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Figure S1. ORTEP view (50% probability ellipsoids) of complex **9**. Disorder omitted for clarity.

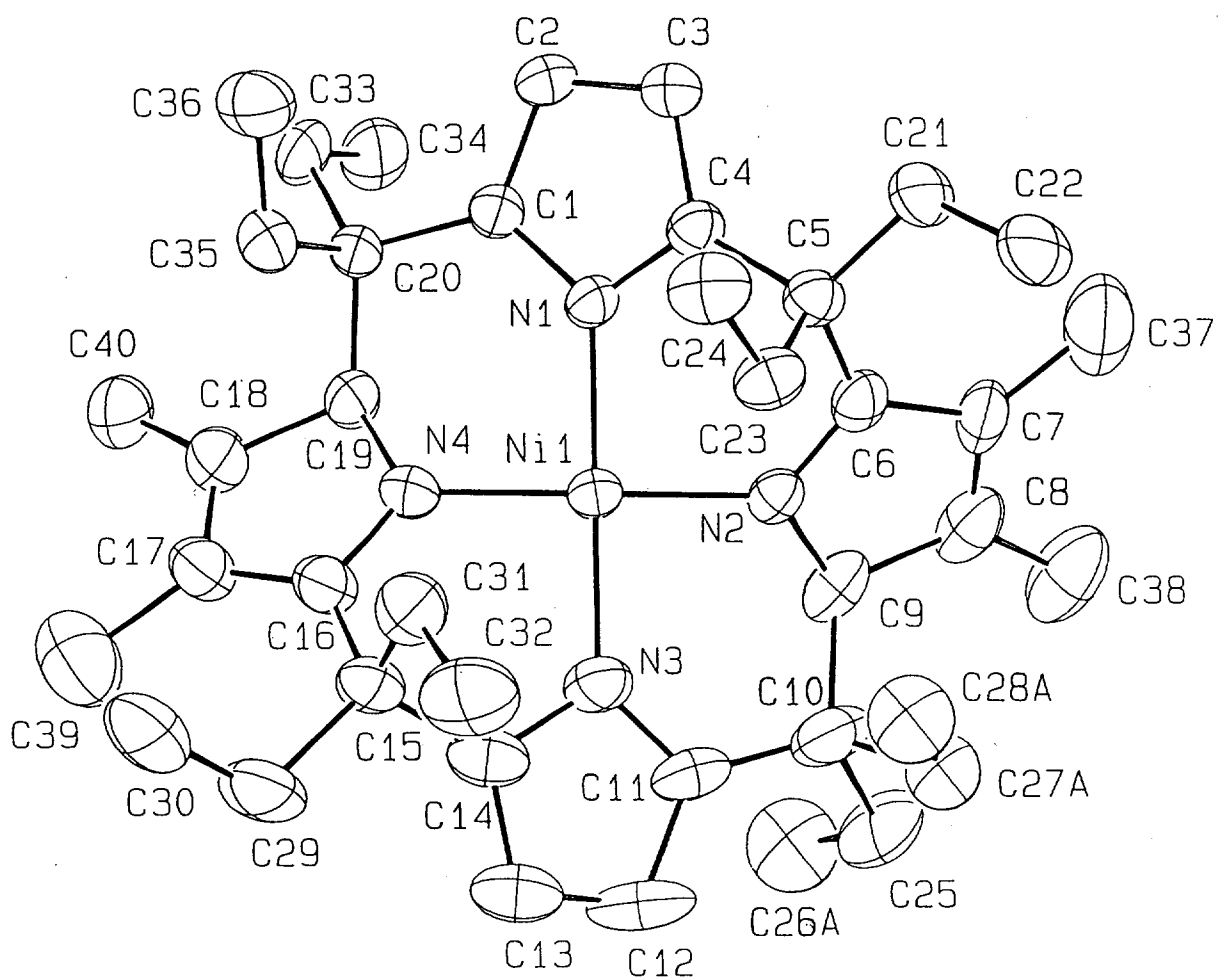


Figure S2. SCHAKAL view of complex 9. Disorder omitted for clarity.

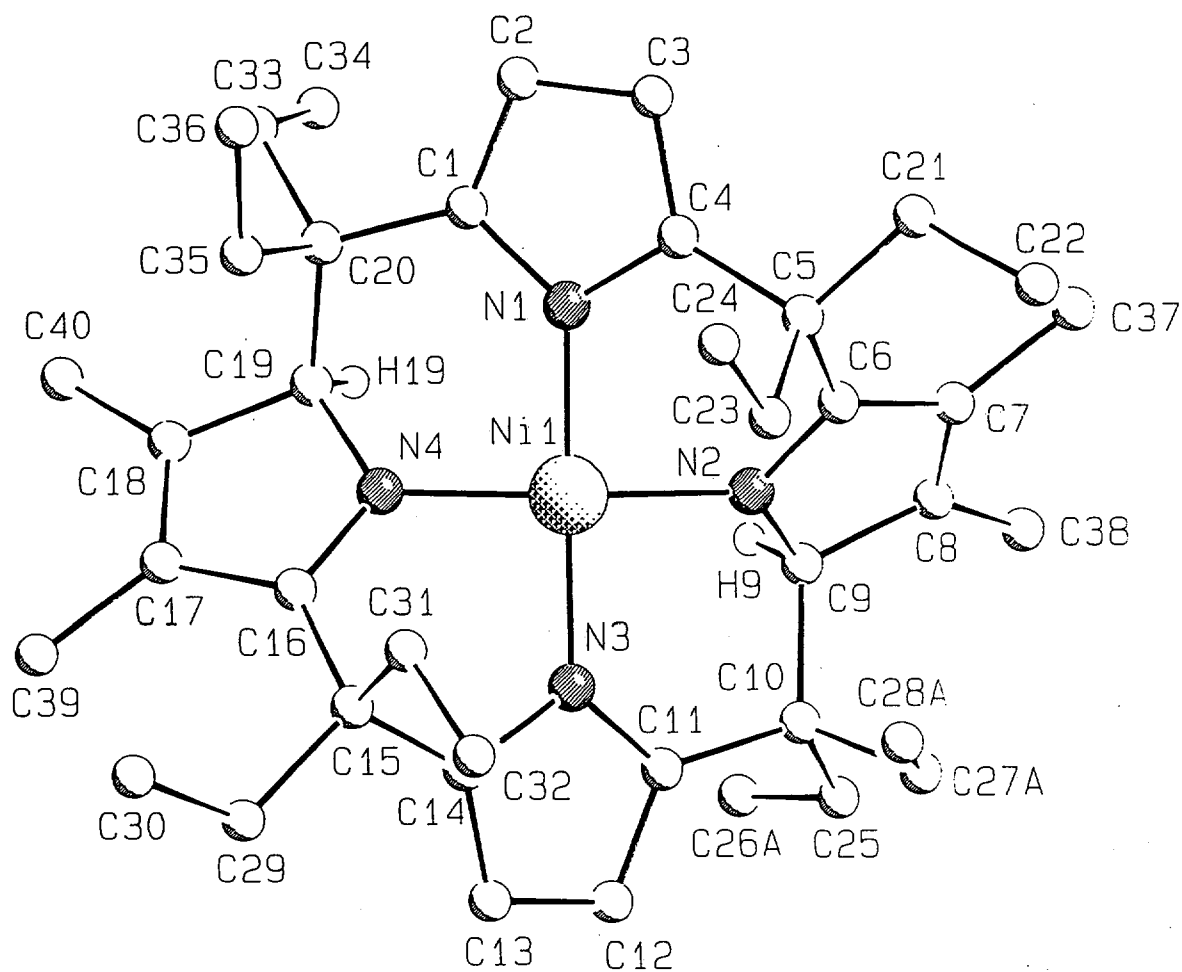


Figure S3. ORTEP view (30% probability ellipsoids) of complex **11**.

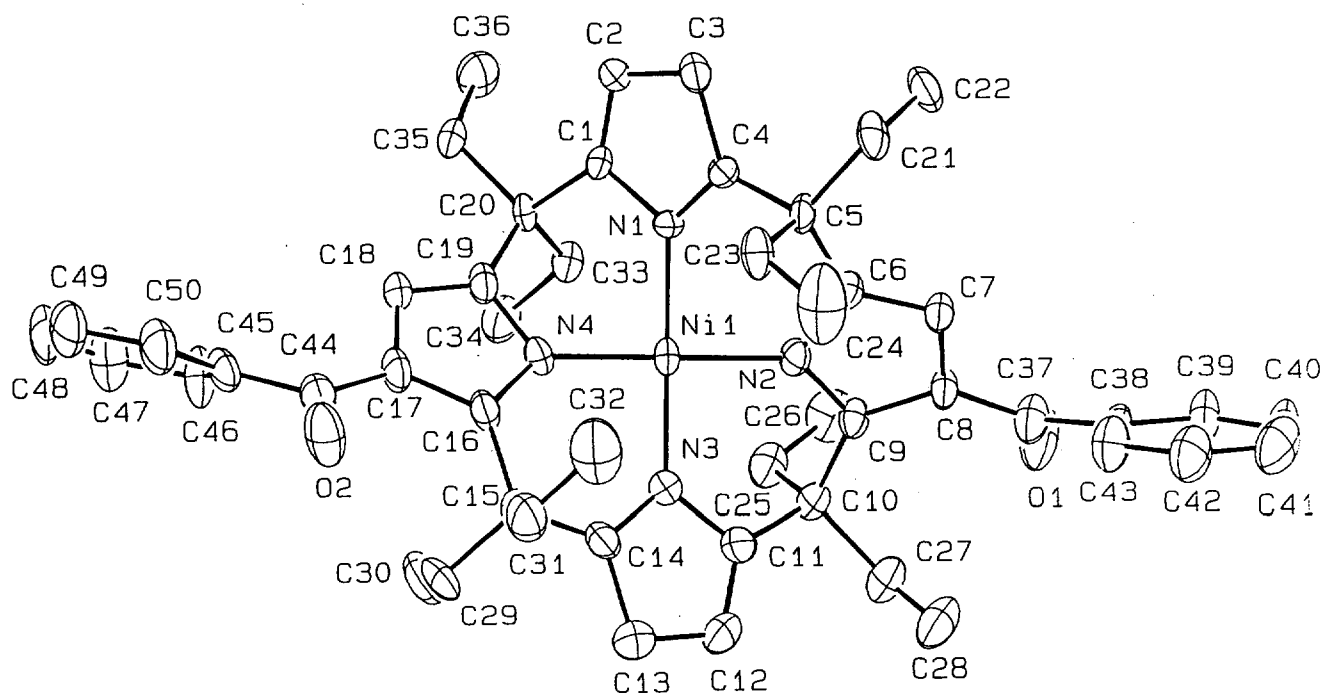
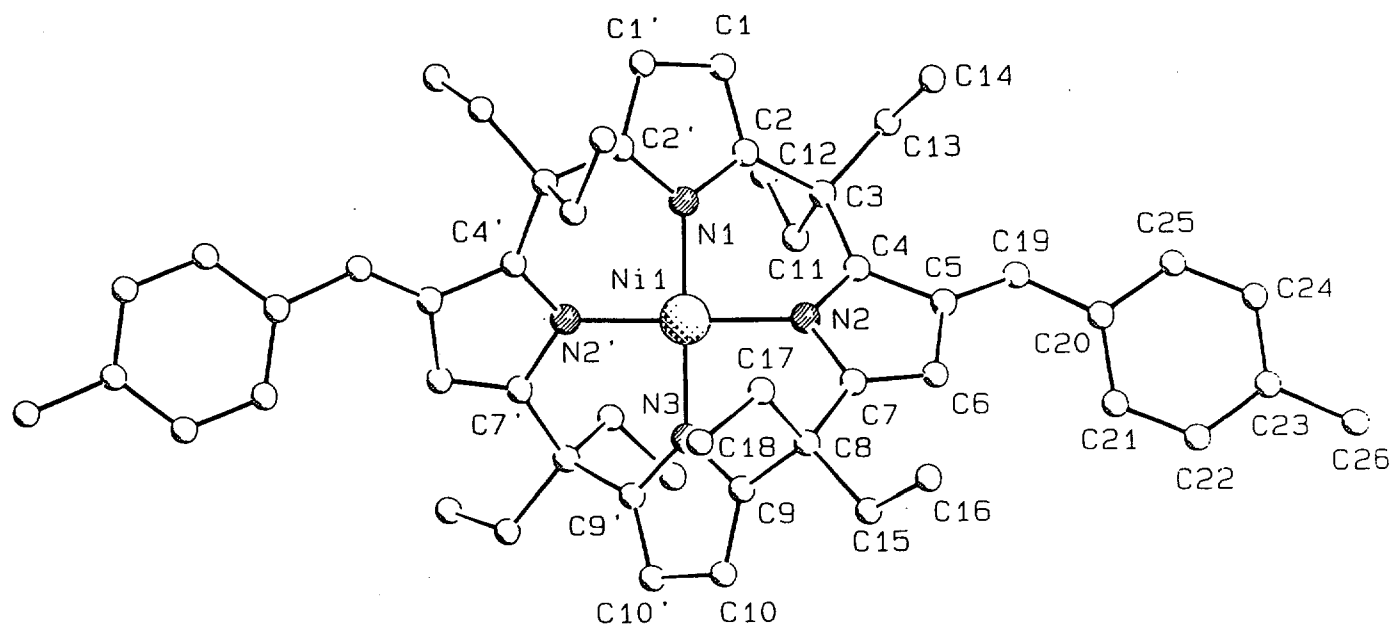


Figure S5. SCHAKAL view of complex 14. A prime denotes a transformation of $-x, y, 0.5-z$.



