Supplementary Information

Synthesis and Carbene-Transfer Reactivity of Dimeric Nickel Carbene Cations Supported by *N*-Heterocyclic Carbene Ligands

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I. Experimental

General Considerations. Unless stated otherwise, all manipulations were carried out in a MBraun *Lab Master* inert atmosphere box under an atmosphere of purified dinitrogen. Anhydrous diethyl ether was purchased from Fischer, stirred over sodium metal, and filtered through activated alumina. Pentane was purchased from Sigma Aldrich and dried by passage through activated alumina and Q-5 columns. C_6D_6 and CD_2Cl_2 were purchased from Cambridge Isotope Laboratories, degassed by freeze-pump-thaw cycles, and dried over CaH_2 or activated 4 Å molecular sieves. Celite and 4 Å molecular sieves were activated by evacuation overnight at 180°C. 1,3-di(2',6'-diisopropylphenyl)imidazolin-2-ylidene, N_2CPh_2, $\{(Pr)Ni(\mu\text{-}Cl)\}_2$, and $NaB(Ar^F)_4$ were prepared according to literature procedures.[1-4] All other chemicals were used as received. Elemental analyses were performed by Midwest Microlab (Indianapolis, IN). ^1H NMR spectra were recorded on a Bruker 500-MHz NMR spectrometer and reported with reference to solvent resonances (residual C_6D_5H in C_6D_6, 7.16 ppm; residual $CDHCl_2$ in CD_2Cl_2, 5.32 ppm). Solution magnetic susceptibilities were determined by ^1H NMR spectroscopy using the Evans method (diamagnetic corrections were not applied).[5] X-ray diffraction data were collected on a Siemens 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).

$[\{(IPr)Ni\}_2(\mu\text{-}Cl)(\mu\text{-}CPh_2)][B(Ar^F)_4]$ (6). $\{(IPr)Ni(\mu\text{-}Cl)\}_2$ (**3**, 456 mg, 0.472 mmol) was dissolved in 5 mL Et_2O and cooled to -35°C. $NaB(Ar^F)_4$ (418 mg, 0.472 mmol) and N_2CPh_2 (92 mg, 0.474 mmol) were added to a scintillation vial, dissolved in 10 mL Et_2O, and cooled to -35°C. While stirring, $NaB(Ar^F)_4$ and N_2CPh_2 were added to **3**, causing an immediate color change from yellow to brown. The reaction was allowed to stir at room temperature for 30 minutes before being filtered through Celite. The filtrate was then dried under reduced pressure, and the green solid recrystallized by layering a concentrated Et_2O solution with pentane. 825 mg (89% yield) forest green **6** was isolated.

For **6**: ^{1}H NMR (20ºC, 500.133 MHz, CD_2Cl_2): δ 7.78 (s, 8H, Ar^F), 7.61 (s, 4H, Ar^F), 7.49 (t, 4H, J = 7.8 Hz, Ar^{IPr}), 7.22 (d, 8H, J = 7.8 Hz, Ar^{IPr}), 7.10 (t, 2H, J = 7.6 Hz, p-C_6H_5), 7.03 (s, 4H, CH=CH), 6.76 (t, 4H, J = 7.6 Hz, m-C_6H_5), 6.22 (d, 4H, J = 7.6 Hz, o-C_6H_5), 2.26 (sept., 8H, J = 6.8 Hz, -$CH(CH_3)_2$), 1.01 (d, 24H, J = 6.8 Hz, -$CH(CH_3)_2$), 0.94 (d, 24H, J = 6.8 Hz, -$CH(CH_3)_2$). ^{19}F NMR (20ºC, 470.545 MHz, CD_2Cl_2): δ -62.96. ^{13}C{^{1}H} NMR (20ºC, 125.769 MHz, CD_2Cl_2): δ 274.1, 177.5, 163.0, 162.6, 162.2, 161.8, 146.0, 136.2, 135.5, 131.1, 130.9, 129.6, 126.3, 125.9, 124.9, 124.2, 120.6, 118.1, 29.2, 25.8, 23.0. Elemental analysis for $BC_{99}ClF_{24}H_{90}N_4Ni_2$: %C = 60.8, %H = 4.64, %N = 2.87; found: %C = 60.5, %H = 4.94, %N = 2.73.

[{(IPr)Ni}$_2$(μ-Cl)(μ-CHSiMe$_3$)][B(Ar^F)$_4$] (**7**). **3** (432 mg, 0.447 mmol) was dissolved in 5 mL Et_2O and cooled to -35°C. $NaB(Ar^F)_4$ (396 mg, 0.447 mmol) and $N_2CHSiMe_3$ (0.24 mL, 2 M, 0.448 mmol) were added to a scintillation vial, dissolved in 10 mL Et_2O, and cooled to -35°C. While stirring, $NaB(Ar^F)_4$ and $N_2CHSiMe_3$ were added to **3**, causing an immediate color change from yellow to blue-violet. The reaction was allowed to stir at room temperature for 30 minutes before being filtered through celite. Filtrate was then dried under reduced pressure, and the purple solid recrystallized by layering a concentrated Et_2O solution with pentane. 762 mg (91% yield) blue-violet **7** was isolated.

For **7**: ^{1}H NMR (20ºC, 500.133 MHz, CD_2Cl_2): δ 14.27 (s, 1H, -$CHSiMe_3$), 7.77 (s, 8H, o-Ar^F), 7.62 (t, 4H, J = 8 Hz, p-Ar^{IPr}), 7.60 (s, 4H p-Ar^F), 7.37 (d, 4H, J = 7.8 Hz, Ar^{IPr}), 7.27 (d, 4H, J = 7.8 Hz, Ar^{IPr}), 7.15 (s, 4H, CH=CH), 2.65 (sept., 4H, J = 7 Hz, -$CH(CH_3)_2$), 2.15 (sept., 4H, J = 7 Hz, -$CH(CH_3)_2$), 1.35 (d, 12H, J = 7 Hz, -$CH(CH_3)_2$), 1.17 (d, 12H, J = 7 Hz, -$CH(CH_3)_2$), 1.13 (d, 12H, J = 7 Hz, -$CH(CH_3)_2$), 0.95 (d, 12H, J = 7 Hz, -$CH(CH_3)_2$). ^{19}F NMR (20ºC, 470.545 MHz, CD_2Cl_2): δ -63.00. ^{13}C{^{1}H} NMR (20ºC, 125.769 MHz, CD_2Cl_2): δ 294.3, 177.6, 163.0, 162.6, 162.2, 161.8, 146.0, 145.2, 135.5, 134.7, 131.7, 129.9, 129.6, 129.4, 129.2, 128.5, 126.4, 125.7, 125.2, 124.2, 118.1, 29.3, 26.5, 23.9, 22.7, 3.8. Elemental analysis for $BC_{90}ClF_{24}H_{90}N_4Ni_2Si$: %C = 57.6, %H = 4.84, %N = 2.99; found: %C = 57.9, %H = 4.79, %N = 2.90.

[{(IPr)Ni(CO)}$_2$(μ-Cl)]B(Ar^F)$_4$ (**8**). Complex **6** (312 mg in 25 mL Et_2O, 0.160 mmol) was placed in a Schlenk flask and cooled to -78°C. Carbon monoxide (11.6 mL, 0.480 mmol) was then introduced via syringe, causing a gradual color change from brown/yellow to blue-violet. The reaction was stirred at -78°C for 30 min before being warmed to room temperature and stirred for an additional 30 min. The solution was then dried under vacuum and the purple solid washed with 20 mL pentane to remove $Ph_2C{=}C{=}O$ (isolation and characterization reported below). Recrystallization of a concentrated Et_2O solution layered with pentane afforded 296 mg of **8** (91% yield).

For **8**: ^{1}H NMR (20ºC, 500.133 MHz, CD_2Cl_2): δ 7.74 (s, 8H, Ar^F), 7.57 (s, 4H, Ar^F), 7.49 (t, 4H, J = 7.8 Hz, Ar^{IPr}), 7.25 (d, 8H, J = 7.8 Hz, Ar^{IPr}), 7.25 (s, 2H, CH=CH), 2.42 (sept., 4H, J = 6.9 Hz, -$CH(CH_3)_2$), 1.15 (d, 24H, J = 6.9 Hz, -$CH(CH_3)_2$), 1.13 (d, 24H, J = 6.9 Hz, -

$CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (20ºC, 125.769 MHz, CD_2Cl_2): δ 192.2, 168.9, 163.0, 162.6, 162.2, 161.8, 145.9, 135.4, 135.2, 131.5, 129.9, 129.6, 129.37, 128.5, 126.4, 126.3, 125.1, 124.1, 122.0, 118.1, 29.3, 25.4, 24.0. IR (KBr/Nujol): ν_{CO} = 2063, 2023 cm^{-1}. Elemental analysis for $BC_{88}ClF_{24}H_{84}N_4Ni_2O_2$: %C = 57.2, %H = 4.58, %N = 3.03; found: %C = 57.0, %H = 4.53, %N = 2.99.

