Nickel(I) Monomers and Dimers with Cyclopentadienyl and Indenyl Ligands


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Supporting Information: Nickel(I) Monomers and Dimers with Cyclopentadienyl and Indenyl Ligands

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Experimental Procedures and Characterizing Data for New Compounds

(μ-Cp)(μ-Cl)Ni₂(IPr)₂ (1a)

To a solution of (μ-Cl)₂Ni₂(IPr)₂ (83.4 mg, 0.086 mmol) in 4 mL diethyl ether at -35°C, NaCp (7.0 mg, 0.08 mmol) was added. The mixture was stirred at -35°C for 6 hours. The volatiles were removed under vacuum. The resulting residue was extracted with pentane (2 x 5 mL). The combined solution from the extractions was filtered through celite and dried under reduced pressure to give 1a as a green solid which was purified by recrystallization from a benzene/pentane solution. Single crystals for X-ray analysis were grown from a pentane solution at -35°C. Yield: 44.7 mg (52%).

![Diagram of 1a]

Anal. calcd (found) for C₅₉H₇₇N₄ClNi₂: C, 71.21 (71.18); H, 7.80 (7.89); N, 5.63 (5.39). ¹H NMR (400 MHz, C₇D₈, 223 K): 7.16-6.97 (m, 12H, H₈ and H₇), 6.43 (s, 4H, H₉), 3.93 (s, 5H, Cp), 3.17 (septet, J = 6.4 Hz, 8H, H₆), 1.43 (d, J = 6.2 Hz, 24H, H₅), 1.13 (d, J = 6.4 Hz, 24H, H₅). ¹³C{¹H} NMR (125.7 MHz, C₇D₈, 223 K): 188.1, 145.8, 137.6, 123.6, 122.6, 79.5, 28.7, 25.8, 23.1. UV-Vis λmax (ε): 272 nm (88016), 326 nm (63095), 384 nm (71111), 608 nm (786, br).

(μ-Cp)(μ-Cl)Ni₂(SIPr)₂ (1b)

To a solution of (μ-Cl)₂Ni₂(SIPr)₂ (82.4 mg, 0.084 mmol) in 8 mL diethyl ether at -35°C, NaCp (7.4 mg, 0.084 mmol) was added. The mixture was stirred at -35°C for 8 hours. The volatiles were removed under vacuum. The resulting residue was extracted with pentane (2 x 5 mL). The combined solution from the extractions was filtered through celite and dried under reduced pressure to give 1b as a green solid which was purified by recrystallization from a benzene/pentane solution. Yield: 65 mg (77%).

![Diagram of 1b]
Anal. calcd (found) for C_{59}H_{77}ClNi_2: C, 70.93 (70.56); H, 8.17 (7.76); N, 5.61 (5.43). \(^1\)H NMR (500 MHz, C\(_7\)D\(_8\), 203 K): 7.16 (m, 12H, H8 and H7), 3.91 (s, 5H, Cp), 3.49 (m, 8H, H6), 3.31 (br s, 8H, H9), 1.47 (br s, 24H, H5), 1.24 (br s, 24H, H5). \(^1^3\)C\{\(^1\)H\} NMR (125.7 MHz, C\(_7\)D\(_8\), 203 K): 214.3, 148.1, 138.4, 188.0, 137.6, 124.7, - 81.1, 54.2, 29.1, 26.9, 24.5. UV-Vis \(\lambda_{\text{max}}\) (\(\varepsilon\)): 280 nm (78464), 331 nm (41531), 382 nm (65693), 633 nm (571, br).

(\(\mu\)-Ind)(\(\mu\)-Cl)Ni_2(IPr)_2 (2a)

To a solution of (\(\mu\)-Cl)_2Ni_2(IPr)_2 (46 mg, 0.048 mmol) in 6 mL diethyl ether at -35°C, LiInd (5.8 mg, 0.048 mmol) was added. The mixture was stirred at -35°C for 6 hours. The volatiles were removed under vacuum. The resulting residue was extracted with benzene (2 x 3 mL). The combined solution from the extractions was filtered through celite and dried under reduced pressure to give 2a as a green solid which was purified by recrystallization from a benzene/pentane solution.

Anal. calcd (found) for C_{63}H_{79}ClNi_2: C, 72.40 (72.41); H, 7.62 (8.06); N, 5.36 (5.14). \(^1\)H NMR (400 MHz, C\(_6\)D\(_6\)): 7.22 (t, \(J = 7.3\) Hz, 4H, H8), 7.10 (d, \(J = 7.3\) Hz, 8H, H7), 6.76 (m, 2H, H3/H3’ or H4/H4’), 6.57 (s, 4H, H9), 6.55 (m, 2H, H3/H3’ or H4/H4’), 3.59 (d, \(J = 4.0\) Hz, 2H, H2), 3.31 (septet, \(J = 6.8\) Hz, 4H, H6), 3.03 (septet, \(J = 6.8\) Hz, 4H, H6), 2.48 (t, \(J = 4.3\) Hz, 1H, H1), 1.34 (d, \(J = 6.8\) Hz, 12H, H5), 1.15 (d, \(J = 6.8\) Hz, 12H, H5), 1.12 (d, \(J = 6.8\) Hz, 12H, H5), 1.08 (d, \(J = 6.8\) Hz, 12H, H5). \(^1^3\)Cl\{\(^1\)H\} NMR (125.7 MHz, C\(_6\)D\(_6\)): 190.7, 148.9, 146.7, 146.2, 138.1, 124.5, 124.3, 124.2, 122.3, 121.5, 52.1, 34.6, 29.2, 26.5, 25.9, 23.9. UV-Vis \(\lambda_{\text{max}}\) (\(\varepsilon\)): 265 nm (18798, sh), 316 nm (18224, sh), 344 nm (20066), 382 nm (19392), 614 nm (867, br).

(\(\mu\)-Ind)(\(\mu\)-Cl)Ni_2(SIPr)_2 (2b)

To a solution of (\(\mu\)-Cl)_2Ni_2(SIPr)_2 (97.3 mg, 0.099 mmol) in 8 mL diethyl ether at -35°C, LiInd (12.1 mg, 0.099 mmol) was added. The mixture was stirred at -35°C for 6 hours. The volatiles were removed under vacuum. The resulting residue was washed with pentane and extracted with benzene (3 x 4 mL). The combined solution from the extractions was filtered
through celite and the volume of solution was reduced to ~1 mL under reduced pressure. Approximately 4 mL pentane was then added, which caused a solid to precipitate. The resulting precipitate was collected by filtration, washed with pentane and dried in vacuo to give 2b as a green solid. Single crystals for X-ray analysis were grown from a benzene/pentane solution at room temperature. Yield: 81 mg (78%).

Anal. calcd (found) for C_{63}H_{81}ClN_{4}Ni_{2}: C, 72.26 (72.03); H, 7.80 (7.92); N, 5.35 (4.91). \(^1\)H NMR (400 MHz, C\(_6\)D\(_6\)): 7.20 (d, \(J = 8\) Hz, 4H, H8), 7.08 (t, \(J = 8\) Hz, 8H, H7), 6.76 (m, 2H, H3/H3’ or H4/H4’), 6.52 (m, 2H, H3/H3’ or H4/H4’), 3.74 (d, \(J = 4\) Hz, 2H, H2), 3.50 (s, 8H, H9), 3.47 (septet, \(J = 6.8\) Hz, 8H, H6), 2.49 (t, \(J = 4\) Hz, 1H, H1), 1.37 (d, \(J = 6.8\) Hz, 12H, H5), 1.19 (d, \(J = 6.8\) Hz, 12H, H5), 1.18 (d, \(J = 6.8\) Hz, 12H, H5), 1.13 (d, \(J = 6.8\) Hz, 12H, H5). \(^{13}\)C\(^{1}\)H NMR (125.7 MHz, C\(_6\)D\(_6\)): 217.3, 149.1, 147.7, 147.2, 138.9, 125.0, 124.7, 122.5, 121.6, 54.4, 35.4, 29.2, 29.1, 26.6, 24.8, 24.5. UV-Vis \(\lambda_{\text{max}}(\varepsilon)\): 316 nm (12802), 344 nm (11622, sh), 384 nm (10863), 604 nm (572, br).

\((\mu\text{-Ind})(\mu\text{-Cl})\text{Ni}_2(\text{IPr})(\text{SIPr})\) (2ab)

To a solution of 4b (20.3 mg, 0.036 mmol) in 1 mL benzene, (\(\mu\text{-Cl})_2\text{Ni}_2(\text{IPr})_2\) (17.3 mg, 0.018 mmol) was added. The solution changed from red to green. The mixture was stirred for 0.5 hours and the volatiles were removed under vacuum. The resulting residue was washed with pentane and dried in vacuo to give crude 2ab as a green solid which was purified by recrystallization from a benzene/pentane solution. Yield: 31 mg (82%).

Anal. calcd (found) for C_{63}H_{81}ClN_{4}Ni_{2}: C, 72.26 (71.83); H, 7.80 (8.12); N, 5.35 (4.94). \(^1\)H NMR (400 MHz, C\(_6\)D\(_6\)): 7.23-7.02 (m, 12H, Ph), 6.82 (t, \(J = 5.6\) Hz, 1H), 6.78 (m, 2H, H3/H3’ or H4/H4’), 6.68 (t, 2H, H3/H3’ or H4/H4’), 6.58 (s, 2H, H5), 3.65 (d, \(J = 2.4\) Hz,
1H, H2 or H2’), 3.57 (d, J = 2.4 Hz, 1H, H2 or H2’), 3.47 (m, 4H, H8), 3.29 (septet, J = 5.2 Hz, 2H, H6), 3.02 (septet, J = 5.2 Hz, 2H, H6), 2.38 (t, J = 5.2 Hz, 1H, H1), 1.41 (d, J = 5.2 Hz, 6H, H9 or H10), 1.35 (d, J = 5.2 Hz, 6H, H9 or H10), 1.23 (d, J = 5.2 Hz, 12H, H9 or H10), 1.20 (d, J = 5.2 Hz, 6H, H9 or H10), 1.10 (d, J = 5.2 Hz, 6H, H9 or H10), 1.04 (d, J = 5.2 Hz, 6H, H9 or H10), 0.98 (d, J = 5.2 Hz, 6H, H9 or H10). \(^{13}\text{C}^{1\text{H}}\) NMR (125.7 MHz, C\(_6\)D\(_6\)): 217.5, 190.9, 149.3, 149.2, 147.9, 146.7, 146.6, 146.4, 138.2, 129.7, 128.9, 128.7, 125.4, 124.5, 124.4, 124.2, 122.6, 122.3, 121.6, 121.5, 54.6, 52.8, 29.2, 29.1, 26.8, 26.6, 26.4, 26.0, 24.8, 24.7, 23.8, 23.6. UV-Vis \(\lambda_{\text{max}}\) (\(\varepsilon\)): 346 nm (385895), 379 nm (406667), 601 nm (4451, br).