Crystal data (9): $C_{40}H_{58}N_4Ni \cdot C_7H_8$, $M = 745.8$, monoclinic, space group $P2_1/c$, $a = 13.394(2)$, $b = 19.107(3)$, $c = 15.714(2)$ Å, $\beta = 93.14(1)^\circ$, $V = 4015.5(10)$ Å³, $Z = 4$, $D_{\text{calcd}} = 1.234$ g/cm³, $F(000) = 1616$, $\lambda(\text{Cu-K}\alpha) = 1.54178$ Å, $\mu(\text{Cu-K}\alpha) = 9.38$ cm⁻¹: crystal dimensions 0.22x0.23x0.36 mm. The structure was solved by the heavy atom method and anisotropically refined for all the non-H atoms except for the disordered atoms. The C(25)-C(26) and C(27)-C(28) ethyl groups were found to be affected by high thermal parameters indicating the presence of disorder. The best fit was obtained by splitting the C(26), C(27), C(28) carbon atoms over two positions (A and B) isotropically refined with site occupation factors of 0.5. During the refinement the C-C bond distances within the disordered ethyl groups were constrained to be 1.54(1) Å. The toluene solvent molecules of crystallization were found to lie about a centre of symmetry requiring the statistical distribution over two positions of the C(44) and C(48) methyl carbon atoms. All the hydrogen atoms, but those related to the disordered atoms and to the methyl groups of the toluene molecules, which were ignored, were located from a difference Fourier map and introduced as fixed contributors in the last stage of refinement ($U_{\text{iso}} = 0.05$ Å²). For 4111 unique observed reflections [$I > 2\sigma(I)$] collected at $T = 143$ K on a Rigaku AFC6S diffractometer ($5 < 2\theta < 140^\circ$) the conventional R is 0.073 ($wR2 = 0.231$ calculated over 6605 unique total data having $I > 0$).

(11) $C_{50}H_{58}N_4NiO_2 \cdot 0.5C_6H_{14}$, $M = 848.8$, triclinic, space group P 1, $a = 11.702(2)$, $b = 18.799(3)$, $c = 10.572(2)$ Å, $\alpha = 98.05(2)$, $\beta = 96.13(2)$, $\gamma = 92.10(2)^\circ$, $V = 2286.5(7)$ Å³, $Z = 2$, $D_{\text{calcd}} = 1.233$ g/cm³, $F(000) = 910$, $\lambda(\text{Cu-K}\alpha) = 1.54178$ Å, $\mu(\text{Cu-K}\alpha) = 9.19$ cm⁻¹: crystal dimensions 0.16x0.25x0.30 mm. The structure was solved by the heavy atom method and anisotropically refined for all the non-H atoms except for the disordered atoms. The *n*-hexane solvent molecule of crystallization was found to be disordered about a centre of symmetry. The best fit was obtained by splitting the C(51), C(52), C(53) carbon atoms over two positions (A and B) isotropically refined with site occupation factors of 0.5. During the refinement the C-C bond distances were constrained to be 1.54(1) Å. All the hydrogen atoms, but those associated to the disordered *n*-hexane molecule, which were ignored, were located from a difference Fourier map and introduced as fixed contributors in the last stage of refinement ($U_{\text{iso}} = 0.08$ Å²). For 2312 unique observed reflections [$I > 2\sigma(I)$] collected at $T = 295$ K on a Rigaku AFC6S diffractometer ($5 < 2\theta < 140^\circ$) and corrected for absorption the conventional R is 0.063 ($wR2 = 0.201$ calculated over 6376 unique total data having $I > 0$).

(14) $C_{52}H_{62}N_4Ni$, $M = 801.8$, monoclinic, space group $C2/c$, $a = 15.100(2)$, $b = 17.249(2)$, $c = 17.720(2)$ Å, $\beta = 113.35(2)^\circ$, $V = 4237.4(11)$ Å³, $Z = 4$, $D_{\text{calcd}} = 1.257$ g/cm³, $F(000) = 1720$, $\lambda(\text{Cu-K}\alpha) = 1.54178$ Å, $\mu(\text{Cu-K}\alpha) = 9.29$ cm⁻¹: crystal dimensions 0.10x0.22x0.40 mm. The structure was solved by the heavy atom method and anisotropically refined for all the non-H atoms. All the hydrogen atoms were located from a difference Fourier map and introduced as fixed contributors in the last stage of refinement ($U_{\text{iso}} = 0.05$ Å²). For 2272 unique observed reflections [$I > 2\sigma(I)$] collected at $T = 143$ K on a Rigaku AFC6S diffractometer ($5 < 2\theta < 140^\circ$) and corrected for absorption the conventional R is 0.052 ($wR2 = 0.127$ calculated over 3455 unique total data having $I > 0$).

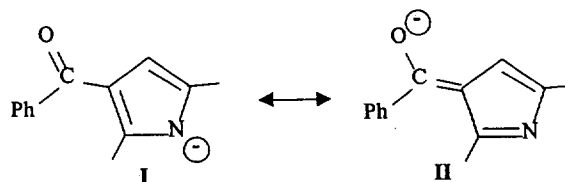
All calculations were carried out on a QUANSAN Personal Computer equipped with an INTEL PENTIUM processor.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (England).

Description of the structures

Complex 9 crystallizes with toluene solvent molecules of crystallization in a complex/solvent molar ratio of 1/1. The macrocycle derives from the protonation of porphyrinogen at the C(9), C(19) α -carbon atoms of two opposite pyrrole rings (Figure 1) and methylation of the β -carbon atoms of the same rings. The resulting dianionic ligand provides a distorted square planar coordination to nickel, as indicated by the remarkable tetrahedral distortion observed for the N_4 core (deviations from the planarity ranging from $-0.272(5)$ to $0.129(3)$ Å for N(3) and N(4), respectively). The metal is displaced by $0.103(1)$ Å from the mean plane through the N_4 core. The Ni-N bond distances fall in rather narrow range (mean value $1.877(4)$ Å) and are in good agreement with those already observed. The trend of the N-C and C-C bond distances and angles within the pyrrole rings containing the neutral N(2) and N(4) nitrogen atoms is consistent with a double bond localization on the N(2)-C(6) ($1.303(6)$ Å), N(4)-C(16) ($1.308(6)$ Å), C(7)-C(8) ($1.336(8)$ Å) and C(17)-C(18) ($1.349(8)$ Å) bonds, while the pyrrole rings containing the negatively charged N(1) and N(3) nitrogen atoms substantially maintain their bond delocalization. As a possible consequence of the sp^3 character of the C(9), C(19) α -carbon atoms and the presence of the methyl groups at the β -carbon atoms, the conformation of the macrocycle deviates from the regular saddle-shape conformation, as indicated by the dihedral angles between the N_4 core and the mean planes through the pyrrole rings ($N_4 \wedge N(1), C(1) \dots C(4)$, $23.7(1)^\circ$; $N_4 \wedge N(2), C(16) \dots C(9)$, $42.1(1)^\circ$; $N_4 \wedge N(3), C(11) \dots C(14)$, $24.2(2)^\circ$; $N_4 \wedge N(4), C(16) \dots C(19)$, $46.0(1)^\circ$) and by the dihedral angles between opposite pyrrole rings ($N(1), C(1) \dots C(4) \wedge N(3), C(11) \dots C(14)$, $47.7(2)^\circ$; $N(2), C(6) \dots C(9) \wedge N(4), C(16) \dots C(19)$, $88.0(2)^\circ$). In this conformation the H(9), H(19) hydrogen atoms and the H(231), H(311) from two methylene groups are arranged on opposite sides of the N_4 core providing a flattened tetrahedral cage for the nickel atom. The H atoms provided by the methylene groups approach more closely the metal from the same side (Ni $\cdots$ H(231), 2.56 Å; Ni $\cdots$ H(311), 2.43 Å), the other Ni $\cdots$ H separations being: Ni $\cdots$ H(9), 3.10 Å; Ni $\cdots$ H(19), 3.01 Å.

Complex 11 (Figure 2) crystallizes with *n*-hexane solvent molecules of crystallization in a complex/solvent molar ratio of 1/0.5. A square planar co-ordination to nickel is provided by the N(1), N(3) nitrogen atoms of two β -protonated pyrrole rings and by the N(2), N(4) nitrogen atoms of two pyrrole rings functionalized at the C(8), C(17) β -carbon atoms by benzoyl groups. The N_4 core is planar (maximum deviation from the planarity: $0.006(6)$ Å), the metal being displaced by $0.045(2)$ Å. The Ni-N bond distances involving the N(2), N(3), N(4) nitrogen atoms (mean value $1.873(3)$ Å) are in agreement with those found in 9, while the Ni-N(1) bond distance ($1.901(5)$ Å) is a little but significantly longer. As observed in 9, the N-C and C-C bond distances and angles within the pyrrole rings containing the neutral N(1) and N(3) nitrogen atoms indicate a significant double bond localization on the N(1)-C(4) ($1.284(9)$ Å), N(3)-C(14) ($1.302(10)$ Å) and C(1)-C(2) ($1.330(9)$ Å), C(11)-C(12) ($1.331(12)$ Å) bonds. Although the C-O bond distances in the benzoyl groups are consistent with a double bond character (C(37)-O(1), $1.212(11)$ Å; C(44)-O(2), $1.225(11)$ Å), the trend of bond distances and angles within the pyrrole rings containing the N(2) and N(4) nitrogen atoms suggests a partial contribution of the enolic form of the PhCOPy fragment corresponding to the following canonical forms:



The contribution of form **II** seems to be particularly important for the pyrrole ring containing N(4), where the N(4)-C(16) (1.349(10) Å) and C(18)-C(19) (1.344(11) Å) show a remarkable double bond character. The macrocycle assumes a regular saddle-shape conformation, the dihedral angles between the N₄ core and the mean planes through the pyrrole rings being: N₄ ^ N(1),C(1)...C(4), 36.9(2)°; N₄ ^ N(2),C(6)...C(9), 36.8(3)°; N₄ ^ N(3),C(11)...C(14), 29.5(3)°; N₄ ^ N(4),C(16)...C(19), 38.3(2)°. The dihedral angles between opposite pyrrole rings are 66.4(3) and 72.6(3)° for N(1),C(1)...C(4) ^ N(3),C(11)...C(14) and N(2),C(6)...C(9) ^ N(4),C(16)...C(19), respectively. This conformation leads three hydrogen (H(252), H(332) from one side; H(231) from the opposite side) atoms from three methylene groups to approach the metal along the d_z² direction at distances varying from 2.64 to 2.75 Å.

Complex **14** consists of discrete molecules of formula [Ni(Et₃N₂(Py-CHPh)₂)]. The complex has a crystallographically imposed C₂ symmetry, the two-fold axis running the Ni, N(1), N(3) atoms. The N₄ core is perfectly planar for symmetry requirements. The Ni-N bond distances (mean value 1.869(13) Å) fall in the usual range. The values of the N-C and C-C bond distances within the independent β-substituted pyrrole ring are consistent with a remarkable double bond localization at the N(2)-C(4) (1.307(4) Å), C(6)-C(7) (1.341(4) Å) and C(5)-C(19) (1.343(5)) bonds. The macrocycle assumes the usual saddle-shape conformation, as indicated by the dihedral angles between the N₄ core and the mean planes through the pyrrole rings (N₄ ^ N(1),C(1),C(2),C(1)',C(2)', 31.6(1)°; N₄ ^ N(2),C(4)...C(7), 35.2(1)°; N₄ ^ N(3),C(9),C(10),C(9)',C(10)', 34.3(1)°; ' = -x, y, 0.5-z). The dihedral angle between opposite pyrrole rings are 65.9(1) and 66.2(1)° for N(1),C(1),C(2),C(1)',C(2)' ^ N(3),C(9),C(10),C(9)',C(10)' and N(2),C(4)...C(7) ^ N(2)',C(4)'...C(7)', respectively. As observed in **9** and **11**, four hydrogen atoms [H(111), H(171)'; H(111)', H(171)] from four methylene groups are arranged on opposite sides of the N₄ core providing a flattened tetrahedral cage for the nickel atom at distances of 2.83 Å [H(111), H(111)'] and 2.42 [H(171), H(171)'].

Table S1. Experimental Data for the X-ray Diffraction Studies on Crystalline Complexes 9, 11 and 14.

