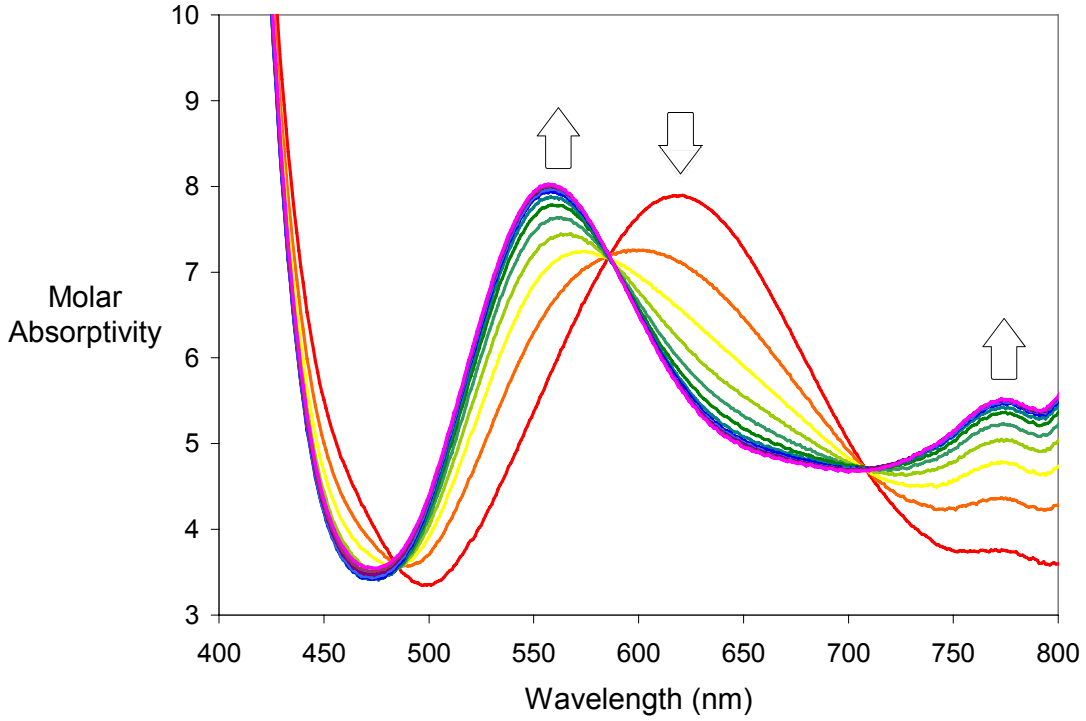

Fig. S1 The conversion of **1** to **2**, 60 μM per-nickel in benzonitrile solvent, over a period of approximately 1h.

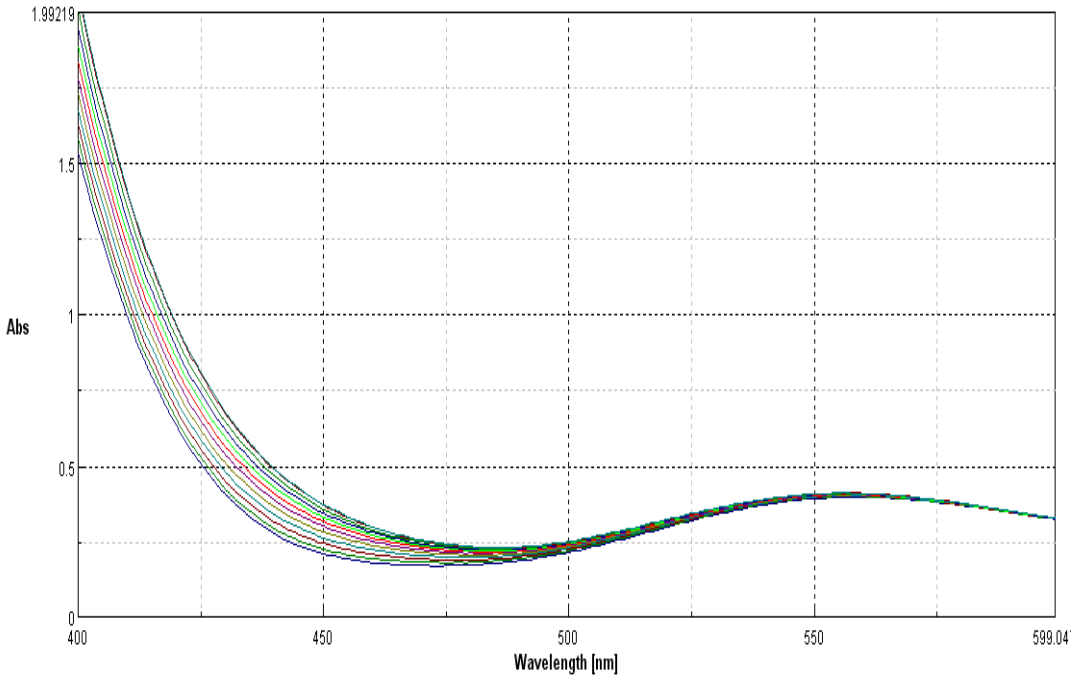

Fig. S2 The conversion of **2** to **3**, 60 μM per-nickel in benzonitrile solvent, over a period of approximately 6h.