The pentane extract described above was filtered through Celite and then the solvent was removed under reduced pressure to afford 23 mg (74% yield) of $Ph_2C{=}C{=}O$ as a pale yellow oil.[6] For $Ph_2C{=}C{=}O$: ^1H NMR (20ºC, 500.133 MHz, C_6D_6): δ 7.05 (m, 8H), 6.95 (m, 2H). $^{13}C\{^1H\}$ NMR (20ºC, 125.769 MHz, C_6D_6): δ 201.7, 129.5, 128.3, 127.9, 126.3, 46.12. GC-MS (m/z) = 194.0 (M^+), 165.1.

Stoichiometric Reaction of 6 with CO. At -78°C, CO (2.3 mL, 0.095 mmol) was added with a syringe to **6** (185 mg in 20 mL Et_2O, 0.095 mmol). The color of the solution darkened slightly. After stirring for 1 hr at -78°C, the reaction was allowed to warm to room temperature. After removal of solvent under vacuum, the ^1H-NMR spectrum of the crude product mixture indicated a 30% conversion to $Ph_2C{=}C{=}O$ and **8**.

Reaction of 6 with N_3Mes. Complex **6** (37 mg, 0.019 mmol) and N_3Mes (31 mg, 0.19 mmol) were loaded into a sealable NMR tube and dissolved in CD_2Cl_2 (0.6 mL). The reaction was removed from light, and monitored for formation of $[\{(IPr)Ni\}_2(\mu\text{-NMes})(\mu\text{-Cl})][B(Ar^F)_4]$ and depletion of **6**. Identification of $Ph_2C{=}NMes$ was made by comparison to an authentic sample.[7] Heating a sealed NMR tube of **6** and N_3Mes to 60°C with an oil bath resulted in rapid decomposition of **6** without formation of $Ph_2C{=}NMes$.

[(IPr)Ni(CN^tBu)$_3$]B(Ar^F)$_4$ (9). At -35°C, CN^tBu (51 mg in 5 mL Et_2O, 0.678 mmol) was added to **6** (220 mg in 10 mL Et_2O, 0.113 mmol), causing a gradual color change from dark brown to light orange with formation of a fine white precipitate. The reaction was allowed to warm to room temperature and stirred for an additional 30 min. Removal of solvent under reduced pressure formed an orange, waxy solid which was triturated with 15 mL pentane (see below for the workup of this pentane extract). The solid was then extracted with 15 mL Et_2O, to separate **9** from (IPr)Ni(Cl)(CN^tBu) (**10**) which was identified by comparison with an authentic sample.[8] Evaporation of the Et_2O extract to 5 mL, followed by layering with pentane afforded 67 mg (76% yield) or **9** as pale yellow/green blocks.

For **9**: ^1H NMR (20ºC, 500.133 MHz, CD_2Cl_2): δ 12.7 (s, 2H, br, $\Delta_{½}$ = 45 Hz), 7.72 (s, 8H, Ar^F), 7.57 (s, 4H, Ar^F), 7.19 (s, 4H, br, $\Delta_{½}$ = 18 Hz), 6.96 (s, 2H, br, $\Delta_{½}$ = 17 Hz), 4.63 (s, 4H, br, $\Delta_{½}$ = 170 Hz), 2.63 (s, 27H, br, $\Delta_{½}$ = 20 Hz), 2.40 (s, 12H, br, $\Delta_{½}$ = 75 Hz), 2.04 (s, 12H, br, $\Delta_{½}$ = 11 Hz). μ_{eff} = 1.9 μ_B (Evans, 20ºC, CD_2Cl_2). IR (CaF_2/Fluorolube): 2168, 2134 cm^{-1}. $BC_{74}F_{24}H_{75}N_5Ni$: %C = 57.0, %H = 4.85, %N = 4.49; found: %C = 56.6, %H = 4.84, %N = 4.15.

The pentane extract described above was filtered through Celite. Solvent was the removed under reduced pressure to afford 17 mg (61% yield) of $Ph_2C{=}C{=}N^tBu$ as a pale orange

oil.[9] For $Ph_2C=C=N^tBu$: ^1H NMR (20ºC, 500.133 MHz, C_6D_6): δ 7.42 (d, 4H, J = 8.0 Hz, *o*-C_6H_5), 7.16 (t, 4H, J = 8.0 Hz, *m*-C_6H_5), 7.01 (t, 2H, J = 8.0 Hz, *p*-C_6H_5), 1.17 (s, 9H, -$C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (20ºC, 125.769 MHz, C_6D_6): δ 182.03, 136.0, 129.1, 127.7, 126.0, 76.8, 60.2, 30.3. GC-MS (m/z) = 249.0 (M^+), 193.1.

References:

1. V. Bohm, C. Gstattmayr, T. Weskamp, W. Herrmann, *Angew. Chem. Int., Ed.*, 2001, **40**(*18*), 3387.
2. S. B. Duckett, M.-D. Galvez-Lopez, R. N. Preutz, D. Schott, *Dalton Trans.*, 2004, **17**, 2746.
3. B. R. Dible, M. S. Sigman, A. M. Arif, *Inorg. Chem*. 2005, **44**, 3774.
4. D. L. Reger, T. D. Wright, C. A. Little, J. J. S. Lambda, M. D. Smith, *Inorg. Chem.*, 2001, **40**, 3810.
5. D. F. Evans, *J. Chem. Soc.*, 1959, 2003.
6. (a) E. C. Taylor, A. McKillop, G. H. Hawks, *Org. Synth.*, 1972, **52**, 36. (b) J. M. Goll, E. Fillion, *Organometallics*, 2008, **27**, 3622.
7. N. D. Harrold, R. Waterman, G. L. Hillhouse, *J. Am . Chem. Soc.*, 2009, **131**, 12871.
8. C. A., Laskowski, G. L. Hillhouse, *Organometallics* 2009, **28**, 6114
9. (a) J. A. Green, L. A. Singer, *Tetrahedron Lett.* 1969, 5093. (b) H.-J. Cristau, I. Jouanin, M. Taillefer, *J. Organomet. Chem.*, 1999, **584**(*1*), 68.

II. X-Ray

X-Ray Structure Determination. A crystal of suitable size and appearance was selected under a stereomicroscope while immersed in Paratone-N oil to minimize exposure to air. The crystal was extracted from the oil using a tapered glass filament that also held the crystal during data collection. The crystal was mounted and aligned on a Bruker SMART APEX system. All images showed sharp diffractions. Frames separated in reciprocal space were collected and provided an orientation matrix and initial cell parameters. The full data set provided final cell parameters.

A hemisphere of data was obtained at 100 K in reciprocal space to a resolution of 0.84 Å using 0.3° steps in ω using integration times of 10-30 s per frame, depending on the sample. Integration of intensities and refinement of cell parameters were completed with SAINT. Absorption corrections were applied using SADABS or psi-scans and were small. Crystals showed no visual signs of decomposition after data collection.

[{(IPr)Ni}$_2$(μ-Cl)(μ-CPh$_2$)][B(Ar^F)$_4$] (6)

The space group was determined as P-1 based on systematic absences and intensity statistics. Patterson method was used to locate Ni and Cl atoms. Direct methods were used to locate B, C, F, and N atoms. All non-hydrogen atoms were converted to and refined anisotropically. All hydrogen atoms were refined isotropically and fixed at calculated positions.

