Supporting Information for:

Interactions of Aziridines with Nickel Complexes. Oxidative-Addition and Reductive-Elimination Reactions that Break and Make C–N Bonds

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Experimental Section

General Considerations. Unless stated otherwise, all operations were performed in a Braun inert atmosphere glove box under an atmosphere of purified nitrogen, or using high-vacuum and standard Schlenk techniques under an argon or dinitrogen atmosphere. Anhydrous solvents such as THF, benzene, toluene, diethylether, *n*-hexanes, pentane, and CH_2Cl_2 were purchased from Acros Chemicals or EM Science, stirred over sodium metal and filtered through activated alumina. All other solvents were dried and degassed by using standard high-vacuum and Schlenk techniques.[1] C_6D_6 and CD_2Cl_2 were purchased form Cambridge Isotope Laboratory (CIL) and degassed and dried over activated 4Å molecular sieves. Celite, alumina and 4Å molecular sieves were activated in vacuo overnight at a temperature above 180°C. Infrared data (Nujol mulls, KBr or CaF_2 plates) were measured by using a Nicolet 20SXB instrument. Elemental analysis were performed by Desert Analytics (Tucson, AZ). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 500 and 400 MHz NMR spectrometers. ^{1}H and ^{13}C NMR are reported with reference to solvent resonances (residual C_6D_5H in C_6D_6, δ 7.16 and 128.0; CD_2Cl_2, δ 5.32 and 53.8. X-ray diffraction data were collected on a Siemens APEX Platform goniometer with a Charged Coupled Device (CCD) detector. Structures were solved by direct or Patterson methods using the SHELXTL (version 5.1) program library (G. Sheldrick, Bruker Analytical X-ray Systems, Madison, WI).[2]

N-tosyl aziridine (**1a**), N-tosyl-2-methyl aziridine (**1b**), and N-tosyl-2-*n*-butyl aziridine (**1c**) were prepared by literature methods.[3] N-tosyl-2-*i*-propyl aziridine (**1d**) was a gift of Dr. Anne LaPointe (Symyx Technologies). $Ni(cod)_2$ was purchased from Strem Chemical Co. and used without further purification. (bpy)Ni(cod) (**2**)[4] and (bpy)$NiEt_2$ (**3**)[5] were prepared by literature methods.

Preparation of *syn*-(*p*-$CH_3C_6H_4SO_2$)NCHDCH-*n*-Bu (1e). The procedure was carried out as in the literature for **1c**,[3a] except that *cis*-1-deutero-1-hexene was used. A 20-mg (0.055 mmol) sample of $Cu(OTf)_2$ was dissolved in 3 mL of CH_3CN under an inert atmosphere. To the solution was added *cis*-1-deutero-1-hexene (0.4 mL, 3.2 mmol,) and PhI=NTs (0.30 g, 0.8 mmol). The solution was stirred for 15 min at ambient temperature and then filtered through a plug of silica gel and washed with 50 mL of EtOAc. The solvent was removed using a rotovap to give a yellow oil which was purified by flash chromatography (3x18-cm silica gel column;4:1 hexanes:EtOAc) to give *syn*-(*p*-$CH_3C_6H_4SO_2$)NCHDCH-*n*-Bu (**1e**) as a colorless oil (0.059 g, 29% yield based on PhI=NTs). For **1e**: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.81(d, 2 H, C_6H_4), 7.31 (d, 2 H, C_6H_4), 2.70 (m, 1 H, C*H*(*n*-Bu)), 2.60 (d, 1 H, ^{3}J = 7.0 Hz, *syn*-NC*H*D), 2.43 (s, 3 H, $C_6H_4CH_3$), 1.52 (m, 2 H, $(CH_2)_3CH_3$), 1.24 (m, 4 H, $(CH_2)_3CH_3$), 0.82 (t, 3 H, $(CH_2)_3CH_3$). [Note: In unlabeled **1c**, the *anti*-NC*H*H resonance appears at δ 2.05 (dd, 1 H, J= 3.14, 4.5 Hz).]

General Comments on the Preparation of the Azametallcyclobutane Complexes. Preparations for complexes **4a-e** are given below. It should be noted that similar yields are obtained using either **2** or **3** as the Ni source, but typically use of **2** requires longer reaction times and/or heating (as noted). The metallacycles can be conveniently recrystallized from cold acetonitrile layered with diethyl ether.

Preparation of (bpy)Ni($NTsCH_2CH_2$) (4a). ***Method A:*** A 30-mg (0.15 mmol) solid sample of N-p-tolylsulfonyl aziridine (**1a**) was added to 50 mg (0.15 mmol) of (bpy)Ni(cod) (**2**) in 10 mL of THF, and stirred for 2 h at 60 ^{o}C. The reaction mixture was filtered and concentrated under vacuum to ~1 mL, then 20 mL of pentane were slowly added to the solution and the mixture was stirred at ambient temperature for 30 min. The mixture was filtered and the solids were washed