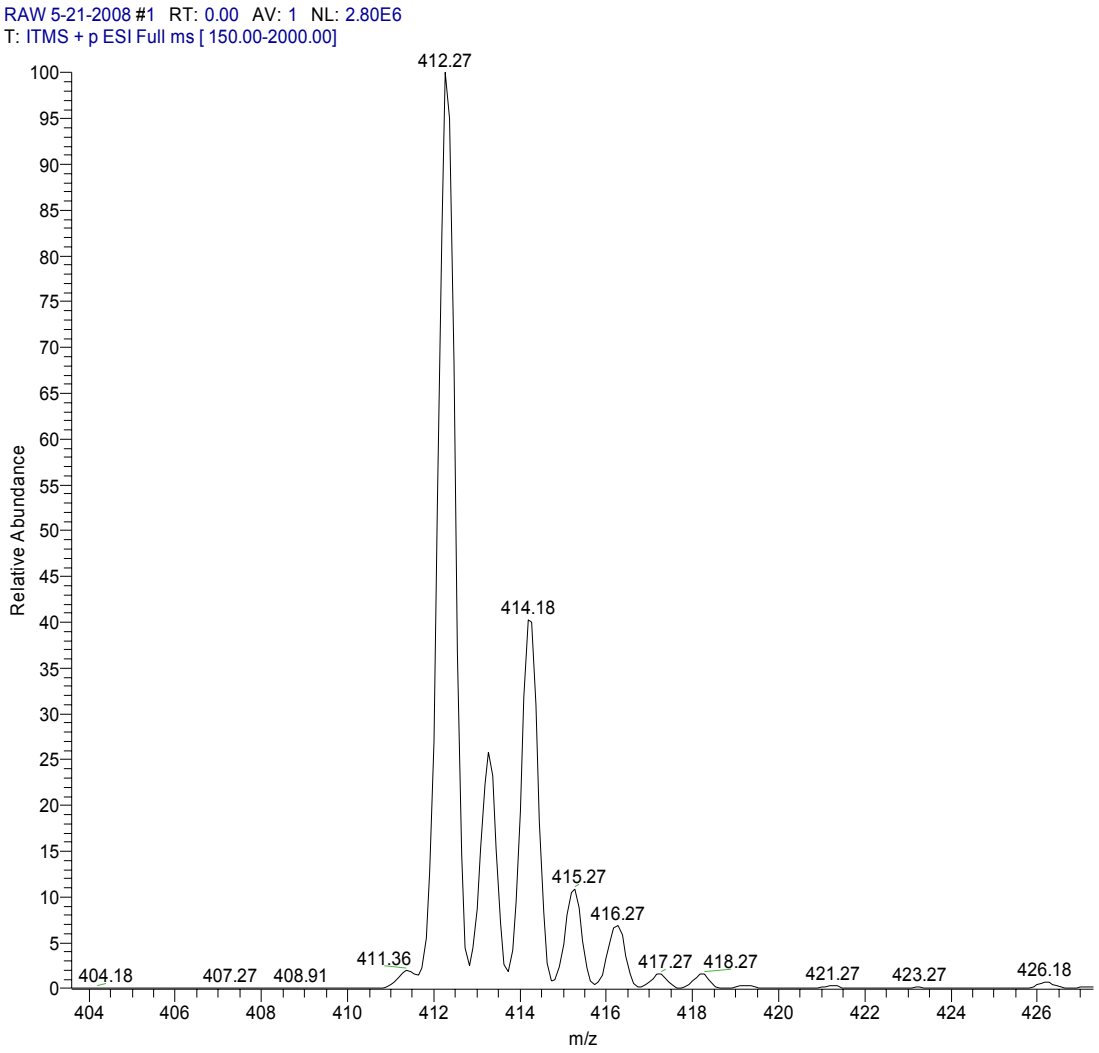

Fig. S3. ESI-MS of methanolic solution of acetonitrile-derived analog of **3**, formed from acetamide lacking an isotopic label.