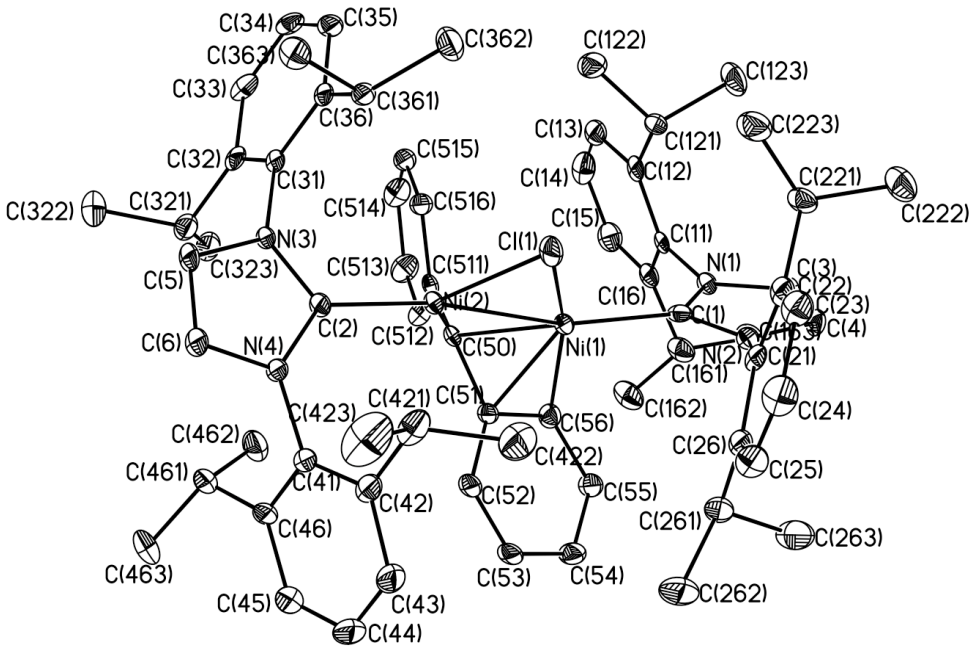
Crystal data and structure refinement for **6**:

Identification code	carl90a	Theta range for data collection	1.88 to 25.00°.
Empirical formula	$C_{100}H_{96}BCl_3F_{24}N_4Ni_2$	Index ranges	-17<=h<=17
Formula weight	2044.39		-21<=k<=15
Temperature	100(2) K		-22<=l<=24
Wavelength	0.71073 Å	Reflections collected	24831
Crystal system	Triclinic	Independent reflections	16471 [R(int) = 0.0615]
Space group	P-1	Completeness to theta = 25.00°	98.6 %
Unit cell dimensions	a = 15.022(3) Å	Absorption correction	None
	b = 18.047(4) Å	Max. and min. transmission	0.6757 and 0.4364
	c = 20.367(4) Å	Refinement method	Full-matrix least-squares on F^2
	α= 105.350(4)°		
	β= 111.153(4)°	Data / restraints / parameters	16471 / 0 / 1223
	γ = 100.049(4)°	Goodness-of-fit on F^2	0.921
Volume	4736.7(17) Å^3	Final R indices [I>2sigma(I)]	R1 = 0.0690
Z	2		wR2 = 0.1728
Density (calculated)	1.433 Mg/m^3	R indices (all data)	R1 = 0.1157
Absorption coefficient	0.579 mm^{-1}		wR2 = 0.1866
F(000)	2104	Largest diff. peak and hole	2.192 and -0.789 e.Å^{-3}
Crystal size	0.60 x 0.20 x 0.20 mm^3		

Bond Distances (Å) for **6**:

Ni(2)-C(50)	1.831(5)	C(51)-C(50)	1.458(7)	C(514)-C(515)	1.352(7)
Ni(2)-C(2)	1.893(5)	C(56)-C(55)	1.403(7)	C(22)-C(23)	1.387(7)
Ni(2)-Cl(1)	2.1641(15)	C(31)-C(32)	1.390(7)	C(22)-C(221)	1.543(7)
Ni(2)-Ni(1)	2.4312(10)	C(31)-C(36)	1.396(7)	C(361)-C(363)	1.536(7)
Ni(1)-C(50)	1.958(5)	C(32)-C(33)	1.405(7)	C(515)-C(516)	1.386(7)
Ni(1)-C(1)	1.975(5)	C(32)-C(321)	1.511(7)	C(511)-C(516)	1.406(7)
Ni(1)-C(51)	2.134(5)	C(16)-C(15)	1.377(7)	C(511)-C(50)	1.474(7)
Ni(1)-Cl(1)	2.2244(15)	C(16)-C(161)	1.528(8)	C(24)-C(25)	1.377(8)
Ni(1)-C(56)	2.368(5)	C(15)-C(14)	1.383(8)	C(24)-C(23)	1.390(8)
N(1)-C(1)	1.362(6)	C(34)-C(33)	1.368(7)	C(122)-C(121)	1.517(7)
N(1)-C(3)	1.399(6)	C(52)-C(53)	1.335(7)	C(121)-C(123)	1.524(7)
N(1)-C(11)	1.441(6)	C(13)-C(14)	1.392(8)	C(41)-C(42)	1.382(8)
N(3)-C(2)	1.354(6)	C(55)-C(54)	1.369(7)	C(41)-C(46)	1.400(8)
N(3)-C(5)	1.391(6)	C(36)-C(361)	1.512(7)	C(43)-C(44)	1.366(9)
N(3)-C(31)	1.446(6)	C(6)-N(4)	1.376(6)	C(43)-C(42)	1.392(8)
C(12)-C(13)	1.388(7)	C(26)-C(25)	1.378(7)	C(42)-C(421)	1.479(8)
C(12)-C(11)	1.401(7)	C(26)-C(21)	1.414(7)	C(221)-C(222)	1.526(7)
C(12)-C(121)	1.508(7)	C(26)-C(261)	1.496(8)	C(221)-C(223)	1.530(8)
C(5)-C(6)	1.344(7)	C(321)-C(323)	1.518(7)	C(46)-C(45)	1.406(8)
C(2)-N(4)	1.361(6)	C(321)-C(322)	1.546(7)	C(46)-C(461)	1.516(8)
C(3)-C(4)	1.330(7)	C(161)-C(162)	1.512(7)	C(421)-C(422)	1.539(8)
C(1)-N(2)	1.348(6)	C(161)-C(163)	1.553(7)	C(421)-C(423)	1.547(8)
N(2)-C(4)	1.400(6)	C(21)-C(22)	1.373(7)	C(44)-C(45)	1.354(9)
N(2)-C(21)	1.456(6)	C(53)-C(54)	1.416(7)	C(261)-C(263)	1.520(8)
C(11)-C(16)	1.393(7)	N(4)-C(41)	1.453(6)	C(261)-C(262)	1.551(7)
C(35)-C(34)	1.350(7)	C(513)-C(512)	1.379(7)	C(461)-C(463)	1.545(7)
C(35)-C(36)	1.403(7)	C(513)-C(514)	1.395(8)	C(461)-C(462)	1.556(8)
C(51)-C(56)	1.403(7)	C(362)-C(361)	1.515(7)		
C(51)-C(52)	1.430(7)	C(512)-C(511)	1.385(7)		

Fully Label Ortep Diagram (35%) of **6**:



Bond Angles (°) for **6**:

