673000	-0.492133000
H	-1.852469000	-4.746086000	1.072818000
C	-2.874254000	0.804077000	-0.145012000
C	-3.180722000	1.010489000	-1.522357000
C	-3.328161000	2.334954000	-1.983372000
H	-3.569256000	2.513114000	-3.043040000
C	-3.163117000	3.428100000	-1.122622000
H	-3.298030000	4.454733000	-1.499480000
C	-2.793873000	3.210720000	0.211362000
H	-2.619528000	4.074357000	0.871852000
C	-2.631074000	1.907468000	0.726318000
C	-3.215007000	-0.144842000	-2.524109000
H	-3.374107000	-1.078825000	-1.950024000
C	-1.826797000	-0.282141000	-3.181999000
H	-1.054750000	-0.443011000	-2.394015000
H	-1.559307000	0.630353000	-3.756263000
H	-1.802611000	-1.148460000	-3.876939000
C	-4.337173000	-0.035074000	-3.571797000
H	-4.362080000	-0.946500000	-4.205457000
H	-4.185780000	0.826577000	-4.256054000
H	-5.335556000	0.081692000	-3.101026000
C	-2.089481000	1.721464000	2.144250000
H	-2.326895000	0.687165000	2.458187000
C	-0.549823000	1.827805000	2.126890000
H	-0.132953000	1.664054000	3.142972000
H	-0.214316000	2.825426000	1.774561000
H	-0.121379000	1.052390000	1.448984000
C	-2.710774000	2.677212000	3.179718000
H	-2.360007000	2.416586000	4.200368000
H	-3.820134000	2.631252000	3.177981000
H	-2.417989000	3.733764000	3.001476000
N	2.842917000	-0.361768000	-0.572562000
C	1.713216000	-1.071132000	-0.826810000
C	4.118732000	-0.807057000	-1.291045000
C	3.512046000	-1.766495000	-2.340430000
H	3.371522000	-1.216498000	-3.295352000
H	4.183996000	-2.623505000	-2.553210000

C	2.124234000	-2.207029000	-1.795444000
C	5.107803000	-1.514212000	-0.338087000
H	4.671177000	-2.411653000	0.140803000
H	5.998016000	-1.841124000	-0.914897000
H	5.461785000	-0.828179000	0.457916000
C	4.862208000	0.373636000	-1.942319000
H	4.237513000	0.895358000	-2.692008000
H	5.197812000	1.113551000	-1.187542000
H	5.763330000	-0.009567000	-2.464472000
C	2.215020000	-3.533300000	-0.999439000
H	2.574029000	-4.353746000	-1.658373000
H	2.904745000	-3.458466000	-0.135211000
H	1.218688000	-3.814046000	-0.605774000
C	1.102834000	-2.390099000	-2.931484000
H	0.103271000	-2.616183000	-2.507846000
H	1.007732000	-1.469353000	-3.542467000
H	1.405448000	-3.223220000	-3.603181000
C	2.863160000	0.797154000	0.294853000
C	2.595762000	2.083069000	-0.262716000
C	2.747495000	3.213249000	0.566678000
H	2.552359000	4.214665000	0.152521000
C	3.132233000	3.086924000	1.908510000
H	3.258058000	3.984570000	2.535067000
C	3.326415000	1.813050000	2.457570000
H	3.582527000	1.717779000	3.524390000
C	3.189689000	0.647731000	1.674065000
C	2.046351000	2.254637000	-1.679745000
H	2.299652000	1.337711000	-2.248678000
C	0.505653000	2.320242000	-1.629993000
H	0.099879000	1.391055000	-1.166589000
H	0.153980000	3.188720000	-1.034923000
H	0.082106000	2.410543000	-2.652203000
C	2.641151000	3.456050000	-2.437579000
H	2.279282000	3.463793000	-3.487193000
H	2.337327000	4.424898000	-1.987467000
H	3.750860000	3.428503000	-2.457566000
C	3.260094000	-0.723972000	2.346672000
H	3.420653000	-1.476313000	1.551740000
C	1.890900000	-1.052057000	2.977972000
H	1.899376000	-2.065453000	3.434117000
H	1.622879000	-0.319266000	3.768606000
H	1.099566000	-1.026283000	2.191648000
C	4.405359000	-0.863745000	3.366139000
H	4.462024000	-1.907434000	3.740692000
H	5.390906000	-0.606261000	2.924229000
H	4.255783000	-0.212037000	4.252916000

$(L)_2Ni$
E = -2323.35445

Ni	-0.009060000	-0.130973000	-0.209861000
N	2.743922000	0.668789000	-0.569105000
C	1.825155000	-0.175798000	-0.052781000
C	4.182297000	0.403612000	-0.237023000
C	4.034664000	-0.652558000	0.892442000
H	4.161853000	-0.153782000	1.876386000
H	4.815753000	-1.437973000	0.825170000
C	2.586968000	-1.218606000	0.779963000
C	4.921591000	-0.148073000	-1.477104000
H	4.445841000	-1.077228000	-1.849418000
H	5.977832000	-0.377573000	-1.224955000
H	4.930016000	0.589754000	-2.306591000
C	4.883447000	1.682134000	0.261564000
H	4.319886000	2.142606000	1.099249000