Complex	9	11	14
formula	$C_{40}H_{58}N_4Ni \cdot C_7H_8$	$C_{50}H_{58}N_4NiO_2$ $0.5C_6H_{14}$	$C_{52}H_{62}N_4Ni$
cryst habit	prism	flattened prism	prism
cryst colour	yellow	pink	green
fw	745.8	848.8	801.8
cryst syst	monoclinic	triclinic	monoclinic
space group	$P2_1/c$	$\bar{P}1$	$C2/c$
cell parameters ^a			
a , Å	13.394(2)	11.702(2)	15.100(2)
b , Å	19.107(3)	18.799(3)	17.249(2)
c , Å	15.714(2)	10.572(2)	17.720(2)
α , deg	90	98.05(2)	90
β , deg	93.14(1)	96.13(2)	113.35(2)
γ , deg	90	92.10(2)	90
V , Å ³	4015.5(10)	2286.5(7)	4237.4(11)
Z	4	2	4
d_{calc} , Mg m ⁻³	1.234	1.233	1.257
cryst dimens, mm	0.22x0.23x0.36	0.16x0.25x0.30	0.10x0.22x0.40
linear abs coeff, cm ⁻¹	9.38	9.19	9.29
diffractometer	Rigaku AFC6S	Rigaku AFC6S	Rigaku AFC6S
diffraction geometry	equatorial	equatorial	equatorial
scan type	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
scan speed, deg min ⁻¹	4-16	4-16	4-16
scan width, deg	$1.78 + 0.30\text{tg}\theta$	$1.42 + 0.30\text{tg}\theta$	$1.68 + 0.30\text{tg}\theta$
radiation	b	b	b
data collcn range of 2θ , deg	5-140	5-140	5-140
reflcn measd	$h, k, \pm l$	$h, \pm k, \pm l$	$h, k, \pm l$
unique total data	7620	8540	4020
unique obs data [$I > 2\sigma(I)$]	4111	2312	2272
unique data used in rfmnt [$I > 0$] (NO)	6605	6376	3455
no. of params refined (NV)	475	538	259
overdetermn ratio (NO/NV)	13.9	11.9	13.3
transm factors	0.954-1.000	0.801-1.000	0.808-1.000
$R = \sum \Delta F / \sum F_o $ ^c	0.073	0.063	0.052
$wR2 = [\sum w \Delta F ^2 / \sum w F_o ^2]^{1/2}$ ^d	0.231	0.201	0.127
GOF= $[\sum w \Delta F ^2 / (NO-NV)]^{1/2}$	1.052	0.960	1.000
largest shift/esd, final cycle	<0.001	0.001	<0.001
largest peak, e Å ⁻³	0.86 ^e	0.62	0.28

^a Unit cell parameters were obtained by least-squares analysis of the setting angles of 25 carefully centered reflections chosen from diverse regions of reciprocal space collected at 143 K for 9, 14 and at 295 K for 11

^b Graphite monochromated Cu K α ($\lambda = 1.54178$ Å)

^c Calculated on the unique observed data [$I > 2\sigma(I)$]

^d Calculated on the unique data with $I > 0$

^e Midway along the Ni(1)-N(3) bond

S10

Table S2. Fractional atomic coordinates ($\times 10^4$) for complex 9.

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
Ni(1)	2639.0(5)	543.9(3)	2436.8(5)	C(24)	1235(5)	615(3)	4768(3)
N(1)	1782(2)	-181(2)	2761(2)	C(25)	2358(6)	2508(4)	543(5)
N(2)	1549(3)	1122(2)	2130(2)	C(26)A	2874(14)	2122(10)	-143(10)
N(3)	3502(3)	1293(2)	2232(3)	C(26)B	2526(15)	1969(9)	-194(10)
N(4)	3697(3)	-94(2)	2457(2)	C(27)A	1861(10)	2770(7)	1845(8)
C(1)	1897(3)	-894(2)	2697(3)	C(28)A	1896(12)	2655(8)	2808(9)
C(2)	1018(4)	-1215(2)	2903(3)	C(27)B	1911(9)	2621(6)	2234(10)
C(3)	350(3)	-685(2)	3124(3)	C(28)B	2398(11)	3335(7)	2376(9)
C(4)	847(3)	-55(2)	3036(3)	C(29)	6064(4)	801(4)	3273(5)
C(5)	512(3)	686(2)	3224(3)	C(30)	6519(5)	319(4)	3963(5)
C(6)	648(3)	1085(2)	2401(3)	C(31)	4398(4)	711(3)	3939(4)
C(7)	-60(4)	1437(2)	1793(4)	C(32)	4538(6)	1385(4)	4443(4)
C(8)	462(4)	1700(2)	1167(3)	C(33)	2671(4)	-1946(2)	2053(3)
C(9)	1541(4)	1526(2)	1341(3)	C(34)	2170(4)	-1880(3)	1174(4)
C(10)	2296(5)	2143(3)	1425(4)	C(35)	3445(4)	-1410(2)	3421(3)
C(11)	3330(4)	1881(2)	1729(3)	C(36)	2925(4)	-1880(3)	4021(4)
C(12)	4240(6)	2231(3)	1671(4)	C(37)	-1175(6)	1458(4)	1777(5)
C(13)	4963(5)	1856(3)	2153(4)	C(38)	38(6)	2066(3)	401(4)
C(14)	4516(4)	1277(3)	2500(4)	C(39)	6375(6)	-591(4)	2254(5)
C(15)	4909(4)	699(3)	3088(4)	C(40)	4882(4)	-1644(3)	1416(4)
C(16)	4649(3)	24(3)	2629(3)	C(41)	4249(6)	-434(4)	-327(4)
C(17)	5245(4)	-538(3)	2277(3)	C(42)	4750(6)	603(4)	458(4)
C(18)	4608(4)	-1011(3)	1912(3)	C(43)	4006(6)	173(4)	139(4)
C(19)	3551(3)	-768(2)	2019(3)	C(44)	3506(10)	-898(9)	-679(9)
C(20)	2880(3)	-1248(2)	2549(3)	C(45)	-704(7)	-189(4)	575(5)
C(21)	-575(4)	688(2)	3495(4)	C(46)	973(6)	-117(4)	241(5)
C(22)	-934(4)	1386(3)	3865(5)	C(47)	293(7)	-293(4)	794(5)
C(23)	1225(4)	1015(2)	3927(3)	C(48)	-1308(11)	-375(9)	1102(9)

The site occupation factors are 0.5 for the A and B positions of C(26), C(27), C(28) and for C(44), C(48).

Table S3. Fractional atomic coordinates ($\times 10^4$) for complex 11.

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
Ni(1)	-1895.1(10)	2806.3(7)	4510.6(11)	C(26)	-2693(8)	3912(5)	1157(9)
O(1)	-32(5)	3920(4)	131(6)	C(27)	-1542(8)	2549(5)	2(8)
O(2)	-3491(5)	619(3)	7448(7)	C(28)	-510(8)	2096(6)	-269(9)
N(1)	-1499(5)	3597(3)	5835(5)	C(29)	-4028(8)	650(4)	4282(9)
N(2)	-731(5)	3136(3)	3615(5)	C(30)	-5026(9)	1030(6)	3755(10)
N(3)	-2234(5)	2008(3)	3241(6)	C(31)	-1951(8)	678(4)	5166(9)
N(4)	-3001(5)	2448(3)	5452(5)	C(32)	-800(10)	1086(6)	5599(12)
C(1)	-2317(6)	3945(4)	6650(6)	C(33)	-4054(6)	3849(4)	4988(6)
C(2)	-1751(6)	4429(4)	7561(7)	C(34)	-5256(7)	3552(5)	4527(8)
C(3)	-491(6)	4399(4)	7420(7)	C(35)	-4260(6)	4044(4)	7387(7)
C(4)	-480(6)	3863(4)	6252(6)	C(36)	-4511(7)	4814(4)	7338(9)
C(5)	594(5)	3594(4)	5651(6)	C(37)	639(7)	3678(5)	895(8)
C(6)	314(6)	3478(4)	4215(6)	C(38)	1868(7)	3607(5)	650(7)
C(7)	961(6)	3643(4)	3265(7)	C(39)	2311(7)	4058(5)	-151(8)
C(8)	308(6)	3441(4)	2097(7)	C(40)	3430(9)	3973(7)	-460(9)
C(9)	-731(5)	3099(4)	2320(7)	C(41)	4104(8)	3490(7)	-8(10)
C(10)	-1758(6)	2720(4)	1453(7)	C(42)	3667(8)	3038(6)	789(10)
C(11)	-2052(6)	2028(5)	1924(8)	C(43)	2568(8)	3101(5)	1103(9)
C(12)	-2265(8)	1365(5)	1292(9)	C(44)	-4080(7)	1142(5)	7402(8)
C(13)	-2639(8)	874(5)	2176(9)	C(45)	-5141(7)	1182(4)	8087(8)
C(14)	-2607(6)	1374(4)	3428(8)	C(46)	-6143(8)	1446(5)	7602(9)
C(15)	-2911(7)	1142(4)	4633(7)	C(47)	-7118(8)	1420(6)	8247(11)
C(16)	-3169(6)	1758(4)	5635(8)	C(48)	-7082(10)	1141(6)	9363(12)
C(17)	-3806(6)	1741(4)	6702(7)	C(49)	-6113(11)	875(6)	9829(10)
C(18)	-4081(6)	2462(4)	7092(7)	C(50)	-5130(8)	888(5)	9200(9)
C(19)	-3582(6)	2874(4)	6342(7)	C(51)A	1187(28)	1023(14)	2414(30)
C(20)	-3577(5)	3678(4)	6326(6)	C(52)A	957(27)	267(15)	1621(27)
C(21)	1624(6)	4145(5)	6076(7)	C(53)A	644(8)	-26(16)	203(28)
C(22)	1581(7)	4867(5)	5690(8)	C(51)B	511(36)	537(25)	2430(30)
C(23)	828(6)	2877(4)	6153(7)	C(52)B	631(22)	757(13)	1115(24)
C(24)	1786(10)	2485(6)	5590(13)	C(53)B	170(27)	-20(13)	718(9)
C(25)	-2839(6)	3187(5)	1525(7)				

The site occupation factors for the A and B positions of C(51), C(52), C(53) are 0.5.

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Table S4. Fractional atomic coordinates ($\times 10^4$) for complex 14.

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
Ni(1)	0(-)	-57.8(4)	2500(-)	C(12)	2492(3)	-1519(3)	4292(2)
N(1)	0(-)	-1122(2)	2500(-)	C(13)	2401(2)	-1890(2)	2629(2)
N(2)	897(2)	-67(2)	1999(2)	C(14)	2154(3)	-2228(2)	1776(2)
N(3)	0(-)	1020(2)	2500(-)	C(15)	379(2)	1762(2)	642(2)
C(1)	484(2)	-2346(2)	2543(2)	C(16)	302(3)	1517(2)	-210(2)
C(2)	760(2)	-1584(2)	2573(2)	C(17)	-801(2)	707(2)	647(2)
C(3)	1741(2)	-1245(2)	2712(2)	C(18)	-1695(3)	1206(3)	420(2)
C(4)	1623(2)	-543(2)	2161(2)	C(19)	3129(2)	-492(2)	1854(2)
C(5)	2268(2)	-222(2)	1791(2)	C(20)	3823(2)	-130(2)	1577(2)
C(6)	1777(2)	465(2)	1354(2)	C(21)	3938(2)	667(2)	1538(2)
C(7)	958(2)	541(2)	1473(2)	C(22)	4632(2)	972(2)	1298(2)
C(8)	159(2)	1131(2)	1161(2)	C(23)	5248(2)	495(2)	1105(2)
C(9)	93(2)	1500(2)	1916(2)	C(24)	5135(3)	-299(2)	1133(2)
C(10)	63(3)	2259(2)	2125(2)	C(25)	4440(3)	-602(2)	1372(2)
C(11)	2227(2)	-909(2)	3610(2)	C(26)	6047(3)	832(2)	903(3)

Table S5. Fractional atomic coordinates ($\times 10^4$) for hydrogen atoms for complex 9.

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
H(2)	868	-1701	2987	H(331)	3247	-2244	2014
H(3)	-372	-757	3241	H(332)	2196	-2257	2408
H(9)	1685	1217	793	H(341)	2105	-2305	924
H(12)	4349	2578	1296	H(342)	2532	-1628	847
H(13)	5669	1972	2219	H(343)	1524	-1598	1243
H(19)	3258	-680	1386	H(351)	4037	-1624	3254
H(211)	-572	308	3868	H(352)	3558	-889	3724
H(212)	-1044	456	2900	H(361)	3331	-1937	4516
H(221)	-1575	1382	3976	H(362)	2807	-2333	3832
H(222)	-783	1842	3529	H(363)	2220	-1674	4176
H(223)	-567	1459	4363	H(371)	-1403	1276	2269
H(231)	1908	1045	3783	H(372)	-1472	1209	1275
H(232)	979	1500	4032	H(373)	-1478	1938	1663
H(241)	1741	768	5163	H(381)	489	2105	-9
H(242)	1496	150	4643	H(382)	-247	2487	522
H(243)	506	586	5013	H(383)	-359	1814	57
H(291)	6353	814	2654	H(391)	6791	-86	2653
H(292)	6231	1315	3388	H(392)	6635	-558	1563
H(301)	7152	375	3955	H(393)	6769	-1061	2632
H(302)	6308	-186	3834	H(401)	4320	-1897	1103
H(303)	6193	504	4547	H(402)	5159	-1988	1745
H(311)	3613	648	3780	H(403)	5233	-1581	963
H(312)	4619	296	4276	H(42)	4564	1196	781
H(321)	4153	1309	4940	H(43)	3105	371	237
H(322)	4266	1785	4116	H(46)	1724	-221	373
H(323)	5229	1485	4516	H(47)	521	-526	1278

Table S6. Fractional atomic coordinates ($\times 10^4$) for hydrogen atoms for complex 11.