with 3 x 2 mL of pentane and dried under vacuum to yield maroon microcrystals of **4a** (49 mg, 77% yield). ***Method B:*** In an inert atmosphere glovebox, a solution of N-p-tolylsulfonyl aziridine (**1a**; 72 mg, 0.36 mmol) in THF (2 mL) was added to a solution of (bpy)$NiEt_2$ (**3**; 90 mg, 0.33 mmol) in THF (7 mL) and stirred for 2 h, during which time the dark green solution had turned crimson-red in color. The solution was concentrated to 1 mL and the product was precipitated by slow addition of hexanes (~5 mL). The mixture was then cooled to -35 °C for 30 min and the red solids were filtered and washed several times with cold hexanes. The solid was then dried under vacuum to remove excess solvent to yield **4a** (93 mg, 70%). For **4a**: ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 9.47 (d, 1 H, bpy), 8.11-7.24 (multiplets, 11 H, bpy & C_6H_4), 3.65 (t, 2 H, ^{3}J = 7.6 Hz, N-CH_2), 2.38 (s, 3 H, $C_6H_4CH_3$), 0.30 (t, 2 H, ^{3}J = 7.6 Hz, Ni-CH_2). ^{13}C{^{1}H} NMR (CD_2Cl_2, 126 MHz): δ 156.1, 152.6, 152.0, 150.1, 142.5, 140.9, 138.6, 137.7, 129.3, 127.7, 127.1, 126.4, 121.5, 120.4, 54.4, 21.6, -12.2. Anal. Calcd. for $C_{19}H_{19}N_3NiO_2S$: C, 55.4; H, 4.65; N, 10.20. Found: C, 55.5; H, 4.71; N, 10.11.

Preparation of (bpy)Ni{NTsCH(CH_3)CH_2} (4b). A procedure similar to *Method B* (above) was followed using (bpy)$NiEt_2$ (**3**; 0.25 g, 0.7 mmol), N-p-tolylsulfonyl-2-methyl aziridine (**1b**; 0.15 g, 0.7 mmol, and 10 mL of THF. The solution was stirred at ambient temperature for 3 h; workup afforded **4b** (0.18 g, 56% yield) as a red powder. Crystals of **4b** suitable for the crystallographic study were obtained by dissolving the compound in a minimum of methylene chloride and layering with diethyl ether. After several days at -35 °C, maroon blocks were harvested. For **4b**: ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 9.50 (d, 1 H, bpy), 8.21-7.23 (multiplets, 11 H, bpy & C_6H_4), 3.79 (m, 1 H, C*H*CH_3), 2.40 (s, 3 H, $C_6H_4CH_3$), 1.14 (d, 3 H, CHCH_3), 0.44 (dd, 1H, ^{3}J = 7.8 Hz, ^{2}J = 5.0 Hz, *syn*-C*H*H), -0.05 (t, 1 H, ^{3}J = 5.0 Hz, ^{2}J = 5.0 Hz, *anti*-C*H*H). ^{13}C{^{1}H} NMR (CD_2Cl_2, 126 MHz): δ 156.9, 152.4, 152.0, 149.8, 143.7, 140.2, 138.3, 137.4, 129.0, 127.6, 126.7, 126.2, 121.3, 120.2, 60.9, 26.4, 21.4, -3.4. Anal. Calcd. for $C_{20}H_{21}N_3NiO_2S$: C, 56.4; H, 4.97; N, 9.86. Found: C, 56.4; H, 4.73; N, 9.77.

Preparation of (bpy)Ni{NTsCH($CH_2CH_2CH_2CH_3$)CH_2} (4c). A procedure similar to *Method B* (above) was followed using130 mg (0.5 mmol) of N-p-tolylsulfonyl-2-n-butyl aziridine

(**1c**) and 110 mg (0.4 mmol) of (bpy)$NiEt_2$ in 15 mL of THF and stirring for 1 h at ambient temperature. Workup as described above gave **4c** as a light-maroon powder (0.084 g, 47% yield). For **4c**: ^{1}H NMR (CD_2Cl_2, 500 MHz): 9.47 (d, 1 H, bpy), 8.22-7.22 (multiplets, 11 H, bpy & C_6H_4), 3.62 (m, 1 H, C*H*Bu), 2.37 (s, 3 H, $C_6H_4CH_3$), 1.57 (br m, 2 H, $(CH_2)_3CH_3$), 1.24 (br m, 4 H, $(CH_2)_3CH_3$), 0.85 (t, 3 H, $(CH_2)_3CH_3$), 0.30 (dd, 1 H, $^3J = 8.3$ Hz, $^2J = 5.2$ Hz, *syn*-C*H*HCHBu), -0.01 (pseudo t, 1 H, $^3J = 4.1$ Hz, $^2J = 5.2$ Hz, *anti*-C*H*HCHBu). $^{13}C\{^1H\}$ (CD_2Cl_2, 126 MHz): δ156.2, 152.6, 152.1, 150.0, 143.5, 140.8, 138.5, 137.5, 129.2, 128.0, 127.1, 126.4, 121.5, 120.3, 65.4, 40.2, 28.1, 23.5, 21.7, 14.6, -5.1. Anal. Calcd. for $C_{23}H_{27}N_3NiO_2S$: C, 59.0 ; H, 5.81; N, 8.97. Found: C, 58.7; H, 5.72; N, 8.88.