H	4.996309000	2.438883000	-0.542719000
H	5.901962000	1.435661000	0.627097000
C	2.527526000	-2.565572000	0.019071000
H	3.029388000	-3.371191000	0.598734000
H	3.010670000	-2.503693000	-0.977907000
H	1.466479000	-2.846086000	-0.146352000
C	1.917039000	-1.396235000	2.156707000
H	0.859166000	-1.705059000	2.019352000
H	1.912261000	-0.444575000	2.728103000
H	2.442753000	-2.166723000	2.763025000
N	-2.844638000	-0.594315000	-0.645961000
C	-1.830509000	0.093180000	-0.079456000
C	-4.240652000	-0.159398000	-0.310049000
C	-3.965932000	1.198350000	0.392507000
H	-4.155601000	2.025346000	-0.323871000
H	-4.645190000	1.357216000	1.255484000
C	-2.459329000	1.190995000	0.794173000
C	-4.911482000	-1.187530000	0.629368000
H	-4.332383000	-1.316118000	1.565512000
H	-5.933769000	-0.850069000	0.899326000
H	-5.008372000	-2.181862000	0.145036000
C	-5.086760000	0.010799000	-1.586418000
H	-4.581691000	0.682894000	-2.310654000
H	-5.284472000	-0.959442000	-2.088519000
H	-6.070485000	0.456944000	-1.331304000
C	-2.241461000	0.820351000	2.280901000
H	-2.673029000	1.597951000	2.948781000
H	-2.705148000	-0.154315000	2.537989000
H	-1.154455000	0.733505000	2.485801000
C	-1.764553000	2.537504000	0.507877000
H	-0.672630000	2.422563000	0.676087000
H	-1.904858000	2.844950000	-0.549661000
H	-2.155877000	3.346295000	1.164010000
C	2.366364000	1.757548000	-1.460177000
H	1.258812000	1.735543000	-1.526627000
H	2.689783000	2.743642000	-1.062285000
H	2.800200000	1.631921000	-2.477312000
C	-2.609065000	-1.747997000	-1.502976000
H	-2.898507000	-1.548306000	-2.558256000
H	-1.522193000	-1.963036000	-1.458123000
H	-3.173449000	-2.638954000	-1.150562000

$(L)_2Ni(Ph)(Cl)$
E = -3015.08270

Ni	-0.046876000	-0.381195000	-0.092520000
Cl	-0.613852000	-2.596552000	-0.352633000
N	-2.770064000	-0.228671000	-0.920290000
C	-1.916071000	-0.176150000	0.091965000
C	-4.232989000	-0.356287000	-0.567143000
C	-4.146223000	-0.542818000	0.969980000
H	-4.280113000	-1.616538000	1.214918000
H	-4.942488000	0.018732000	1.499876000
C	-2.715227000	-0.095927000	1.397780000
C	-4.989599000	0.920251000	-0.984559000
H	-4.574907000	1.818922000	-0.485914000
H	-6.060311000	0.833574000	-0.707103000
H	-4.944965000	1.082062000	-2.082014000
C	-4.833684000	-1.596865000	-1.254223000
H	-4.212870000	-2.492685000	-1.047853000
H	-4.920340000	-1.471012000	-2.353355000
H	-5.854243000	-1.780469000	-0.859438000
C	-2.702412000	1.365150000	1.915294000

H	-3.322686000	1.435408000	2.834383000
H	-3.106766000	2.078599000	1.168991000
H	-1.673133000	1.692499000	2.157704000
C	-2.128725000	-1.027804000	2.476018000
H	-1.129519000	-0.672892000	2.800312000
H	-2.009852000	-2.057345000	2.082846000
H	-2.792185000	-1.045236000	3.367429000
N	2.738054000	-0.050364000	-0.885485000
C	1.837897000	-0.636039000	-0.097577000
C	4.186801000	-0.158652000	-0.466465000
C	4.029404000	-0.836715000	0.918532000
H	4.839578000	-1.567345000	1.119434000
H	4.079258000	-0.061181000	1.711864000
C	2.618004000	-1.488768000	0.923172000
C	4.800239000	1.250102000	-0.345359000
H	4.167080000	1.905659000	0.287098000
H	5.803076000	1.177510000	0.124303000
H	4.932366000	1.736939000	-1.333842000
C	4.998234000	-0.997453000	-1.475817000
H	4.583410000	-2.016943000	-1.596171000
H	5.030445000	-0.515627000	-2.475122000
H	6.046055000	-1.092695000	-1.124509000
C	1.964323000	-1.497666000	2.314975000
H	2.556223000	-2.122518000	3.017650000
H	1.890276000	-0.478076000	2.746779000
H	0.943438000	-1.922949000	2.243048000
C	2.668823000	-2.950211000	0.398755000
H	1.645581000	-3.369143000	0.335744000
H	3.117574000	-3.015120000	-0.612378000
H	3.283407000	-3.565448000	1.090775000
C	-2.347199000	-0.367152000	-2.310540000
H	-1.336947000	0.070007000	-2.415748000
H	-2.280475000	-1.440954000	-2.580662000
H	-3.054448000	0.153382000	-2.987388000
C	2.397921000	0.730804000	-2.070177000
H	1.350547000	0.514221000	-2.341943000
H	2.493106000	1.818727000	-1.877695000
H	3.062712000	0.449912000	-2.913220000
C	-0.336134000	2.436234000	-0.842212000
C	0.191639000	1.504738000	0.091874000
C	-0.150800000	3.825924000	-0.707714000
C	0.903093000	2.064706000	1.187062000
C	0.561671000	4.347632000	0.386423000
H	-0.576558000	4.507515000	-1.464005000
C	1.084644000	3.453791000	1.337652000
H	1.332355000	1.400835000	1.956009000
H	0.702923000	5.434730000	0.498870000
H	1.641185000	3.838811000	2.209288000
H	-0.917499000	2.079262000	-1.709403000