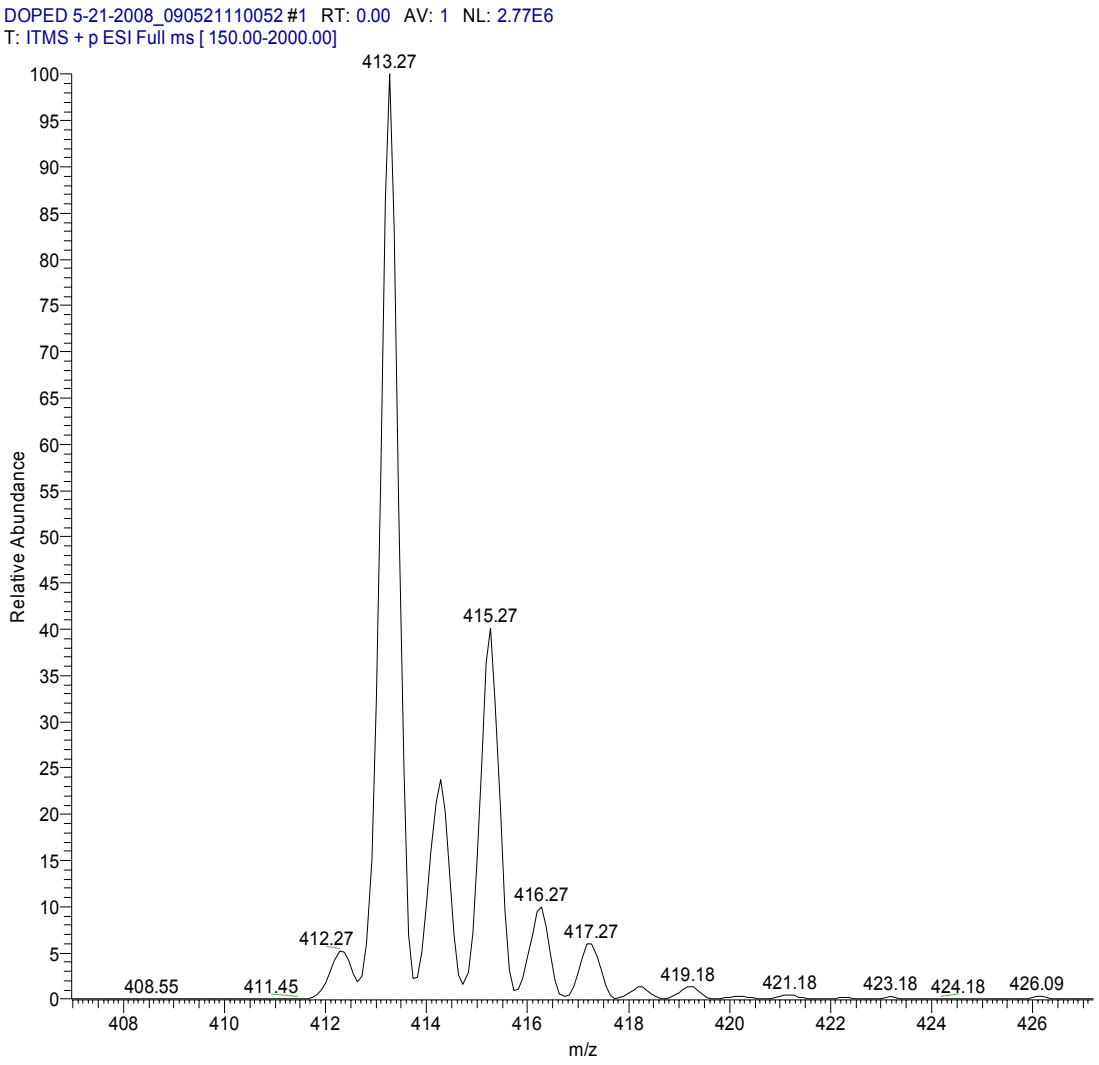

Fig. S4. ESI-MS of methanolic solution of acetonitrile-derived analog of 3, formed in from ^{15}N-labelled acetamide.

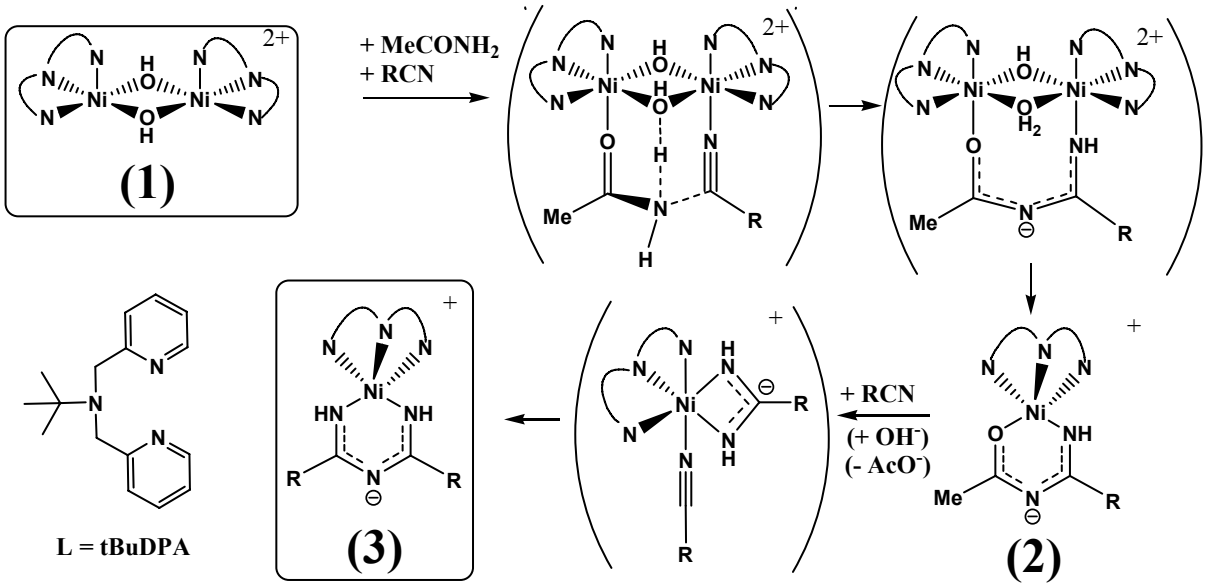

Fig. S5. One possible mechanism for the formation of **3** from **1**. R =Me, Ph. Crystallographically characterized compounds are framed; hypothetical, unobserved intermediates are shown in brakets. Monomer-dimer equilibria are possible at various reaction steps.