(\(\eta^5\text{-Cp}\))Ni(IPr) (3a)

NaCp (11 mg, 0.12 mmol) was added to a solution of (\(\mu\text{-Cl}\))\(_2\)Ni\(_2\))(IPr) \(_2\) (58.5 mg, 0.06 mmol) in 6 mL diethyl ether. The mixture was stirred at room temperature for 2 hours. The volatiles were removed under vacuum. The resulting residue was extracted with benzene (2 x 2 mL). The combined solution from the extractions was filtered through celite, dried under reduced pressure, washed with pentane (~2 x 1 mL) and further dried under vacuum to give 3a as a yellow solid. Single crystals for X-ray analysis were grown from a benzene/pentane solution at -35°C. Yield: 52 mg (83%).

Anal. calcd (found) for C\(_{33}\)H\(_{41}\)N\(_2\)Ni: C, 75.01 (74.20); H, 8.07 (7.95); N, 5.47 (5.25). \(^1\text{H}\) NMR (400 MHz, C\(_6\)D\(_6\)): 26.29 (2H), 7.27 (4H), 5.28 (4H), 3.68 (2H), 2.12 (12H), 1.45 (12H), -39.85 (5H). Magnetic susceptibility (C\(_6\)D\(_6\)): 1.87 \(\mu_B\). UV-Vis \(\lambda_{\text{max}}\) (\(\varepsilon\)): 267 nm (8095), 333 nm (6358), 416 nm (5723).

(\(\eta^5\text{-Cp}\))Ni(SIPr) (3b)

NaCp (35.6 mg, 0.40 mmol) was added to a solution of (\(\mu\text{-Cl}\))\(_2\)Ni\(_2\))(SIPr) \(_2\) (195.2 mg, 0.20 mmol) in 12 mL diethyl ether. The mixture was stirred at room temperature for 2 hours. The volatiles were removed under vacuum. The resulting residue was extracted with benzene (2 x 4 mL). The combined solution from the extractions was filtered through celite, dried under reduced pressure, washed with pentane (~2 x 1 mL) and further dried under vacuum to give 3b as a yellow solid. Yield: 153 mg (73%).
Anal. calcd (found) for C$_{33}$H$_{43}$N$_2$Ni: C, 74.72 (73.37); H, 8.43 (8.39); N, 5.45 (4.91). $^1$H NMR (400 MHz, C$_6$D$_6$): 7.26 (4H), 6.29 (6H), 3.95 (10H), 2.83 (2H), 1.92 (13H), -11.49 (4H), -44.96 (5H). Magnetic susceptibility (C$_6$D$_6$): 1.71 $\mu$B. UV-Vis $\lambda_{\text{max}}$ (ε): 247 nm (14700), 329 nm (5870), 411 nm (5314).

$(\eta^5$-Ind)Ni(IPr) (4a)

LiInd (21.5 mg, 0.176 mmol) was added to a solution of (µ-Cl)$_2$Ni$_2$(IPr)$_2$ (84.9 mg, 0.088 mmol) in 10 mL diethyl ether. The mixture was stirred at room temperature for 2 hours. The volatiles were removed under vacuum. The resulting residue was extracted with pentane (4 x 5 mL). The combined solution from the extractions was filtered through celite and reduced to ~0.5 mL under reduced pressure. The mixture was left to stand at -35ºC for 6 hours. The resulting precipitate was collected and dried under vacuum to give 4a as an orange solid. Single crystals for X-ray analysis were grown from a pentane solution at -35ºC. Yield: 70 mg (72%).

Anal. calcd (found) for C$_{36}$H$_{45}$N$_2$Ni: C, 76.88 (75.07); H, 7.71 (7.66); N, 4.98 (4.79). $^1$H NMR (400 MHz, C$_6$D$_6$): 19.27 (2H), 6.08 (5H), 4.51 (4H), 2.58 (12H), 1.92 (14H), 1.34 (1H), 1.13 (2H), 0.94 (1H), -14.56 (2H). Magnetic susceptibility (C$_6$D$_6$): 1.61 $\mu$B. UV-Vis $\lambda_{\text{max}}$ (ε): 247 nm (20933), 333 nm (6358), 416 nm (5723).

$(\eta^5$-Ind)Ni(SIPr) (4b)

LiInd (35.4 mg, 0.29 mmol) was added to a solution of (µ-Cl)$_2$Ni$_2$(SIPr)$_2$ (140.3 mg, 0.14 mmol) in 14 mL diethyl ether. The mixture was stirred at room temperature for 2 hours. The volatiles were removed under vacuum. The resulting residue was extracted with pentane (4 x 8 mL). The combined solution from the extractions was filtered through celite and reduced to ~0.5 mL under reduced pressure. The mixture was left to stand at -35ºC for 6 hours. The resulting precipitate was collected and further dried under vacuum to give 4b as an orange solid. Single crystals for X-ray analysis were grown from a saturated pentane solution at -35ºC. Yield: 123 mg (76%).

Anal. calcd (found) for C$_{36}$H$_{48}$N$_2$Ni: C, 76.60 (75.87); H, 8.04 (7.95); N, 4.96 (4.82). $^1$H NMR (400 MHz, C$_6$D$_6$): 7.26 (6H), 6.43 (5H), 4.48 (12H), 3.33 (3H), 1.91 (13H), -3.80 (4H),
-15.61 (2H). Magnetic susceptibility (C₆D₆): 1.57 μB. UV-Vis λ_max (ε): 312 nm (8438, sh), 362 nm (7720), 451 nm (1729, sh), 524 nm (1158, br).

(η⁵-C₅)Ni(IPr)(THF)PF₆

FcPF₆ (30 mg, 0.09 mmol) was added to a solution of (η⁵-C₅)Ni(IPr) (47.6 mg, 0.09 mmol) in 2 mL THF. The mixture was stirred for 16 hours at room temperature. The solution was reduced to ~0.2 mL under vacuum and a solid formed upon addition of diethyl ether. The resulting precipitate was collected by filtration, washed with diethyl ether and dried under vacuum to give (η⁵-C₅)Ni(IPr)(THF)PF₆ as a red solid. Yield: 42 mg (63%).

¹H NMR (400 MHz, CD₂Cl₂, 203 K): 7.57 (t, J = 7.7 Hz, 2H, Ph), 7.42 (d, J = 7.8 Hz, 4H, Ph), 7.30 (s, 2H, CH=CH from IPr), 4.54 (s, 5H, C₅p), 2.88 (m, 4H, CHMe₂), 2.67 (br s, 4H, THF), 1.35 (br s, 16H, C₆H₃ from IPr and THF).

¹³C{¹H} NMR (125.7 MHz, C₆D₆, 203 K): 157.2, 144.5, 135.0, 130.6, 126.8, 124.5, 92.56, 80.9, 67.8, 28.7, 25.6, 25.3, 21.9.

Exposure of (η⁵-C₅)Ni(IPr)(THF)PF₆ to high vacuum resulted in the formation of a new compound which was insoluble except in the presence of THF, when it reverted back to (η⁵-C₅)Ni(IPr)(THF)PF₆. Elemental analysis on the new compound was consistent with (η⁵-C₅)Ni(IPr)PF₆ Anal. calcd (found) for C₃₃H₄₁N₂PF₆Ni: C, 59.22 (58.94); H, 6.17 (6.14); N, 4.19 (3.98).

Reaction of (η⁵-C₅)Ni(IPr)(THF)PF₆ with tetrabutylammonium chloride

To a suspension of (η⁵-C₅)Ni(IPr)(THF)PF₆ (10 mg, 0.012 mmol) in 0.7 mL C₆D₆, tetrabutylammonium chloride (3.8 mg, 0.012 mmol) was added. After 5 min, an orange-red solution formed. ¹H NMR spectroscopy indicated quantitative conversion into (η⁵-C₅)Ni(IPr)(Cl).[1]

Reaction of 3a with methyl iodide

To a solution of 3a (22 mg, 0.042 mmol) in 2 mL C₆H₆, methyl iodide (1.3 μL, 0.021 mmol) was added. After 5 min, the volatiles were removed under vacuum. ¹H NMR spectroscopy of the residue in C₆D₆ indicated the quantitative formation of 1:1 mixture of (η⁵-
Cp)Ni(IPr)(Me) and (η⁵-Cp)Ni(IPr)(I), which have been synthesized by alternative routes and fully characterized.

(η⁵-Cp)Ni(IPr)(Me)
To a suspension of CpNi(IPr)Cl (200 mg, 0.36 mmol) in 8 mL diethyl ether at -35°C, methylmagnesium chloride (3M in THF, 0.12 mL, 0.36 mmol) was added. The mixture was slowly warmed to room temperature. The volatiles were removed under vacuum. The resulting residue was extracted with benzene (2 x 3 mL). The combined solution from the extractions was filtered through Celite and dried under reduced pressure to give (η⁵-Cp)Ni(IPr)(Me) as an olive green solid. Yield: 126 mg (64%).

¹H NMR (400 MHz, C⁶D₆): 7.28 (t, J = 7.8 Hz, 2H, Ph), 7.18 (d, J = 7.4 Hz, 4H, Ph), 6.55 (s, 2H, CH=CH from IPr), 4.88 (s, 5H, Cp), 3.04 (septet, 4H, CHMe₂), 1.42 (d, J = 6.4 Hz, 12H, CH₃ from IPr), 1.00 (d, J = 6.4 Hz, 12H, CH₃ from IPr), -0.71 (s, 3H, CH₃). ¹³C{¹H} NMR (125.7 MHz, C⁶D₆): 190.8, 146.8, 138.0, 130.2, 124.4, 90.3, 29.4, 26.3, 23.0, -34.4.