$(L)_2Ni(Ph)(F)$
E = -2654.70873

Ni	-0.042068000	-0.362261000	-0.055335000
N	-2.723943000	-0.472894000	-0.953709000
C	-1.926836000	-0.276751000	0.082792000
C	-4.196555000	-0.629954000	-0.655564000
C	-4.166689000	-0.752348000	0.890329000
H	-4.279511000	-1.818939000	1.174550000
H	-5.002034000	-0.196164000	1.362226000
C	-2.767164000	-0.238408000	1.356413000
C	-4.957007000	0.618526000	-1.147328000
H	-4.566537000	1.540913000	-0.673231000
H	-6.034247000	0.529203000	-0.897504000

H	-4.881271000	0.737992000	-2.248387000
C	-4.751681000	-1.899197000	-1.325138000
H	-4.145545000	-2.787878000	-1.054443000
H	-4.779502000	-1.813341000	-2.431262000
H	-5.791915000	-2.073777000	-0.980849000
C	-2.826053000	1.208768000	1.903114000
H	-3.433373000	1.231203000	2.833197000
H	-3.279989000	1.913417000	1.176750000
H	-1.809715000	1.584040000	2.132861000
C	-2.144456000	-1.174636000	2.413565000
H	-1.186097000	-0.760196000	2.786224000
H	-1.925495000	-2.165195000	1.968295000
H	-2.832764000	-1.289567000	3.278421000
N	2.794196000	0.015381000	-0.784353000
C	1.842975000	-0.619566000	-0.102812000
C	4.226301000	-0.313083000	-0.419524000
C	4.007817000	-1.201775000	0.831027000
H	4.730394000	-2.042444000	0.875651000
H	4.158080000	-0.589389000	1.745507000
C	2.531602000	-1.682509000	0.766148000
C	4.989113000	0.982172000	-0.082254000
H	4.437313000	1.583551000	0.669039000
H	5.983331000	0.727797000	0.339794000
H	5.159836000	1.612918000	-0.979022000
C	4.931724000	-1.052250000	-1.576162000
H	4.408595000	-1.991038000	-1.843747000
H	5.001538000	-0.421323000	-2.486661000
H	5.968147000	-1.310245000	-1.276600000
C	1.874474000	-1.805399000	2.151536000
H	2.396441000	-2.571695000	2.764443000
H	1.902326000	-0.844679000	2.707970000
H	0.818676000	-2.110172000	2.013578000
C	2.376007000	-3.039189000	0.025029000
H	1.291879000	-3.236514000	-0.101700000
H	2.853199000	-3.023906000	-0.975931000
H	2.850655000	-3.847723000	0.622230000
C	-2.224305000	-0.628652000	-2.316586000
H	-1.172917000	-0.280699000	-2.325919000
H	-2.238324000	-1.696190000	-2.616107000
H	-2.832556000	-0.037486000	-3.032014000
C	2.542053000	1.005308000	-1.827482000
H	1.483042000	0.937304000	-2.126469000
H	2.734213000	2.034472000	-1.461715000
H	3.191964000	0.804995000	-2.704428000
C	-0.489422000	2.432934000	-0.833357000
C	0.111457000	1.523261000	0.078202000
C	-0.372883000	3.829155000	-0.690920000
C	0.818819000	2.109692000	1.163238000
C	0.338907000	4.377788000	0.390988000
H	-0.850886000	4.495013000	-1.430037000
C	0.930390000	3.504931000	1.322283000
H	1.304366000	1.459864000	1.911718000
H	0.427537000	5.469879000	0.509491000
H	1.488108000	3.913135000	2.182757000
H	-1.069261000	2.048300000	-1.690636000
F	-0.442567000	-2.226938000	-0.043048000

$(cAAC)_2NiCl_2$
E = -4098.28940

Ni	0.000000000	0.000000000	0.000000000
Cl	0.828833000	-1.496776000	1.413818000
N	0.329190000	1.868592000	2.321384000
C	0.735769000	1.317058000	1.176320000

C	1.428969000	2.657494000	3.083738000
C	2.674757000	2.292682000	2.249347000
H	3.214515000	1.457411000	2.742155000
H	3.380076000	3.145178000	2.171735000
C	2.161271000	1.816553000	0.870176000
C	1.128438000	4.164504000	3.106216000
H	1.038140000	4.596369000	2.092535000
H	1.956965000	4.688123000	3.625687000
H	0.195781000	4.376912000	3.665459000
C	1.574558000	2.173117000	4.531180000
H	1.804006000	1.092247000	4.580448000
H	0.666020000	2.379030000	5.130904000
H	2.418613000	2.720352000	5.000403000
C	2.046008000	2.995834000	-0.134941000
H	3.065799000	3.349083000	-0.397202000
H	1.483818000	3.854543000	0.281304000
H	1.518978000	2.678666000	-1.054897000
C	3.082301000	0.742026000	0.264553000
H	2.711066000	0.400998000	-0.723550000
H	3.143062000	-0.145238000	0.923515000
H	4.101209000	1.163075000	0.123444000
C	-1.027307000	1.893162000	2.881451000
C	-1.396292000	0.990765000	3.931415000
C	-2.612850000	1.216072000	4.611754000
H	-2.898865000	0.529799000	5.424102000
C	-3.464079000	2.272768000	4.277497000
H	-4.399665000	2.435250000	4.836166000
C	-3.128677000	3.097850000	3.201125000
H	-3.820725000	3.900211000	2.901465000
C	-1.929086000	2.932592000	2.474931000
C	-0.628461000	-0.281065000	4.307874000
H	0.310470000	-0.312140000	3.719293000
C	-1.454416000	-1.515999000	3.879804000
H	-1.727593000	-1.459291000	2.809749000
H	-2.387093000	-1.601848000	4.477776000
H	-0.864229000	-2.444306000	4.024906000
C	-0.296040000	-0.395061000	5.811584000
H	0.325128000	-1.297261000	5.993106000
H	-1.214103000	-0.508031000	6.426650000
H	0.257645000	0.480720000	6.202230000
C	-1.746779000	3.847366000	1.255587000
H	-0.789724000	3.587321000	0.760229000
C	-2.871363000	3.580785000	0.228020000
H	-2.684442000	4.158616000	-0.700867000
H	-3.860279000	3.891595000	0.627637000
H	-2.914617000	2.512753000	-0.051379000
C	-1.746313000	5.352464000	1.607344000
H	-1.554789000	5.955435000	0.694838000
H	-0.983380000	5.625941000	2.360548000
H	-2.733055000	5.671864000	2.005042000
Cl	-0.828833000	1.496776000	-1.413818000
N	-0.329190000	-1.868592000	-2.321384000
C	-0.735769000	-1.317058000	-1.176320000
C	-1.428969000	-2.657494000	-3.083738000
C	-2.674757000	-2.292682000	-2.249347000
H	-3.214515000	-1.457411000	-2.742155000
H	-3.380076000	-3.145178000	-2.171735000
C	-2.161271000	-1.816553000	-0.870176000
C	-1.128438000	-4.164504000	-3.106216000
H	-1.038140000	-4.596369000	-2.092535000
H	-1.956965000	-4.688123000	-3.625687000
H	-0.195781000	-4.376912000	-3.665459000
C	-1.574558000	-2.173117000	-4.531180000