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
H(2)	-2190	4699	8407	H(292)	-4388	382	4933
H(31)	173	4257	8192	H(301)	-5683	720	3381
H(32)	-384	4898	7270	H(302)	-5063	1253	2963
H(7)	1884	3905	3562	H(303)	-5198	1306	4417
H(12)	-2301	1135	312	H(311)	-1874	288	4367
H(131)	-3419	638	1901	H(312)	-2395	397	5747
H(132)	-2118	467	2258	H(321)	-469	839	5803
H(18)	-4416	2646	8014	H(322)	-842	1605	6438
H(211)	2252	3850	5941	H(323)	-608	1214	4932
H(212)	1916	4157	6946	H(331)	-3946	4317	4956
H(221)	2151	5167	6061	H(332)	-3636	3695	4353
H(222)	1009	5181	5960	H(341)	-5520	3534	3626
H(223)	1351	4883	4698	H(342)	-5904	3724	5001
H(231)	33	2562	5881	H(343)	-5393	3043	4342
H(232)	867	2892	7097	H(351)	-4851	3721	7337
H(241)	1920	2053	5918	H(352)	-4139	3953	8397
H(242)	2501	2798	5774	H(361)	-4946	4982	8008
H(243)	1627	2392	4657	H(362)	-4972	4834	6509
H(251)	-3639	2881	979	H(363)	-3816	5090	7369
H(252)	-3087	3245	2395	H(39)	1927	4392	-416
H(261)	-3315	4219	1216	H(40)	3674	4349	-978
H(262)	-2638	3953	237	H(41)	4802	3410	-121
H(263)	-2200	4203	1645	H(42)	4101	2568	1226
H(271)	-2421	2196	-642	H(43)	2097	2732	1638
H(272)	-1480	2901	-240	H(46)	-6196	1583	6878
H(281)	-496	2143	-1063	H(47)	-7929	1608	7889
H(282)	-473	1608	206	H(48)	-7771	1112	9663
H(283)	343	2271	110	H(49)	-5981	695	10535
H(291)	-3855	262	3683	H(50)	-4375	637	9451

Table S7. Fractional atomic coordinates ($\times 10^4$) for hydrogen atoms for complex **14**.

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
H(1)	906	-2811	2648	H(162)	469	1956	-481
H(6)	1963	788	993	H(163)	768	1121	-192
H(10)	54	2725	1766	H(171)	-796	250	1051
H(111)	1791	-574	3690	H(172)	-752	564	176
H(112)	2888	-633	3685	H(181)	-1696	1670	134
H(121)	3055	-1830	4351	H(182)	-2317	922	97
H(122)	2645	-1263	4781	H(183)	-1791	1385	893
H(123)	1921	-1922	4245	H(19)	3293	-978	2058
H(131)	3102	-1708	2845	H(21)	3565	994	1682
H(132)	2432	-2292	3002	H(22)	4703	1567	1235
H(141)	2610	-2662	1749	H(24)	5521	-682	988
H(142)	1521	-2509	1498	H(25)	4276	-1127	1408
H(143)	2100	-1860	1392	H(261)	5904	1353	650
H(151)	986	1946	905	H(262)	6201	484	510
H(152)	-100	2192	582	H(263)	6677	925	1399
H(161)	-380	1361	-587				

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Table S8. Anisotropic and isotropic thermal parameters $U_{(i,j)}$ ($\times 10^4 \text{ \AA}^2$) for complex 9. $U_{(i,j)}$ are in the form $\exp[-2\pi^2(U_{11}h^2a^2 + \dots + 2U_{12}hka^*b^* + \dots)]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ni(1)	317(4)	255(3)	438(4)	-17(3)	0(3)	-44(3)
N(1)	333(18)	246(17)	357(18)	-7(13)	4(14)	-15(13)
N(2)	373(19)	267(16)	307(17)	-16(13)	-41(14)	-24(14)
N(3)	501(25)	322(19)	604(26)	-45(18)	66(20)	-92(17)
N(4)	318(19)	352(19)	517(22)	-7(16)	10(16)	-62(15)
C(1)	298(21)	293(21)	491(26)	4(18)	-50(19)	-28(16)
C(2)	400(24)	258(20)	589(29)	12(19)	0(21)	-63(18)
C(3)	374(24)	353(23)	493(26)	6(19)	40(20)	-57(18)
C(4)	376(23)	293(20)	376(22)	-28(17)	4(18)	-30(17)
C(5)	389(23)	328(22)	419(23)	-51(18)	52(19)	-37(17)
C(6)	418(24)	265(20)	481(26)	-69(18)	-56(20)	19(17)
C(7)	450(27)	321(23)	699(34)	-28(23)	-186(25)	88(20)
C(8)	715(35)	341(24)	509(29)	1(21)	-261(26)	0(23)
C(9)	673(32)	314(22)	341(23)	19(18)	-40(21)	48(21)
C(10)	778(40)	312(24)	776(39)	43(25)	214(32)	-70(25)
C(11)	686(34)	304(23)	567(30)	-10(21)	89(26)	-170(22)
C(12)	1046(53)	597(36)	621(36)	44(29)	79(35)	-524(37)
C(13)	632(36)	584(34)	729(38)	-59(29)	22(30)	-305(29)
C(14)	498(30)	504(29)	581(31)	-68(24)	-15(24)	-205(23)
C(15)	391(26)	442(26)	624(31)	-10(22)	-80(23)	-139(20)
C(16)	355(24)	487(26)	499(27)	64(22)	33(20)	-67(20)
C(17)	372(25)	561(29)	550(28)	49(25)	55(21)	-28(22)
C(18)	430(26)	449(26)	484(27)	34(21)	71(21)	19(21)
C(19)	369(23)	297(21)	490(26)	-52(18)	10(20)	4(17)
C(20)	285(22)	301(20)	518(27)	-4(19)	-44(19)	-27(16)
C(21)	424(26)	429(26)	680(33)	-73(23)	206(24)	5(20)
C(22)	519(33)	529(33)	1093(51)	-207(33)	307(33)	-10(26)
C(23)	585(30)	373(24)	419(25)	-31(20)	38(22)	-63(21)
C(24)	701(37)	622(34)	437(27)	31(25)	-18(25)	-125(28)
C(25)	1021(58)	750(47)	1272(66)	719(48)	334(48)	110(41)
C(29)	480(33)	790(43)	968(49)	172(37)	-141(33)	-269(30)
C(30)	431(33)	997(53)	1204(62)	124(47)	-135(37)	-136(34)
C(31)	540(31)	533(31)	553(31)	-13(23)	-121(25)	-46(23)
C(32)	870(47)	739(43)	721(42)	-102(34)	-104(36)	-246(36)
C(33)	452(26)	243(20)	635(30)	-50(20)	-20(22)	53(18)
C(34)	545(30)	405(26)	638(32)	-118(23)	-49(25)	-25(22)
C(35)	349(23)	435(26)	608(30)	2(22)	-16(22)	10(19)
C(36)	530(31)	645(35)	612(34)	180(27)	-127(26)	-139(26)
C(37)	735(45)	714(43)	1106(58)	-71(41)	-220(41)	205(35)
C(38)	1098(55)	528(34)	658(39)	49(28)	-389(38)	89(34)
C(39)	669(45)	1126(62)	957(54)	29(47)	146(39)	86(41)
C(40)	532(31)	494(29)	687(35)	39(26)	160(27)	97(24)
C(41)	872(49)	893(49)	486(32)	109(32)	-16(31)	-100(38)
C(42)	1007(56)	746(42)	580(35)	111(32)	-58(35)	-57(40)
C(43)	1035(56)	889(52)	503(36)	60(33)	-12(35)	-79(43)
C(44)	617(78)	1125(115)	674(80)	-125(78)	64(64)	-207(77)
C(45)	1136(63)	568(40)	930(54)	-300(37)	-284(47)	149(39)
C(46)	941(52)	575(39)	859(50)	-187(35)	-440(42)	227(36)
C(47)	1017(58)	595(38)	771(46)	-155(34)	-431(42)	256(38)
C(48)	713(88)	1204(127)	639(78)	289(82)	-12(66)	-261(83)

Atom	U_{iso}	Atom	U_{iso}
C(26)A	927(57)	C(26)B	879(54)
C(27)A	614(31)	C(27)B	601(29)
C(28)A	808(39)	C(28)B	852(42)

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Table S9. Anisotropic and isotropic thermal parameters $U_{(i,j)}$ ($\times 10^4 \text{ \AA}^2$) for complex 11. $U_{(i,j)}$ are in the form $\exp[-2\pi^2(U_{11}h^2a^2 + \dots + 2U_{12}hka^*b^* + \dots)]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ni (1)	427 (8)	469 (8)	444 (7)	103 (6)	177 (6)	-60 (6)
O (1)	689 (42)	1698 (68)	703 (42)	581 (44)	150 (34)	49 (41)
O (2)	874 (46)	758 (45)	1505 (63)	590 (44)	417 (43)	144 (37)
N (1)	452 (37)	365 (34)	302 (31)	-6 (26)	35 (27)	-76 (29)
N (2)	500 (39)	476 (38)	346 (35)	151 (30)	74 (30)	-18 (30)
N (3)	606 (43)	551 (45)	508 (41)	-20 (35)	154 (33)	-127 (34)
N (4)	528 (40)	419 (40)	519 (39)	128 (33)	133 (32)	-128 (32)
C (1)	474 (43)	427 (44)	331 (39)	74 (34)	163 (33)	-22 (34)
C (2)	535 (49)	543 (50)	426 (44)	0 (39)	93 (37)	-166 (38)
C (3)	445 (46)	659 (53)	463 (45)	177 (41)	30 (36)	-118 (38)
C (4)	565 (49)	512 (47)	261 (38)	47 (34)	43 (34)	-135 (38)
C (5)	309 (39)	686 (52)	416 (42)	102 (38)	125 (32)	-72 (35)
C (6)	430 (43)	559 (48)	375 (41)	128 (36)	58 (34)	21 (36)
C (7)	389 (43)	664 (53)	419 (44)	149 (39)	94 (35)	-34 (37)
C (8)	380 (42)	689 (54)	434 (46)	178 (40)	122 (36)	-55 (37)
C (9)	283 (39)	623 (51)	431 (43)	139 (38)	55 (34)	28 (35)
C (10)	575 (52)	643 (53)	389 (43)	31 (38)	129 (37)	-57 (41)
C (11)	500 (49)	608 (56)	656 (57)	-64 (47)	166 (41)	-82 (41)
C (12)	1153 (83)	752 (70)	861 (70)	-137 (58)	611 (61)	-96 (59)
C (13)	1182 (85)	696 (66)	895 (72)	-173 (58)	463 (62)	-186 (58)
C (14)	538 (51)	468 (52)	840 (63)	-44 (47)	225 (44)	-105 (40)
C (15)	610 (52)	481 (50)	591 (50)	60 (41)	238 (41)	-45 (41)
C (16)	455 (46)	414 (47)	756 (57)	127 (42)	243 (41)	-42 (36)
C (17)	589 (52)	625 (58)	579 (51)	252 (45)	141 (41)	-115 (43)
C (18)	550 (49)	466 (49)	505 (47)	102 (39)	190 (38)	-76 (37)
C (19)	453 (45)	545 (49)	471 (45)	173 (39)	120 (36)	-67 (37)
C (20)	280 (38)	510 (46)	508 (44)	91 (36)	152 (33)	-87 (32)
C (21)	288 (41)	988 (65)	585 (50)	260 (48)	-30 (35)	-143 (40)
C (22)	784 (63)	806 (66)	710 (58)	202 (50)	63 (47)	-427 (50)
C (23)	508 (48)	746 (58)	690 (54)	429 (47)	132 (41)	68 (42)
C (24)	1213 (98)	1291 (103)	2032 (136)	979 (101)	700 (94)	542 (83)
C (25)	485 (49)	911 (67)	519 (49)	146 (47)	46 (38)	55 (45)
C (26)	843 (69)	929 (75)	919 (73)	211 (60)	89 (56)	177 (57)
C (27)	900 (69)	987 (73)	524 (52)	81 (50)	276 (47)	-42 (55)
C (28)	966 (77)	1253 (88)	739 (66)	77 (62)	415 (58)	155 (66)
C (29)	874 (70)	445 (53)	1054 (75)	52 (51)	246 (59)	-320 (48)
C (30)	880 (77)	1183 (91)	961 (78)	178 (67)	-14 (61)	-575 (68)
C (31)	880 (71)	569 (59)	1073 (78)	77 (55)	423 (61)	-11 (53)
C (32)	1145 (93)	989 (85)	1639 (111)	414 (79)	435 (83)	244 (73)
C (33)	452 (44)	606 (51)	458 (44)	160 (38)	108 (35)	34 (37)
C (34)	564 (55)	1029 (71)	619 (54)	134 (50)	140 (43)	15 (49)
C (35)	524 (48)	614 (53)	519 (47)	81 (40)	268 (38)	-4 (39)
C (36)	769 (62)	618 (59)	990 (71)	102 (52)	374 (52)	174 (48)
C (37)	462 (52)	1004 (71)	567 (54)	209 (51)	117 (43)	-9 (47)
C (38)	655 (58)	960 (69)	360 (44)	71 (45)	216 (40)	-145 (51)
C (39)	593 (57)	1069 (74)	738 (59)	334 (54)	283 (47)	-78 (49)
C (40)	757 (74)	1709 (117)	611 (63)	247 (69)	277 (55)	-365 (72)
C (41)	449 (60)	1643 (116)	822 (76)	68 (75)	168 (54)	60 (64)
C (42)	616 (65)	1197 (88)	964 (75)	190 (66)	263 (55)	80 (58)
C (43)	561 (59)	1036 (77)	889 (68)	286 (60)	259 (52)	76 (54)
C (44)	621 (57)	576 (56)	747 (59)	148 (48)	201 (46)	-29 (46)

Table S9. Anisotropic and isotropic thermal parameters $U_{(i,j)}$
($\times 10^4 \text{ \AA}^2$) for complex 11 (cont.).