(η⁵-Cp)Ni(IPr)(I)
To a solution of CpNi(IPr)Cl (92 mg, 0.17 mmol) in 4 mL THF, sodium iodide (252 mg, 1.7 mmol) was added. The mixture was stirred at room temperature for 16 hours. The volatiles were removed under vacuum. The resulting residue was extracted with toluene (2 x 4 mL). The combined solution from the extractions was filtered through celite and the volume of solution was reduced to ~0.5 mL under reduced pressure. Pentane was then added until a precipitate formed. The resulting precipitate was collected by filtration, washed with pentane and dried in vacuo to give (η⁵-Cp)Ni(IPr)(I) as a purple solid. Yield: 78 mg (72%).

Anal. calcd (found) for C₃₃H₄₁N₂NiI: C, 60.86 (60.65); H, 6.35 (6.42); N, 4.30 (4.20). ¹H NMR (400 MHz, C₆D₆): 7.29 (t, J = 8.4 Hz, 2H, Ph), 7.20 (d, J = 8.1 Hz, 4H, Ph), 6.64 (s, 2H, CH=CH from IPr), 4.84 (s, 5H, Cp), 3.07 (br s, 4H, CHMe₂), 1.45 (d, J = 6.7 Hz, 12H, CH₃ from IPr), 0.95 (d, J = 6.8 Hz, 12H, CH₃ from IPr). ¹³C{¹H} NMR (125.7 MHz, C₆D₆): 176.8, 147.1, 137.8, 130.8, 126.4, 124.7, 92.8, 29.4, 26.8, 23.4.
After three freeze-pump-thaw cycles, excess 1 atm CO was introduced via a dual manifold Schlenk line to a solution of 3a (6 mg, 0.01 mmol) in 0.5 mL C₆D₆ at room temperature. ¹H NMR spectroscopy indicated quantitative conversion into (CO)₃Ni(IPr).[²]

(allylether)Ni(IPr)
To a solution of 3a (8 mg, 0.019 mmol) in 0.5 mL C₆D₆ at room temperature, allylether (2.3 µL, 0.019 mmol) was added. The mixture was heated at 50ºC for 29 hours. ¹H NMR spectroscopy indicated quantitative conversion into (allylether)Ni(IPr).[³]

(dvse)Ni(IPr)
To a solution of 3a (8 mg, 0.015 mmol) in 0.5 mL C₆D₆ at room temperature, dvse (3.4 µL, 0.015 mmol) was added. The mixture was heated at 50ºC for 92 hours. ¹H NMR spectroscopy indicated 96% conversion into (dvse)Ni(IPr).[³]

General procedure for the Suzuki-Miyaura Reaction
To a suspension of p-chlorotoluene (6.4 mg, 0.05 mmol), phenylboronic acid (6.7 mg, 0.05 mmol) and KO²Bu (16.8 mg, 0.15 mmol) in 0.5 mL benzene in a J. Young NMR tube, the appropriate Ni precatalyst (0.005 mmol) was added. The mixture was heated at 70ºC for 3.5 hours. The solvent was removed under vacuum. The residue was extracted with 0.8 mL CDCl₃ and filtered through celite. To this extraction, 1,3,5-trimethoxybenzene (8.4 mg, 0.05 mmol) was added as an internal standard. The yield of product was determined by ¹H NMR spectroscopy.
Procedure for EPR Spectroscopy and Spectra of Selected Compounds

Samples for EPR spectroscopy were prepared in a nitrogen filled glovebox by dissolving each complex in toluene. For each sample, 200 μL volume of 1 mM complex was pipetted into an EPR tube and the EPR tube was sealed in the glovebox. X-band EPR spectra were acquired on a Bruker ELEXSYS E500 EPR spectrometer equipped with a SHQ resonator and an Oxford ESR-900 helium-flow cryostat. EPR scans were acquired at 7 K with the following instrumental parameters: microwave frequency 9.39 GHz, modulation frequency 100 kHz, modulation amplitude 5 G, and microwave power 0.1 mW. Simulations of the EPR spectra were done using MATLAB 7.8 software and the EasySpin 4.0.0 package. Table S1 gives the Gaussian FWHM broadenings along the x-, y-, and z-axis used for each simulation.

Table S1: Gaussian FWHM broadenings along the x-, y-, and z-axis used for EPR simulation of 3a, 3b, 4a, and 4b.

<table>
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<tr>
<th>Compound/Gaussian broadening</th>
<th>Along x-axis FWHM (MHz)</th>
<th>Along y-axis FWHM (MHz)</th>
<th>Along z-axis FWHM (MHz)</th>
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<tr>
<td>3a</td>
<td>280</td>
<td>85</td>
<td>75</td>
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<tr>
<td>3b</td>
<td>120</td>
<td>210</td>
<td>48</td>
</tr>
<tr>
<td>4a</td>
<td>115</td>
<td>140</td>
<td>100</td>
</tr>
<tr>
<td>4b</td>
<td>120</td>
<td>210</td>
<td>48</td>
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Figure S1: X-band CW EPR spectrum of 3b (blue) in toluene at 7K and the corresponding simulation (green). The g-values from the simulation are $g_1 = 2.349$, $g_2 = 2.267$ and $g_3 = 2.062$. 

![EPR Spectrum](image-url)
**Figure S2:** X-band CW EPR spectrum of 4a (blue) in toluene at 7K and the corresponding simulation (green). The g-values from the simulation are $g_1 = 2.328$, $g_2 = 2.242$ and $g_3 = 2.085$.

**Figure S3:** X-band CW EPR spectrum of 4b (blue) in toluene at 7K and the corresponding simulation (green). The g-values from the simulation are $g_1 = 2.340$, $g_2 = 2.207$ and $g_3 = 2.072$. 
**Figure S4**: Overlay of X-band CW EPR spectra of 3a (IPrNiCp, black), 3b (SIPrNiCp, blue), 4a (IPrNiInd, red) and 4b (SIPrNiInd, magenta) in toluene at 7K.

![EPR Spectra Overlay](image)

**Table S2**: Simulated g-values for the EPR spectra of 3a, 3b, 4a and 4b.

<table>
<thead>
<tr>
<th>Compound/g-value</th>
<th>g₁</th>
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<th>g₃</th>
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<tbody>
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<td>3a</td>
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</tr>
<tr>
<td>4b</td>
<td>2.340</td>
<td>2.207</td>
<td>2.072</td>
</tr>
</tbody>
</table>
Procedure for SQUID Experiments and Data of Selected Compounds
The magnetic susceptibility measurements were obtained using a Quantum Design SQUID magnetometer MPMS operating between 2 and 300 K for dc-applied fields at 0.1 T. Dc analyses were performed on polycrystalline samples of 39.8, 12.7, 38.9 and 14.9 mg for 3a, 3b, 4a and 4b, respectively, wrapped in a polyethylenemembrane.

DC susceptibility measurements
The measured molar magnetic susceptibility of 3a-4b in a field of 0.1 T are plotted as a function of temperature in Figure S5. At room temperature, the $\chi T$ product is 0.45, 0.47, 0.51 and 0.55 cm$^3$K/mol for 3a, 3b, 4a and 4b, respectively. The theoretical $\chi T$ value for S=1/2 is 0.375 cm$^3$K/mol and for S=1, 1 cm$^3$K/mol if g is equal to 2. All measured $\chi T$ values are close to the S=1/2 value which is consistent with a one unpaired electron system. The $\chi T$ values can also be converted by

$$\mu_{eff} = \sqrt{8 \chi MT} \text{ (no units)}$$

At room temperature, the $\mu_{eff}$ values are 1.90, 1.93, 2.0 and 2.09 for 3a, 3b, 4a and 4b, respectively. Theoretical values, $\mu_{eff}$ of S=1/2 is 1.732 and S=1 is 2.828.

The g values can be calculated from the equation:

$$\chi T = \frac{g^2 * S(S + 1)}{8}$$

At room temperature, the $\chi T$ values correspond to g = 2.19, 2.24, 2.33 and 2.42 for 3a, 3b, 4a and 4b, respectively, when S = 1/2.
Figure S5: Temperature dependence of the $\chi$ products at 0.1 T for 3a (IPrNiCp, blue), 3b (SIPrNiCp, red), 4a (IPrNiInd, black) and 4b (SIPrNiInd, green) (with $\chi = M/H$ normalized per mol).

For mononuclear paramagnetic metal systems, the $\chi T$ vs $T$ plot should be a horizontal straight line which obeys the Curie Law (Figures S6 and S7). However, the $\chi T$ values of all complexes decreased slightly with the decrease in temperature. The obvious reason for the decreasing $\chi T$ values may be a small diamagnetic contribution since the $\chi T$ value of $S = 1/2$ is very small; however, this effect is normally considered negligible in high spin systems. The $\chi T$ values decreased to reach 0.35 (1.67), 0.20 (1.25), 0.23 (1.36) and 0.24 (1.38) cm$^3$K/mol ($\mu_{eff}$) for 3a, 3b, 4a and 4b, respectively, at 2.0 K due to the weak intermolecular antiferromagnetic interaction.
Figure S6: Temperature dependence of the $\chi T$ products at 0.1 T for 3a (IPrNiCp, red), 3b (SIPrNiCp, blue), 4a (IPrNiInd, black) and 4b (SIPrNiInd, green) (with $\chi = M/H$ normalized per mol).

Figure S7: Temperature dependence of $\mu_{\text{eff}}$ at 0.1 T for 3a (IPrNiCp, black), 3b (SIPrNiCp, blue), 4a (IPrNiInd, red) and 4b (SIPrNiInd, green) (with $\chi = M/H$ normalized per mol).
Procedure for Electrochemistry and CVs of Selected Compounds

Electrochemistry voltammetric data were collected using an air tight three-electrode system, which was assembled in a nitrogen filled glovebox. The working electrode was a 2 mm diameter platinum electrode. The reference and counter electrodes were 0.8 mm platinum wires. The electrolyte was 0.10 M \textsuperscript{n}Bu\textsubscript{4}NPF\textsubscript{6} in THF, which was synthesized by the metathesis of Bu\textsubscript{4}NBr and HPF\textsubscript{6}, recrystallized from hot ethanol, and dried under vacuum overnight. The THF used in the experiment was HPLC grade and dried before use. Ferrocene was used as internal standard. Cyclic voltammetry data were measured with Princeton Applied Research VersaSTAT 4 potentiostatic instrumentation.