H	-1.804006000	-1.092247000	-4.580448000
H	-0.666020000	-2.379030000	-5.130904000
H	-2.418613000	-2.720352000	-5.000403000
C	-2.046008000	-2.995834000	0.134941000
H	-3.065799000	-3.349083000	0.397202000
H	-1.483818000	-3.854543000	-0.281304000
H	-1.518978000	-2.678666000	1.054897000
C	-3.082301000	-0.742026000	-0.264553000
H	-2.711066000	-0.400998000	0.723550000
H	-3.143062000	0.145238000	-0.923515000
H	-4.101209000	-1.163075000	-0.123444000
C	1.027307000	-1.893162000	-2.881451000
C	1.396292000	-0.990765000	-3.931415000
C	2.612850000	-1.216072000	-4.611754000
H	2.898865000	-0.529799000	-5.424102000
C	3.464079000	-2.272768000	-4.277497000
H	4.399665000	-2.435250000	-4.836166000
C	3.128677000	-3.097850000	-3.201125000
H	3.820725000	-3.900211000	-2.901465000
C	1.929086000	-2.932592000	-2.474931000
C	0.628461000	0.281065000	-4.307874000
H	-0.310470000	0.312140000	-3.719293000
C	1.454416000	1.515999000	-3.879804000
H	1.727593000	1.459291000	-2.809749000
H	2.387093000	1.601848000	-4.477776000
H	0.864229000	2.444306000	-4.024906000
C	0.296040000	0.395061000	-5.811584000
H	-0.325128000	1.297261000	-5.993106000
H	1.214103000	0.508031000	-6.426650000
H	-0.257645000	-0.480720000	-6.202230000
C	1.746779000	-3.847366000	-1.255587000
H	0.789724000	-3.587321000	-0.760229000
C	2.871363000	-3.580785000	-0.228020000
H	2.684442000	-4.158616000	0.700867000
H	3.860279000	-3.891595000	-0.627637000
H	2.914617000	-2.512753000	0.051379000
C	1.746313000	-5.352464000	-1.607344000
H	1.554789000	-5.955435000	-0.694838000
H	0.983380000	-5.625941000	-2.360548000
H	2.733055000	-5.671864000	-2.005042000

$(L)_2NiCl_2$
E = -3243.88252

Ni	-0.000044000	-0.000113000	0.000476000
Cl	0.298342000	0.917777000	2.007904000
N	2.723674000	0.719966000	-0.341832000
C	1.873139000	-0.243889000	-0.039212000
C	4.180436000	0.456732000	-0.045470000
C	4.086019000	-0.918597000	0.671882000
H	4.196938000	-0.769337000	1.765858000
H	4.893859000	-1.607372000	0.350553000
C	2.664662000	-1.485576000	0.370683000
C	4.993865000	0.407636000	-1.353482000
H	4.621337000	-0.383462000	-2.034281000
H	6.059365000	0.196467000	-1.127959000
H	4.956402000	1.375515000	-1.895620000
C	4.716786000	1.553060000	0.893591000
H	4.057126000	1.658472000	1.779225000
H	4.790481000	2.539092000	0.389653000
H	5.733826000	1.281208000	1.244147000
C	2.671407000	-2.465741000	-0.831880000
H	3.211801000	-3.395408000	-0.552246000
H	3.169541000	-2.027784000	-1.720527000

H	1.635888000	-2.716838000	-1.135675000
C	2.045936000	-2.181992000	1.596943000
H	1.055916000	-2.610997000	1.340221000
H	1.895108000	-1.466754000	2.429908000
H	2.701255000	-3.012292000	1.937731000
Cl	-0.297834000	-0.916874000	-2.007635000
N	-2.723939000	-0.720393000	0.341083000
C	-1.873238000	0.243785000	0.039872000
C	-4.180524000	-0.456968000	0.044095000
C	-4.085806000	0.919122000	-0.671726000
H	-4.196201000	0.771025000	-1.765914000
H	-4.893823000	1.607518000	-0.350040000
C	-2.664605000	1.485851000	-0.369208000
C	-4.994822000	-0.409345000	1.351625000
H	-4.622800000	0.381041000	2.033523000
H	-6.060178000	-0.197975000	1.125610000
H	-4.957700000	-1.377804000	1.892749000
C	-4.716149000	-1.552368000	-0.896469000
H	-4.055857000	-1.656822000	-1.781748000
H	-4.790114000	-2.538929000	-0.393603000
H	-5.732962000	-1.280223000	-1.247450000
C	-2.672025000	2.464955000	0.834205000
H	-3.212529000	3.394734000	0.555155000
H	-3.170430000	2.026129000	1.722276000
H	-1.636669000	2.716010000	1.138602000
C	-2.045147000	2.183320000	-1.594507000
H	-1.055261000	2.612046000	-1.336795000
H	-1.893874000	1.468770000	-2.427986000
H	-2.700222000	3.013936000	-1.934993000
C	2.275439000	2.028337000	-0.817497000
H	1.384438000	1.875241000	-1.455549000
H	1.995358000	2.671741000	0.042011000
H	3.073639000	2.518443000	-1.409096000
C	-2.276018000	-2.029298000	0.815516000
H	-1.996675000	-2.672245000	-0.044570000
H	-1.384594000	-1.877012000	1.453162000
H	-3.074087000	-2.519472000	1.407249000