C(45)	666(58)	642(56)	545(52)	268(45)	46(44)	-212(46)
C(46)	657(62)	1110(81)	939(70)	563(63)	301(55)	-27(55)
C(47)	756(69)	1156(88)	1264(93)	484(74)	389(65)	42(60)
C(48)	990(85)	1026(86)	1131(93)	379(72)	561(73)	-218(69)
C(49)	1132(92)	1110(89)	759(71)	391(63)	284(68)	-281(72)
C(50)	891(70)	1018(75)	778(64)	413(58)	174(54)	-192(57)

Atom	U_{iso}	Atom	U_{iso}
C(51)A	1704(116)	C(51)B	2308(157)
C(52)A	1635(105)	C(52)B	1301(85)
C(53)A	1489(108)	C(53)B	1368(93)

Table S10. Anisotropic thermal parameters $U_{(i,j)}$ ($\times 10^4 \text{ \AA}^2$) for complex 14. $U_{(i,j)}$ are in the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{12}hka^*b^* + \dots)]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ni(1)	224(4)	223(4)	222(4)	0(-)	80(3)	0(-)
N(1)	228(19)	231(20)	213(21)	0(-)	69(16)	0(-)
N(2)	233(12)	250(14)	210(13)	28(12)	83(10)	0(12)
N(3)	247(19)	241(20)	237(21)	0(-)	91(17)	0(-)
C(1)	357(19)	212(17)	429(21)	27(15)	165(17)	42(15)
C(2)	268(16)	260(17)	276(17)	5(14)	125(14)	13(14)
C(3)	254(16)	288(17)	249(17)	24(14)	86(14)	47(14)
C(4)	248(16)	258(16)	215(16)	-37(14)	43(13)	-13(14)
C(5)	288(16)	336(19)	213(16)	10(14)	99(14)	-13(14)
C(6)	277(17)	299(18)	228(17)	31(14)	55(14)	-45(14)
C(7)	261(16)	239(16)	235(16)	22(14)	86(13)	-22(14)
C(8)	237(16)	242(16)	230(17)	37(13)	76(14)	-35(13)
C(9)	249(16)	221(16)	251(17)	59(14)	65(14)	-17(13)
C(10)	330(18)	262(18)	375(21)	60(15)	124(17)	9(15)
C(11)	289(17)	451(21)	261(18)	18(16)	103(15)	106(16)
C(12)	504(24)	605(27)	229(19)	106(18)	108(17)	185(20)
C(13)	333(18)	287(19)	362(20)	58(16)	171(16)	78(15)
C(14)	415(21)	367(20)	436(23)	-17(17)	211(19)	64(17)
C(15)	304(18)	321(19)	400(20)	174(16)	164(16)	55(15)
C(16)	399(21)	614(26)	294(20)	144(19)	152(17)	26(20)
C(17)	309(18)	397(21)	218(16)	39(15)	76(14)	-25(16)
C(18)	282(19)	650(28)	335(21)	-15(19)	73(16)	37(19)
C(19)	282(17)	405(20)	251(18)	12(16)	95(14)	11(16)
C(20)	259(15)	351(20)	205(16)	32(14)	58(13)	23(15)
C(21)	324(19)	322(20)	399(21)	-47(16)	156(16)	15(16)
C(22)	307(19)	344(21)	380(22)	-3(16)	91(17)	-20(16)
C(23)	313(19)	453(21)	215(17)	12(16)	84(14)	-90(17)
C(24)	336(19)	367(20)	526(25)	-34(18)	237(18)	26(16)
C(25)	334(18)	300(19)	462(22)	-4(17)	187(17)	-5(16)
C(26)	368(21)	509(24)	518(25)	-31(20)	213(19)	-79(19)

Table S11. Bond distances (Å) and angles (°) for complex 9.

Ni(1) - N(1)	1.887(4)	C(13) - C(14)	1.384(8)
Ni(1) - N(2)	1.873(4)	C(14) - C(15)	1.516(8)
Ni(1) - N(3)	1.879(4)	C(15) - C(16)	1.509(8)
Ni(1) - N(4)	1.868(4)	C(15) - C(29)	1.570(8)
N(1) - C(1)	1.375(5)	C(15) - C(31)	1.535(9)
N(1) - C(4)	1.368(5)	C(16) - C(17)	1.465(8)
N(2) - C(6)	1.303(6)	C(17) - C(18)	1.349(8)
N(2) - C(9)	1.460(6)	C(17) - C(39)	1.519(10)
N(3) - C(11)	1.386(6)	C(18) - C(19)	1.508(7)
N(3) - C(14)	1.400(7)	C(18) - C(40)	1.495(8)
N(4) - C(16)	1.308(6)	C(19) - C(20)	1.557(6)
N(4) - C(19)	1.468(6)	C(20) - C(33)	1.562(6)
C(1) - C(2)	1.382(6)	C(20) - C(35)	1.560(6)
C(1) - C(20)	1.510(6)	C(21) - C(22)	1.542(8)
C(2) - C(3)	1.407(6)	C(23) - C(24)	1.526(7)
C(3) - C(4)	1.386(6)	C(25) - C(26)A	1.505(19)
C(4) - C(5)	1.519(6)	C(25) - C(26)B	1.575(18)
C(5) - C(6)	1.521(6)	C(27)A - C(28)A	1.527(19)
C(5) - C(21)	1.539(7)	C(27)B - C(28)B	1.523(18)
C(5) - C(23)	1.553(6)	C(29) - C(30)	1.524(10)
C(6) - C(7)	1.471(7)	C(31) - C(32)	1.518(9)
C(7) - C(8)	1.336(8)	C(33) - C(34)	1.507(8)
C(7) - C(37)	1.493(10)	C(35) - C(36)	1.501(8)
C(8) - C(9)	1.494(7)	C(41) - C(42)'	1.405(11)
C(8) - C(38)	1.478(8)	C(41) - C(43)	1.419(10)
C(9) - C(10)	1.554(8)	C(41) - C(44)	1.422(17)
C(10) - C(11)	1.525(8)	C(42) - C(43)	1.365(11)
C(10) - C(25)	1.558(10)	C(45) - C(46)"	1.437(11)
C(10) - C(27)A	1.501(15)	C(45) - C(47)	1.375(13)
C(10) - C(27)B	1.670(16)	C(45) - C(48)	1.241(17)
C(11) - C(12)	1.398(9)	C(46) - C(47)	1.336(12)
C(12) - C(13)	1.394(9)		
N(3) - Ni(1) - N(4)	91.5(2)	N(3) - C(11) - C(10)	124.4(4)
N(2) - Ni(1) - N(4)	165.7(2)	C(10) - C(11) - C(12)	127.1(4)
N(2) - Ni(1) - N(3)	89.1(2)	N(3) - C(11) - C(12)	107.9(4)
N(1) - Ni(1) - N(4)	89.3(2)	C(11) - C(12) - C(13)	107.5(5)
N(1) - Ni(1) - N(3)	174.1(2)	C(12) - C(13) - C(14)	108.8(6)
N(1) - Ni(1) - N(2)	91.4(2)	N(3) - C(14) - C(13)	107.3(5)
Ni(1) - N(1) - C(4)	122.5(3)	C(13) - C(14) - C(15)	132.8(5)
Ni(1) - N(1) - C(1)	129.4(2)	N(3) - C(14) - C(15)	119.9(5)
C(1) - N(1) - C(4)	107.8(4)	C(14) - C(15) - C(31)	111.3(5)
Ni(1) - N(2) - C(9)	120.0(3)	C(14) - C(15) - C(29)	109.2(5)
Ni(1) - N(2) - C(6)	127.3(3)	C(14) - C(15) - C(16)	105.6(5)
C(6) - N(2) - C(9)	110.0(4)	C(29) - C(15) - C(31)	108.6(5)
Ni(1) - N(3) - C(14)	121.8(3)	C(16) - C(15) - C(31)	109.1(4)
Ni(1) - N(3) - C(11)	129.1(3)	C(16) - C(15) - C(29)	113.2(5)
C(11) - N(3) - C(14)	108.5(4)	N(4) - C(16) - C(15)	116.3(4)
Ni(1) - N(4) - C(19)	118.9(3)	C(15) - C(16) - C(17)	133.7(4)
Ni(1) - N(4) - C(16)	128.4(4)	N(4) - C(16) - C(17)	109.9(4)
C(16) - N(4) - C(19)	110.6(4)	C(16) - C(17) - C(39)	128.5(5)
N(1) - C(1) - C(20)	123.9(3)	C(16) - C(17) - C(18)	107.9(5)
N(1) - C(1) - C(2)	108.8(4)	C(18) - C(17) - C(39)	123.6(5)
C(2) - C(1) - C(20)	126.8(4)	C(17) - C(18) - C(40)	126.6(5)
C(1) - C(2) - C(3)	107.4(4)	C(17) - C(18) - C(19)	108.8(4)
C(2) - C(3) - C(4)	106.6(4)	C(19) - C(18) - C(40)	124.5(4)
N(1) - C(4) - C(3)	109.4(4)	N(4) - C(19) - C(18)	102.7(4)

Table S11. Bond distances (Å) and angles (°) for complex 9 (cont.).

C(4) - C(5) - C(23)	109.8(3)	C(1) - C(20) - C(19)	110.6(3)
C(4) - C(5) - C(21)	110.5(3)	C(19) - C(20) - C(35)	108.7(3)
C(4) - C(5) - C(6)	104.6(3)	C(19) - C(20) - C(33)	109.2(4)
C(21) - C(5) - C(23)	110.9(4)	C(1) - C(20) - C(35)	109.8(4)
C(6) - C(5) - C(23)	107.7(3)	C(1) - C(20) - C(33)	109.0(3)
C(6) - C(5) - C(21)	113.2(4)	C(33) - C(20) - C(35)	109.5(3)
N(2) - C(6) - C(5)	117.5(4)	C(5) - C(21) - C(22)	115.2(4)
C(5) - C(6) - C(7)	132.7(4)	C(5) - C(23) - C(24)	112.9(4)
N(2) - C(6) - C(7)	109.8(4)	C(10) - C(25) - C(26)B	112.2(8)
C(6) - C(7) - C(37)	129.2(5)	C(10) - C(25) - C(26)A	117.8(9)
C(6) - C(7) - C(8)	107.8(4)	C(10) - C(27)A - C(28)A	109.2(10)
C(8) - C(7) - C(37)	122.8(5)	C(10) - C(27)B - C(28)B	117.0(10)
C(7) - C(8) - C(38)	125.8(5)	C(15) - C(29) - C(30)	114.1(5)
C(7) - C(8) - C(9)	108.8(4)	C(15) - C(31) - C(32)	114.8(5)
C(9) - C(8) - C(38)	125.4(5)	C(20) - C(33) - C(34)	116.4(4)
N(2) - C(9) - C(8)	103.6(4)	C(20) - C(35) - C(36)	116.8(4)
C(8) - C(9) - C(10)	117.7(4)	C(43) - C(41) - C(44)	122.3(8)
N(2) - C(9) - C(10)	110.8(4)	C(42)' - C(41) - C(44)	116.9(9)
C(9) - C(10) - C(27)B	104.7(6)	C(42)' - C(41) - C(43)	120.7(7)
C(9) - C(10) - C(27)A	112.1(7)	C(41) - C(42)' - C(43)'	119.4(7)
C(9) - C(10) - C(25)	109.3(5)	C(41) - C(43) - C(42)	119.9(7)
C(9) - C(10) - C(11)	110.7(4)	C(47) - C(45) - C(48)	116.8(10)
C(25) - C(10) - C(27)B	117.8(6)	C(46)" - C(45) - C(48)	124.8(10)
C(25) - C(10) - C(27)A	94.3(7)	C(46)" - C(45) - C(47)	118.3(7)
C(11) - C(10) - C(27)B	104.7(6)	C(45) - C(46)' - C(47)"	122.4(8)
C(11) - C(10) - C(27)A	119.5(7)	C(45) - C(47) - C(46)	119.2(8)
C(11) - C(10) - C(25)	109.5(5)		

A prime and double prime denotes a transformation of 1-x, -y, -z and -x, -y, -z respectively.