Table S3: Tabulated cyclic voltammetry data of 1.6 mM Ni complexes (3a, 3b, 4a and 4b) in 0.1 M \textsuperscript{n}Bu\textsubscript{4}NP\textsubscript{F} in THF at a Pt working electrode.

<table>
<thead>
<tr>
<th></th>
<th>3a</th>
<th>3b</th>
<th>4a</th>
<th>4b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidation Potential vs. Fc\textsuperscript{+}/Fc</td>
<td>-0.66 V</td>
<td>-0.75 V</td>
<td>-0.41 V</td>
<td>-0.64 V</td>
</tr>
<tr>
<td>Reduction Potential vs. Fc\textsuperscript{+}/Fc</td>
<td>-2.57 V</td>
<td>-2.73 V</td>
<td>-2.27 V</td>
<td>-2.30 V</td>
</tr>
</tbody>
</table>

Figure S8: CV of 3a (1.6 mM) at reductive potentials in a 0.10 M \textsuperscript{n}Bu\textsubscript{4}NP\textsubscript{F} solution of THF under N\textsubscript{2} at room temperature. The working electrode was a 2.0 mm diameter platinum disk, and the scan rate was 0.50 V s\textsuperscript{-1}. 

![Cyclic Voltammetry Graph](image)
**Figure S9:** CV of 3b (1.6 mM) at reductive potentials in a 0.10 M {\textsuperscript{6}Bu}_{4}NPF_{6} solution of THF under \textsubscript{N}2 at room temperature. The working electrode was a 2.0 mm diameter platinum disk, and the scan rate was 0.50 V s\textsuperscript{-1}.

**Figure S10:** CV of 4a (1.6 mM) at reductive potentials in a 0.10 M {\textsuperscript{6}Bu}_{4}NPF_{6} solution of THF under \textsubscript{N}2 at room temperature. The working electrode was a 2.0 mm diameter platinum disk, and the scan rate was 0.50 V s\textsuperscript{-1}.
Figure S11: CV of 4b (1.6 mM) at reductive potentials in a 0.10 M nBu4PF6 solution of THF under N2 at room temperature. The working electrode was a 2.0 mm diameter platinum disk, and the scan rate was 0.50 V s⁻¹.

![Graph showing redox behavior of 4b](image1.png)

Figure S12: CV of 3a (1.6 mM) at oxidative potentials in a 0.10 M nBu4PF6 solution of THF under N2 at room temperature. The working electrode was a 2.0 mm diameter platinum disk, and the scan rate was 0.50 V s⁻¹.

![Graph showing redox behavior of 3a](image2.png)
Figure S13: CV of 3b (1.6 mM) at oxidative potentials in a 0.10 M "Bu4NPF6 solution of THF under N2 at room temperature. The working electrode was a 2.0 mm diameter platinum disk, and the scan rate was 0.50 V s\(^{-1}\).

Figure S14: CV of 4a (1.6 mM) at oxidative potentials in a 0.10 M "Bu4NPF6 solution of THF under N2 at room temperature. The working electrode was a 2.0 mm diameter platinum disk, and the scan rate was 0.50 V s\(^{-1}\).
**Figure S15:** CV of 4b (1.6 mM) at oxidative potentials in a 0.10 M "Bu4NPF6 solution of THF under N2 at room temperature. The working electrode was a 2.0 mm diameter platinum disk, and the scan rate was 0.50 V s⁻¹.
Reactions Relating to Equilibrium Between Ni(I) Monomers and Dimers

Addition of 3a to an equilibrated mixture of 1a

To a solution of 1a (6.5 mg, 0.0065 mmol) in 0.5 mL C₆D₆ in a J. Young NMR tube, 3a (5.3 mg, 0.01 mmol) was added. After 10 minutes ¹H NMR spectroscopy showed that the reaction equilibrium had shifted to 1a and 3a. The NMR spectra are shown in Figure S16.
Figure S16: \( ^1\)H NMR spectrum of an equilibrated mixture of 1a; b) \( ^1\)H NMR spectrum of equilibrated mixture of 1a after addition of 3a.

a)  

b)
**Reaction of 1a and 1b**

To a solution of 1a (6.5 mg, 0.0065 mmol) in 0.5 mL C₆D₆, 1b (6.5 mg, 0.0065 mmol) was added. ¹H NMR spectroscopy indicated that the solution is a mixture of 1a, 1b, 3a, 3b, (µ-Cl)₂Ni₂(SIPr)₂, (µ-Cl)₂Ni₂(IPr)₂ and a new product which has been assigned as (µ-Cp)(µ-Cl)Ni₂(IPr)(SIPr). Although many peaks are overlapping in the spectrum, we believe that the new peaks at 4.67 (s) for Cp and 3.25 (s) for the saturated backbone peak of SIPr are consistent with the formation of (µ-Cp)(µ-Cl)Ni₂(IPr)(SIPr). The ¹H NMR spectrum of the mixture is shown in Figure S17.

**Figure S17:** ¹H NMR spectrum of reaction between 1a and 1b.
Reaction of (µ-Cl)$_2$Ni$_2$(SIPr)$_2$ and (µ-Cl)$_2$Ni$_2$(IPr)$_2$

To a solution of (µ-Cl)$_2$Ni$_2$(IPr)$_2$ (7.6 mg, 0.0078 mmol) in 0.5 mL C$_6$D$_6$, (µ-Cl)$_2$Ni$_2$(SIPr)$_2$ (7.6 mg, 0.0078 mmol) was added. After 20 minutes $^1$H NMR spectroscopy showed a mixture of (µ-Cl)$_2$Ni$_2$(SIPr)$_2$, (µ-Cl)$_2$Ni$_2$(IPr)$_2$ and (µ-Cl)$_2$Ni$_2$(IPr)(SIPr). The $^1$H NMR spectrum of the mixture is shown in Figure S18.

$^1$H NMR (400 MHz, C$_6$D$_6$) for (µ-Cl)$_2$Ni$_2$(IPr)(SIPr): 7.11 (m, 12H) (Ph from IPr and SIPr), 6.72 (s, 2H, CH=CH from IPr), 3.66 (m, 4H, CHMe$_2$ from SIPr overlapping with (µ-Cl)$_2$Ni$_2$(SIPr)$_2$), 3.11 (m, 4H, CHMe$_2$ from IPr overlapping with (µ-Cl)$_2$Ni$_2$(IPr)$_2$), 2.74 (s, 4H, CH$_2$-CH$_2$ from SIPr), 2.82 (d, $J$ = 8 Hz, 12H, Me), 2.41 (d, $J$ = 8 Hz, 12H, Me), 1.29 (d, $J$ = 8 Hz, 12H, Me), 1.15 (d, $J$ = 8 Hz, 12H, Me) (CH$_3$ from IPr and SIPr).

**Figure S18:** $^1$H NMR spectrum of reaction between (µ-Cl)$_2$Ni$_2$(SIPr)$_2$ and (µ-Cl)$_2$Ni$_2$(IPr)$_2$. 

---

**Figure S18:** $^1$H NMR spectrum of reaction between (µ-Cl)$_2$Ni$_2$(SIPr)$_2$ and (µ-Cl)$_2$Ni$_2$(IPr)$_2$. 

---

S24
Figure S19: EPR spectrum $(\mu$-Cl)$_2$Ni$_2$(IPr)$_2$ which shows presence of $S = \frac{1}{2}$ compound.

Figure S20: EPR spectrum $(\mu$-Cl)$_2$Ni$_2$(SIPr)$_2$ which shows presence of $S = \frac{1}{2}$ compound.
Reaction of 4a and (µ-Cl)₂Ni₂(IPr)₂
To a solution of 4a (7.5 mg, 0.014 mmol) in 0.5 mL C₆D₆, (µ-Cl)₂Ni₂(IPr)₂ (6.8 mg, 0.007 mmol) was added. Upon addition, the yellow solution turned green. After 20 minutes, ¹H NMR spectroscopy indicated quantitative conversion to 2a.

Reaction of 3a and (µ-Cl)₂Ni₂(IPr)₂
To a solution of 3a (7.3 mg, 0.014 mmol) in 0.5 mL C₆D₆, (µ-Cl)₂Ni₂(IPr)₂ (6.8 mg, 0.007 mmol) was added. After 20 minutes, ¹H NMR spectroscopy indicated a mixture of 1a with small amount of 3a and (µ-Cl)₂Ni₂(IPr)₂, as shown in Figure S21.

Figure S21: ¹H NMR spectrum reaction between 3a and (µ-Cl)₂Ni₂(IPr)₂.

Reaction of 1a and 4a
To a solution of 1a (7.4 mg, 0.074 mmol) in 0.5 mL C₆D₆, 4a (4.2 mg, 0.0074 mmol) was added. After 48 hours, ¹H NMR spectroscopy indicated full conversion to 2a and 3a.
Figure S22: EPR spectrum 1a which shows presence of 3a.

Figure S23: EPR spectrum 1b which shows presence of 3b.
**Figure S24:** EPR spectra for 2a, which shows no $S = \frac{1}{2}$ impurities.

![EPR spectra for 2a](image)

**Figure S25:** EPR spectra for 2b, which shows no $S = \frac{1}{2}$ impurities.

![EPR spectra for 2b](image)
Reaction of 1a and LiInd
To a solution of 1a (23 mg, 0.024 mmol) in 1 mL THF, a solution of LiInd (1.4 mg, 0.012 mmol) in 1 mL THF was added dropwise. After 1 hour, the volatiles were removed under vacuum. The resulting residue was dissolved in 0.8 mL C₆D₆. ¹H NMR spectroscopy indicated quantitative conversion to 2a and 3a.

Reaction of 1a and NaCp
To a solution of 1a (35 mg, 0.035 mmol) in 1 mL THF, NaCp (3.1 mg, 0.035 mmol) was added. After 4 hours, the volatiles were removed under vacuum. ¹H NMR spectroscopy of the resulting residue in C₆D₆ indicated that only 3a was present. The residue was extracted with benzene and the solvent removed under vacuum to provide yellow 3a. Yield: 33 mg (92%).