$(L)_2NiF_2$
E = -2523.13086

Ni	0.004923000	-0.002931000	-0.024063000
N	2.817661000	0.776033000	-0.196218000
C	1.923192000	-0.180436000	-0.019489000
C	4.267043000	0.392545000	0.017339000
C	4.102738000	-1.015359000	0.645071000
H	4.219849000	-0.938562000	1.746616000
H	4.876256000	-1.722056000	0.281249000
C	2.657799000	-1.483409000	0.301156000
C	5.006113000	0.391632000	-1.335960000
H	4.547034000	-0.319280000	-2.051248000
H	6.066427000	0.099367000	-1.190489000
H	4.997502000	1.401157000	-1.797330000
C	4.952412000	1.365352000	0.995178000
H	4.356370000	1.483141000	1.923156000
H	5.120509000	2.369093000	0.553206000
H	5.947291000	0.960513000	1.274012000
C	2.622357000	-2.388904000	-0.958380000
H	3.097838000	-3.366541000	-0.727976000
H	3.171441000	-1.932636000	-1.807518000
H	1.568387000	-2.528760000	-1.266545000
C	1.973882000	-2.211483000	1.474648000
H	0.935929000	-2.477650000	1.193243000
H	1.931222000	-1.571404000	2.380656000

H	2.523944000	-3.142716000	1.730680000
N	-2.821352000	-0.798662000	0.066241000
C	-1.920616000	0.170443000	0.012498000
C	-4.269699000	-0.387066000	-0.095815000
C	-4.104992000	1.099068000	-0.504319000
H	-4.224431000	1.191759000	-1.604351000
H	-4.876074000	1.743968000	-0.035462000
C	-2.659240000	1.507131000	-0.099074000
C	-5.026072000	-0.585366000	1.233214000
H	-4.572798000	0.005141000	2.053685000
H	-6.081094000	-0.261973000	1.118949000
H	-5.035671000	-1.652331000	1.538605000
C	-4.943261000	-1.205775000	-1.213746000
H	-4.337591000	-1.184812000	-2.142710000
H	-5.112099000	-2.264211000	-0.926883000
H	-5.936338000	-0.765381000	-1.440085000
C	-2.617706000	2.193889000	1.292868000
H	-3.128160000	3.179693000	1.237004000
H	-3.129825000	1.587229000	2.067986000
H	-1.559514000	2.323481000	1.590739000
C	-1.989143000	2.422373000	-1.141064000
H	-0.954400000	2.643706000	-0.816530000
H	-1.949500000	1.939142000	-2.140003000
H	-2.549689000	3.377065000	-1.239610000
C	2.457762000	2.132281000	-0.624662000
H	1.483322000	2.356591000	-0.145790000
H	3.222629000	2.855737000	-0.284954000
H	2.382619000	2.183556000	-1.730983000
C	-2.483541000	-2.200202000	0.333179000
H	-3.188718000	-2.870359000	-0.194581000
H	-1.458103000	-2.354059000	-0.059091000
H	-2.541221000	-2.409882000	1.422331000
F	0.201257000	1.514533000	1.001974000
F	-0.158981000	-1.492037000	-1.091110000

$(L)_2NiCl$
E = -2783.61736

Ni	-0.016926000	0.114546000	-0.101394000
Cl	0.582892000	2.305675000	-0.429502000
N	2.724635000	-0.314480000	-0.851927000
C	1.803689000	-0.322326000	0.108548000
C	4.167578000	-0.322410000	-0.419374000
C	4.018416000	-0.211912000	1.123246000
H	4.281013000	0.816735000	1.444687000
H	4.706513000	-0.903446000	1.651624000
C	2.518591000	-0.487993000	1.452635000
C	4.850047000	-1.631961000	-0.864288000
H	4.344892000	-2.518655000	-0.430510000
H	5.908883000	-1.642005000	-0.532567000
H	4.849344000	-1.739996000	-1.969306000
C	4.896756000	0.899487000	-1.010281000
H	4.337682000	1.830016000	-0.781918000
H	5.016797000	0.823434000	-2.110915000
H	5.911892000	0.981660000	-0.569515000
C	2.283566000	-1.935581000	1.950669000
H	2.777838000	-2.091980000	2.933799000
H	2.683001000	-2.690002000	1.240921000
H	1.197562000	-2.128981000	2.071294000
C	1.962457000	0.512215000	2.486219000
H	0.899001000	0.289437000	2.712356000
H	2.001234000	1.547975000	2.093031000
H	2.540519000	0.453939000	3.434146000
N	-2.661485000	-1.014794000	-0.323039000