Preparation of (bpy)Ni{NTsCH{CH(CH$_3$)$_2$}CH$_2$} (4d). A procedure similar to *Method B* (above) was followed using 55 mg (0.23 mmol) N-p-tolylsulfonyl-2-i-propyl aziridine (**1d**) and 55 mg (0.2mmol) (bpy)$NiEt_2$ in 15 mL of THF and stirring for 12 h at ambient temperature. Workup as described above gave 63 mg (69%) of **4d** as a light maroon powder. For **4d**: ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 9.39 (d, 1 H, bpy), 8.27-7.17 (multiplets, 11 H, bpy & C_6H_4), 3.45 (m, 1 H, N-C*H*), 2.37 (s, 3 H, $C_6H_4CH_3$), 1.73 (m, 1 H, C*H*$(CH_3)_2$), 1.04 (d, 3 H, CH$(CH_3)_2$), 0.82 (d, 3 H, CH$(CH_3)_2$), 0.04 (dd, 1 H, Ni-CH*H*), -0.02 (t, 1 H, Ni-CH*H*); ^{13}C NMR (CD_2Cl_2, 126 MHz): δ 156.2, 152.2., 152.1, 149.9, 143.8, 140.7, 138.4, 137.5, 129.0, 128.1, 126.9, 126.4, 121.5, 120.3, 70.5, 35.1, 21.6, 19.4, 17.9, -8.9. Anal. Calcd. for $C_{22}H_{25}N_3NiO_2S$: C, 58.2 ; H, 5.55; N, 9.25. Found: C, 58.8; H, 5.64; N, 8.56.

Preparation of (bpy)Ni{NTsCH(CH$_2$CH$_2$CH$_2$CH$_3$)CHD} (4e). A procedure similar to *Method B* (above) was followed using130 mg (0.5 mmol) of the monodeuterated N-p-tolylsulfonyl-2-n-butyl aziridine *syn*-(*p*-$CH_3C_6H_4SO_2$)NCHDCH-*n*-Bu (**1e**) and 139 mg (0.4 mmol) of (bpy)$NiEt_2$ in 15 mL of THF and stirring for 2 h at ambient temperature. Workup as described above gave **4e** as a light-maroon powder (0.132 g, 62% yield). Carrying out the reaction using (bpy)Ni(cod) (**2**) according to *Method A* (above) gave a spectroscopically identical product (**4e**). For **4e**: ^{1}H NMR (CD_2Cl_2, 500 MHz): 9.47 (d, 1 H, bpy), 8.22-7.22 (multiplets, 11 H, bpy &

C_6H_4), 3.62 (m, 1 H, C*H*Bu), 2.37 (s, 3 H, $C_6H_4CH_3$), 1.57 (br m, 2 H, $(CH_2)_3CH_3$), 1.24 (br m, 4 H, $(CH_2)_3CH_3$), 0.85 (t, 3 H, $(CH_2)_3CH_3$), -0.01 (d, 1 H, $^3J = 4.1$ Hz, *anti*-C*H*DCHBu).

Reaction of 4e with oxygen. A representative procedure for oxidation of **4a-e** is given for **4e**. A 25-mg sample of **4e** (0.05 mmol) was dissolved in 10 mL of benzene and stirred under 1 atm of O_2 for 1 h. GC-MS analysis of the supernatant showed only **1e** and bipyridine to be present. Solvent was removed under vacuum from the resulting heterogeneous mixture, and the aziridine **1e** (4 mg, 46% yield) was isolated by flash chromatography (silica; hexanes/EtOAc, 4:1, $R_f = 0.44$). ^{1}H NMR analysis of the purified product, specifically integration of the ring-methylene resonances at δ 2.60 and 2.05, showed the product to be **1e** in 92-96% isomeric purity (3 independent experiments).

References

(1) For a general description of the equipment and techniques, see: Burger, B. J.; Bercaw, J. E. In *Experimental Organometallic Chemistry*; Wayda, A. L., Darensbourg, M. Y., Eds.; ACS Symposium Series 357; American Chemical Society; Washington, DC, 1987; pp 79-98.

(2) All software and sources of scattering factors are contained in the SHELXTL (version 5.1) program library; G. Sheldrick, Bruker Analytical Systems, Madison, WI.

(3) (a) Evans, D. A.; Faul, M. M.; Bilodeau, M. T. *J. Am. Chem. Soc.* **1994**, *116*, 2742. (b) Nadir, U. K.; Sharma, R. L.; Koul, V. K. *J. Chem. Soc., Perk. Trans.* **1991**, 2015.

(4) Han, K. I.; Pitrowski, A. M.; Eisch, J. J. in *Organometallic Syntheses, Vol. 3*; King, R. B.; Eisch, J. J., Eds.; Elsevier: Amsterdam, 1986; p 112.

(5) Saito, T.; Uchida, Y.; Misono, A.; Yamamoto, A.; Morifuji, K.; Ikeda, S. *J. Am. Chem. Soc*. **1966**, *88*, 5198.

Data Collection

A red cube was selected under a stereo-microscope while immersed in mineral oil to avoid possible reaction with air. The crystal was removed from the oil using a tapered fiber that also served to hold the crystal for data collection. The crystal was mounted and centered on a Bruker SMART APEX system. Rotation and still images showed diffractions to be sharp while frames separated in reciprocal space were obtained and provided an orientation matrix and initial cell parameters. Final cell parameters were obtained from the full data set.

A "hemisphere" data set was obtained which samples approximately 1.2 hemispheres of reciprocal space to a resolution of 0.84A using 0.3 degree steps in ω using 30 sec integration times for each frame. Absorption corrections were applied using SADABS [1].