Reaction of 1b and NaCp
To a solution of 1b (35 mg, 0.035 mmol) in 1 mL THF, NaCp (3.1 mg, 0.035 mmol) was added. After 4 hours, the volatiles were removed under vacuum. The residue was extracted with benzene and the solvent removed under vacuum to provide yellow 3b. Yield: 31 mg (90%).
General procedure for Van’t Hoff analysis

1a (7.3 mg, 0.0073 mmol) or 1b (5.6 mg, 0.0056 mmol) was dissolved in 0.5 mL C₆D₆ in a J. Young NMR tube. The sample was placed into a 400 MHz NMR spectrometer. ¹H NMR spectra were recorded at the following temperatures: 25, 30, 35, 40, 45, 50, 55, 60, 65, 70°C. The methyl peaks of the NHC ligand in 1a (or 1b) and (μ-Cl)₂Ni₂(NHC)₂ were integrated to determine the concentration of the corresponding complexes in the mixture. The concentration of the paramagnetic species 3a or 3b was determined from the concentration of (μ-Cl)₂Ni₂(NHC)₂.

Table S4: Experimentally determined equilibrium constants for 1a and 1b.

<table>
<thead>
<tr>
<th>Temperature(Kelvin)</th>
<th>1/Temperature</th>
<th>Kₐ</th>
<th>K₈</th>
</tr>
</thead>
<tbody>
<tr>
<td>298.24</td>
<td>0.003353</td>
<td>0.006021</td>
<td>0.03739</td>
</tr>
<tr>
<td>302.28</td>
<td>0.003308</td>
<td>0.009043</td>
<td>0.051617</td>
</tr>
<tr>
<td>309.35</td>
<td>0.003233</td>
<td>0.012343</td>
<td>0.069071</td>
</tr>
<tr>
<td>314.4</td>
<td>0.003181</td>
<td>0.015863</td>
<td>0.091171</td>
</tr>
<tr>
<td>318.44</td>
<td>0.00314</td>
<td>0.022114</td>
<td>0.120831</td>
</tr>
<tr>
<td>324.50</td>
<td>0.003082</td>
<td>0.028736</td>
<td>0.153849</td>
</tr>
<tr>
<td>328.54</td>
<td>0.003044</td>
<td>0.037052</td>
<td>0.190134</td>
</tr>
<tr>
<td>334.60</td>
<td>0.002989</td>
<td>0.04714</td>
<td>0.236962</td>
</tr>
<tr>
<td>339.65</td>
<td>0.002944</td>
<td>0.06056</td>
<td>0.294398</td>
</tr>
<tr>
<td>344.70</td>
<td>0.002901</td>
<td>0.080575</td>
<td>0.359495</td>
</tr>
</tbody>
</table>

\[
K_a = \frac{[3a][(\mu-Cl)_2Ni_2(IPr)_2]^{0.5}}{[1a]}
\]

\[
K_b = \frac{[3b][(\mu-Cl)_2Ni_2(SiPr)_2]^{0.5}}{[1b]}
\]
Figure S26: Van’t Hoff Plot for 1a

![Graph showing the Van’t Hoff plot for 1a with the equation y = -5550.3x + 13.564 and R² = 0.9966.]

Figure S27: Van’t Hoff Plot for 1b.

![Graph showing the Van’t Hoff plot for 1b with the equation y = -4956.3x + 13.386 and R² = 0.9973.]

S31
DFT Calculations

NBO analysis details

NBO calculations (version 6.0) were carried out with Gaussian09 (revision D.01) on the optimized geometries of 3a and 4a. In order to simplify the analysis, the 2,6-diisopropylphenyl substituents on the NHC ligand (IPr) were replaced by hydrogens. The N-H distance of these models was obtained by geometry optimization keeping the rest of the molecule frozen. In addition, 3c-2e interactions were excluded between the Cp/indenyl ligands and Ni, in order to compare only the donor-acceptor interactions with these two ligands. The $\pi$(Cp/indenyl) $\rightarrow$ $d$ (Ni) interactions were identified in the $\beta$-electron configuration (both 3a and 4a have a doublet spin ground state) as donations from $\pi$(C=C) and LP(C) (LP = Lone Pair) orbitals to the Ni $d$ orbital with a single-electron vacancy. The $\pi$(Cp/indenyl) $\rightarrow$ $\sigma^*$ (Ni-C) interactions were found both in the $\alpha$ and $\beta$-electron configurations and involve electron-donation from $\pi$(C=C) and LP(C) orbitals to the antibonding $\sigma^*$ (Ni-C) orbital. In the second order perturbation analysis, the $\pi$(Cp/indenyl) $\rightarrow$ $d$ (Ni) and $\pi$(Cp/indenyl) $\rightarrow$ $\sigma^*$ (Ni-C) interactions yield several natural localized molecular orbitals (NLMOs). Those shown in Figures 9 and S31 were selected as the most representative examples. The stabilization energies given in the manuscript are the summation of all components contributing to these interactions in the $\beta$-electron configuration.

Additional figures

Figure S28: Spin densities of complexes 3b (left) and 4b (right).
**Figure S29:** SOMO (left) and spin density (right) of complex 3a.

![SOMO and Spin Density](image1)

**Figure S30:** Optimized geometry of the Ni(II) species derived from the one-electron oxidation of complex 3a.

![Optimized Geometry](image2)

**Figure S31:** Natural localized molecular orbitals (NLMOs) for the $\pi(L) \rightarrow \sigma^*(\text{Ni-C})$ donation. $L = \text{Cp}$ (left) or indenyl (right). The substituents on the NHC ligand (IPr) were removed for clarity.

![NLMO Diagram](image3)
**Figure S32:** Top (top) and side (bottom) views of the spin densities of the dinuclear complexes 1\textit{a} (left) and 2\textit{a} (right).

**Results with other DFT functionals**

In addition to M06L, other pure and hybrid DFT functionals were tested for determining the ground electronic state of 1\textit{a}. These calculations showed that the nature of the singlet ground state depends on the functional used (Table S5). With the pure functionals, M06L and BP86* (* = D3 Grimme’s corrections for dispersion forces), the singlet is closed-shell, whereas with the hybrid functionals, M06, B3LYP* and PBE0*, the singlet is open-shell, with two antiferromagnetically-coupled unpaired electrons located on the metal centers, \textit{i.e.} Ni(↑)Ni(↓). Furthermore, the triplet state, Ni(↑)Ni(↑), is more stable with the latter functionals. This is due to the Hartree-Fock exchange introduced in hybrid functionals. The best fit between the experimental X-Ray structure and the DFT-optimized geometry of the ground state was given by the closed-shell singlet state determined as the ground state using the BP86* and M06L functionals (Table S6).
### Table S5: Relative energies (ΔH), in kJ mol\(^{-1}\), for the closed-shell singlet (S), open-shell singlet (OSS) and triplet (T) states of 1a, with different DFT functionals. Geometries were fully-optimized in the gas phase for the real systems by using the double-ζ quality basis set.

<table>
<thead>
<tr>
<th></th>
<th>S</th>
<th>OSS</th>
<th>T</th>
</tr>
</thead>
<tbody>
<tr>
<td>M06L</td>
<td>0.0</td>
<td>63.3</td>
<td>32.5</td>
</tr>
<tr>
<td>BP86*</td>
<td>0.0</td>
<td>60.0</td>
<td></td>
</tr>
<tr>
<td>M06</td>
<td>8.9</td>
<td>0.0</td>
<td>1.7</td>
</tr>
<tr>
<td>B3LYP*</td>
<td>32.2</td>
<td>0.0</td>
<td>5.1</td>
</tr>
<tr>
<td>PBE0*</td>
<td>42.4</td>
<td>0.0</td>
<td>5.5</td>
</tr>
</tbody>
</table>

### Table S6: Selected bond distances, in Å, for the comparison of the X-ray structure of 1a with the DFT geometries of the ground state optimized with different functionals.

<table>
<thead>
<tr>
<th></th>
<th>Ni1-Ni2</th>
<th>Ni1-C4</th>
<th>Ni2-C4</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-Ray (exp.)</td>
<td>2.4015(3)</td>
<td>2.2067(18)</td>
<td>2.1879(19)</td>
</tr>
<tr>
<td>M06L</td>
<td>2.37</td>
<td>2.18</td>
<td>2.17</td>
</tr>
<tr>
<td>BP86*</td>
<td>2.37</td>
<td>2.20</td>
<td>2.20</td>
</tr>
<tr>
<td>M06</td>
<td>2.55</td>
<td>2.22</td>
<td>2.65</td>
</tr>
<tr>
<td>B3LYP*</td>
<td>2.64</td>
<td>2.23</td>
<td>2.75</td>
</tr>
<tr>
<td>PBE0*</td>
<td>2.67</td>
<td>2.26</td>
<td>2.76</td>
</tr>
</tbody>
</table>

In addition to M06L, M06 was also used for modeling complex 2a. With both functionals, the ground state is a closed shell singlet (Table S7). The energy differences between the S and T states are 63.3 and 16.6 kJ mol\(^{-1}\) with M06L and M06, respectively. When this data is compared to that obtained for 1a (Table S5), it becomes apparent that the triplet state is less accessible with an indenyl bridging ligand (2a) compared with a Cp bridging ligand (1a), regardless of the functional used.

### Table S7: Relative energies (ΔH), in kJ mol\(^{-1}\), for the closed-shell singlet (S) and triplet (T) states of 2a, with the M06L and M06 functionals. Geometries were fully-optimized in the gas phase for the real systems by using the double-ζ quality basis set.

<table>
<thead>
<tr>
<th></th>
<th>S</th>
<th>T</th>
</tr>
</thead>
<tbody>
<tr>
<td>M06L</td>
<td>0.0</td>
<td>63.3</td>
</tr>
<tr>
<td>M06</td>
<td>0.0</td>
<td>16.6</td>
</tr>
</tbody>
</table>

**DFT results on the (μ-Cl)\(_2\)Ni\(_2\)(IPr)\(_2\) dimer**

All attempts to model the electronic and geometrical structures of the (μ-Cl)\(_2\)Ni\(_2\)(IPr)\(_2\) dimer were unsuccessful. Both pure and hybrid DFT functionals predicted a triplet ground state for this species (Table S8), which is in contradiction with the diamagnetism observed in the experiments. In addition, there are rather large differences between the X-Ray structure of...
this species and the DFT-optimized geometries for all functionals tested (Table S9). These experiment-theory discrepancies may be due to the lack of crystal-packing effects in the gas phase calculations. The DFT models of (μ-Cl)2Ni2(IPr)2 were thus not considered any further.