Table S12. Bond distances (Å) and angles (°) for complex 11.

Ni(1) - N(1)	1.901(5)	C(15) - C(29)	1.553(11)
Ni(1) - N(2)	1.875(6)	C(15) - C(31)	1.554(12)
Ni(1) - N(3)	1.868(6)	C(16) - C(17)	1.420(11)
Ni(1) - N(4)	1.876(6)	C(17) - C(18)	1.419(10)
O(1) - C(37)	1.212(11)	C(17) - C(44)	1.475(12)
O(2) - C(44)	1.225(11)	C(18) - C(19)	1.344(11)
N(1) - C(1)	1.467(9)	C(19) - C(20)	1.514(11)
N(1) - C(4)	1.284(9)	C(20) - C(33)	1.545(9)
N(2) - C(6)	1.405(8)	C(20) - C(35)	1.545(10)
N(2) - C(9)	1.361(9)	C(21) - C(22)	1.472(14)
N(3) - C(11)	1.436(11)	C(23) - C(24)	1.495(14)
N(3) - C(14)	1.302(10)	C(25) - C(26)	1.478(14)
N(4) - C(16)	1.349(10)	C(27) - C(28)	1.532(14)
N(4) - C(19)	1.398(9)	C(29) - C(30)	1.489(14)
C(1) - C(2)	1.330(9)	C(31) - C(32)	1.519(14)
C(1) - C(20)	1.527(9)	C(33) - C(34)	1.499(10)
C(2) - C(3)	1.500(10)	C(35) - C(36)	1.494(11)
C(3) - C(4)	1.482(10)	C(37) - C(38)	1.496(12)
C(4) - C(5)	1.538(10)	C(38) - C(39)	1.403(13)
C(5) - C(6)	1.502(9)	C(38) - C(43)	1.381(13)
C(5) - C(21)	1.546(10)	C(39) - C(40)	1.392(14)
C(5) - C(23)	1.539(11)	C(40) - C(41)	1.330(17)
C(6) - C(7)	1.382(11)	C(41) - C(42)	1.398(17)
C(7) - C(8)	1.378(10)	C(42) - C(43)	1.367(14)
C(8) - C(9)	1.412(10)	C(44) - C(45)	1.502(12)
C(8) - C(37)	1.488(12)	C(45) - C(46)	1.367(12)
C(9) - C(10)	1.520(9)	C(45) - C(50)	1.367(13)
C(10) - C(11)	1.498(12)	C(46) - C(47)	1.393(14)
C(10) - C(25)	1.568(11)	C(47) - C(48)	1.354(18)
C(10) - C(27)	1.572(11)	C(48) - C(49)	1.330(17)
C(11) - C(12)	1.331(12)	C(49) - C(50)	1.390(16)
C(12) - C(13)	1.489(14)	C(51)A- C(52)A	1.54(4)
C(13) - C(14)	1.508(12)	C(52)A- C(53)A	1.52(4)
C(14) - C(15)	1.477(12)	C(51)B- C(52)B	1.52(5)
C(15) - C(16)	1.518(10)	C(52)B- C(53)B	1.52(3)
N(3) - Ni(1) - N(4)	89.2(3)	N(3) - C(14) - C(15)	128.4(7)
N(2) - Ni(1) - N(4)	176.9(3)	C(14) - C(15) - C(31)	109.4(6)
N(2) - Ni(1) - N(3)	90.7(3)	C(14) - C(15) - C(29)	106.9(6)
N(1) - Ni(1) - N(4)	90.9(2)	C(14) - C(15) - C(16)	113.7(6)
N(1) - Ni(1) - N(3)	177.6(3)	C(29) - C(15) - C(31)	107.4(6)
N(1) - Ni(1) - N(2)	89.0(3)	C(16) - C(15) - C(31)	111.9(6)
Ni(1) - N(1) - C(4)	126.4(5)	C(16) - C(15) - C(29)	107.0(6)
Ni(1) - N(1) - C(1)	124.3(4)	N(4) - C(16) - C(15)	121.0(7)
C(1) - N(1) - C(4)	108.9(6)	C(15) - C(16) - C(17)	129.0(7)
Ni(1) - N(2) - C(9)	127.8(5)	N(4) - C(16) - C(17)	108.7(6)
Ni(1) - N(2) - C(6)	123.8(4)	C(16) - C(17) - C(44)	130.4(7)
C(6) - N(2) - C(9)	108.3(6)	C(16) - C(17) - C(18)	106.1(6)
Ni(1) - N(3) - C(14)	125.7(6)	C(18) - C(17) - C(44)	123.4(7)
Ni(1) - N(3) - C(11)	122.1(5)	C(17) - C(18) - C(19)	107.3(7)
C(11) - N(3) - C(14)	112.2(7)	N(4) - C(19) - C(18)	110.2(6)
Ni(1) - N(4) - C(19)	124.3(5)	C(18) - C(19) - C(20)	130.7(7)

Table S12. Bond distances (Å) and angles (°) for complex 11 (cont.).

Ni(1) - N(4) - C(16)	126.4(5)	N(4) - C(19) - C(20)	119.1(6)
C(16) - N(4) - C(19)	107.5(6)	C(1) - C(20) - C(19)	105.3(5)
N(1) - C(1) - C(20)	116.5(6)	C(19) - C(20) - C(35)	110.6(6)
N(1) - C(1) - C(2)	109.4(6)	C(19) - C(20) - C(33)	111.0(6)
C(2) - C(1) - C(20)	134.1(6)	C(1) - C(20) - C(35)	108.0(5)
C(1) - C(2) - C(3)	108.1(6)	C(1) - C(20) - C(33)	110.5(5)
C(2) - C(3) - C(4)	102.4(6)	C(33) - C(20) - C(35)	111.2(6)
N(1) - C(4) - C(3)	111.1(6)	C(5) - C(21) - C(22)	119.8(6)
C(3) - C(4) - C(5)	126.2(6)	C(5) - C(23) - C(24)	114.2(7)
N(1) - C(4) - C(5)	122.5(6)	C(10) - C(25) - C(26)	115.2(6)
C(4) - C(5) - C(23)	105.2(5)	C(10) - C(27) - C(28)	115.9(7)
C(4) - C(5) - C(21)	110.3(6)	C(15) - C(29) - C(30)	113.1(7)
C(4) - C(5) - C(6)	108.2(5)	C(15) - C(31) - C(32)	114.3(7)
C(21) - C(5) - C(23)	111.0(6)	C(20) - C(33) - C(34)	114.8(6)
C(6) - C(5) - C(23)	110.8(6)	C(20) - C(35) - C(36)	116.5(6)
C(6) - C(5) - C(21)	111.1(6)	O(1) - C(37) - C(8)	123.3(8)
N(2) - C(6) - C(5)	121.7(6)	C(8) - C(37) - C(38)	116.8(7)
C(5) - C(6) - C(7)	130.3(6)	O(1) - C(37) - C(38)	119.9(8)
N(2) - C(6) - C(7)	108.0(6)	C(37) - C(38) - C(43)	124.1(8)
C(6) - C(7) - C(8)	107.8(6)	C(37) - C(38) - C(39)	117.5(8)
C(7) - C(8) - C(37)	121.7(7)	C(39) - C(38) - C(43)	118.3(8)
C(7) - C(8) - C(9)	108.2(6)	C(38) - C(39) - C(40)	118.7(9)
C(9) - C(8) - C(37)	129.3(7)	C(39) - C(40) - C(41)	122.7(10)
N(2) - C(9) - C(8)	107.6(6)	C(40) - C(41) - C(42)	118.9(9)
C(8) - C(9) - C(10)	134.2(6)	C(41) - C(42) - C(43)	120.1(10)
N(2) - C(9) - C(10)	118.3(6)	C(38) - C(43) - C(42)	121.4(9)
C(9) - C(10) - C(27)	113.6(6)	O(2) - C(44) - C(17)	123.4(8)
C(9) - C(10) - C(25)	110.6(6)	C(17) - C(44) - C(45)	117.7(7)
C(9) - C(10) - C(11)	108.7(6)	O(2) - C(44) - C(45)	118.9(8)
C(25) - C(10) - C(27)	107.9(6)	C(44) - C(45) - C(50)	118.1(8)
C(11) - C(10) - C(27)	108.6(6)	C(44) - C(45) - C(46)	123.2(8)
C(11) - C(10) - C(25)	107.2(6)	C(46) - C(45) - C(50)	118.4(8)
N(3) - C(11) - C(10)	121.5(7)	C(45) - C(46) - C(47)	120.1(9)
C(10) - C(11) - C(12)	130.7(8)	C(46) - C(47) - C(48)	120.6(9)
N(3) - C(11) - C(12)	107.6(7)	C(47) - C(48) - C(49)	119.5(11)
C(11) - C(12) - C(13)	110.0(8)	C(48) - C(49) - C(50)	121.2(10)
C(12) - C(13) - C(14)	102.2(7)	C(45) - C(50) - C(49)	120.2(9)
N(3) - C(14) - C(13)	107.9(7)	C(51)A- C(52)A- C(53)A	135(3)
C(13) - C(14) - C(15)	123.6(7)	C(51)B- C(52)B- C(53)B	80(2)

Table S13. Bond distances (Å) and angles (°) for complex 14.

Ni(1) - N(1)	1.836(4)	C(8) - C(9)	1.520(5)
Ni(1) - N(2)	1.891(4)	C(8) - C(15)	1.544(5)
Ni(1) - N(3)	1.859(4)	C(8) - C(17)	1.555(4)
N(1) - C(2)	1.361(4)	C(9) - C(10)	1.366(5)
N(2) - C(4)	1.307(4)	C(10) - C(10)'	1.415(6)
N(2) - C(7)	1.430(5)	C(11) - C(12)	1.531(6)
N(3) - C(9)	1.375(4)	C(13) - C(14)	1.522(5)
C(1) - C(1)'	1.408(4)	C(15) - C(16)	1.527(5)
C(1) - C(2)	1.373(5)	C(17) - C(18)	1.515(6)
C(2) - C(3)	1.519(4)	C(19) - C(20)	1.462(5)
C(3) - C(4)	1.521(5)	C(20) - C(21)	1.391(5)
C(3) - C(11)	1.575(4)	C(20) - C(25)	1.390(6)
C(3) - C(13)	1.539(5)	C(21) - C(22)	1.382(5)
C(4) - C(5)	1.480(5)	C(22) - C(23)	1.382(5)
C(5) - C(6)	1.449(4)	C(23) - C(24)	1.383(5)
C(5) - C(19)	1.343(5)	C(23) - C(26)	1.505(6)
C(6) - C(7)	1.341(5)	C(24) - C(25)	1.381(7)
C(7) - C(8)	1.506(4)		

N(2) - Ni(1) - N(3)	90.5(1)	N(2) - C(7) - C(6)	109.4(3)
N(2) - Ni(1) - N(2)'	180.0(-)	C(6) - C(7) - C(8)	131.5(3)
N(1) - Ni(1) - N(3)	180.0(-)	N(2) - C(7) - C(8)	119.1(3)
N(1) - Ni(1) - N(2)	89.5(1)	C(7) - C(8) - C(17)	108.8(3)
Ni(1) - N(1) - C(2)	125.8(2)	C(7) - C(8) - C(15)	111.4(3)
C(2) - N(1) - C(2)'	108.3(2)	C(7) - C(8) - C(9)	106.4(3)
Ni(1) - N(2) - C(7)	122.9(2)	C(15) - C(8) - C(17)	110.7(3)
Ni(1) - N(2) - C(4)	126.6(3)	C(9) - C(8) - C(17)	109.9(3)
C(4) - N(2) - C(7)	109.8(3)	C(9) - C(8) - C(15)	109.5(3)
Ni(1) - N(3) - C(9)'	127.0(2)	N(3) - C(9) - C(8)	118.2(3)
Ni(1) - N(3) - C(9)	127.0(1)	C(8) - C(9) - C(10)	131.4(3)
C(9) - N(3) - C(9)'	106.0(2)	N(3) - C(9) - C(10)	110.4(3)
C(1)' - C(1) - C(2)	106.9(3)	C(9) - C(10) - C(10)'	106.6(3)
N(1) - C(2) - C(1)	109.0(3)	C(3) - C(11) - C(12)	114.6(3)
C(1) - C(2) - C(3)	129.5(3)	C(3) - C(13) - C(14)	117.3(3)
N(1) - C(2) - C(3)	121.4(3)	C(8) - C(15) - C(16)	116.3(3)
C(2) - C(3) - C(13)	109.4(3)	C(8) - C(17) - C(18)	114.4(3)
C(2) - C(3) - C(11)	109.8(3)	C(5) - C(19) - C(20)	128.5(3)
C(2) - C(3) - C(4)	110.1(3)	C(19) - C(20) - C(25)	118.8(3)
C(11) - C(3) - C(13)	107.6(3)	C(19) - C(20) - C(21)	124.0(3)
C(4) - C(3) - C(13)	115.4(3)	C(21) - C(20) - C(25)	117.2(3)
C(4) - C(3) - C(11)	104.2(3)	C(20) - C(21) - C(22)	121.1(3)
N(2) - C(4) - C(3)	121.0(3)	C(21) - C(22) - C(23)	121.1(3)
C(3) - C(4) - C(5)	130.7(3)	C(22) - C(23) - C(26)	120.7(3)
N(2) - C(4) - C(5)	108.0(3)	C(22) - C(23) - C(24)	118.4(3)
C(4) - C(5) - C(19)	128.2(3)	C(24) - C(23) - C(26)	120.9(4)
C(4) - C(5) - C(6)	104.8(3)	C(23) - C(24) - C(25)	120.3(3)
C(6) - C(5) - C(19)	127.0(3)	C(20) - C(25) - C(24)	121.9(3)
C(5) - C(6) - C(7)	107.7(3)		

Syntheses and analytical data of all compounds reported in Schemes 1 and 2.