Table S1. Crystal data and structure refinement for **3**.

Identification code	3	
Empirical formula	$C_{30}H_{33}N_6NiClO_4$	
Formula weight	635.78	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 12.3250(9) Å	α= 90°.
	b = 17.1390(12) Å	β= 104.3250(10)°.
	c = 14.1153(10) Å	γ = 90°.
Volume	2889.0(4) $Å^3$	
Z	4	
Density (calculated)	1.462 $g \cdot cm^{-3}$	
Absorption coefficient	0.812 mm^{-1}	
F(000)	1328	
Crystal size	0.18 x 0.16 x 0.04 mm^3	
Theta range for data collection	1.91 to 27.03°.	
Index ranges	-15<=h<=15, -21<=k<=21, -18<=l<=18	
Reflections collected	24185	
Independent reflections	6292 [R(int) = 0.0408]	
Completeness to theta = 25.00°	99.9 %	
Max. and min. transmission	0.9683 and 0.8677	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6292 / 0 / 388	
Goodness-of-fit on F^2	1.019	
Final R indices [I>2sigma(I)]	R1 = 0.0443, wR2 = 0.1020	
R indices (all data)	R1 = 0.0619, wR2 = 0.1128	
Largest diff. peak and hole	0.615 and -0.356 $e.Å^{-3}$	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **3**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ni(1)	6441(1)	3809(1)	8120(1)	25(1)
N(1)	4903(2)	3866(1)	7810(2)	28(1)
N(2)	4486(2)	3902(1)	6075(1)	27(1)
N(3)	6424(2)	3865(1)	6817(2)	28(1)

N(4)	8053(2)	3822(1)	8448(1)	26(1)
N(5)	6907(2)	2424(1)	8724(1)	26(1)
N(6)	6584(2)	3893(1)	9508(1)	26(1)
C(1)	4206(2)	3911(1)	6939(2)	25(1)
C(2)	2976(2)	3960(1)	6842(2)	27(1)
C(3)	2349(2)	4521(2)	6227(2)	33(1)
C(4)	1202(2)	4557(2)	6098(2)	42(1)
C(5)	660(2)	4013(2)	6549(2)	48(1)
C(6)	1270(2)	3454(2)	7152(2)	46(1)
C(7)	2428(2)	3437(2)	7318(2)	36(1)
C(8)	5562(2)	3880(1)	6049(2)	25(1)
C(9)	5761(2)	3857(1)	5046(2)	27(1)
C(10)	4954(2)	4169(1)	4263(2)	29(1)
C(11)	5080(2)	4111(2)	3319(2)	36(1)
C(12)	6005(3)	3738(2)	3142(2)	40(1)
C(13)	6821(2)	3440(2)	3915(2)	40(1)
C(14)	6701(2)	3502(2)	4859(2)	32(1)
C(15)	8612(2)	4505(2)	8566(2)	33(1)
C(16)	9760(2)	4546(2)	8914(2)	38(1)
C(17)	10354(2)	3863(2)	9177(2)	41(1)
C(18)	9782(2)	3164(2)	9053(2)	38(1)
C(19)	8633(2)	3150(2)	8673(2)	30(1)
C(20)	7993(2)	2394(2)	8472(2)	37(1)
C(21)	6138(2)	1766(2)	8277(2)	32(1)
C(22)	5810(2)	1869(2)	7163(2)	39(1)
C(23)	6696(3)	966(2)	8538(2)	41(1)
C(24)	5064(2)	1813(2)	8632(2)	41(1)
C(25)	7094(2)	2502(2)	9788(2)	35(1)
C(26)	7095(2)	3335(1)	10140(2)	26(1)
C(27)	7580(2)	3516(2)	11108(2)	33(1)
C(28)	7533(2)	4268(2)	11443(2)	37(1)
C(29)	6964(2)	4830(2)	10805(2)	38(1)
C(30)	6500(2)	4617(2)	9849(2)	33(1)
Cl(1)	6284(1)	6750(1)	9316(1)	43(1)
O(1)	7030(2)	6282(2)	8914(2)	70(1)
O(2)	5260(2)	6337(2)	9179(2)	64(1)
O(3)	6126(2)	7479(1)	8803(2)	82(1)
O(4)	6792(3)	6859(2)	10322(2)	94(1)

Table S3. Bond lengths [Å] and angles [°] for **3**.