Table S8: Relative energies (ΔH), in kJ mol⁻¹, for the closed-shell singlet (S), open-shell singlet (OSS) and triplet (T) states of (μ-Cl)2Ni2(IPr)2, with different DFT functionals. Geometries were fully-optimized in gas phase for the real systems by using the double-ζ quality basis set.

<table>
<thead>
<tr>
<th></th>
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<th>OSS</th>
<th>T</th>
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<tbody>
<tr>
<td>M06L</td>
<td>58.1</td>
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<tr>
<td>M06</td>
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<td>1.5</td>
<td>0</td>
</tr>
<tr>
<td>B3LYP*</td>
<td>119.9</td>
<td>0.7</td>
<td>0</td>
</tr>
<tr>
<td>PBE0*</td>
<td>141.9</td>
<td>0.4</td>
<td>0</td>
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</tbody>
</table>

*= D3 Grimme’s corrections for dispersion forces.

Table S9: Selected geometrical parameters, in Å and °, for the comparison of the X-ray structure of (μ-Cl)2Ni2(IPr)2 with the DFT geometries of the ground state (T) optimized with different functionals.

<table>
<thead>
<tr>
<th></th>
<th>Ni-Ni</th>
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<th>Ni1-Cl2</th>
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<th>N2C2N2C11</th>
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<tbody>
<tr>
<td>X-Ray (exp.)</td>
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<td>2.2085(8)</td>
<td>2.2467(8)</td>
<td>88.8(2)</td>
<td>4.6(3)</td>
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<tr>
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<td>2.28</td>
<td>2.35</td>
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<td>2.31</td>
<td>48.4</td>
<td>-6.0</td>
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*= D3 Grimme’s corrections for dispersion forces.

Optimized energies and geometries of all stationary points

Optimized Cartesian coordinates, in Å, and absolute energies, in hartrees, of all stationary points reported in the text. Enthalpies (H_Bz) and Gibbs (G_THF) energies were obtained from Eqs S1 and S2, respectively, in which the thermochemistry corrections found in gas phase, (H – E) and (G – E), were added to the single-point energies computed with the continuum SMD model for solvation (solvent = Benzene (Bz) or THF).

\[
H_{Bz} = (H - E) + E_{SMD}(Bz)
\]

Eq. S1

\[
G_{THF} = (G - E) + E_{SMD}(THF)
\]

Eq. S2
Cp anion
$H_{Bz} = -193.510984$

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S40
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C   1.57039500  -0.09745800  2.66287100
H   2.57826800  -0.23133600  2.28557700
C  -0.07357200  -0.18470900  3.76135200
N  -1.15193000  -0.41909500  -1.25946400
C  -2.47580700  -0.20943900  -0.76191000
C  -3.28353000  -1.33399400  -0.51736500
C  -2.75107700  -2.72935700  -0.77409900
H  -2.05620600  -2.66030800  -1.62243300
C  -1.94180800  -3.22715900  0.42593300
H  -1.11762000  -2.54637300  0.66974700
H  -1.52107300  -4.21949300  0.22771000
H  -2.57966300  -3.30416700  1.31462500
C  -3.83987600  -3.73060100  -1.14214100
H  -4.49740200  -3.94438000  -0.29147800
H  -3.39396600  -4.68313700  -1.44272600
H  -4.46699200  -3.37454900  -1.96467900
C  -4.55845800  -1.12023500  0.01027100
H  -5.20341400  -1.97018100  0.21634200
C  -5.01362600  0.16624800  0.27895600
3b-oxidized (Ni(II))

\[ G_{\text{THF}} = -1525.85854 \]

Ni  
-0.71800600  -0.07046200  1.15135300

S57
4a

$H_{Bz} = -1677.7278$

Ni  
-0.259304  -0.086948  -1.233944
C  
0.334641  0.536760  -3.129099
H  
0.257103  1.575395  -3.433063
C  
-0.703411  -0.438148  -3.226571
H  
-1.687752  -0.281157  -3.652060
C  
-0.160579  -1.702832  -2.798927
C  
-0.708691  -2.998008  -2.702974
H  
-1.733136  -3.181798  -3.020722
C  
0.072036  -4.027484  -2.208434
H  
-0.340850  -5.031111  -2.141948
C  
1.396069  -3.796401  -1.780661
H  
1.982637  -4.625437  -1.391102
C  
1.958913  -2.533216  -1.846647
H  
2.979035  -2.357801  -1.508177
C  
1.199353  -1.468074  -2.367491
C  
1.474286  -0.070057  -2.534334
H  
2.416850  0.416082  -2.309237
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N  
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C  
2.268958  0.776089  0.944500
C  
2.720730  1.773780  0.060030
C  
1.782983  2.857263  -0.438892
H  
0.822617  2.367128  -0.657524
C  
2.245521  3.512167  -1.733696
H  
1.461480  4.173204  -2.117008
H  
2.466546  2.772983  -2.510304
H  
3.141323  4.127241  -1.588708
C  
1.536330  3.921557  0.632643
H  
1.147174  3.491563  1.560538
H  
0.807412  4.659960  0.279228
H  
2.462593  4.456150  0.873470

S59
\((\text{IPr})\text{Ni}\)

\(H_{\text{Lz}} = -1330.57218\)

\[
\begin{align*}
\text{Ni} & \quad 0.000510 \quad -0.137862 \quad -1.860193
\end{align*}
\]
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X-ray crystallography

Low-temperature diffraction data (ω-scans) were collected on either a Rigaku R-AXIS RAPID diffractometer coupled to a R-AXIS RAPID imaging plate detector with Mo $K_\alpha$ radiation ($\lambda = 0.71073$ Å) for the structure of 1a or a Rigaku MicroMax-007HF diffractometer coupled to a Saturn994+ CCD detector with Cu $K_\alpha$ ($\lambda = 1.54178$ Å) for the structures of 2b, 3a, 4a and 4b. All structures were solved by direct methods using SHELXS[4] and refined against $F^2$ on all data by full-matrix least squares with SHELXL-97[5] using established refinement techniques.[6] All hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the $U$ value of the atoms they are linked to (1.5 times for methyl groups).

_Canting of central carbon atoms of the bridging ligands are canted towards the Ni-Ni-Cl plane_

As noted in the main text a feature of the binding of the bridging Cp and indenyl ligands in 1a and 2b is that the central carbon atoms of the bridging Cp or indenyl ligand is canted towards the Ni-Ni-Cl plane. As a result, the dihedral angle between the bridging Cp or indenyl plane and the plane containing the two Ni atoms and the two terminal carbon atoms of the bridging Cp or indenyl ligand (the dihedral angle $\theta$ in Figure S33 below) is significantly less than $90^\circ$.

**Figure S33:** Values of the dihedral angle formed between the Cp or indenyl plane and the plane containing the two Ni centers and the two terminal carbon atoms of the bridging Cp or indenyl ligand in 1a or 2b.

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<th>Compound</th>
<th>$\theta$</th>
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<tr>
<td>1a</td>
<td>69.9°</td>
</tr>
<tr>
<td>2b</td>
<td>67.7°</td>
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X-Ray Data for 1a (CCDC 939469)

Compound 1a crystallizes in the monoclinic space group $P2(1)/n$ with one molecule in the asymmetric unit. Two of the iso-propyl groups of the ligand were disordered over two sites. The coordinates for the hydrogen atoms bound to C1, C2, C3, C4, and C5 were taken from the difference Fourier synthesis and the hydrogen atoms were subsequently refined semi-freely with the help of a distance restraint.

**Table S10: Crystal data and structure refinement for 1a**

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</tr>
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<tr>
<td>Temperature</td>
<td>150(2) K</td>
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<tr>
<td>Wavelength</td>
<td>0.71075 Å</td>
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<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>$P2(1)/n$</td>
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<tr>
<td>Unit cell dimensions</td>
<td>$a = 20.5396(4)$ Å $b = 12.1359(2)$ Å $c = 23.7443(17)$ Å $\alpha = 90^\circ$ $\beta = 112.504(8)^\circ$ $\gamma = 90^\circ$</td>
</tr>
<tr>
<td>Volume</td>
<td>5468.0(4) Å$^3$</td>
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<tr>
<td>Z</td>
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<tr>
<td>Density (calculated)</td>
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<td>Absorption coefficient</td>
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<td>Crystal size</td>
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<tr>
<td>Theta range for data collection</td>
<td>3.07 to 30.51°</td>
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<td>Independent reflections</td>
<td>16595 [R(int) = 0.0703]</td>
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<td>Completeness to theta = 30.51°</td>
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<td>Absorption correction</td>
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<td>Max. and min. transmission</td>
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<td>Refinement method</td>
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<td>R indices (all data)</td>
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<td>Largest diff. peak and hole</td>
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**Table S11: Atomic coordinates (x 10$^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for 1a.** U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

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C(70A)-C(71A)   1.513(10)
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C(70A)-C(72A)-H(72F)  109.5
H(72D)-C(72A)-H(72F)  109.5
H(72E)-C(72A)-H(72F)  109.5
C(17)-C(16)-N(3)  106.70(15)
C(17)-C(16)-H(16)  126.7
N(3)-C(16)-H(16)  126.7
C(16)-C(17)-N(4)  106.83(14)
C(16)-C(17)-H(17)  126.6
N(4)-C(17)-H(17)  126.6
C(15)-N(4)-C(17)  111.88(14)
C(15)-N(4)-C(81)  124.37(13)
C(17)-N(4)-C(81)  123.42(13)
C(82)-C(81)-C(86)  123.09(16)
C(82)-C(81)-N(4)  119.30(15)
C(86)-C(81)-N(4)  117.60(15)
C(83)-C(82)-C(81)  116.92(17)
C(83)-C(82)-C(87)  120.28(17)
C(81)-C(82)-C(87)  122.80(16)
C(82)-C(87)-C(88)  110.52(16)
C(82)-C(87)-C(89)  111.45(18)
C(88)-C(87)-C(89)  110.65(17)
C(82)-C(87)-H(87)  108.0
C(88)-C(87)-H(87)  108.0
C(89)-C(87)-H(87)  108.0
C(87)-C(88)-H(88A)  109.5
C(87)-C(88)-H(88B)  109.5
H(88A)-C(88)-H(88B)  109.5
C(87)-C(88)-H(88C)  109.5
H(88A)-C(88)-H(88C)  109.5
H(88B)-C(88)-H(88C)  109.5
C(87)-C(89)-H(89A)  109.5
C(87)-C(89)-H(89B)  109.5
H(89A)-C(89)-H(89B)  109.5
C(87)-C(89)-H(89C)  109.5
H(89A)-C(89)-H(89C)  109.5
H(89B)-C(89)-H(89C)  109.5
C(84)-C(83)-C(82)  121.3(2)
C(84)-C(83)-H(83)  119.3
C(82)-C(83)-H(83)  119.3
C(85)-C(84)-C(83)  120.08(19)
C(85)-C(84)-H(84)  120.0
C(83)-C(84)-H(84)  120.0
C(84)-C(85)-C(86)  121.47(19)
C(84)-C(85)-H(85)  119.3
Compound 2b crystallizes in the monoclinic space group $P2(1)/n$ with one molecule in the asymmetric unit. The coordinates for the hydrogen atoms bound to C1, C2 and C9 were taken from the difference Fourier synthesis and the hydrogen atoms were subsequently refined semi-freely with the help of a distance restraint.