Structure Solution and Refinement

The space group was determined as C2/c based on systematic absences and intensity statistics. Patterson method was used to locate the heavy atoms of Ni and S and heteroatoms from the E-map.

Prior to location of H, all atoms were converted to and refined anisotropically. H atoms were refined isotropically and fixed at calculated positions. Hydrogens H1, H2 and H3 were located in the electron map and refined isotropically. Selected torsion angles were defined based on these positions and were compared to selected torsion angles obtained using hydrogens fixed at calculated positions. No anomalous bond lengths or thermal parameters were noted.

$R_{int} = \Sigma \mid F_o^2 - \langle F_o^2 \rangle \mid / \Sigma \mid F_o^2 \mid$

$wR_2 = [\Sigma [w (F_o^2 - F_c^2)^2] / \Sigma [w (F_o^2)^2]]^{1/2}$

$GooF = S = [\Sigma [w (F_o^2 - F_c^2)^2] / (n-p)^{1/2}$

$R_1 = \Sigma \mid \mid F_o \mid - \mid F_c \mid \mid / \Sigma \mid F_o \mid$

where: $w = q / \sigma^2 (F_o^2) + (aP)^2 + bP$;

n = number of independent reflections;

p = number of parameters refined.

References

[1] All software and sources of scattering factors are contained in the SHELXTL (version 5.1) program library (G. Sheldrick, Bruker Analytical X-ray Systems, Madison, WI).

Table 1. Crystal and structure refinement for (bpy)Ni(N(Tos)CH(CH_3)CH_2).

Identification Code	danm11s	
Empirical formula	$C_{20}H_{21}N_3NiO_2S$	
Formula weight	426.17	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space Group	C2/c	
Unit cell dimensions	a = 13.7055(13) Å	α = 90 °
	b = 14.4807(14) Å	β = 102.477(2) °
	c = 20.1202(19) Å	γ = 90 °
Volume	3898.9(6) $Å^3$	
Z	8	
Density (calculated)	1.452 Mg/m^3	
Absorption coefficient	1.122 mm^{-1}	
F(000)	1776	
Crystal size	40 x 40 x 30 μm, red cube	
Theta range for data collection	2.07 to 25.10	
Index ranges	$-16 \le h \le 12$, $-17 \le k \le 14$ $-23 \le l \le 22$	
Reflections collected	9679	
Independent reflections	3446 (R_{int} = 0.0374)	
Completeness to theta = 25.10°	99.5%	
Absorption correction	SADABS	
Max. and min. transmission	0.9671 and 0.9565	
Refinement method	Full-matrix least squares on F^2	
Data / restraints / parameters	3446 / 0 / 257	
Goodness-of-fit on F^2	1.325	
Final R indices [I > 2 sigma(I)]	R_1 = 0.0814, wR_2 = 0.1593	
R indices (all data)	R_1 = 0.0884, wR_2 = 0.1623	
Largest diff. peak and hole	0.908 and -0.689 $eÅ^{-3}$	

Table 2. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for danm11s. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ni	911(1)	752(1)	6318(1)	19(1)
S(1)	3043(1)	1311(1)	6668(1)	19(1)
O(2)	2792(3)	2106(3)	7033(2)	22(1)
N(21)	-244(4)	283(4)	6567(3)	23(1)
N(11)	345(3)	1954(3)	6501(2)	19(1)
O(1)	3435(3)	530(3)	7095(2)	24(1)
N(1)	2128(4)	1079(3)	6059(3)	21(1)
C(1)	1425(5)	-361(5)	6001(4)	29(2)
C(31)	4006(4)	1630(4)	6243(3)	19(1)
C(11)	-544(4)	1874(4)	6692(3)	22(1)
C(25)	-464(5)	-612(4)	6626(3)	28(2)
C(12)	-1081(5)	2653(5)	6800(3)	25(1)
C(32)	3806(4)	2223(4)	5690(3)	21(1)
C(22)	-1691(5)	663(5)	7000(3)	25(1)
C(33)	4556(5)	2465(4)	5365(3)	23(1)
C(14)	180(5)	3589(5)	6501(3)	32(2)
C(21)	-858(4)	920(4)	6760(3)	20(1)
C(35)	5699(5)	1548(5)	6138(3)	34(2)
C(2)	2206(5)	151(4)	5729(3)	23(1)
C(24)	-1297(5)	-905(5)	6863(3)	32(2)
C(36)	4961(5)	1297(5)	6474(3)	30(2)
C(15)	691(5)	2793(4)	6406(3)	23(1)
C(23)	-1912(5)	-256(5)	7049(3)	31(2)
C(34)	5516(5)	2123(5)	5576(3)	26(1)
C(3)	1990(5)	263(5)	4966(3)	35(2)
C(13)	-712(5)	3519(5)	6710(3)	33(2)
C(37)	6330(5)	2359(5)	5205(3)	31(2)

Table 3. Bond lengths [Å] and angles [°] for danm11s.