C	-1.922584000	0.067923000	-0.045708000
C	-4.152528000	-0.899419000	-0.130669000
C	-4.238832000	0.453612000	0.621335000
H	-5.111846000	1.053466000	0.291774000
H	-4.367522000	0.260302000	1.707306000
C	-2.880964000	1.182375000	0.380617000
C	-4.688045000	-2.068558000	0.717342000
H	-4.125599000	-2.161729000	1.669330000
H	-5.753980000	-1.888655000	0.967659000
H	-4.635985000	-3.038466000	0.179784000
C	-4.862778000	-0.874687000	-1.501758000
H	-4.499278000	-0.038059000	-2.130682000
H	-4.710606000	-1.821741000	-2.060667000
H	-5.955773000	-0.748492000	-1.358900000
C	-2.365580000	1.891451000	1.649514000
H	-3.071885000	2.691308000	1.961725000
H	-2.259346000	1.178550000	2.494880000
H	-1.374207000	2.345122000	1.447484000
C	-2.956510000	2.208961000	-0.780270000
H	-1.947691000	2.628493000	-0.972820000
H	-3.324265000	1.745839000	-1.719536000
H	-3.650747000	3.033929000	-0.510009000
C	2.373178000	-0.119987000	-2.256411000
H	1.364674000	-0.547177000	-2.421015000
H	2.321987000	0.963009000	-2.492887000
H	3.106533000	-0.621908000	-2.919974000
C	-2.075185000	-2.251817000	-0.827373000
H	-0.984889000	-2.073410000	-0.935594000
H	-2.241592000	-3.097288000	-0.126569000
H	-2.499070000	-2.526296000	-1.817046000

$(L)_2NiF$
E = -2423.24202

Ni	0.002530000	0.106001000	-0.047494000
F	0.315059000	1.668783000	-1.074617000
N	2.703315000	-0.660819000	-0.663082000
C	1.858358000	-0.118553000	0.212265000
C	4.175655000	-0.473051000	-0.401187000
C	4.134494000	0.585302000	0.733827000
H	4.355467000	1.586034000	0.308282000
H	4.900465000	0.384574000	1.511045000
C	2.679257000	0.575376000	1.299858000
C	4.802529000	-1.810791000	0.046689000
H	4.310023000	-2.202401000	0.959317000
H	5.880749000	-1.671727000	0.268678000
H	4.725902000	-2.584983000	-0.745603000
C	4.887994000	0.053675000	-1.660033000
H	4.390961000	0.967947000	-2.044010000
H	4.911826000	-0.701546000	-2.473045000
H	5.939484000	0.310203000	-1.415050000
C	2.564487000	-0.231617000	2.615831000
H	3.127028000	0.275032000	3.429580000
H	2.965382000	-1.261794000	2.512944000
H	1.501982000	-0.314310000	2.924405000
C	2.130989000	2.002807000	1.512249000
H	1.123686000	1.965122000	1.975886000
H	2.009378000	2.522792000	0.541195000
H	2.803962000	2.584754000	2.178978000
N	-2.697377000	-0.971430000	0.295570000
C	-1.899354000	0.056137000	-0.014242000
C	-4.184495000	-0.732569000	0.210548000
C	-4.221477000	0.809279000	0.040186000
H	-5.000088000	1.122362000	-0.685250000

H	-4.474650000	1.280024000	1.013585000
C	-2.786634000	1.241269000	-0.391296000
C	-4.886635000	-1.195273000	1.500427000
H	-4.422808000	-0.730832000	2.395059000
H	-5.953905000	-0.892858000	1.473480000
H	-4.859639000	-2.298527000	1.622166000
C	-4.767720000	-1.480368000	-1.008356000
H	-4.282734000	-1.153845000	-1.949658000
H	-4.645207000	-2.580122000	-0.916693000
H	-5.854900000	-1.275390000	-1.092769000
C	-2.298909000	2.515319000	0.330257000
H	-2.934933000	3.386271000	0.059547000
H	-2.332655000	2.393596000	1.434152000
H	-1.251383000	2.703458000	0.017686000
C	-2.638281000	1.453895000	-1.921039000
H	-1.569684000	1.667672000	-2.131298000
H	-2.948333000	0.558484000	-2.500269000
H	-3.265537000	2.311180000	-2.248945000
C	2.240649000	-1.364890000	-1.854484000
H	1.171587000	-1.610557000	-1.693082000
H	2.318063000	-0.721435000	-2.755381000
H	2.824749000	-2.294491000	-2.022465000
C	-2.178253000	-2.287471000	0.649777000
H	-1.076982000	-2.248059000	0.524729000
H	-2.417608000	-2.552193000	1.701874000
H	-2.593509000	-3.076611000	-0.012784000

$(L)_2Ni(F_2)(Ph)_2$
E = -2985.94114

Ni	-0.072312000	0.003292000	-0.556346000
C	0.367047000	-2.655942000	0.493598000
C	-0.310408000	-1.441264000	0.753688000
C	0.222126000	-3.764656000	1.347145000
C	-1.198710000	-1.408987000	1.847532000
C	-0.628450000	-3.702426000	2.465979000
H	0.771782000	-4.693876000	1.121048000
C	-1.351512000	-2.523059000	2.701497000
H	-1.828948000	-0.527535000	2.037496000
H	-0.742068000	-4.572008000	3.133080000
H	-2.054831000	-2.460928000	3.548738000
H	0.978406000	-2.747889000	-0.414284000
C	0.365620000	1.461415000	0.712458000
C	-0.120691000	1.625772000	2.021948000
C	1.262503000	2.436372000	0.213525000
H	-0.809608000	0.898050000	2.468421000
H	1.601550000	2.351249000	-0.828282000
C	0.271153000	2.727744000	2.814397000
C	1.663342000	3.527373000	1.005692000
H	-0.134672000	2.826636000	3.835302000
H	2.363676000	4.269530000	0.586422000
C	1.170114000	3.682140000	2.314814000
H	1.481344000	4.538121000	2.935233000
F	0.086604000	1.322256000	-1.969519000
F	-0.299361000	-1.369543000	-1.877678000
N	-3.028020000	-0.548843000	-0.747246000
N	-2.637274000	1.583838000	-0.629881000
C	-2.012421000	0.363052000	-0.605862000
C	-4.258133000	0.089670000	-0.835553000
H	-5.192646000	-0.465560000	-0.963950000
C	-4.011662000	1.434821000	-0.762676000
H	-4.686978000	2.294636000	-0.815487000
C	-2.885378000	-2.002180000	-0.887736000
H	-3.648437000	-2.356042000	-1.608477000