**X-Ray Data for 2b (CCDC 939470)**

**Table S15: Crystal data and structure refinement for 2b**

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<td></td>
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<td>Crystal size</td>
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<td>Independent reflections</td>
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<td>Absorption correction</td>
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Max. and min. transmission 0.9263 and 0.8001
Refinement method Full-matrix least-squares on \( F^2 \)
Data / restraints / parameters 9726 / 3 / 656
Goodness-of-fit on \( F^2 \) 1.090
Final R indices [I>2sigma(I)]
\[ R1 = 0.0482, \quad wR2 = 0.1182 \]
R indices (all data)
\[ R1 = 0.0623, \quad wR2 = 0.1339 \]
Largest diff. peak and hole 0.500 and -0.514 e.Å\(^{-3}\)

**Table S16:** Atomic coordinates (x 10\(^4\)) and equivalent isotropic displacement parameters (Å\(^2\)x 10\(^3\)) for 2b. U(eq) is defined as one third of the trace of the orthogonalized \( U_{ij} \) tensor.

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Table S17: Anisotropic displacement parameters (Å² x 10³) for 2b. The anisotropic displacement factor exponent takes the form: -2π²[h²a*²U¹¹ + ... + 2hkab*U¹²]

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C(3)-C(4) 1.385(4)  
C(3)-C(8) 1.421(4)  
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H(52B)-C(52)-H(52C) 109.5
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C(11)-Ni(2)-C(1) 135.80(10)
C(9)-Ni(2)-C(1) 40.52(10)
C(11)-Ni(2)-Cl(1) 111.34(7)
C(9)-Ni(2)-Cl(1) 146.13(8)
C(1)-Ni(2)-Cl(1) 108.22(7)
C(11)-Ni(2)-Ni(1) 89.83(8)
C(9)-Ni(2)-Ni(1) 55.70(7)
Cl(1)-Ni(2)-Ni(1) 56.31(2)
N(4)-C(16)-N(3) 105.4(2)
N(4)-C(16)-Ni(1) 131.45(18)
N(3)-C(16)-Ni(1) 122.79(18)
C(16)-N(3)-C(61) 125.9(2)
C(16)-N(3)-C(17) 113.8(2)
C(61)-N(3)-C(17) 118.0(2)
C(66)-C(61)-C(62) 122.0(3)
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C(62)-C(61)-N(3) 119.7(3)
C(63)-C(62)-C(61) 117.8(3)
C(63)-C(62)-C(67) 119.2(3)
C(61)-C(62)-C(67) 122.9(3)
C(62)-C(67)-C(69) 113.6(3)
C(62)-C(67)-C(68) 110.5(3)
C(69)-C(67)-C(68) 109.2(3)
C(62)-C(67)-H(67) 107.8
C(69)-C(67)-H(67) 107.8
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C(67)-C(68)-H(68B) 109.5
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C(64)-C(63)-C(62) 121.3(3)
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C(63)-C(64)-C(65) 120.7(3)
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C(65)-C(64)-H(64) 119.7
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C(66)-C(65)-H(65) 119.5
C(61)-C(66)-C(65) 117.2(3)
C(61)-C(66)-C(70) 123.1(3)
The compound 3a crystallizes in the triclinic space group $P\overline{1}$ with one molecule in the asymmetric unit.

**Table S20: Crystal data and structure refinement for 3a**

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X-Ray Data for 3a (CCDC 939471)

The compound 3a crystallizes in the triclinic space group $P\overline{1}$ with one molecule in the asymmetric unit.
Theta range for data collection 2.43 to 68.29°.
Index ranges -11<=h<=11, -10<=k<=10, -21<=l<=21
Reflections collected 48798
Independent reflections 4964 [R(int) = 0.0533]
Completeness to theta = 68.29° 97.7 %
Absorption correction Semi-empirical from equivalents
Max. and min. transmission 0.9238 and 0.8463
Refinement method Full-matrix least-squares on F²
Data / restraints / parameters 4964 / 0 / 324
Goodness-of-fit on F² 1.033
Final R indices [I>2sigma(I)] R1 = 0.0288, wR2 = 0.0733
R indices (all data) R1 = 0.0291, wR2 = 0.0735
Largest diff. peak and hole 0.265 and -0.258 e.Å⁻³

Table S21: Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å² x 10³) for 3a. U(eq) is defined as one third of the trace of the orthogonalized Uᵢⱼ tensor.

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Table S22: Anisotropic displacement parameters ($\AA^2 \times 10^3$) for 3a. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2a^*U^{11} + ... + 2hk a^* b^* U^{12}]$

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Table S23: Bond lengths ($\AA$) for 3a

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| Ni(1)-C(2)  | 2.1246(14) |
| Ni(1)-C(3)  | 2.1315(13) |
| Ni(1)-C(1)  | 2.1755(14) |
| Ni(1)-C(4)  | 2.1835(13) |
| Ni(1)-C(5)  | 2.1835(13) |
| C(1)-C(2)   | 1.410(2)   |
| C(1)-C(5)   | 1.415(2)   |
| C(1)-H(1)   | 0.9500     |
| C(2)-C(3)   | 1.426(2)   |
| C(2)-H(2)   | 0.9500     |
| C(3)-C(4)   | 1.412(2)   |
| C(3)-H(3)   | 0.9500     |
| C(4)-C(5)   | 1.416(2)   |
C(4)-H(4)  0.9500
C(5)-H(5)  0.9500
C(11)-N(1)  1.3701(16)
C(11)-N(2)  1.3726(16)
N(1)-C(12)  1.3870(17)
N(1)-C(21)  1.4392(16)
C(21)-C(26)  1.4006(18)
C(21)-C(22)  1.4028(18)
C(22)-C(23)  1.3944(19)
C(22)-C(27)  1.5206(18)
C(27)-C(28)  1.529(2)
C(27)-C(29)  1.529(2)
C(27)-H(27)  1.0000
C(28)-H(28A)  0.9800
C(28)-H(28B)  0.9800
C(28)-H(28C)  0.9800
C(29)-H(29A)  0.9800
C(29)-H(29B)  0.9800
C(29)-H(29C)  0.9800
C(23)-C(24)  1.384(2)
C(23)-H(23)  0.9500
C(24)-C(25)  1.384(2)
C(24)-H(24)  0.9500
C(25)-C(26)  1.3973(19)
C(25)-H(25)  0.9500
C(26)-C(30)  1.5218(18)
C(30)-C(31)  1.529(2)
C(30)-C(32)  1.5297(19)
C(30)-H(30)  1.0000
C(31)-H(31A)  0.9800
C(31)-H(31B)  0.9800
C(31)-H(31C)  0.9800
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C(32)-H(32B)  0.9800
C(32)-H(32C)  0.9800
C(12)-C(13)  1.3440(19)
C(12)-H(12)  0.9500
C(13)-N(2)  1.3942(17)
C(13)-H(13)  0.9500
N(2)-C(41)  1.4423(16)
C(41)-C(42)  1.4013(18)
C(41)-C(46)  1.4035(18)
C(42)-C(43)  1.3953(19)
C(42)-C(47)  1.5241(18)
C(47)-C(49)  1.5288(19)
C(47)-C(48)  1.529(2)
C(47)-H(47)  1.0000
C(48)-H(48A)  0.9800
C(48)-H(48B)  0.9800
C(48)-H(48C)  0.9800
C(49)-H(49A)  0.9800
C(49)-H(49B)  0.9800
C(49)-H(49C)  0.9800
C(43)-C(44)  1.381(2)
C(43)-H(43)  0.9500
C(44)-C(45)  1.385(2)
Table S24: Bond angles (°) for 3a