Ni-N(21)	1.888(5)
Ni-N(1)	1.911(5)
Ni-C(1)	1.921(7)
Ni-N(11)	1.973(5)
Ni-C(2)	2.493(6)
S(1)-O(2)	1.447(4)
S(1)-O(1)	1.451(4)
S(1)-N(1)	1.588(5)
S(1)-C(31)	1.782(6)
N(21)-C(25)	1.341(8)
N(21)-C(21)	1.361(8)
N(11)-C(15)	1.333(8)
N(11)-C(11)	1.361(8)
N(1)-C(2)	1.513(8)
C(1)-C(2)	1.500(9)
C(1)-H(2)	0.91(7)
C(1)-H(1)	0.94(6)
C(31)-C(36)	1.378(8)
C(31)-C(32)	1.384(8)
C(11)-C(12)	1.388(9)
C(11)-C(21)	1.462(9)
C(25)-C(24)	1.395(9)
C(25)-H(25A)	0.9300
C(12)-C(13)	1.378(10)
C(12)-H(12A)	0.9300
C(32)-C(33)	1.378(8)
C(32)-H(32A)	0.9300
C(22)-C(23)	1.373(9)
C(22)-C(21)	1.383(9)
C(22)-H(22A)	0.9300
C(33)-C(34)	1.384(9)
C(33)-H(33A)	0.9300
C(14)-C(13)	1.380(10)
C(14)-C(15)	1.383(9)
C(14)-H(14A)	0.9300
C(35)-C(36)	1.381(9)
C(35)-C(34)	1.382(9)
C(35)-H(35A)	0.9300
C(2)-C(3)	1.507(9)
C(2)-H(3)	0.98(5)
C(24)-C(23)	1.367(10)
C(24)-H(24A)	0.9300
C(36)-H(36A)	0.9300
C(15)-H(15A)	0.9300
C(23)-H(23A)	0.9300
C(34)-C(37)	1.509(8)
C(3)-H(3A)	0.9600
C(3)-H(3B)	0.9600
C(3)-H(3C)	0.9600
C(13)-H(13A)	0.9300
C(37)-H(37A)	0.9600
C(37)-H(37B)	0.9600
C(37)-H(37C)	0.9600

N(21)-Ni-N(1)	173.3(2)
N(21)-Ni-C(1)	100.1(3)
N(1)-Ni-C(1)	73.4(3)
N(21)-Ni-N(11)	83.2(2)
N(1)-Ni-N(11)	103.5(2)
C(1)-Ni-N(11)	171.5(3)
N(21)-Ni-C(2)	136.5(2)
N(1)-Ni-C(2)	37.3(2)
C(1)-Ni-C(2)	36.9(2)
N(11)-Ni-C(2)	138.2(2)
O(2)-S(1)-O(1)	114.7(3)
O(2)-S(1)-N(1)	108.9(3)
O(1)-S(1)-N(1)	115.0(3)
O(2)-S(1)-C(31)	108.6(3)
O(1)-S(1)-C(31)	105.6(3)
N(1)-S(1)-C(31)	103.2(3)
C(25)-N(21)-C(21)	117.7(5)
C(25)-N(21)-Ni	126.1(4)
C(21)-N(21)-Ni	116.0(4)
C(15)-N(11)-C(11)	119.1(5)
C(15)-N(11)-Ni	127.7(4)
C(11)-N(11)-Ni	113.0(4)
C(2)-N(1)-S(1)	114.0(4)
C(2)-N(1)-Ni	92.7(3)
S(1)-N(1)-Ni	115.7(3)
C(2)-C(1)-Ni	92.7(4)
C(2)-C(1)-H(2)	110(4)
Ni-C(1)-H(2)	105(4)
C(2)-C(1)-H(1)	110(4)
Ni-C(1)-H(1)	112(4)
H(2)-C(1)-H(1)	124(6)
C(36)-C(31)-C(32)	119.8(5)
C(36)-C(31)-S(1)	119.7(5)
C(32)-C(31)-S(1)	120.5(4)
N(11)-C(11)-C(12)	120.8(6)
N(11)-C(11)-C(21)	114.0(5)
C(12)-C(11)-C(21)	125.2(6)
N(21)-C(25)-C(24)	122.7(6)
N(21)-C(25)-H(25A)	118.6
C(24)-C(25)-H(25A)	118.6
C(13)-C(12)-C(11)	119.8(6)
C(13)-C(12)-H(12A)	120.1
C(11)-C(12)-H(12A)	120.1
C(33)-C(32)-C(31)	120.0(6)
C(33)-C(32)-H(32A)	120.0
C(31)-C(32)-H(32A)	120.0
C(23)-C(22)-C(21)	119.8(6)
C(23)-C(22)-H(22A)	120.1
C(21)-C(22)-H(22A)	120.1
C(32)-C(33)-C(34)	121.4(6)
C(32)-C(33)-H(33A)	119.3
C(34)-C(33)-H(33A)	119.3
C(13)-C(14)-C(15)	119.3(6)
C(13)-C(14)-H(14A)	120.3
C(15)-C(14)-H(14A)	120.3
N(21)-C(21)-C(22)	121.7(6)
N(21)-C(21)-C(11)	113.7(5)
C(22)-C(21)-C(11)	124.6(6)