H	-1.866580000	-2.187879000	-1.284501000
H	-3.030754000	-2.506753000	0.087984000
C	-1.978855000	2.893488000	-0.659620000
H	-2.649097000	3.604513000	-1.179913000
H	-1.770864000	3.257820000	0.365106000
H	-1.035007000	2.764184000	-1.223339000
N	2.524544000	-0.513317000	-1.856816000
N	2.822505000	-0.513022000	0.295539000
C	1.861663000	-0.349565000	-0.670260000
C	3.869770000	-0.775101000	-1.635497000
H	4.570961000	-0.941755000	-2.459353000
C	4.060822000	-0.773389000	-0.278782000
H	4.962237000	-0.928121000	0.322524000
C	1.941332000	-0.446191000	-3.204394000
H	2.747255000	-0.160588000	-3.908629000
H	1.506378000	-1.425301000	-3.474760000
H	1.134906000	0.311961000	-3.174837000
C	2.648453000	-0.372568000	1.739596000
H	3.376812000	-1.032162000	2.249678000
H	2.810327000	0.679275000	2.049478000
H	1.625788000	-0.675887000	2.017661000

$(L)_2Ni(Cl_2)(Ph)_2$
E = -3706.64849

Ni	-0.050174000	-0.012428000	-0.511401000
C	0.888260000	-2.551466000	0.663308000
C	-0.042293000	-1.497527000	0.833558000
C	0.963559000	-3.614342000	1.581731000
C	-0.930215000	-1.592222000	1.923580000
C	0.098619000	-3.670948000	2.689079000
H	1.705244000	-4.413550000	1.416074000
C	-0.859202000	-2.659415000	2.846108000
H	-1.731461000	-0.855211000	2.071759000
H	0.159457000	-4.503291000	3.408439000
H	-1.572980000	-2.691643000	3.686173000
H	1.538195000	-2.568860000	-0.221876000
C	0.060471000	1.520696000	0.776948000
C	-0.691711000	1.626932000	1.960534000
C	0.941623000	2.584287000	0.466055000
H	-1.410006000	0.849380000	2.246605000
H	1.501510000	2.570498000	-0.479604000
C	-0.563439000	2.739674000	2.820328000
C	1.075297000	3.692959000	1.322949000
H	-1.174637000	2.783876000	3.737275000
H	1.770801000	4.502864000	1.045623000
C	0.327389000	3.778131000	2.511105000
H	0.432238000	4.647283000	3.180185000
Cl	-0.069160000	1.568638000	-2.291101000
Cl	-0.033496000	-1.677390000	-2.185169000
N	-2.934876000	-1.028431000	-0.572457000
N	-2.879512000	1.144033000	-0.535760000
C	-2.055394000	0.035623000	-0.523816000
C	-4.251342000	-0.589741000	-0.613994000
H	-5.091554000	-1.288513000	-0.671454000
C	-4.216263000	0.774571000	-0.590995000
H	-5.019772000	1.516640000	-0.625720000
C	-2.660255000	-2.469703000	-0.566369000
H	-3.393829000	-2.959323000	-1.236372000
H	-1.643310000	-2.649124000	-0.958506000
H	-2.761757000	-2.876353000	0.458957000
C	-2.526544000	2.567523000	-0.507531000
H	-3.291960000	3.117849000	-1.088303000
H	-2.504557000	2.943661000	0.533573000

H	-1.542701000	2.704690000	-0.989754000
N	2.831802000	-0.107452000	-1.530364000
N	2.770575000	-0.021316000	0.640356000
C	1.952498000	-0.039135000	-0.472048000
C	4.146760000	-0.132940000	-1.083658000
H	4.989844000	-0.193374000	-1.778752000
C	4.109343000	-0.077915000	0.280597000
H	4.911982000	-0.067773000	1.024456000
C	2.557070000	-0.194383000	-2.970742000
H	3.400566000	0.290768000	-3.500557000
H	2.462775000	-1.253259000	-3.275285000
H	1.612613000	0.333004000	-3.194830000
C	2.401012000	0.099035000	2.050896000
H	3.095374000	-0.523712000	2.647899000
H	2.467069000	1.156426000	2.375926000
H	1.373506000	-0.262225000	2.205736000

(S11). References

[S1] a) V. Lavallo, Y. Canac, C. Präsang, B. Donnadieu, G. Bertrand, *Angew. Chem. Int. Ed*. **2005**, *44*, 5705–5709; *Angew. Chem.* **2005**, *117*, 5851-5855; b) P. C. Andrikopoulos, D. R. Armstrong, A. R. Kennedy, R. E. Mulvey, C. T. O'Hara, R. B. Rowlings, *Eur. J. Inorg. Chem*. **2003**, 3354-3362; c) P. P. Power, *Chem. Rev*. **2012**, *112*, 3482−3507; d) see reference S37.

[S2] K. C. Mondal, H. W. Roesky, M. C.bSchwarzer, G. Frenking, B. Niepötter, H. Wolf, R. Herbst-Irmer, D. Stalke, *Angew. Chem., Int. Ed.* **2013**, **52**, 2963-2967; *Angew. Chem.* **2013**, *125*, 3036-3040.