C(50)-Ni(2)-C(2)	117.6(2)	C(11)-C(12)-C(121)	122.8(5)	C(31)-C(32)-C(321)	122.8(4)
C(50)-Ni(2)-Cl(1)	108.24(15)	C(6)-C(5)-N(3)	105.8(5)	C(33)-C(32)-C(321)	121.1(5)
C(2)-Ni(2)-Cl(1)	133.63(16)	N(3)-C(2)-N(4)	103.9(4)	C(15)-C(16)-C(11)	118.3(5)
C(50)-Ni(2)-Ni(1)	52.41(15)	N(3)-C(2)-Ni(2)	127.2(3)	C(15)-C(16)-C(161)	119.1(5)
C(2)-Ni(2)-Ni(1)	168.05(15)	N(4)-C(2)-Ni(2)	127.8(4)	C(11)-C(16)-C(161)	122.5(5)
Cl(1)-Ni(2)-Ni(1)	57.55(4)	C(4)-C(3)-N(1)	106.7(4)	C(16)-C(15)-C(14)	120.8(5)
C(50)-Ni(1)-C(1)	152.4(2)	N(2)-C(1)-N(1)	104.7(4)	C(35)-C(34)-C(33)	120.5(5)
C(50)-Ni(1)-C(51)	41.47(19)	N(2)-C(1)-Ni(1)	129.8(3)	C(53)-C(52)-C(51)	121.1(5)
C(1)-Ni(1)-C(51)	125.09(19)	N(1)-C(1)-Ni(1)	125.4(4)	C(12)-C(13)-C(14)	120.8(5)
C(50)-Ni(1)-Cl(1)	101.49(15)	C(1)-N(2)-C(4)	110.8(4)	C(54)-C(55)-C(56)	121.0(5)
C(1)-Ni(1)-Cl(1)	102.37(15)	C(1)-N(2)-C(21)	125.8(4)	C(31)-C(36)-C(35)	115.5(5)
C(51)-Ni(1)-Cl(1)	128.93(14)	C(4)-N(2)-C(21)	121.1(4)	C(31)-C(36)-C(361)	122.4(4)
C(50)-Ni(1)-C(56)	68.31(19)	C(3)-C(4)-N(2)	107.1(5)	C(35)-C(36)-C(361)	122.0(5)
C(1)-Ni(1)-C(56)	90.79(19)	C(16)-C(11)-C(12)	122.4(5)	C(5)-C(6)-N(4)	107.5(4)
C(51)-Ni(1)-C(56)	35.84(18)	C(16)-C(11)-N(1)	119.6(4)	C(25)-C(26)-C(21)	116.4(5)
Cl(1)-Ni(1)-C(56)	164.23(13)	C(12)-C(11)-N(1)	117.9(4)	C(25)-C(26)-C(261)	122.3(5)
C(50)-Ni(1)-Ni(2)	47.82(14)	C(34)-C(35)-C(36)	122.3(5)	C(21)-C(26)-C(261)	121.2(5)
C(1)-Ni(1)-Ni(2)	157.51(15)	C(56)-C(51)-C(52)	117.9(5)	C(32)-C(321)-C(323)	113.1(4)
C(51)-Ni(1)-Ni(2)	76.62(13)	C(56)-C(51)-C(50)	118.0(4)	C(32)-C(321)-C(322)	111.4(5)
Cl(1)-Ni(1)-Ni(2)	55.18(4)	C(52)-C(51)-C(50)	123.2(4)	C(323)-C(321)-C(322)	109.7(4)
C(56)-Ni(1)-Ni(2)	111.59(13)	C(56)-C(51)-Ni(1)	81.2(3)	C(162)-C(161)-C(16)	113.5(5)
Ni(2)-Cl(1)-Ni(1)	67.27(5)	C(52)-C(51)-Ni(1)	118.2(4)	C(162)-C(161)-C(163)	108.7(5)
C(1)-N(1)-C(3)	110.6(4)	C(50)-C(51)-Ni(1)	62.8(3)	C(16)-C(161)-C(163)	110.5(4)
C(1)-N(1)-C(11)	125.7(4)	C(51)-C(56)-C(55)	119.7(5)	C(22)-C(21)-C(26)	122.7(5)
C(3)-N(1)-C(11)	123.0(4)	C(51)-C(56)-Ni(1)	62.9(3)	C(22)-C(21)-N(2)	117.2(4)
C(2)-N(3)-C(5)	111.6(4)	C(55)-C(56)-Ni(1)	127.1(4)	C(26)-C(21)-N(2)	120.0(5)
C(2)-N(3)-C(31)	125.6(4)	C(32)-C(31)-C(36)	124.2(4)	C(52)-C(53)-C(54)	121.0(5)
C(5)-N(3)-C(31)	122.2(4)	C(32)-C(31)-N(3)	117.4(4)	C(2)-N(4)-C(6)	111.1(4)
C(13)-C(12)-C(11)	117.4(5)	C(36)-C(31)-N(3)	118.4(4)	C(2)-N(4)-C(41)	125.7(4)
C(13)-C(12)-C(121)	119.6(5)	C(31)-C(32)-C(33)	116.1(5)	C(6)-N(4)-C(41)	123.0(4)

C(512)-C(513)-C(514)	120.0(5)	C(51)-C(50)-Ni(1)	75.8(3)	C(223)-C(221)-C(22)	113.0(4)
C(515)-C(514)-C(513)	119.6(5)	C(511)-C(50)-Ni(1)	115.5(3)	C(41)-C(46)-C(45)	115.9(6)
C(21)-C(22)-C(23)	118.8(5)	Ni(2)-C(50)-Ni(1)	79.8(2)	C(41)-C(46)-C(461)	123.1(5)
C(21)-C(22)-C(221)	123.5(5)	C(24)-C(25)-C(26)	122.2(5)	C(45)-C(46)-C(461)	120.9(6)
C(23)-C(22)-C(221)	117.6(5)	C(15)-C(14)-C(13)	120.2(6)	C(22)-C(23)-C(24)	119.9(6)
C(34)-C(33)-C(32)	121.3(5)	C(12)-C(121)-C(122)	114.8(5)	C(42)-C(421)-C(422)	113.3(5)
C(36)-C(361)-C(362)	113.6(4)	C(12)-C(121)-C(123)	109.6(4)	C(42)-C(421)-C(423)	108.7(5)
C(36)-C(361)-C(363)	109.0(4)	C(122)-C(121)-C(123)	109.1(4)	C(422)-C(421)-C(423)	111.8(5)
C(362)-C(361)-C(363)	110.0(4)	C(42)-C(41)-C(46)	124.1(5)	C(45)-C(44)-C(43)	121.7(6)
C(514)-C(515)-C(516)	120.6(5)	C(42)-C(41)-N(4)	119.6(5)	C(26)-C(261)-C(263)	111.4(5)
C(55)-C(54)-C(53)	119.1(5)	C(46)-C(41)-N(4)	116.2(5)	C(26)-C(261)-C(262)	112.1(5)
C(512)-C(511)-C(516)	117.1(5)	C(515)-C(516)-C(511)	121.1(5)	C(263)-C(261)-C(262)	109.0(5)
C(512)-C(511)-C(50)	122.4(5)	C(44)-C(43)-C(42)	120.8(6)	C(46)-C(461)-C(463)	114.2(5)
C(516)-C(511)-C(50)	120.5(5)	C(41)-C(42)-C(43)	116.6(6)	C(46)-C(461)-C(462)	109.7(5)
C(25)-C(24)-C(23)	119.9(5)	C(41)-C(42)-C(421)	123.3(5)	C(463)-C(461)-C(462)	108.0(5)
C(51)-C(50)-C(511)	120.7(4)	C(43)-C(42)-C(421)	120.0(6)	C(44)-C(45)-C(46)	120.8(6)
C(51)-C(50)-Ni(2)	119.0(4)	C(222)-C(221)-C(223)	111.0(5)		
C(511)-C(50)-Ni(2)	120.4(4)	C(222)-C(221)-C(22)	109.9(5)		

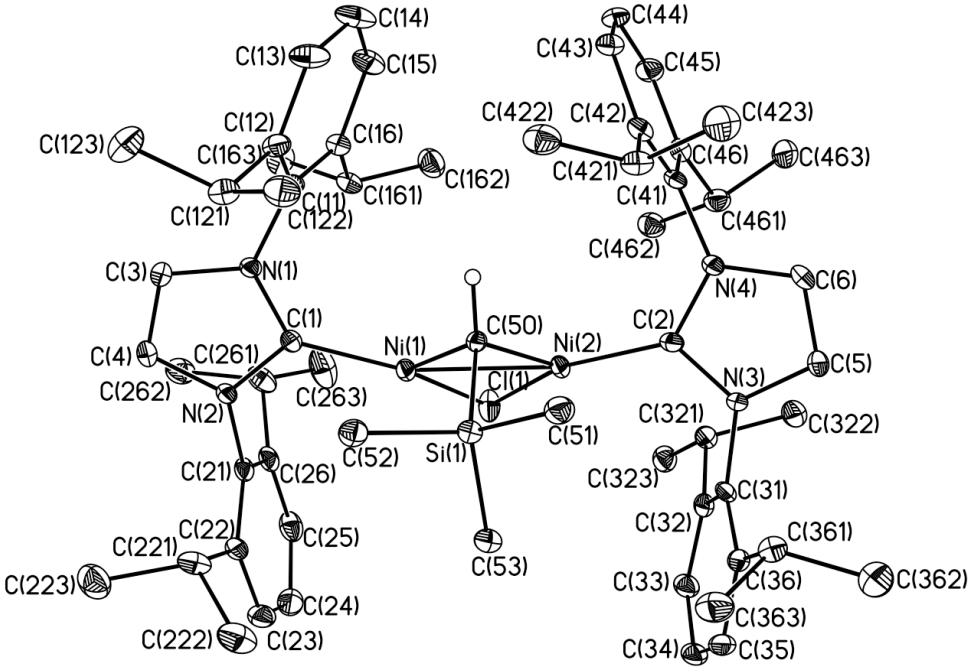
[{(IPr)Ni}$_2$(μ-Cl)(μ-CHSiMe$_3$)][B(Ar^F)$_4$] (7)

The space group was determined as P-1 based on systematic absences and intensity statistics. Patterson method was used to locate Ni and Cl atoms. Direct methods were used to locate B, C, F, N, and Si atoms. All non-hydrogen atoms were converted to and refined anisotropically. The carbene hydrogen was located in the difference map and refined isotropically. All other hydrogen atoms were refined isotropically and fixed at calculated positions.