C(36)-C(35)-C(34)	122.4(6)
C(36)-C(35)-H(35A)	118.8
C(34)-C(35)-H(35A)	118.8
C(1)-C(2)-C(3)	115.2(6)
C(1)-C(2)-N(1)	98.9(5)
C(3)-C(2)-N(1)	109.6(5)
C(1)-C(2)-Ni	50.3(3)
C(3)-C(2)-Ni	116.3(4)
N(1)-C(2)-Ni	49.9(3)
C(1)-C(2)-H(3)	114(3)
C(3)-C(2)-H(3)	108(3)
N(1)-C(2)-H(3)	110(3)
Ni-C(2)-H(3)	135(3)
C(23)-C(24)-C(25)	118.9(6)
C(23)-C(24)-H(24A)	120.6
C(25)-C(24)-H(24A)	120.6
C(31)-C(36)-C(35)	119.0(6)
C(31)-C(36)-H(36A)	120.5
C(35)-C(36)-H(36A)	120.5
N(11)-C(15)-C(14)	122.2(6)
N(11)-C(15)-H(15A)	118.9
C(14)-C(15)-H(15A)	118.9
C(24)-C(23)-C(22)	119.2(6)
C(24)-C(23)-H(23A)	120.4
C(22)-C(23)-H(23A)	120.4
C(35)-C(34)-C(33)	117.3(6)
C(35)-C(34)-C(37)	121.2(6)
C(33)-C(34)-C(37)	121.5(6)
C(2)-C(3)-H(3A)	109.5
C(2)-C(3)-H(3B)	109.5
H(3A)-C(3)-H(3B)	109.5
C(2)-C(3)-H(3C)	109.5
H(3A)-C(3)-H(3C)	109.5
H(3B)-C(3)-H(3C)	109.5
C(12)-C(13)-C(14)	118.7(6)
C(12)-C(13)-H(13A)	120.6
C(14)-C(13)-H(13A)	120.6
C(34)-C(37)-H(37A)	109.5
C(34)-C(37)-H(37B)	109.5
H(37A)-C(37)-H(37B)	109.5
C(34)-C(37)-H(37C)	109.5
H(37A)-C(37)-H(37C)	109.5
H(37B)-C(37)-H(37C)	109.5

Table 4. Anisotropic displacement parameters [$Å^2$ x 10^3]
for danm11s. The anisotropic displacement factor exponent takes the form: -
$2\pi^2[h^2a^{*2}U^{11} + ... + 2hka^*b^*U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ni	17(1)	15(1)	24(1)	-3(1)	5(1)	0(1)
S(1)	19(1)	19(1)	20(1)	1(1)	5(1)	-1(1)
O(2)	23(2)	20(2)	26(2)	-6(2)	9(2)	-6(2)
N(21)	23(3)	21(3)	22(3)	-6(2)	4(2)	-4(2)
N(11)	15(2)	19(3)	21(3)	-3(2)	-1(2)	2(2)
O(1)	23(2)	22(2)	27(2)	5(2)	8(2)	1(2)
N(1)	22(3)	16(3)	25(3)	1(2)	6(2)	0(2)
C(1)	29(4)	21(4)	38(4)	-4(3)	11(3)	3(3)
C(31)	16(3)	21(3)	20(3)	-2(2)	5(2)	-1(2)
C(11)	19(3)	28(3)	16(3)	0(3)	0(2)	2(3)
C(25)	36(4)	21(3)	29(3)	-15(3)	13(3)	-9(3)
C(12)	19(3)	34(4)	22(3)	-1(3)	2(3)	6(3)
C(32)	19(3)	24(3)	22(3)	1(3)	4(2)	0(2)
C(22)	24(3)	33(4)	19(3)	-6(3)	3(3)	-3(3)
C(33)	30(3)	19(3)	21(3)	1(3)	11(3)	2(3)
C(14)	40(4)	25(4)	30(4)	0(3)	2(3)	1(3)
C(21)	19(3)	23(3)	16(3)	-5(2)	-2(2)	-1(2)
C(35)	17(3)	53(5)	31(4)	4(3)	5(3)	0(3)
C(2)	22(3)	21(3)	25(3)	-5(3)	6(3)	3(3)
C(24)	36(4)	28(4)	34(4)	-7(3)	12(3)	-15(3)
C(36)	21(3)	42(4)	24(3)	9(3)	0(3)	-6(3)
C(15)	24(3)	20(3)	23(3)	2(3)	4(3)	0(3)
C(23)	29(4)	41(4)	24(3)	-9(3)	7(3)	-15(3)
C(34)	21(3)	30(4)	27(3)	-6(3)	9(3)	-7(3)
C(3)	42(4)	31(4)	29(4)	3(3)	3(3)	1(3)
C(13)	39(4)	26(4)	28(4)	-3(3)	-4(3)	15(3)
C(37)	27(4)	40(4)	31(4)	0(3)	17(3)	-1(3)

Table 5. Hydrogen coordinates [x 10^4] and isotropic displacement parameters [$Å^2$ x 10^3] for danm11s.