Ni(1)-N(3)	1.836(2)	N(3)-C(8)	1.317(3)
Ni(1)-N(1)	1.840(2)	N(3)-H(3N)	0.84(3)
Ni(1)-N(4)	1.926(2)	N(4)-C(15)	1.347(3)
Ni(1)-N(6)	1.930(2)	N(4)-C(19)	1.351(3)
N(1)-C(1)	1.316(3)	N(5)-C(25)	1.468(3)
N(1)-H(1N)	0.80(3)	N(5)-C(20)	1.469(3)
N(2)-C(8)	1.337(3)	N(5)-C(21)	1.507(3)
N(2)-C(1)	1.347(3)	N(6)-C(30)	1.345(3)
		N(6)-C(26)	1.351(3)
		C(1)-C(2)	1.490(3)

C(2)-C(7)	1.392(4)	C(28)-H(28)	0.9500
C(2)-C(3)	1.394(3)	C(29)-C(30)	1.378(4)
C(3)-C(4)	1.381(4)	C(29)-H(29)	0.9500
C(3)-H(3)	0.9500	C(30)-H(30)	0.9500
C(4)-C(5)	1.391(4)	Cl(1)-O(4)	1.414(2)
C(4)-H(4)	0.9500	Cl(1)-O(2)	1.418(2)
C(5)-C(6)	1.375(5)	Cl(1)-O(3)	1.433(2)
C(5)-H(5)	0.9500	Cl(1)-O(1)	1.439(3)
C(6)-C(7)	1.389(4)		
C(6)-H(6)	0.9500	N(3)-Ni(1)-N(1)	90.20(9)
C(7)-H(7)	0.9500	N(3)-Ni(1)-N(4)	89.78(9)
C(8)-C(9)	1.496(3)	N(1)-Ni(1)-N(4)	176.27(9)
C(9)-C(14)	1.390(4)	N(3)-Ni(1)-N(6)	171.49(9)
C(9)-C(10)	1.397(3)	N(1)-Ni(1)-N(6)	93.83(9)
C(10)-C(11)	1.383(3)	N(4)-Ni(1)-N(6)	85.71(8)
C(10)-H(10)	0.9500	C(1)-N(1)-Ni(1)	128.40(18)
C(11)-C(12)	1.383(4)	C(1)-N(1)-H(1N)	112(2)
C(11)-H(11)	0.9500	Ni(1)-N(1)-H(1N)	120(2)
C(12)-C(13)	1.385(4)	C(8)-N(2)-C(1)	120.3(2)
C(12)-H(12)	0.9500	C(8)-N(3)-Ni(1)	129.22(18)
C(13)-C(14)	1.380(4)	C(8)-N(3)-H(3N)	112.2(19)
C(13)-H(13)	0.9500	Ni(1)-N(3)-H(3N)	118.4(19)
C(14)-H(14)	0.9500	C(15)-N(4)-C(19)	119.2(2)
C(15)-C(16)	1.380(4)	C(15)-N(4)-Ni(1)	120.33(17)
C(15)-H(15)	0.9500	C(19)-N(4)-Ni(1)	120.07(17)
C(16)-C(17)	1.382(4)	C(25)-N(5)-C(20)	109.2(2)
C(16)-H(16)	0.9500	C(25)-N(5)-C(21)	114.8(2)
C(17)-C(18)	1.380(4)	C(20)-N(5)-C(21)	112.84(19)
C(17)-H(17)	0.9500	C(30)-N(6)-C(26)	118.8(2)
C(18)-C(19)	1.385(3)	C(30)-N(6)-Ni(1)	115.84(17)
C(18)-H(18)	0.9500	C(26)-N(6)-Ni(1)	121.83(16)
C(19)-C(20)	1.507(4)	N(1)-C(1)-N(2)	126.2(2)
C(20)-H(20A)	0.9900	N(1)-C(1)-C(2)	120.2(2)
C(20)-H(20B)	0.9900	N(2)-C(1)-C(2)	113.6(2)
C(21)-C(24)	1.530(4)	C(7)-C(2)-C(3)	119.1(2)
C(21)-C(22)	1.534(4)	C(7)-C(2)-C(1)	121.5(2)
C(21)-C(23)	1.537(4)	C(3)-C(2)-C(1)	119.3(2)
C(22)-H(22A)	0.9800	C(4)-C(3)-C(2)	120.2(3)
C(22)-H(22B)	0.9800	C(4)-C(3)-H(3)	119.9
C(22)-H(22C)	0.9800	C(2)-C(3)-H(3)	119.9
C(23)-H(23A)	0.9800	C(3)-C(4)-C(5)	120.2(3)
C(23)-H(23B)	0.9800	C(3)-C(4)-H(4)	119.9
C(23)-H(23C)	0.9800	C(5)-C(4)-H(4)	119.9
C(24)-H(24A)	0.9800	C(6)-C(5)-C(4)	119.9(3)
C(24)-H(24B)	0.9800	C(6)-C(5)-H(5)	120.0
C(24)-H(24C)	0.9800	C(4)-C(5)-H(5)	120.0
C(25)-C(26)	1.511(3)	C(5)-C(6)-C(7)	120.1(3)
C(25)-H(25A)	0.9900	C(5)-C(6)-H(6)	119.9
C(25)-H(25B)	0.9900	C(7)-C(6)-H(6)	119.9
C(26)-C(27)	1.385(3)	C(6)-C(7)-C(2)	120.3(3)
C(27)-C(28)	1.379(4)	C(6)-C(7)-H(7)	119.8
C(27)-H(27)	0.9500	C(2)-C(7)-H(7)	119.8
C(28)-C(29)	1.386(4)	N(3)-C(8)-N(2)	125.6(2)