2. PyHCl (2.93 g, 25.4 mmol) was added in one portion to a solution of **1** (11.40 g, 12.7 mmol) in toluene (200 mL). The resulting amber solution was stirred overnight and the undissolved white solid, LiCl, was filtered off. The solvent was partially evaporated and *n*-pentane (200 mL) was added, resulting in the formation of an orange-yellow powder which was collected and dried *in vacuo* (5.96 g; 78.6%). Crystals suitable for X-ray diffraction were grown in a mixture of toluene/*n*-pentane. Anal. Calcd for **2**, C₃₆H₅₀N₄Ni: C, 72.37; H, 8.43; N, 9.38. Found: C, 72.19; H, 8.52; N, 9.47. ¹H NMR of dihydro-2,12 isomer, **2a** + dihydro-2,13 isomer, **2b** (C₆D₆, 400 MHz, 298 K, ppm): δ 6.35 (d, *J*=3.2 Hz, 2H, C₄H₂N, **2a**); 6.30 (s, 2H, C₄H₂N, **2b**); 6.23 (s, 2H, C₄H₂N, **2b**); 6.16 (d, *J*=3.2 Hz, 2H, C₄H₂N, **2a**); 5.34 (s broad, 2H, C₄H₃N, **2a**); 5.32 (t, *J*=2.0 Hz, 2H, C₄H₃N, **2b**); 3.83 (dq, *J*_{gem}=13.8 Hz, *J*_{vic}=7.2 Hz, 4H, CH₂); 3.54 (dq, *J*_{gem}=13.6 Hz, *J*_{vic}=7.2 Hz 2H, CH₂); 3.42 (dq, *J*_{gem}=13.8 Hz, *J*_{vic}=7.2 Hz, 2H, CH₂); 3.24 (dq, *J*_{gem}=13.6 Hz, *J*_{vic}=7.2 Hz, 2H, CH₂); 3.04 (dq, *J*_{gem}=13.2 Hz, *J*_{vic}=7.6 Hz 2H, CH₂); 2.80-2.70 (m, 4H, CH₂ overlapping with d, *J*=2.0 Hz, 4H, C₄H₃N, d, *J*=2.0 Hz, 2H, C₄H₃N, d, *J*=2.0 Hz, 2H, C₄H₃N); 2.44 (dq, *J*_{gem}=13.6 Hz, *J*_{vic}=7.2 Hz, 2H, CH₂); 2.1-2.0 (m, 8H, CH₂); 1.97 (m, 4H, CH₂); 1.67 (dq, *J*_{gem}=14.4 Hz, *J*_{vic}=7.2 Hz, 2H, CH₂); 1.57 (dq, *J*_{gem}=14.4 Hz, *J*_{vic}=7.2 Hz, 2H, CH₂); 1.22 (t, *J*=7.2 Hz, 6H, CH₃); 1.19 (t, *J*=7.6 Hz, 6H, CH₃); 0.92 (t, *J*=7.2 Hz, 6H, CH₃, overlapping with t, *J*=7.2 Hz, 6H, CH₃, t, *J*=7.6 Hz, 6H, CH₃); 0.86 (t, *J*=7.2 Hz, 6H, CH₃); 0.81 (t, *J*=7.2 Hz, 6H, CH₃); 0.73 (t, *J*=7.2 Hz, 6H, CH₃). Complexes **2a** and **2b** were deprotonated and fully deuterated in C₅D₅N: ¹H NMR (C₅D₅N, 200 MHz, 298 K, ppm): δ 3.13 (q, *J*=7.3 Hz, 8H, CH₂); 2.04 (q, *J*=7.3 Hz, , 8H, CH₂); 1.00 (t, *J*=7.3 Hz, , 12H, CH₃); 0.83 (t, *J*=7.3 Hz, , 12H, CH₃). The reaction of **1** with two equivalents of weak acids, like chloroacetone or ethyl-chloroacetate gave **2**, while in H₂O demetallation of **1** was observed.

3. Complex **2** (2.50 g, 4.19 mmol) was reacted with 1,4-diazabicyclo [2.2.2] octane (0.47 g, 4.19 mmol) in THF (100 mL). The resulting yellow solution was stirring at room temperature for 3 h and the solvent was evaporated to dryness. The solid residue was triturated with *n*-pentane to give a yellow powder which was collected and dried *in vacuo* (2.6 g, 87.6 %). Anal. Calcd for **3**, C₄₂H₆₂N₆Ni: C, 71.08; H, 8.81; N, 11.84. Found: C, 71.18; H, 9.11; N, 11.16. ¹H NMR (C₆D₆, 400 MHz, 298 K, ppm): δ 6.26 (s, 8H, C₄H₂N); 3.33 (s broad, 2H, C₆H₁₂N₂H₂); 2.50 (s, 12H, C₆H₁₂N₂H₂); 2.04 (s broad, 8H, CH₂); 1.92 (m, 8H, CH₂); 0.99 (s broad, 12H, CH₃); 0.91 (t, *J*=7.2 Hz, 12H, CH₃).

4. A CD₃OD solution of **2** (4.00 g, 6.70 mmol) was stirred for 1 h at room temperature. The resulting amber solution was evaporated to dryness and the solid residue was triturated with *n*-pentane to give a yellow powder which was collected and dried *in vacuo* (3.74 g, 92 %). ¹H NMR (C₆D₆, 400 MHz, 298 K, ppm): δ 3.83 (dq, *J*_{gem}=13.8 Hz, *J*_{vic}=7.2 Hz, 4H, CH₂); 3.54 (dq, *J*_{gem}=13.6 Hz, *J*_{vic}=7.2 Hz, 2H, CH₂); 3.42 (dq, *J*_{gem}=13.8 Hz, *J*_{vic}=7.2 Hz, 2H, CH₂); 3.24 (dq, *J*_{gem}=13.6 Hz, *J*_{vic}=7.2 Hz, 2H, CH₂); 3.04 (dq, *J*_{gem}=13.2 Hz, *J*_{vic}=7.6 Hz 2H, CH₂); 2.75 (dq, *J*_{gem}=13.6 Hz, *J*_{vic}=7.2 Hz, 2H, CH₂); 2.65 (dq, *J*_{gem}=13.2 Hz, *J*_{vic}=7.6 Hz 2H, CH₂); 2.44 (dq, *J*_{gem}=13.6 Hz, *J*_{vic}=7.2 Hz, 2H, CH₂); 2.1-2.0 (m, 8H, CH₂); 1.97 (m, 4H, CH₂); 1.67 (dq, *J*_{gem}=14.4 Hz, *J*_{vic}=7.2 Hz, 2H, CH₂); 1.57 (dq, *J*_{gem}=14.4 Hz, *J*_{vic}=7.2 Hz, 2H, CH₂); 1.22 (t, *J*=7.2 Hz, 6H, CH₃); 1.19 (t, *J*=7.6 Hz, 6H, CH₃); 0.92 (t, *J*=7.2 Hz, 6H, CH₃, overlapping with t, *J*=7.2 Hz, 6H, CH₃, t, *J*=7.6 Hz, 6H, CH₃); 0.86 (t, *J*=7.2 Hz, 6H, CH₃); 0.81 (t, *J*=7.2 Hz, 6H, CH₃); 0.73 (t, *J*=7.2 Hz, 6H, CH₃). ²H NMR (C₆D₆, 600 MHz, 298 K, ppm): δ 6.24 (s, 8D, C₄D₂N); 5.37 (s, 4D, C₄D₃N); 2.77 (s, 8D, C₄D₃N).

5. BuⁿLi (7.2 mL, 1.6 M in *n*-hexane, 11.52 mmol) was added dropwise to a THF (100 mL) solution of **4** (3.50 g, 5.76 mmol). The reaction mixture was refluxed for 2 h and then evaporated to dryness. The resulting green yellow solid was triturated with *n*-hexane, collected and dried *in vacuo* (4.32 g, 82 %). ¹H NMR (C₆D₆, 400 MHz, 298 K, ppm): δ 3.25 (t, *J*=6.8 Hz, 16H, THF overlapping with m, 8H, CH₂); 2.28 (q, *J*=7.2 Hz, 8H, CH₂); 1.26 (t, *J*=6.8 Hz, 16H, THF overlapping with t, *J*=7.2 Hz, 12H, CH₃); 1.01 (t, *J*=7.2 Hz, 12H, CH₃). ²H NMR (C₆D₆, 600 MHz, 298 K, ppm): δ 6.19 (s, 8D, C₄D₂N).

6. To a suspension of trimethyloxonium tetrafluoroborate (1.01 g, 6.85 mmol) in toluene (50 mL) was added dropwise a red solution of **1** (3.07 g, 3.43 mmol) in toluene (100 mL) at -50 °C. The reaction mixture was warmed to room temperature and stirred overnight. The undissolved white solid, LiBF₄, was filtered off and the resulting red-orange solution was evaporated to dryness. The solid residue was triturated with *n*-pentane (50 mL) to give a yellow-orange powder which was collected and dried *in vacuo* (1.6 g, 75 %). Anal. Calcd for **6**, C₃₈H₅₄N₄Ni: C, 72.96; H, 8.70; N, 8.96. Found: C, 72.84; H, 8.65; N, 8.05. ¹H NMR analysis of the collected powder showed

2H, CH₂); 2.4 (m, 2H, CH₂); 2.2-1.7(m, 8H, CH₂); 1.59 (m, 4H, CH₂ overlapping with s, 6H, H₃CC₄H₂N); 1.06 (t, *J*=7.3 Hz, 6H, CH₃); 0.97 (t, *J*=7.3 Hz, 6H, CH₃ overlapping with t, *J*=7.3 Hz, 6H, CH₃); 0.55 (t, *J*=7.3 Hz, 6H, CH₃). The NMR spectrum of the solution, before the solid was isolated, showed the single isomer we obtained in the solid state.

7. **6** (1.6 g, 2.56 mmol) was recrystallized from hot DME (20 mL) to obtained the 3,13-dihydro 2,12-dimethyl derivative, **7** like microcrystalline light yellow solid which was collected and dried *in vacuo* (1.5 g, 94 %). Crystals suitable for X-ray diffraction were grown in a mixture of toluene/*n*-hexane. Anal. Calcd for **7**, C₃₈H₅₄N₄Ni: C, 72.96; H, 8.70; N, 8.96. Found: C, 72.25; H, 8.92; N, 8.56. ¹H NMR (C₆D₆, 200 MHz, 298 K, ppm): δ 6.36 (d, *J*=2.9 Hz, 2H, C₄H₂N); 6.19 (d, *J*=2.9 Hz, 2H, C₄H₂N); 3.90 (m, 2H, CH₂); 3.0 (m, 2H, CH₂); 2.7(m, 2H, CH₂ overlapping with s, 4H, H₃CC₄H₂N); 2.30 (m, 4H, CH₂); 1.90 (m, 2H, CH₂); 1.60 (m, 4H, CH₂ overlapping with s, 6H, H₃CC₄H₂N); 1.20 (t, *J*=7.3 Hz, 6H, CH₃); 0.86 (t, *J*=7.3 Hz, 6H, CH₃ overlapping with t, *J*=7.3 Hz, 6H, CH₃); 0.77 (t, *J*=7.3 Hz, 6H, CH₃).