Crystal data and structure refinement for **7**:

Identification code	carl92a	Theta range for data collection	1.33 to 25.00°.
Empirical formula	$C_{91}H_{96}BClF_{24}N_4Ni_2Si$	Index ranges	-12<=h<=16
Formula weight	1964.39		-16<=k<=21
Temperature	100(2) K		-23<=l<=24
Wavelength	0.71073 Å	Reflections collected	23070
Crystal system	Triclinic	Independent reflections	15798 [R(int) = 0.1402]
Space group	P-1	Completeness to theta = 25.00°	97.3 %
Unit cell dimensions	a = 13.729(5) Å	Absorption correction	None
	b = 17.963(6) Å	Max. and min. transmission	0.6215 and 0.3775
	c = 20.822(7) Å	Refinement method	Full-matrix least-squares on F^2
	a= 69.525(6)°		
	b= 73.169(6)°	Data / restraints / parameters	15798 / 0 / 1158
	g = 82.761(6)°	Goodness-of-fit on F^2	0.942
Volume	4603(3) Å^3	Final R indices [I>2sigma(I)]	R1 = 0.0493
Z	2		wR2 = 0.1105
Density (calculated)	1.417 Mg/m^3	R indices (all data)	R1 = 0.0765
Absorption coefficient	0.604 mm^{-1}		wR2 = 0.1230
F(000)	2024	Largest diff. peak and hole	0.961 and -0.624 e.Å^{-3}
Crystal size	0.60 x 0.20 x 0.20 mm^3		

Fully Label Ortep Diagram (35%) of **7**:



Bond Distances (Å) for **7**:

Ni(1)-C(50)	1.849(3)	C(32)-C(31)	1.404(4)	C(122)-C(121)	1.529(5)
Ni(1)-C(1)	1.899(3)	C(32)-C(321)	1.530(4)	C(362)-C(361)	1.523(5)
Ni(1)-Cl(1)	2.1559(9)	C(36)-C(31)	1.392(5)	C(42)-C(41)	1.387(4)
Ni(1)-Ni(2)	2.4385(9)	C(36)-C(35)	1.396(4)	C(42)-C(421)	1.518(4)
Ni(2)-C(50)	1.858(3)	C(36)-C(361)	1.518(5)	C(34)-C(35)	1.370(5)
Ni(2)-C(2)	1.898(3)	C(4)-C(3)	1.344(4)	C(222)-C(221)	1.509(5)
Ni(2)-Cl(1)	2.1672(10)	C(6)-C(5)	1.337(4)	C(41)-C(46)	1.400(4)
Si(1)-C(51)	1.861(3)	C(12)-C(11)	1.394(4)	C(23)-C(22)	1.396(4)
Si(1)-C(52)	1.866(3)	C(12)-C(13)	1.400(4)	C(26)-C(25)	1.388(4)
Si(1)-C(53)	1.870(3)	C(12)-C(121)	1.516(4)	C(26)-C(261)	1.522(5)
Si(1)-C(50)	1.882(3)	C(322)-C(321)	1.540(4)	C(421)-C(423)	1.525(5)
C(1)-N(1)	1.350(4)	C(321)-C(323)	1.526(4)	C(16)-C(15)	1.392(4)
C(1)-N(2)	1.365(4)	C(21)-C(22)	1.393(4)	C(461)-C(46)	1.521(4)
N(4)-C(2)	1.363(3)	C(21)-C(26)	1.399(4)	C(461)-C(462)	1.527(5)
N(4)-C(6)	1.376(4)	C(11)-C(16)	1.400(4)	C(461)-C(463)	1.536(4)
N(4)-C(41)	1.457(4)	C(33)-C(34)	1.381(5)	C(15)-C(14)	1.375(5)
N(1)-C(3)	1.388(4)	C(161)-C(163)	1.511(5)	C(361)-C(363)	1.531(4)
N(1)-C(11)	1.460(3)	C(161)-C(16)	1.519(4)	C(121)-C(123)	1.535(4)
N(2)-C(4)	1.389(4)	C(161)-C(162)	1.532(4)	C(46)-C(45)	1.394(5)
N(2)-C(21)	1.448(4)	C(43)-C(44)	1.377(4)	C(223)-C(221)	1.539(5)
N(3)-C(2)	1.357(4)	C(43)-C(42)	1.390(4)	C(13)-C(14)	1.374(5)
N(3)-C(5)	1.384(4)	C(24)-C(25)	1.376(5)	C(261)-C(263)	1.523(5)
N(3)-C(31)	1.458(3)	C(24)-C(23)	1.379(5)	C(261)-C(262)	1.527(5)
C(32)-C(33)	1.390(4)	C(44)-C(45)	1.384(4)	C(221)-C(22)	1.520(4)

Bond Angles (°) for **7**:

C(50)-Ni(1)-C(1)	107.42(13)	C(31)-C(32)-C(321)	122.4(3)	C(46)-C(41)-N(4)	117.0(2)
C(50)-Ni(1)-Cl(1)	104.87(9)	C(31)-C(36)-C(35)	116.7(3)	C(24)-C(23)-C(22)	121.1(3)
C(1)-Ni(1)-Cl(1)	147.11(10)	C(31)-C(36)-C(361)	124.1(3)	C(25)-C(26)-C(21)	117.0(3)
C(50)-Ni(1)-Ni(2)	49.04(9)	C(35)-C(36)-C(361)	119.1(3)	C(25)-C(26)-C(261)	121.5(3)
C(1)-Ni(1)-Ni(2)	155.22(9)	C(3)-C(4)-N(2)	106.6(3)	C(21)-C(26)-C(261)	121.1(3)
Cl(1)-Ni(1)-Ni(2)	55.88(3)	C(5)-C(6)-N(4)	107.2(3)	C(42)-C(421)-C(423)	110.8(3)
C(50)-Ni(2)-C(2)	108.27(12)	C(36)-C(31)-C(32)	123.4(3)	C(42)-C(421)-C(422)	111.8(3)
C(50)-Ni(2)-Cl(1)	104.10(10)	C(36)-C(31)-N(3)	119.2(3)	C(423)-C(421)-C(422)	111.0(3)
C(2)-Ni(2)-Cl(1)	147.59(8)	C(32)-C(31)-N(3)	117.4(3)	C(15)-C(16)-C(11)	116.3(3)
C(50)-Ni(2)-Ni(1)	48.71(9)	N(3)-C(2)-N(4)	103.5(2)	C(15)-C(16)-C(161)	119.4(3)
C(2)-Ni(2)-Ni(1)	156.71(8)	N(3)-C(2)-Ni(2)	123.8(2)	C(11)-C(16)-C(161)	124.1(2)
Cl(1)-Ni(2)-Ni(1)	55.44(3)	N(4)-C(2)-Ni(2)	132.0(2)	C(46)-C(461)-C(462)	110.5(3)
C(51)-Si(1)-C(52)	106.21(15)	C(4)-C(3)-N(1)	106.9(3)	C(46)-C(461)-C(463)	111.7(2)
C(51)-Si(1)-C(53)	112.41(16)	C(11)-C(12)-C(13)	116.6(3)	C(462)-C(461)-C(463)	111.1(3)
C(52)-Si(1)-C(53)	109.41(14)	C(11)-C(12)-C(121)	124.7(3)	C(14)-C(15)-C(16)	121.5(3)
C(51)-Si(1)-C(50)	109.52(14)	C(13)-C(12)-C(121)	118.6(3)	C(36)-C(361)-C(362)	110.2(3)
C(52)-Si(1)-C(50)	111.14(14)	C(323)-C(321)-C(32)	114.2(2)	C(36)-C(361)-C(363)	112.4(3)
C(53)-Si(1)-C(50)	108.17(14)	C(323)-C(321)-C(322)	109.5(2)	C(362)-C(361)-C(363)	108.8(3)
Ni(1)-Cl(1)-Ni(2)	68.67(3)	C(32)-C(321)-C(322)	110.2(3)	C(12)-C(121)-C(122)	111.5(3)
Ni(1)-C(50)-Ni(2)	82.25(12)	C(6)-C(5)-N(3)	106.5(3)	C(12)-C(121)-C(123)	111.0(3)
Ni(1)-C(50)-Si(1)	109.51(14)	C(22)-C(21)-C(26)	123.2(3)	C(122)-C(121)-C(123)	109.8(3)
Ni(2)-C(50)-Si(1)	111.16(16)	C(22)-C(21)-N(2)	119.2(3)	C(45)-C(46)-C(41)	116.7(3)
N(1)-C(1)-N(2)	104.3(2)	C(26)-C(21)-N(2)	117.5(3)	C(45)-C(46)-C(461)	120.0(3)
N(1)-C(1)-Ni(1)	134.2(2)	C(12)-C(11)-C(16)	123.8(3)	C(41)-C(46)-C(461)	123.3(3)
N(2)-C(1)-Ni(1)	120.3(2)	C(12)-C(11)-N(1)	117.8(3)	C(14)-C(13)-C(12)	120.9(3)
C(2)-N(4)-C(6)	111.3(2)	C(16)-C(11)-N(1)	118.3(3)	C(26)-C(261)-C(263)	113.8(3)
C(2)-N(4)-C(41)	125.4(3)	C(34)-C(33)-C(32)	120.9(3)	C(26)-C(261)-C(262)	110.3(3)
C(6)-N(4)-C(41)	122.2(2)	C(163)-C(161)-C(16)	111.2(3)	C(263)-C(261)-C(262)	110.0(3)
C(1)-N(1)-C(3)	111.3(2)	C(163)-C(161)-C(162)	111.8(3)	C(24)-C(25)-C(26)	121.3(3)
C(1)-N(1)-C(11)	126.6(2)	C(16)-C(161)-C(162)	112.7(3)	C(44)-C(45)-C(46)	120.9(3)
C(3)-N(1)-C(11)	121.6(2)	C(44)-C(43)-C(42)	120.8(3)	C(222)-C(221)-C(22)	113.7(3)
C(1)-N(2)-C(4)	111.0(2)	C(25)-C(24)-C(23)	120.3(3)	C(222)-C(221)-C(223)	110.5(3)
C(1)-N(2)-C(21)	121.4(2)	C(43)-C(44)-C(45)	120.6(3)	C(22)-C(221)-C(223)	109.3(3)
C(4)-N(2)-C(21)	126.3(2)	C(41)-C(42)-C(43)	117.5(3)	C(34)-C(35)-C(36)	121.2(3)
C(2)-N(3)-C(5)	111.6(2)	C(41)-C(42)-C(421)	122.3(3)	C(21)-C(22)-C(23)	116.8(3)
C(2)-N(3)-C(31)	123.7(2)	C(43)-C(42)-C(421)	120.2(3)	C(21)-C(22)-C(221)	121.8(3)
C(5)-N(3)-C(31)	124.4(3)	C(35)-C(34)-C(33)	120.7(3)	C(23)-C(22)-C(221)	121.2(3)
C(33)-C(32)-C(31)	116.8(3)	C(42)-C(41)-C(46)	123.5(3)	C(13)-C(14)-C(15)	120.8(3)
C(33)-C(32)-C(321)	120.6(3)	C(42)-C(41)-N(4)	119.4(3)		