N(3)-C(8)-C(9)	119.4(2)
N(2)-C(8)-C(9)	115.1(2)
C(14)-C(9)-C(10)	118.8(2)
C(14)-C(9)-C(8)	122.0(2)
C(10)-C(9)-C(8)	119.1(2)
C(11)-C(10)-C(9)	120.4(2)
C(11)-C(10)-H(10)	119.8
C(9)-C(10)-H(10)	119.8
C(10)-C(11)-C(12)	120.2(3)
C(10)-C(11)-H(11)	119.9
C(12)-C(11)-H(11)	119.9
C(11)-C(12)-C(13)	119.8(2)
C(11)-C(12)-H(12)	120.1
C(13)-C(12)-H(12)	120.1
C(14)-C(13)-C(12)	120.2(3)
C(14)-C(13)-H(13)	119.9
C(12)-C(13)-H(13)	119.9
C(13)-C(14)-C(9)	120.6(3)
C(13)-C(14)-H(14)	119.7
C(9)-C(14)-H(14)	119.7
N(4)-C(15)-C(16)	122.4(2)
N(4)-C(15)-H(15)	118.8
C(16)-C(15)-H(15)	118.8
C(15)-C(16)-C(17)	118.8(3)
C(15)-C(16)-H(16)	120.6
C(17)-C(16)-H(16)	120.6
C(18)-C(17)-C(16)	118.8(3)
C(18)-C(17)-H(17)	120.6
C(16)-C(17)-H(17)	120.6
C(17)-C(18)-C(19)	120.4(3)
C(17)-C(18)-H(18)	119.8
C(19)-C(18)-H(18)	119.8
N(4)-C(19)-C(18)	120.5(2)
N(4)-C(19)-C(20)	117.8(2)
C(18)-C(19)-C(20)	121.7(2)
N(5)-C(20)-C(19)	113.0(2)
N(5)-C(20)-H(20A)	109.0
C(19)-C(20)-H(20A)	109.0
N(5)-C(20)-H(20B)	109.0
C(19)-C(20)-H(20B)	109.0
H(20A)-C(20)-H(20B)	107.8
N(5)-C(21)-C(24)	109.2(2)
N(5)-C(21)-C(22)	108.8(2)
C(24)-C(21)-C(22)	107.5(2)
N(5)-C(21)-C(23)	111.7(2)
C(24)-C(21)-C(23)	109.9(2)
C(22)-C(21)-C(23)	109.7(2)
C(21)-C(22)-H(22A)	109.5
C(21)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
C(21)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
C(21)-C(23)-H(23A)	109.5
C(21)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
C(21)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(21)-C(24)-H(24A)	109.5
C(21)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
C(21)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
N(5)-C(25)-C(26)	114.1(2)
N(5)-C(25)-H(25A)	108.7
C(26)-C(25)-H(25A)	108.7
N(5)-C(25)-H(25B)	108.7
C(26)-C(25)-H(25B)	108.7
H(25A)-C(25)-H(25B)	107.6
N(6)-C(26)-C(27)	120.7(2)
N(6)-C(26)-C(25)	119.3(2)
C(27)-C(26)-C(25)	120.0(2)
C(28)-C(27)-C(26)	120.2(2)
C(28)-C(27)-H(27)	119.9
C(26)-C(27)-H(27)	119.9
C(27)-C(28)-C(29)	119.0(2)
C(27)-C(28)-H(28)	120.5
C(29)-C(28)-H(28)	120.5
C(30)-C(29)-C(28)	118.2(2)
C(30)-C(29)-H(29)	120.9
C(28)-C(29)-H(29)	120.9
N(6)-C(30)-C(29)	123.0(2)
N(6)-C(30)-H(30)	118.5
C(29)-C(30)-H(30)	118.5
O(4)-Cl(1)-O(2)	111.15(19)
O(4)-Cl(1)-O(3)	111.32(17)
O(2)-Cl(1)-O(3)	111.16(15)
O(4)-Cl(1)-O(1)	107.57(18)
O(2)-Cl(1)-O(1)	107.60(16)
O(3)-Cl(1)-O(1)	107.85(18)