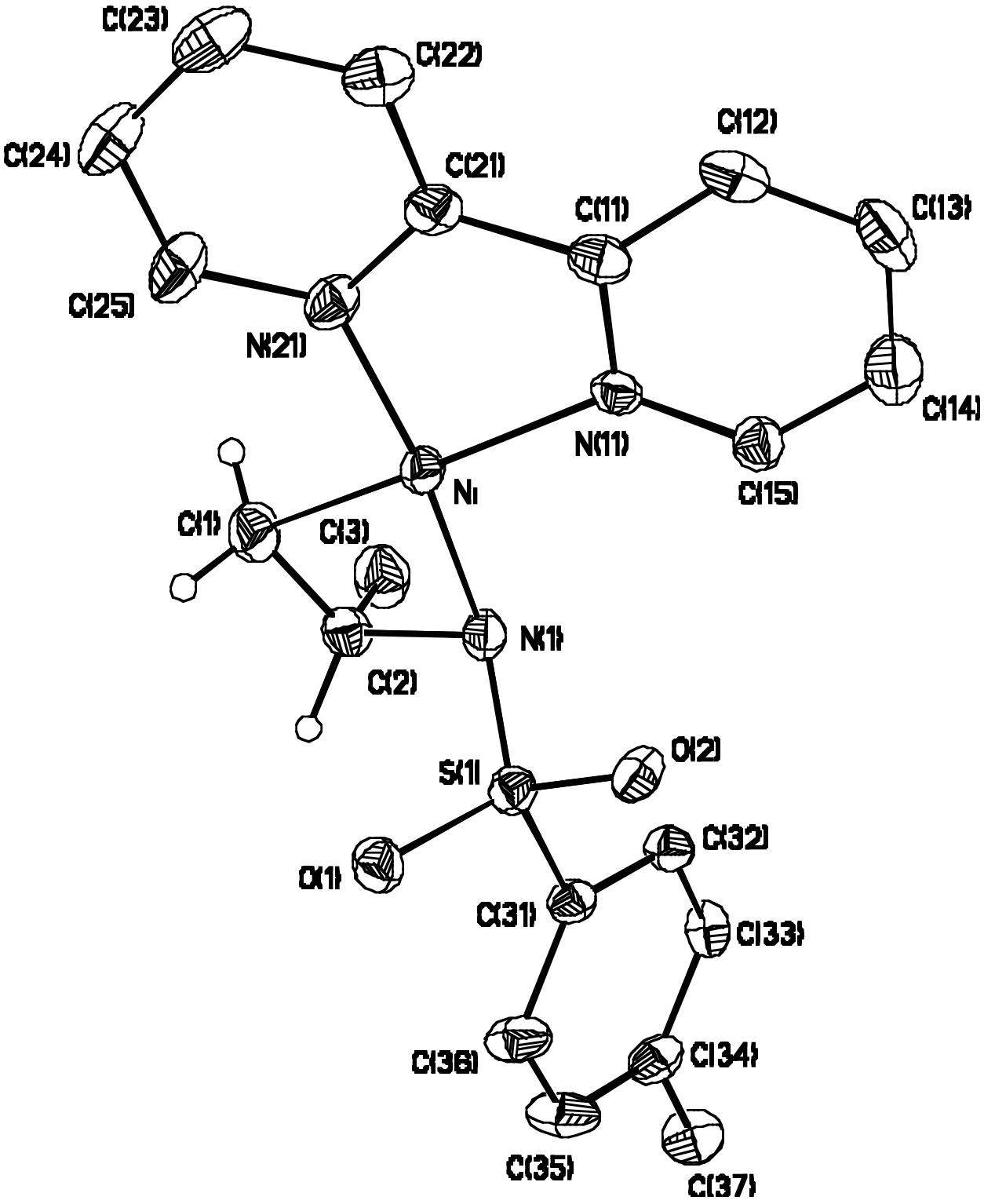
	x	y	z	U(eq)
H(2)	930(50)	-560(50)	5650(40)	30(19)
H(1)	1730(40)	-740(40)	6360(30)	13(15)
H(3)	2880(40)	-90(40)	5880(30)	4(13)
H(25A)	-45	-1055	6504	33
H(12A)	-1687	2590	6932	30
H(32A)	3165	2458	5539	25
H(22A)	-2099	1112	7129	30
H(33A)	4415	2866	4996	27
H(14A)	435	4165	6425	39
H(35A)	6343	1322	6295	41
H(24A)	-1432	-1531	6895	39
H(36A)	5106	909	6850	36
H(15A)	1296	2846	6270	27
H(23A)	-2473	-435	7207	37
H(3A)	2533	11	4792	52
H(3B)	1916	907	4853	52
H(3C)	1385	-58	4768	52
H(13A)	-1058	4046	6789	39
H(37A)	6940	2061	5425	47
H(37B)	6428	3015	5212	47
H(37C)	6139	2150	4742	47

Table 6. Torsion angles [°] for Danm11s.

N(1)-Ni-N(21)-C(25)	-1(2)
C(1)-Ni-N(21)-C(25)	12.1(6)
N(11)-Ni-N(21)-C(25)	-175.8(5)
C(2)-Ni-N(21)-C(25)	19.6(7)
N(1)-Ni-N(21)-C(21)	172.9(16)
C(1)-Ni-N(21)-C(21)	-173.9(5)
N(11)-Ni-N(21)-C(21)	-1.8(4)
C(2)-Ni-N(21)-C(21)	-166.4(4)
N(21)-Ni-N(11)-C(15)	-175.3(5)
N(1)-Ni-N(11)-C(15)	5.4(5)
C(1)-Ni-N(11)-C(15)	-62.1(19)
C(2)-Ni-N(11)-C(15)	-11.2(6)
N(21)-Ni-N(11)-C(11)	-1.0(4)
N(1)-Ni-N(11)-C(11)	179.6(4)
C(1)-Ni-N(11)-C(11)	112.2(17)
C(2)-Ni-N(11)-C(11)	163.1(4)
O(2)-S(1)-N(1)-C(2)	-168.0(4)
O(1)-S(1)-N(1)-C(2)	-37.7(5)
C(31)-S(1)-N(1)-C(2)	76.8(4)
O(2)-S(1)-N(1)-Ni	-62.2(3)
O(1)-S(1)-N(1)-Ni	68.1(4)
C(31)-S(1)-N(1)-Ni	-177.4(3)
N(21)-Ni-N(1)-C(2)	24(2)