[{(IPr)Ni(CO)}$_2$(μ-Cl)][B(Ar^F)$_4$] (8)

The space group was determined as P-1 based on systematic absences and intensity statistics. Patterosn method was used to locate Ni and Cl atoms. Direct methods were used to locate B, C, F, N, and O atoms. All non-hydrogen atoms were converted to and refined anisotropically. All hydrogen atoms were refined isotropically and fixed at calculated positions.

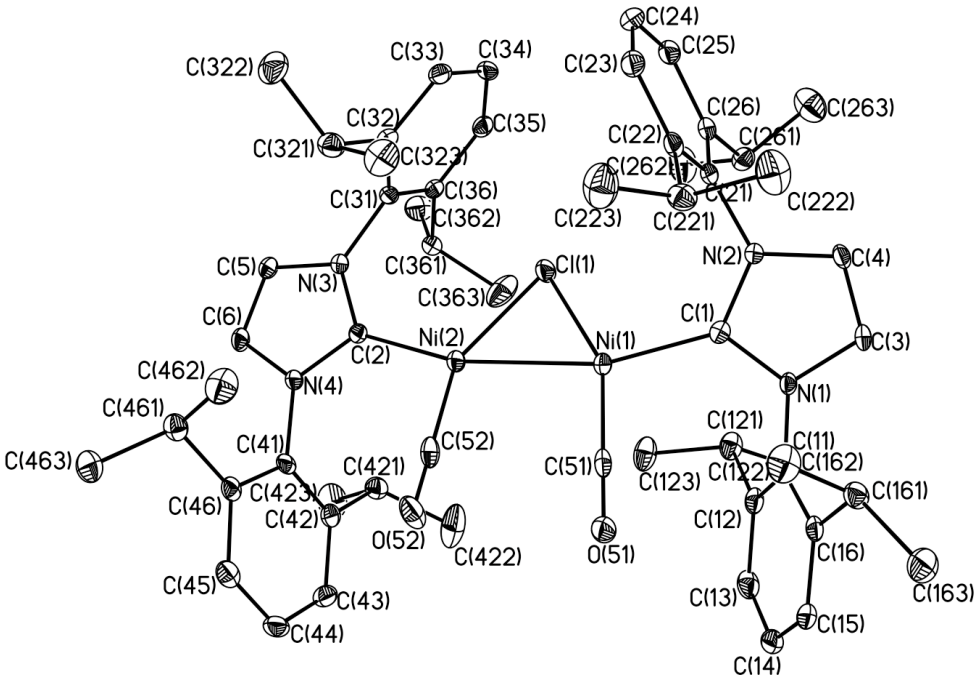
Crystal data and structure refinement for **8**:

Identification code	carl132a	Theta range for data collection	1.69 to 25.00°.
Empirical formula	$C_{88}H_{84}BClF_{24}N_4Ni_2O_2$	Index ranges	-14<=h<=14
Formula weight	1849.27		-20<=k<=20
Temperature	100(2) K		-25<=l<=25
Wavelength	0.71073 Å	Reflections collected	42603
Crystal system	Triclinic	Independent reflections	15284 [R(int) = 0.0549]
Space group	P-1	Completeness to theta = 25.00°	99.8 %
Unit cell dimensions	a = 12.5310(11) Å	Absorption correction	Psi-scan
	b = 17.5339(15) Å	Max. and min. transmission	0.8956 and 0.7284
	c = 21.5138(18) Å	Refinement method	Full-matrix least-squares on F^2
	a= 106.6720(10)°		
	b= 104.999(2)°	Data / restraints / parameters	15284 / 0 / 1115
	g = 91.050(2)°	Goodness-of-fit on F^2	0.952
Volume	4352.0(6) $Å^3$	Final R indices [I>2sigma(I)]	R1 = 0.0464
Z	2		wR2 = 0.1012
Density (calculated)	1.411 Mg/m^3	R indices (all data)	R1 = 0.0619
Absorption coefficient	0.564 mm^{-1}		wR2 = 0.1064
F(000)	1900	Largest diff. peak and hole	0.995 and -0.657 $e.Å^{-3}$
Crystal size	0.60 x 0.20 x 0.20 mm^3		

Bond Distances (Å) for **8**:

Ni(1)-C(51)	1.762(3)	C(24)-C(25)	1.372(4)	C(361)-C(363)	1.523(4)
Ni(1)-C(1)	1.943(3)	C(24)-C(23)	1.389(4)	C(361)-C(362)	1.524(4)
Ni(1)-Cl(1)	2.1260(7)	C(21)-C(26)	1.397(4)	C(321)-C(323)	1.532(4)
Ni(1)-Ni(2)	2.4967(5)	C(21)-C(22)	1.397(4)	C(321)-C(322)	1.532(4)
Ni(2)-C(52)	1.754(3)	C(25)-C(26)	1.389(4)	C(121)-C(122)	1.533(4)
Ni(2)-C(2)	1.958(3)	C(22)-C(23)	1.389(4)	C(121)-C(123)	1.533(4)
Ni(2)-Cl(1)	2.1383(8)	C(22)-C(221)	1.519(4)	N(4)-C(41)	1.448(3)
N(3)-C(2)	1.362(3)	C(26)-C(261)	1.523(4)	C(41)-C(46)	1.391(4)
N(3)-C(5)	1.387(3)	C(6)-C(5)	1.338(4)	C(41)-C(42)	1.395(4)
N(3)-C(31)	1.447(3)	C(6)-N(4)	1.378(3)	C(43)-C(44)	1.372(4)
N(2)-C(1)	1.362(3)	C(2)-N(4)	1.366(3)	C(43)-C(42)	1.387(4)
N(2)-C(4)	1.387(3)	C(4)-C(3)	1.335(4)	C(42)-C(421)	1.519(4)
N(2)-C(21)	1.450(3)	C(161)-C(162)	1.529(4)	C(46)-C(45)	1.391(4)
N(1)-C(1)	1.367(3)	C(161)-C(163)	1.532(4)	C(46)-C(461)	1.519(4)
N(1)-C(3)	1.391(3)	C(222)-C(221)	1.529(4)	C(45)-C(44)	1.376(4)
N(1)-C(11)	1.443(3)	C(221)-C(223)	1.522(4)	C(461)-C(463)	1.529(4)
C(13)-C(14)	1.371(4)	C(34)-C(33)	1.375(4)	C(461)-C(462)	1.532(4)
C(13)-C(12)	1.400(4)	C(34)-C(35)	1.384(4)	C(421)-C(422)	1.521(4)
C(11)-C(12)	1.396(4)	C(35)-C(36)	1.392(4)	C(421)-C(423)	1.523(4)
C(11)-C(16)	1.407(4)	C(36)-C(31)	1.396(4)	C(261)-C(263)	1.524(4)
C(12)-C(121)	1.516(4)	C(36)-C(361)	1.528(4)	C(261)-C(262)	1.539(4)
C(16)-C(15)	1.393(4)	C(31)-C(32)	1.389(4)	C(51)-O(51)	1.134(3)
C(16)-C(161)	1.520(4)	C(33)-C(32)	1.397(4)	C(52)-O(52)	1.145(3)
C(14)-C(15)	1.378(4)	C(32)-C(321)	1.511(4)		