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **3**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ni(1)	25(1)	30(1)	19(1)	1(1)	3(1)	4(1)
N(1)	29(1)	35(1)	20(1)	1(1)	7(1)	6(1)
N(2)	29(1)	29(1)	21(1)	1(1)	5(1)	1(1)
N(3)	24(1)	38(1)	23(1)	3(1)	8(1)	3(1)
N(4)	28(1)	29(1)	21(1)	0(1)	5(1)	1(1)
N(5)	28(1)	25(1)	24(1)	-1(1)	4(1)	1(1)
N(6)	25(1)	29(1)	23(1)	-1(1)	7(1)	1(1)
C(1)	29(1)	22(1)	25(1)	1(1)	5(1)	2(1)
C(2)	29(1)	31(1)	19(1)	-7(1)	3(1)	1(1)
C(3)	35(1)	32(1)	28(1)	-4(1)	1(1)	2(1)
C(4)	35(1)	47(2)	37(2)	-7(1)	-4(1)	11(1)
C(5)	27(1)	69(2)	47(2)	-15(2)	6(1)	4(1)
C(6)	39(2)	60(2)	44(2)	-5(2)	19(1)	-6(2)
C(7)	38(2)	41(2)	31(1)	0(1)	12(1)	3(1)
C(8)	30(1)	22(1)	23(1)	1(1)	6(1)	1(1)
C(9)	33(1)	25(1)	23(1)	-3(1)	7(1)	-6(1)
C(10)	33(1)	27(1)	26(1)	0(1)	5(1)	-7(1)
C(11)	44(2)	36(1)	25(1)	1(1)	4(1)	-14(1)
C(12)	54(2)	47(2)	25(1)	-5(1)	19(1)	-19(1)
C(13)	43(2)	41(2)	42(2)	-10(1)	21(1)	-10(1)
C(14)	34(1)	32(1)	31(1)	0(1)	9(1)	-3(1)
C(15)	36(1)	32(1)	30(1)	5(1)	7(1)	2(1)
C(16)	36(1)	41(2)	39(2)	-2(1)	11(1)	-8(1)
C(17)	28(1)	54(2)	38(2)	-1(1)	3(1)	-1(1)
C(18)	29(1)	40(2)	42(2)	3(1)	6(1)	7(1)
C(19)	30(1)	31(1)	28(1)	-2(1)	7(1)	4(1)
C(20)	33(1)	29(1)	48(2)	-5(1)	7(1)	3(1)
C(21)	34(1)	30(1)	30(1)	-2(1)	4(1)	-2(1)
C(22)	41(2)	40(2)	31(1)	-4(1)	1(1)	-4(1)
C(23)	49(2)	28(1)	40(2)	-1(1)	2(1)	-2(1)
C(24)	37(2)	44(2)	43(2)	1(1)	9(1)	-4(1)
C(25)	49(2)	28(1)	24(1)	2(1)	2(1)	4(1)
C(26)	23(1)	31(1)	22(1)	1(1)	5(1)	0(1)
C(27)	31(1)	44(2)	22(1)	2(1)	3(1)	-3(1)
C(28)	37(1)	50(2)	24(1)	-10(1)	6(1)	-9(1)
C(29)	40(2)	36(2)	39(2)	-13(1)	13(1)	-6(1)
C(30)	36(1)	30(1)	33(1)	-1(1)	13(1)	4(1)
Cl(1)	42(1)	39(1)	40(1)	1(1)	-5(1)	0(1)
O(1)	54(1)	79(2)	85(2)	17(1)	35(1)	10(1)
O(2)	36(1)	83(2)	73(2)	19(1)	15(1)	-6(1)
O(3)	83(2)	46(1)	92(2)	17(1)	-28(2)	-1(1)
O(4)	133(3)	76(2)	46(2)	-16(1)	-30(2)	20(2)

Table S5. Summary of experimental results for various amide and nitrile combinations.

Nitrile	Amide	Imidoylamide species	IDA species
acetonitrile	acetamide	$CH_3CONCNHCH_3$	$CH_3CNHNCNHCH_3$
acetonitrile	^{15}N-acetamide	$CH_3CO^{15}NCNHCH_3$	$CH_3CNH^{15}NCNHCH_3$
d_3-acetonitrile	acetamide	$CH_3CONCNHCD_3$	$CD_3CNHNCNHCD_3$
acetonitrile	1,1-dimethylurea	$(CH_3)_2CHCONCNHCH_3$	$CH_3CNHNCNHCH_3$
benzonitrile	acetamide	$CH_3CONCNHC_6H_5$	$C_6H_5CNHNCNHC_6H_5$
benzonitrile	^{15}N-acetamide	$CH_3CO^{15}NCNHC_6H_5$	$C_6H_5CNH^{15}NCNHC_6H_5$

Synthesis of bis(2-pyridylmethyl)tert-butylamine nickel(II) acetyl(imino(phenyl)methyl)amide perchlorate (2). To a stirred solution of 0.116 mmol tBuDPA(μ-OH)$_2$Ni$_2$(ClO$_4$)$_2$[1] (100 mg) in 2 mL of benzonitrile was added 0.232 mmol (13.2 mg) of acetamide in 2 mL of benzonitrile, in an argon glovebox. The resulting green solution was observed to turn purple over a period of one hour, at which time addition of 50 mL of diethyl ether resulted in the precipitation of 85 mg (64% yield) of **2**, as a fine purple solid. Elemental analysis yields results corresponding to **2** as [tBuDPA]Ni($CH_3CONC(NH)C_6H_5$)(ClO_4) (with inorganic contaminant modeled as 0.735 molecules per **2** of sodium perchlorate also present; this a side effect of the precipitation method and further purification is not possible due to the instability of the intermediate **2**). FT-IR (KBr pellet, cm^{-1}): 3417(m), 2976(m), 1668(s), 1604(ms), 1586(m) 1565(m), 1485(m), 1447(ms), 1419(ms), 1374(m), 1331(ms), 1233(ms), 1098(vs), 1074(vs), 1023(m), 927(m), 773(m), 730(m), 706(w), 622(m). Room temperature magnetic moment 3.2 BM (measured using MSB Mk1 Magnetic Susceptibility Balance, Jonson Matthey). ESI-MS: m/z 474 $[(C_{16}H_{21}N_3)Ni^{2+}(C_6H_5CNHNCOCH_3)^-]^+$. Electronic spectrum in benzonitrile, λ_{max} (ε per mole of **2**): 558(8), 773(6), 827(6), 1112(6). Anal. Calc. for **2**·0.735($NaClO_4$) ($C_{25}H_{30}ClN_5NiO_5$·0.735($NaClO_4$)): C, 45.18; H, 4.55; N, 10.54; Ni, 8.83. Found: C, 45.05; H, 4.68; N, 10.66; Ni, 9.26.