[S3] Simulation of the experimental magnetic data was performed with the *julX* program (E. Bill: Max-Planck Institute for Chemical Energy Conversion, Mülheim/Ruhr, Germany).

[S4] APEX2, SAINT and XPREP, Bruker AXS Inc., Madison, WI, **2009**.

[S5] G. M.Sheldrick, SADABS, University of Goettingen, Goettingen, Germany, **2012**.

[S6] G. M. Sheldrick, *Acta Crystallogr*. **2008**, *A 64*, 112-122.

[S7] C. Huebschle, G. M. Sheldrick, B. J. Dittrich, *J. Appl. Crystallogr*. **2011**, *44*, 1281-1284.

[S8] Full reference: Gaussian 09, Revision A.1, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida,T. Nakajima,Y. Honda,O. Kitao, H. Nakai,T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C.Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

[S9] Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.*, **2008**, *120*, 215-241.

[S10] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.*, **2005**, *7*, 3297-3305.

[S11] C. Y. Peng, P. Y. Ayala, H. B. Schlegel, M. J. Frisch, *J. Comput. Chem.* **1996**, *17*, 49.

[S12] J. W. McIver, A. Komornic *J. Am. Chem. Soc.* **1972**, *94*, 2625.

[S13] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648-5652.

[S14] C. T. Lee, W. T. Yang, R. G. Parr, *Phys. Rev. B*, **1988**, *37*, 785-789.

[S15] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865-3868.

[S16] C. Adamo, V. Barone, *J. Chem. Phys.* **1999**, *110*, 6158-6170.

[S17] J. M. Tao, J. P. Perdew, V. N. Staroverov, G. E. Scuseria, *Phys. Rev. Lett.*, **2003**, *91*, 146401-146404.

[S18] A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098-3100.

[S19] J. P. Perdew, *Phys. Rev. B* **1986**, *33*, 8822-8824.

[S20] A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899-926.

[S21] A. E. Reed, F. Weinhold, *J. Chem. Phys*, **1985**, *83*, 1736-1740.

[S22] A. E. Reed, R. B. Weinstock, F. Weinhold, *J. Chem. Phys*. **1985**, *83*, 735-746.

[S23] J. P. Foster, F. Weinhold, *J. Am. Chem. Soc.* **1980**, *102*, 7211-7218.

[S24] K. B. Wiberg, *Tetrahedron* **1968**, *24*, 1083-1096.

[S25] E. D. Glendening, J. K. Badenhoop, F. Weinhold, *J. Comput. Chem.*, **1998**, *19*, 628-646.

[S26] E. D. Glendening, F. Weinhold, *J. Comput. Chem.* **1998**, *19*, 593-609.

[S27] E. D. Glendening, F. Weinhold, *J. Comput. Chem.* **1998**, *19*, 610-627.

[S28] K. B. Wiberg, *Tetrahedron* **1968**, *24*, 1083.

[S29] E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, F. Weinhold, GENNBO 5.9 ed.; Theoretical Chemistry Institute, University of Wisconsin: Madison, WI, 2009.

[S30] H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz, P. Celani, T. Korona, Lindh, R.; A. Mitrushenkov, G. Rauhut, K. R. Shamasundar, T. B. Adler, R. D. Amos, A. Bernhardsson, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, E. Goll, C. Hampel, A. Hesselmann, G. Hetzer, T. Hrenar, G. Jansen, C. Köppl, Y. Liu, A. W. Lloyd, R. A. Mata, A. J. May, S. J. McNicholas, W. Meyer, M. E. Mura, A. Nicklass, D. P. O'Neill, P. Palmieri, D. Peng, K. Pflüger, R. Pitzer, M. Reiher, T. Shiozaki, H. Stoll, A. J. Stone, R. Tarroni, T. Thorsteinsson, M. Wang, http://www.molpro.net, **2012**.

[S31] V. Bachler, G. Olbrich, F. Neese, K. Wieghardt, *Inorg. Chem.* **2002**, *41*, 4179-4193.

[S32] F. Neese, *J. Phys. Chem. Solids*, **2004**, *65*, 781-785.

[S33] D. Herebian, E. Bothe, F. Neese, T. Weyhermüller, K. Wieghardt, *J. Am. Chem. Soc.* **2003**, *125*, 9116-9128.

[S34] D. Herebian, K. E. Wieghardt, F. Neese, *J. Am. Chem. Soc.* **2003**, *125*, 10997-11005.

[S35] S. Miertus, E. Scrocco, J.Tomasi, *Chem. Phys.* **1981**, *55*, 117-129.

[S36] V. Barone, M. Cossi, J. Tomasi, *J. Comput. Chem*. **1998**, *19*, 404-417.

[S37] T. Yanai, D. P.Tew, N. C.Handy, *Chem. Phys. Lett.* **2004**, *393*, 51-57.

[S38] F. Aquilante, L. De Vico, N. Ferré, G. Ghigo, P. -å. Malmqvist, P. Neogrády, T. B. Pedersen, M. Pitoňák, M. Reiher, B. O. Roos, L. Serrano-Andrés, M. Urban, V. Veryazov, R. Lindh, *J. Comput. Chem.*, **2010**, *31*, 224-247.

[S39] a) A. R. Hajipour, F. Rafiee, *Synth. Commun*. **2013**, *43*, 1314–1327; b) D. Lv, Y.-Y. Zhang, J.-H. Li, *J. Chem. Res*. **2009**, *6*, 397-399.

[S40] J. P. Perdew, *Phys. Rev. B* **1986**, *34*, 7406-7406.

[S41] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida,T. Nakajima,Y. Honda,O. Kitao, H. Nakai,T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C.Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09 (*Revision B.01*), Gaussian, Inc., Wallingford CT, 2009.