Fully Label Ortep Diagram (35%) of **8**:



Bond Angles (°) for **8**:

C(51)-Ni(1)-C(1)	101.47(11)	C(15)-C(16)-C(161)	121.4(2)	C(22)-C(221)-C(222)	110.2(2)
C(51)-Ni(1)-Cl(1)	152.82(9)	C(11)-C(16)-C(161)	122.2(2)	C(223)-C(221)-C(222)	110.0(3)
C(1)-Ni(1)-Cl(1)	105.62(8)	C(13)-C(14)-C(15)	120.5(3)	C(33)-C(34)-C(35)	120.9(3)
C(51)-Ni(1)-Ni(2)	98.44(9)	C(14)-C(15)-C(16)	121.5(3)	C(34)-C(35)-C(36)	120.8(3)
C(1)-Ni(1)-Ni(2)	159.89(8)	C(25)-C(24)-C(23)	120.5(3)	C(35)-C(36)-C(31)	116.4(2)
Cl(1)-Ni(1)-Ni(2)	54.39(2)	C(26)-C(21)-C(22)	123.5(3)	C(35)-C(36)-C(361)	120.4(2)
C(52)-Ni(2)-C(2)	104.06(12)	C(26)-C(21)-N(2)	117.6(2)	C(31)-C(36)-C(361)	123.2(2)
C(52)-Ni(2)-Cl(1)	145.96(9)	C(22)-C(21)-N(2)	118.8(2)	C(32)-C(31)-C(36)	124.3(2)
C(2)-Ni(2)-Cl(1)	109.82(8)	C(24)-C(25)-C(26)	121.4(3)	C(32)-C(31)-N(3)	118.2(2)
C(52)-Ni(2)-Ni(1)	92.35(9)	C(23)-C(22)-C(21)	117.0(3)	C(36)-C(31)-N(3)	117.5(2)
C(2)-Ni(2)-Ni(1)	163.53(8)	C(23)-C(22)-C(221)	121.1(3)	C(34)-C(33)-C(32)	120.7(3)
Cl(1)-Ni(2)-Ni(1)	53.93(2)	C(21)-C(22)-C(221)	121.8(2)	C(31)-C(32)-C(33)	116.7(2)
Ni(1)-Cl(1)-Ni(2)	71.67(3)	C(25)-C(26)-C(21)	116.8(3)	C(31)-C(32)-C(321)	123.1(2)
C(2)-N(3)-C(5)	111.5(2)	C(25)-C(26)-C(261)	119.9(3)	C(33)-C(32)-C(321)	120.3(2)
C(2)-N(3)-C(31)	125.6(2)	C(21)-C(26)-C(261)	123.3(2)	C(363)-C(361)-C(362)	110.3(2)
C(5)-N(3)-C(31)	122.9(2)	C(22)-C(23)-C(24)	120.8(3)	C(363)-C(361)-C(36)	111.2(2)
C(1)-N(2)-C(4)	111.1(2)	C(5)-C(6)-N(4)	106.7(2)	C(362)-C(361)-C(36)	111.9(2)
C(1)-N(2)-C(21)	127.3(2)	N(3)-C(2)-N(4)	103.0(2)	C(32)-C(321)-C(323)	111.3(2)
C(4)-N(2)-C(21)	121.6(2)	N(3)-C(2)-Ni(2)	128.18(19)	C(32)-C(321)-C(322)	111.2(2)
C(1)-N(1)-C(3)	111.1(2)	N(4)-C(2)-Ni(2)	128.83(19)	C(323)-C(321)-C(322)	110.9(3)
C(1)-N(1)-C(11)	125.1(2)	C(3)-C(4)-N(2)	107.2(2)	C(12)-C(121)-C(122)	110.8(2)
C(3)-N(1)-C(11)	123.8(2)	C(4)-C(3)-N(1)	106.8(2)	C(12)-C(121)-C(123)	111.5(2)
C(14)-C(13)-C(12)	121.2(3)	C(6)-C(5)-N(3)	106.8(2)	C(122)-C(121)-C(123)	110.5(2)
C(12)-C(11)-C(16)	123.4(2)	N(2)-C(1)-N(1)	103.8(2)	C(2)-N(4)-C(6)	112.0(2)
C(12)-C(11)-N(1)	118.4(2)	N(2)-C(1)-Ni(1)	128.62(19)	C(2)-N(4)-C(41)	124.6(2)
C(16)-C(11)-N(1)	118.2(2)	N(1)-C(1)-Ni(1)	127.57(19)	C(6)-N(4)-C(41)	123.3(2)
C(11)-C(12)-C(13)	116.8(3)	C(16)-C(161)-C(162)	112.2(2)	C(46)-C(41)-C(42)	123.9(2)
C(11)-C(12)-C(121)	123.6(3)	C(16)-C(161)-C(163)	113.3(2)	C(46)-C(41)-N(4)	118.4(2)
C(13)-C(12)-C(121)	119.6(3)	C(162)-C(161)-C(163)	109.3(2)	C(42)-C(41)-N(4)	117.7(2)
C(15)-C(16)-C(11)	116.4(3)	C(22)-C(221)-C(223)	113.9(3)	C(44)-C(43)-C(42)	121.2(3)

C(43)-C(42)-C(41)	116.6(3)	C(44)-C(45)-C(46)	121.3(3)	C(422)-C(421)-C(423)	109.7(3)
C(43)-C(42)-C(421)	120.5(3)	C(46)-C(461)-C(463)	112.6(2)	C(26)-C(261)-C(263)	111.0(2)
C(41)-C(42)-C(421)	122.8(2)	C(46)-C(461)-C(462)	111.5(2)	C(26)-C(261)-C(262)	112.5(2)
C(45)-C(46)-C(41)	116.3(3)	C(463)-C(461)-C(462)	110.1(3)	C(263)-C(261)-C(262)	108.9(2)
C(45)-C(46)-C(461)	121.4(2)	C(42)-C(421)-C(422)	112.9(3)	O(51)-C(51)-Ni(1)	179.5(3)
C(41)-C(46)-C(461)	122.3(2)	C(42)-C(421)-C(423)	110.4(2)	O(52)-C(52)-Ni(2)	176.6(3)

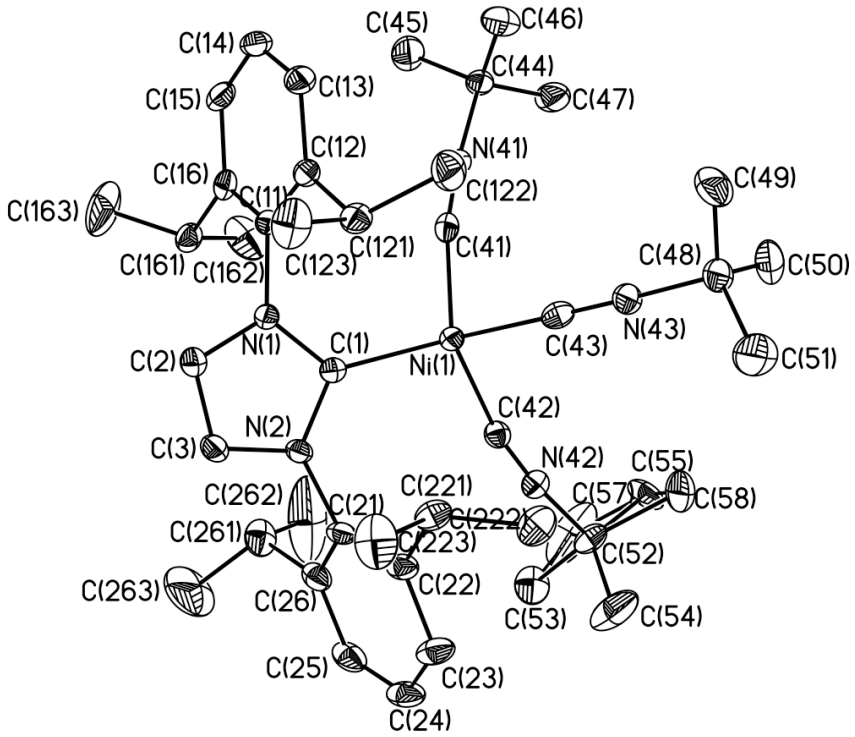
[(IPr)Ni(CN^{t}Bu)$_3$][B(Ar^F)$_4$] (9)

The space group was determined as P2(1)/c based on systematic absences and intensity statistics. Direct methods were used to locate Ni, C, N, and Si atoms. All non-hydrogen atoms were converted to and refined anisotropically. All hydrogen atoms were refined isotropically and fixed at calculated positions. A disordered *tert*-butyl group was detected and modeled to improve GoF and R1.