Synthesis of (2-pyridylmethyl)tert-butylamine nickel (II) bis(imino(phenyl)methyl)amide perchlorate (3). As **2**, but the benzonitrile solution was allowed to stand overnight before ether addition, at which point the resulting orange-brown solution was crashed with 50 mL of diethyl ether, resulting in the precipitation of 114 mg (77% yield) of **3**, as a fine green solid. Diffraction-quality crystals of **3** were grown from a methanolic solution of this crude product, layered under diethyl ether. Only eight crystal structures in the Cambridge Structural Database[2] feature a longer Ni-N bond distance,[3-10] out of more than thirty-nine thousand Ni-N bond lengths reported. FT-IR (KBr pellet, cm^{-1}): 2974(m), 1689(w), 1660(w), 1608(m), 1544(ms), 1450(s), 1426(s), 1297(w), 1255(w), 1226(w), 1192(w), 1158(w), 1093(vs), 1026(s), 929(m), 767(s), 708(s), 623(s). ESI-MS: m/z 535 $[(C_{16}H_{21}N_3)Ni^{2+}(C_6H_5CNHNCNHC_6H_5)^-]^+$ Electronic spectrum in benzonitrile, λ_{max} (ε per mole of **3**): 372(sh), 555(9), 777(6), 827(7), 1176(6). Anal. Calc. for **3**·0.4C_6H_5CN ($C_{30}H_{33}ClN_6NiO_4$·0.4C_6H_5CN) C, 58.19; H, 5.21; N, 13.24; Ni, 8.67. Found: C, 58.53; H, 5.33; N, 13.77; Ni, 9.36.

Crystallographic Details. The X-ray intensity data were measured on a Bruker SMART APEX CCD X-ray diffractometer system equipped with a Mo-target X-ray tube.

The frames were integrated with the Bruker SAINT software package[11] using a narrow-frame integration algorithm. The data were corrected for absorption effects using the empirical method (SADABS).[12] The structures were solved by direct methods and refined using the Bruker SHELXTL (Version 6.14) software package.[13] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms bonded to N(1) and N(3) were located on a difference Fourier map and refined with restraining equivalent isotropic displacement parameters to be 1.2 times the U_{eq} value of the respective nitrogen atom. All other hydrogen atoms were included at idealized positions for structure factor calculations. Selected crystallographic data for all complexes are summarized in Tables S1-S4.

Synthesis of isotopically labeled imidoylamide and imidoylamidine adducts. To a stirred solution of 0.58 mmol tBuDPA(μ-OH)$_2$Ni$_2$(ClO$_4$)$_2$[1] (50 mg) in 1 mL of nitrile solvent (acetonitrile, d3-acetonitrile, benzonitrile) was added 0.116 mmol of amide (acetamide, 1,1-dimethylurea or ^{15}N-acetamide) in 1 mL of nitrile, in an argon glovebox. After a period of 1h, aliquots of the resulting solutions, diluted with methanol, were examined by ESI-MS, and the imidoylamide adducts observed. After 12h, the solutions were examined again, and IDA products observed, as reported in Table S5. Typical results may be seen in Figs. S3 and S4.

1. J. P. Wikstrom, A. Filatov, B. M. Foxman and E. V. Rybak-Akimova, *Dalton Trans.*, 2009, submitted.
2. F. H. Allen, *Acta Crysta.*, 2002, 380-388.
3. A. Bencini, A. Bianchi, M. Castello, P. Dapporto, J. Faus, E. Garcia-Espana, M. Micheloni, P. Paoletti and P. Paoli, *Inorg. Chem.*, 1989, **28,** 3175-3181.
4. F. Cecconi, S. Midollini and A. Orlandini, *J. Chem. Soc., Dalton Trans.*, 1983, 2263-2269.
5. F. Meyer, I. Hyla-Kryspin, E. Kaifer and P. Kircher, *Eur. J. Inorg. Chem.*, 2000, 771-781.
6. H. Adams, D.E. Fenton and P. E. McHugh, *Polyhedron*, 2003, **22**, 75-81.
7. H.-W. Lin, *Acta Crysta. E* 2008, **64**, m295/291-m295/298.
8. M. Hvastijova, J. Kohout, J. G. Diaz, J. Kozisek and J. W. Buchler, *Trans. Met. Chem.*, 2001, **26**, 430-434.
9. R.S. Vagg and E.C. Watton, *Acta Crysta. B*, 1978, **34**, 2715-2720.
10. Y.-X. Sun, *Acta Crysta. C*, 2006, **62**, m109-m111.
11. SAINT, Version 6.02, Bruker AXS, Inc., Madison, WI, 2001.
12. SADABS, Bruker AXS, Inc., Madison, WI, 2001.
13. Sheldrick, G. M. *SHELXTL*, Version 6.14, University of Gottingen, Germany, 2000.