C(1)-Ni-N(1)-C(2)	10.1(4)
N(11)-Ni-N(1)-C(2)	-161.7(3)
N(21)-Ni-N(1)-S(1)	-94.8(18)
C(1)-Ni-N(1)-S(1)	-108.3(4)
N(11)-Ni-N(1)-S(1)	79.9(3)
C(2)-Ni-N(1)-S(1)	-118.4(5)
N(21)-Ni-C(1)-C(2)	171.4(4)
N(1)-Ni-C(1)-C(2)	-10.2(4)
N(11)-Ni-C(1)-C(2)	59.4(19)
O(2)-S(1)-C(31)-C(36)	108.6(5)
O(1)-S(1)-C(31)-C(36)	-14.9(6)
N(1)-S(1)-C(31)-C(36)	-135.9(5)
O(2)-S(1)-C(31)-C(32)	-70.2(5)
O(1)-S(1)-C(31)-C(32)	166.3(5)
N(1)-S(1)-C(31)-C(32)	45.2(6)
C(15)-N(11)-C(11)-C(12)	-1.1(8)
Ni-N(11)-C(11)-C(12)	-175.9(4)
C(15)-N(11)-C(11)-C(21)	178.2(5)
Ni-N(11)-C(11)-C(21)	3.4(6)
C(21)-N(21)-C(25)-C(24)	1.1(9)
Ni-N(21)-C(25)-C(24)	175.0(5)
N(11)-C(11)-C(12)-C(13)	0.2(9)
C(21)-C(11)-C(12)-C(13)	-179.1(6)
C(36)-C(31)-C(32)-C(33)	1.2(9)
S(1)-C(31)-C(32)-C(33)	-180.0(5)
C(31)-C(32)-C(33)-C(34)	0.4(9)
C(25)-N(21)-C(21)-C(22)	-0.8(8)
Ni-N(21)-C(21)-C(22)	-175.3(4)
C(25)-N(21)-C(21)-C(11)	178.6(5)
Ni-N(21)-C(21)-C(11)	4.1(6)
C(23)-C(22)-C(21)-N(21)	0.0(9)
C(23)-C(22)-C(21)-C(11)	-179.4(6)
N(11)-C(11)-C(21)-N(21)	-4.9(7)
C(12)-C(11)-C(21)-N(21)	174.4(6)
N(11)-C(11)-C(21)-C(22)	174.5(5)
C(12)-C(11)-C(21)-C(22)	-6.2(9)
Ni-C(1)-C(2)-C(3)	-104.2(5)
Ni-C(1)-C(2)-N(1)	12.5(5)
S(1)-N(1)-C(2)-C(1)	107.2(5)
Ni-N(1)-C(2)-C(1)	-12.6(5)
S(1)-N(1)-C(2)-C(3)	-131.9(5)
Ni-N(1)-C(2)-C(3)	108.4(5)
S(1)-N(1)-C(2)-Ni	119.8(4)
N(21)-Ni-C(2)-C(1)	-12.3(6)
N(1)-Ni-C(2)-C(1)	163.8(6)
N(11)-Ni-C(2)-C(1)	-169.0(5)
N(21)-Ni-C(2)-C(3)	89.7(5)
N(1)-Ni-C(2)-C(3)	-94.2(6)
C(1)-Ni-C(2)-C(3)	102.0(7)
N(11)-Ni-C(2)-C(3)	-67.0(6)
N(21)-Ni-C(2)-N(1)	-176.1(3)
C(1)-Ni-C(2)-N(1)	-163.8(6)
N(11)-Ni-C(2)-N(1)	27.2(5)
N(21)-C(25)-C(24)-C(23)	-0.5(10)
C(32)-C(31)-C(36)-C(35)	-1.4(10)
S(1)-C(31)-C(36)-C(35)	179.8(5)
C(34)-C(35)-C(36)-C(31)	0.0(11)
C(11)-N(11)-C(15)-C(14)	0.6(9)

Ni-N(11)-C(15)-C(14)	174.6(5)
C(13)-C(14)-C(15)-N(11)	0.8(10)
C(25)-C(24)-C(23)-C(22)	-0.3(10)
C(21)-C(22)-C(23)-C(24)	0.6(9)
C(36)-C(35)-C(34)-C(33)	1.5(10)
C(36)-C(35)-C(34)-C(37)	-177.8(7)
C(32)-C(33)-C(34)-C(35)	-1.7(10)
C(32)-C(33)-C(34)-C(37)	177.7(6)
C(11)-C(12)-C(13)-C(14)	1.2(9)
C(15)-C(14)-C(13)-C(12)	-1.7(10)
H(1)-C(1)-C(2)-H(3)	15(5)
H(2)-C(1)-C(2)-H(3)	-124(6)
H(2)-C(1)-C(2)-C(3)	2(5)
H(1)-C(1)-C(2)-C(3)	142(4)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