8. BuⁿLi (8 mL, 1.64 M in *n*-hexane, 13.2 mmol) was added dropwise to an amber suspension of **7** (4.14 g, 6.62 mmol) in DME (80 mL). An orange solution was almost immediately obtained and gas evolution was observed. The reaction mixture was refluxed overnight, and after cooling a crystalline yellow product separated. The resulting suspension was evaporated to dryness and the residue triturated with *n*-pentane (80 mL) to give a yellow powder which was collected and dried *in vacuo* (5.88 g, 88.9 %). Anal. Calcd for **8**, C₄₆H₇₂Li₂N₄NiO₄·2DME: C, 64.99; H, 9.29; N, 5.61. Found: C, 64.83; H, 9.73; N, 5.76. ¹H NMR (C₃D₈N, 200 MHz, 298 K, ppm): δ 6.25 (s, 2H, H₃CC₄H₂N); 6.20 (s broad, 2H, C₄H₂N); 5.99 (s broad, 2H, C₄H₂N); 4.30 (m, 2H, CH₂); 4.10 (m, 2H, CH₂); 3.5 (m, 4H, CH₂ overlapping with s, 8H, DME); 3.26 (s, 12H, DME); 2.69 (s, 6H, H₃CC₄H₂N); 2.50 (m, 8H, CH₂); 1.45 (m, 6H, CH₃); 1.15 (m, 6H, CH₃). Reprotonation of **8** with two equivalents of PyHCl at room temperature gave a mixture of **6** and **7**, which converted to **7** on heating.

9. Trimethyloxonium tetrafluoroborate (0.89 g, 6.0 mmol) was added in one portion to a yellow solution of **8** (2.99 g, 3.0 mmol) in toluene (100 mL) at -50 °C. The reaction mixture was warmed to room temperature and stirred overnight. The undissolved white solid, LiBF₄, was filtered off and the resulting red solution was evaporated to dryness. The solid residue was dissolved in *n*-pentane (50 mL) and a little black solid was filtered off. The resulting orange solution was evaporated to dryness and the solid residue was dried *in vacuo* and collected (1.55 g, 79%). Crystals suitable for X-ray diffraction were grown in a mixture of toluene/*n*-heptane. Anal. Calcd for **9**, C₄₀H₅₈N₄Ni: C, 73.50; H, 8.94; N, 8.57. Found: C, 73.25; H, 8.71; N, 8.62. ¹H NMR (C₆D₆, 200 MHz, 298 K, ppm): δ 6.43 (d, *J*=3.4 Hz, 2H, C₄H₂N); 6.21 (d, *J*=3.4 Hz, 2H, C₄H₂N); 4.98 (s, 1H, (H₃C)₂C₄H₂N); 4.97 (s, 1H, (H₃C)₂C₄H₂N); 4.60 (m, 2H, CH₂); 3.80 (m, 2H, CH₂); 3.10 (m, 2H, CH₂); 2.25 (m, 6H, CH₂); 1.62 (m, 4H, CH₂); 1.57 (s, 6H, (H₃C)₂C₄H₂N); 1.42 (s, 6H, (H₃C)₂C₄H₂N); 1.5-0.5 (m, 24H, CH₃).

9 (one pot reaction). To a suspension of trimethyloxonium tetrafluoroborate (4.26 g, 28.8 mmol) in toluene (80 mL) was added dropwise a red solution of **1** (12.95 g, 14.4 mmol) in toluene (100 mL) at -50 °C. The reaction mixture was warmed to room temperature and stirred overnight. The undissolved white solid, LiBF₄, was filtered off and the resulting red-orange solution was evaporated to dryness. BuⁿLi (17.1 mL, 1.68 M in *n*-hexane, 28.8 mmol) was added dropwise to a suspension in *n*-pentane (100 mL) of the solid residue. This suspension gave a solution, and after few minutes a yellow solid was obtained. The suspension was refluxed for 2 h and then the solid collected was dissolved in toluene (80 mL) and trimethyloxonium tetrafluoroborate (4.26 g, 28.8 mmol) was added in one portion at -50 °C. The reaction mixture was warmed to room temperature and stirred overnight. The undissolved white solid, LiBF₄, was filtered off and the resulting red solution was evaporated to dryness. The solid residue was dissolved in *n*-pentane (50 mL) and a little black solid was filtered off. The resulting orange solution was evaporated to dryness and the solid residue was dried *in vacuo* and collected (6.87 g, 73 %). Crystals suitable for X-ray diffraction were grown in a mixture of toluene/*n*-heptane. Anal. Calcd for **8**, C₄₀H₅₈N₄Ni: C, 73.50; H, 8.94; N, 8.57. Found: C, 73.15; H, 8.51; N, 8.62. ¹H NMR (C₆D₆, 200 MHz, 298 K, ppm): δ 6.43 (d, *J*=3.4 Hz, 2H, C₄H₂N); 6.21 (d, *J*=3.4 Hz, 2H, C₄H₂N); 4.98 (s, 1H, (H₃C)₂C₄H₂N); 4.97 (s, 1H, (H₃C)₂C₄H₂N); 4.60 (m, 2H, CH₂); 3.80 (m, 2H, CH₂); 3.10 (m, 2H, CH₂); 2.25 (m, 6H, CH₂); 1.62 (m, 4H, CH₂); 1.57 (s, 6H, (H₃C)₂C₄H₂N); 1.42 (s, 6H, (H₃C)₂C₄H₂N); 1.5-0.5 (m, 24H, CH₃).

10. BuⁿLi (5.5 mL, 1.65 M in *n*-hexane, 9.12 mmol) was added dropwise to an orange solution of **8** (2.98 g, 4.56 mmol) in *n*-pentane (80 mL). A gas evolution was observed and an orange solid was almost immediately

In the presence of DME, the unsolvated form gave 10. ^1H NMR ($\text{C}_5\text{D}_5\text{N}$, 200 MHz, 298 K, ppm): δ 6.24 (s, 4H, $\text{C}_4\text{H}_2\text{N}$); 4.20 (m, 2H, CH_2); 3.97 (m, 2H, CH_2); 3.5 (m, 2H, CH_2); 2.69 (m, 6H, CH_2); 2.48 (m, 4H, CH_2 , overlapping with s, 12H, CH_3); 1.37 (m, 12H, CH_3); 1.14 (m, 12H, CH_3).

11. To a THF (100 mL) solution of 1 (10.0 g, 11.1 mmol) was added dropwise a toluene (50 mL) solution of freshly distilled PhCOCl (3.12 g, 22.2 mmol) at -50°C . The reaction mixture was warmed to room temperature and stirred overnight. The orange solution was evaporated to dryness and the solid residue was extracted with ether (80 mL). The yellow-orange solid precipitated during the extraction was collected and dried in *vacuo* (5.33 g, 59.6 %). Crystals suitable for X-ray diffraction were grown in a mixture of THF/*n*-hexane. Anal. Calcd for 11, $\text{C}_{50}\text{H}_{58}\text{N}_4\text{NiO}_2$: C, 74.53; H, 7.25; N, 6.95. Found: C, 74.12; H, 6.99; N, 6.43. ^1H NMR (C_6D_6 , 400 MHz, 298 K, ppm): δ 8.12 (m, 4H, ArH); 7.18 (m, 6H, ArH); 6.31 (s, 1H, $\text{PhCOC}_4\text{H}_1\text{N}$); 6.30 (s, 1H, $\text{PhCOC}_4\text{H}_1\text{N}$); 5.34 (s broad, 1H, $\text{C}_4\text{H}_3\text{N}$); 5.24 (s broad, 1H, $\text{C}_4\text{H}_3\text{N}$); 4.42 (m, 1H, CH_2); 3.94 (m, 2H, CH_2); 3.43 (m, 3H, CH_2); 2.74 (m, 2H, CH_2 , overlapping with m, 4H, $\text{C}_4\text{H}_3\text{N}$); 2.03 (m, 2H, CH_2); 1.90 (m, 2H, CH_2); 1.88 (m, 2H, CH_2); 1.80 (m, 1H, CH_2); 1.49 (m, 1H, CH_2 overlapping with t, $J=7.2$ Hz, 3H, CH_3); 1.22 (t, $J=7.2$ Hz, 3H, CH_3); 1.02 (t, $J=7.2$ Hz, 3H, CH_3); 0.93 (t, $J=7.2$ Hz, 3H, CH_3); 0.90 (t, $J=7.2$ Hz, 3H, CH_3); 0.70 (t, $J=7.2$ Hz, 3H, CH_3); 0.66 (t, $J=7.2$ Hz, 3H, CH_3); 0.31 (t, $J=7.2$ Hz, 3H, CH_3). The NMR spectrum of the solution, before the solid was isolated, showed the single isomer we obtained in the solid state.

12. 11 (3 g, 3.7 mmol) was reacted with 1,4-diazabicyclo[2.2.2]octane (0.42 g, 3.7 mmol) in THF (100 mL). The resulting amber solution was stirred at room temperature for 2h and the solvent was evaporated to dryness. The solid residue was collected and dried in *vacuo* (2.8 g, 82.5 %). ^1H NMR (C_6D_6 , 400 MHz, 298 K, ppm): δ 8.12 (d, $J=6.4$ Hz, 4H, ArH); 7.22 (m, 6H, ArH); 6.07 (s, 2H, $\text{PhCOC}_4\text{H}_1\text{N}$); 5.32 (s broad, 4H, $\text{C}_4\text{H}_2\text{N}$); 3.98 (m, 2H, CH_2); 3.70 (m, 2H, CH_2); 3.16 (s, 2H, $\text{C}_6\text{H}_{12}\text{N}_2\text{H}_2$); 2.90 (m, 2H, CH_2); 2.78 (m, 2H, CH_2); 2.61 (m, 4H, CH_2); 2.27 (m, 4H, CH_2); 2.05 (s broad, 12H, $\text{C}_6\text{H}_{12}\text{N}_2\text{H}_2$); 1.25-1.14 (m, 12, CH_3); 0.92-0.83 (m, 12H, CH_3).

14. To a toluene (100 mL) solution of freshly distilled *p*-tolylaldehyde (2.20 g, 18.3 mmol) was added dropwise a toluene (200 mL) solution of 1 (4.11 g, 4.58 mmol) at -50°C . The reaction mixture was warmed to room temperature in two hours and the resulting dark red solution was stirred overnight. A dark green suspension was obtained and the undissolved white solid, which was the product from the Cannizzaro aldehyde disproportionation, was filtered off. The solvent was completely evaporated and *n*-pentane (100 mL) was added to give a dark green powder which was collected and dried in *vacuo* (3.2 g; 69.9 %). Crystals suitable for X-ray diffraction were grown in a mixture of benzene/isooctane. Anal. Calcd for 14, $\text{C}_{52}\text{H}_{62}\text{N}_4\text{Ni}$: C, 77.90; H, 7.79; N, 6.98. Found: C, 77.82; H, 7.70; N, 6.93. ^1H NMR (C_6D_6 , 400 MHz, 298 K, ppm): δ 8.09 (s, 2H, CHAr); 7.17 (d, $J=8.4$ Hz, 4H, ArH); 6.87 (d, $J=8.4$ Hz, 4H, ArH); 6.54 (s, 2H, $\text{C}_4\text{H}_2\text{N}$); 6.39 (s, 2H, $\text{C}_4\text{H}_2\text{N}$); 6.31 (s, 2H, $\text{C}_4\text{H}_1\text{N}$); 4.07 (dq, $J_{\text{gem}}=14.0$ Hz, $J_{\text{vic}}=7.2$ Hz, 2H, CH_2); 3.50 (dq, $J_{\text{gem}}=14.0$ Hz, $J_{\text{vic}}=7.2$ Hz, 2H, CH_2 overlapping with dq, $J_{\text{gem}}=13.2$ Hz, $J_{\text{vic}}=7.2$ Hz, 2H, CH_2); 2.79 (dq, $J_{\text{gem}}=13.2$ Hz, $J_{\text{vic}}=7.2$ Hz, 2H, CH_2); 2.67 (dq, $J_{\text{gem}}=14.4$ Hz, $J_{\text{vic}}=7.2$ Hz, 2H, CH_2); 2.37 (dq, $J_{\text{gem}}=14.4$ Hz, $J_{\text{vic}}=7.2$ Hz, 2H, CH_2); 2.27 (dq, $J_{\text{gem}}=14.0$ Hz, $J_{\text{vic}}=7.2$ Hz, 2H, CH_2); 2.11 (dq, $J_{\text{gem}}=14.0$ Hz, $J_{\text{vic}}=7.2$ Hz, 2H, CH_2); 2.05 (s, 6H, CH_3); 1.40 (t, $J=7.2$ Hz, 6H, CH_3); 1.26 (t, $J=7.2$ Hz, 6H, CH_3); 1.06 (t, $J=7.2$ Hz, 6H, CH_3); 0.94 (t, $J=7.2$ Hz, 6H, CH_3). The NMR spectrum of the solution, before the solid was isolated, showed the single isomer we obtained in the solid state.