Crystal data and structure refinement for **9**:

Identification code	carl133a	Theta range for data collection	1.72 to 25.00°.
Empirical formula	C_{74} H_{75} B F_{24} N_5 Ni	Index ranges	-24<=h<=24
Formula weight	1559.91		-15<=k<=15
Temperature	100(2) K		-36<=l<=36
Wavelength	0.71073 Å	Reflections collected	77489
Crystal system	Monoclinic	Independent reflections	14313 [R(int) = 0.1713]
Space group	P2(1)/c	Completeness to theta = 25.00°	100.0 %
Unit cell dimensions	a = 20.610(3) Å	Absorption correction	Psi-scan
	b = 12.8020(15) Å	Max. and min. transmission	0.9360 and 0.8244
	c = 30.984(4) Å	Refinement method	Full-matrix least-squares on F^2
	a= 90°		
	b= 95.837(2)°	Data / restraints / parameters	14313 / 0 / 963
	g = 90°	Goodness-of-fit on F^2	0.999
Volume	8132.8(17) $Å^3$	Final R indices [I>2sigma(I)]	R1 = 0.0559
Z	4		wR2 = 0.1406
Density (calculated)	1.274 Mg/m^3	R indices (all data)	R1 = 0.0798
Absorption coefficient	0.335 mm^{-1}		wR2 = 0.1497
F(000)	3212	Largest diff. peak and hole	0.608 and -0.581 e.$Å^{-3}$
Crystal size	0.60 x 0.20 x 0.20 mm^3		

Fully Label Ortep Diagram (35%) of **9**:



Bond Distances (Å) for **9**:

Ni(1)-C(43)	1.906(3)	C(121)-C(122)	1.521(4)	C(26)-C(21)	1.396(4)
Ni(1)-C(42)	1.916(3)	C(121)-C(123)	1.534(4)	C(26)-C(261)	1.512(5)
Ni(1)-C(41)	1.919(3)	C(42)-N(42)	1.152(4)	C(25)-C(24)	1.364(5)
Ni(1)-C(1)	1.988(3)	C(41)-N(41)	1.160(4)	C(21)-C(22)	1.401(4)
C(1)-N(1)	1.368(3)	N(41)-C(44)	1.463(4)	C(22)-C(221)	1.512(4)
C(1)-N(2)	1.368(3)	N(42)-C(52)	1.464(4)	C(43)-N(43)	1.164(4)
C(2)-C(3)	1.345(4)	C(52)-C(53)	1.442(6)	N(43)-C(48)	1.459(4)
C(2)-N(1)	1.377(3)	C(52)-C(55)	1.477(6)	C(48)-C(50)	1.515(5)
C(3)-N(2)	1.380(4)	C(52)-C(54)	1.492(5)	C(48)-C(49)	1.516(5)
C(14)-C(13)	1.377(5)	C(44)-C(45)	1.512(5)	C(48)-C(51)	1.532(5)
C(14)-C(15)	1.384(5)	C(44)-C(47)	1.515(4)	C(221)-C(222)	1.528(5)
C(15)-C(16)	1.390(4)	C(44)-C(46)	1.524(5)	C(221)-C(223)	1.529(4)
C(13)-C(12)	1.388(4)	N(2)-C(21)	1.446(4)	C(261)-C(263)	1.494(5)
C(11)-C(12)	1.397(4)	C(16)-C(161)	1.524(4)	C(261)-C(262)	1.503(6)
C(11)-C(16)	1.398(4)	C(23)-C(24)	1.388(5)	C(161)-C(163)	1.521(5)
C(11)-N(1)	1.443(3)	C(23)-C(22)	1.398(4)	C(161)-C(162)	1.521(5)
C(12)-C(121)	1.524(4)	C(26)-C(25)	1.396(5)		

Bond Angles (°) for **9**:

C(43)-Ni(1)-C(42)	93.04(13)	N(1)-C(1)-Ni(1)	128.36(19)	C(12)-C(11)-C(16)	123.2(3)
C(43)-Ni(1)-C(41)	92.42(12)	N(2)-C(1)-Ni(1)	128.7(2)	C(12)-C(11)-N(1)	118.6(2)
C(42)-Ni(1)-C(41)	125.54(12)	C(3)-C(2)-N(1)	106.1(3)	C(16)-C(11)-N(1)	118.0(2)
C(43)-Ni(1)-C(1)	133.54(12)	C(2)-C(3)-N(2)	106.9(3)	C(13)-C(12)-C(11)	117.1(3)
C(42)-Ni(1)-C(1)	107.03(12)	C(13)-C(14)-C(15)	120.9(3)	C(13)-C(12)-C(121)	121.0(3)
C(41)-Ni(1)-C(1)	107.54(12)	C(14)-C(15)-C(16)	120.5(3)	C(11)-C(12)-C(121)	121.9(3)
N(1)-C(1)-N(2)	102.1(2)	C(14)-C(13)-C(12)	121.0(3)	C(122)-C(121)-C(12)	112.8(3)

C(122)-C(121)-C(123)	110.5(3)	C(1)-N(2)-C(21)	127.1(2)	C(21)-C(22)-C(221)	122.7(3)
C(12)-C(121)-C(123)	110.3(3)	C(3)-N(2)-C(21)	120.8(2)	N(43)-C(43)-Ni(1)	176.1(3)
N(42)-C(42)-Ni(1)	169.4(3)	C(1)-N(1)-C(2)	112.7(2)	C(43)-N(43)-C(48)	175.8(3)
N(41)-C(41)-Ni(1)	169.2(3)	C(1)-N(1)-C(11)	126.0(2)	N(43)-C(48)-C(50)	107.3(3)
C(41)-N(41)-C(44)	174.1(3)	C(2)-N(1)-C(11)	121.3(2)	N(43)-C(48)-C(49)	107.8(3)
C(42)-N(42)-C(52)	173.1(3)	C(15)-C(16)-C(11)	117.3(3)	C(50)-C(48)-C(49)	111.3(3)
C(53)-C(52)-N(42)	108.5(3)	C(15)-C(16)-C(161)	121.0(3)	N(43)-C(48)-C(51)	107.0(3)
C(53)-C(52)-C(55)	114.9(6)	C(11)-C(16)-C(161)	121.7(3)	C(50)-C(48)-C(51)	112.4(3)
N(42)-C(52)-C(55)	107.2(3)	C(24)-C(23)-C(22)	120.7(3)	C(49)-C(48)-C(51)	110.8(3)
C(53)-C(52)-C(54)	109.4(5)	C(25)-C(26)-C(21)	116.8(3)	C(22)-C(221)-C(222)	112.7(3)
N(42)-C(52)-C(54)	108.7(3)	C(25)-C(26)-C(261)	121.2(3)	C(22)-C(221)-C(223)	111.6(3)
C(55)-C(52)-C(54)	108.0(4)	C(21)-C(26)-C(261)	122.0(3)	C(222)-C(221)-C(223)	110.8(3)
N(41)-C(44)-C(45)	108.1(3)	C(24)-C(25)-C(26)	121.3(3)	C(263)-C(261)-C(262)	109.4(4)
N(41)-C(44)-C(47)	107.1(2)	C(26)-C(21)-C(22)	123.6(3)	C(263)-C(261)-C(26)	113.2(4)
C(45)-C(44)-C(47)	113.0(3)	C(26)-C(21)-N(2)	118.2(3)	C(262)-C(261)-C(26)	110.3(3)
N(41)-C(44)-C(46)	107.0(3)	C(22)-C(21)-N(2)	118.0(2)	C(163)-C(161)-C(162)	111.2(3)
C(45)-C(44)-C(46)	110.6(3)	C(25)-C(24)-C(23)	120.8(3)	C(163)-C(161)-C(16)	111.8(3)
C(47)-C(44)-C(46)	110.8(3)	C(23)-C(22)-C(21)	116.6(3)	C(162)-C(161)-C(16)	111.3(3)
C(1)-N(2)-C(3)	112.1(2)	C(23)-C(22)-C(221)	120.7(3)		