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Ni(1)-C(5)-H(5)  123.9
N(1)-C(11)-N(2)  102.92(10)
N(1)-C(11)-Ni(1) 125.66(9)
N(2)-C(11)-Ni(1) 131.37(9)
C(11)-N(1)-C(12) 111.87(10)
C(11)-N(1)-C(21) 122.02(10)
C(12)-N(1)-C(21) 118.00(11)
C(21)-N(1)-C(22) 118.00(11)
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C(22)-C(23)-H(23) 119.5
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C(24)-C(25)-C(26) 121.03(13)
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C(26)-C(30)-H(30) 107.7
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C(30)-C(31)-H(31A) 109.5
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H(31A)-C(31)-H(31B) 109.5
H(31A)-C(31)-H(31B) 109.5
C(30)-C(31)-H(31C)  109.5
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H(31B)-C(31)-H(31C)  109.5
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H(32A)-C(32)-H(32C)  109.5
H(32B)-C(32)-H(32C)  109.5
C(13)-C(12)-N(1)  106.99(11)
C(13)-C(12)-H(12)  126.5
N(1)-C(12)-H(12)  126.5
C(12)-C(13)-N(2)  106.50(11)
C(12)-C(13)-H(13)  126.8
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C(11)-N(2)-C(13)  111.72(10)
C(11)-N(2)-C(41)  122.08(10)
C(13)-N(2)-C(41)  126.14(11)
C(42)-C(41)-C(46)  122.99(12)
C(42)-C(41)-N(2)  119.00(11)
C(46)-C(41)-N(2)  117.99(11)
C(43)-C(42)-C(41)  117.11(12)
C(43)-C(42)-C(47)  120.58(12)
C(41)-C(42)-C(47)  119.4(11)
C(42)-C(47)-C(49)  112.81(11)
C(42)-C(47)-C(48)  110.44(11)
C(49)-C(47)-C(48)  110.00(12)
C(42)-C(47)-H(47)  107.8
C(49)-C(47)-H(47)  107.8
C(48)-C(47)-H(47)  107.8
C(47)-C(48)-H(48A)  109.5
C(47)-C(48)-H(48B)  109.5
H(48A)-C(48)-H(48B)  109.5
C(47)-C(48)-H(48C)  109.5
H(48A)-C(48)-H(48C)  109.5
H(48B)-C(48)-H(48C)  109.5
C(47)-C(49)-H(49A)  109.5
C(47)-C(49)-H(49B)  109.5
H(49A)-C(49)-H(49B)  109.5
C(47)-C(49)-H(49C)  109.5
H(49A)-C(49)-H(49C)  109.5
H(49B)-C(49)-H(49C)  109.5
C(44)-C(43)-C(42)  121.13(13)
C(44)-C(43)-H(43)  119.4
C(42)-C(43)-H(43)  119.4
C(43)-C(44)-C(45)  120.56(12)
C(43)-C(44)-H(44)  119.7
C(45)-C(44)-H(44)  119.7
C(44)-C(45)-C(46)  120.85(13)
C(44)-C(45)-H(45)  119.6
C(46)-C(45)-H(45)  119.6
C(45)-C(46)-C(41)  117.30(12)
C(45)-C(46)-C(50)  121.35(12)
C(41)-C(46)-C(50)  121.28(12)
C(46)-C(50)-C(51)  113.85(12)
C(46)-C(50)-C(52)  109.38(12)
X-Ray Data for 4a (CCDC 939472)

Compound 4a crystallizes in the monoclinic space group Cc with one molecule in the asymmetric unit.

**Table S25: Crystal data and structure refinement for 4a**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
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<tbody>
<tr>
<td>Empirical formula</td>
<td>C36 H43 N2 Ni</td>
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<tr>
<td>Formula weight</td>
<td>562.43</td>
</tr>
<tr>
<td>Temperature</td>
<td>93(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>1.54187 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>Cc</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 16.3437(4) Å, α = 90°,</td>
</tr>
<tr>
<td></td>
<td>b = 13.7905(3) Å, β = 107.721(8)°,</td>
</tr>
<tr>
<td></td>
<td>c = 14.5977(10) Å, γ = 90°.</td>
</tr>
<tr>
<td>Volume</td>
<td>3134.0(2) Å³</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.192 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>1.068 mm⁻¹</td>
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<tr>
<td>F(000)</td>
<td>1204</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.15 x 0.03 x 0.03 mm³</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>4.28 to 68.27°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-19 ≤ h ≤ 19, -16 ≤ k ≤ 16, -17 ≤ l ≤ 17</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>23494</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>5142 [R(int) = 0.0899]</td>
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<tr>
<td>Completeness to theta = 68.27°</td>
<td>98.2 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
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<tr>
<td>Max. and min. transmission</td>
<td>0.9687 and 0.8562</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
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<tr>
<td>Data / restraints / parameters</td>
<td>5142 / 2 / 360</td>
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<tr>
<td>Goodness-of-fit on F²</td>
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<td>Final R indices [I&gt;2σ(I)]</td>
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<tr>
<td>R indices (all data)</td>
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<tr>
<td>Absolute structure parameter</td>
<td>0.07(3)</td>
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<tr>
<td>Largest diff. peak and hole</td>
<td>0.515 and -0.575 e.Å⁻³</td>
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**Table S26:** Atomic coordinates (x $10^4$) and equivalent isotropic displacement parameters (Å$^2$ x $10^3$) for 4a. U(eq) is defined as one third of the trace of the orthogonalized U$_{ij}$ tensor.

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<th>x</th>
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<th>z</th>
<th>U(eq)</th>
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<tr>
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<td>3147(4)</td>
<td>11392(3)</td>
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<td>1707(3)</td>
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<td>6263(3)</td>
<td>8078(3)</td>
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**Table S27:** Anisotropic displacement parameters (Å$^2$ x $10^3$) for 4a. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^*2 U_{11} + ... + 2 h k a^* b^* U_{12} + ...]$
Table S28: Bond lengths (Å) for 4a

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<th>Bond</th>
<th>Length (Å)</th>
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<td>Ni(1)-C(9)</td>
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<td>Ni(1)-C(8)</td>
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<td>1.386(7)</td>
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<td>C(1)-C(9)</td>
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<tr>
<td>C(3)-C(4)</td>
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<td>C(4)-C(5)</td>
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<td>C(4)-H(4)</td>
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<td>C(5)-C(6)</td>
<td>1.409(7)</td>
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<tr>
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<tr>
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<td>0.9500</td>
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<tr>
<td>C(7)-C(8)</td>
<td>1.434(6)</td>
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C(7)-H(7) 0.9500
C(8)-C(9) 1.429(6)
C(9)-H(9) 0.9500
C(11)-N(2) 1.361(5)
C(11)-N(1) 1.389(5)
N(1)-C(12) 1.369(5)
N(1)-C(21) 1.441(5)
C(21)-C(22) 1.397(6)
C(21)-C(26) 1.399(5)
C(22)-C(23) 1.401(6)
C(22)-C(27) 1.516(6)
C(27)-C(28) 1.523(6)
C(27)-H(27) 1.0000
C(28)-H(28A) 0.9800
C(28)-H(28B) 0.9800
C(28)-H(28C) 0.9800
C(29)-H(29A) 0.9800
C(29)-H(29B) 0.9800
C(29)-H(29C) 0.9800
C(23)-C(24) 1.382(7)
C(23)-H(23) 0.9500
C(24)-C(25) 1.366(7)
C(24)-H(24) 0.9500
C(25)-C(26) 1.395(6)
C(25)-H(25) 0.9500
C(26)-C(30) 1.520(6)
C(30)-C(32) 1.509(7)
C(30)-C(31) 1.521(7)
C(30)-H(30) 1.0000
C(31)-H(31A) 0.9800
C(31)-H(31B) 0.9800
C(31)-H(31C) 0.9800
C(32)-H(32A) 0.9800
C(32)-H(32B) 0.9800
C(32)-H(32C) 0.9800
C(12)-C(13) 1.341(6)
C(12)-H(12) 0.9500
C(13)-N(2) 1.386(5)
C(13)-H(13) 0.9500
N(2)-C(41) 1.438(5)
C(41)-C(46) 1.396(5)
C(41)-C(42) 1.405(5)
C(42)-C(43) 1.392(6)
C(42)-C(47) 1.509(6)
C(47)-C(49) 1.517(7)
C(47)-C(48) 1.533(7)
C(47)-H(47) 1.0000
C(48)-H(48A) 0.9800
C(48)-H(48B) 0.9800
C(48)-H(48C) 0.9800
C(49)-H(49A) 0.9800
C(49)-H(49B) 0.9800
C(49)-H(49C) 0.9800
C(43)-C(44) 1.374(6)
C(43)-H(43) 0.9500
Table S29: Bond angles (°) for 4a

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C(7)-C(6)-H(6) 119.5
C(5)-C(6)-H(6) 119.5
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C(6)-C(7)-H(7) 120.6
C(8)-C(7)-H(7) 120.6
C(3)-C(8)-C(9) 109.8(4)
C(3)-C(8)-C(7) 119.7(4)
C(9)-C(8)-C(7) 130.4(4)
C(3)-C(8)-Ni(1) 72.6(2)
C(9)-C(8)-Ni(1) 66.3(2)
C(7)-C(8)-Ni(1) 127.7(3)
C(8)-C(9)-C(1) 105.1(4)
C(8)-C(9)-Ni(1) 76.2(2)
C(1)-C(9)-Ni(1) 67.8(2)
C(8)-C(9)-H(9) 127.5
C(1)-C(9)-H(9) 127.5
Ni(1)-C(9)-H(9) 120.4
N(2)-C(11)-N(1) 102.4(3)
N(2)-C(11)-Ni(1) 123.7(3)
N(1)-C(11)-Ni(1) 133.9(3)
C(12)-N(1)-C(11) 111.5(3)
C(12)-N(1)-C(21) 125.2(3)
C(11)-N(1)-C(21) 123.1(3)
C(22)-C(21)-C(26) 123.8(4)
C(22)-C(21)-N(1) 119.2(3)
C(26)-C(21)-N(1) 117.0(3)
C(21)-C(22)-C(23) 116.3(4)
C(21)-C(22)-C(27) 121.4(4)
C(23)-C(22)-C(27) 122.2(4)
C(22)-C(27)-C(29) 110.7(4)
C(22)-C(27)-C(28) 114.0(4)
C(29)-C(27)-C(28) 110.0(4)
C(22)-C(27)-H(27) 107.3
C(29)-C(27)-H(27) 107.3
C(28)-C(27)-H(27) 107.3
C(27)-C(28)-H(28A) 109.5
C(27)-C(28)-H(28B) 109.5
H(28A)-C(28)-H(28B) 109.5
C(27)-C(28)-H(28C) 109.5
H(28A)-C(28)-H(28C) 109.5
H(28B)-C(28)-H(28C) 109.5
C(27)-C(29)-H(29A) 109.5
C(27)-C(29)-H(29B) 109.5
H(29A)-C(29)-H(29B) 109.5
C(27)-C(29)-H(29C) 109.5
H(29A)-C(29)-H(29C) 109.5
H(29B)-C(29)-H(29C) 109.5
C(24)-C(23)-C(22) 121.0(4)
C(24)-C(23)-H(23) 119.5
C(22)-C(23)-H(23) 119.5
C(25)-C(24)-C(23) 120.8(4)
C(25)-C(24)-H(24) 119.6
C(23)-C(24)-H(24) 119.6
C(24)-C(25)-C(26) 121.2(4)
C(24)-C(25)-H(25) 119.4
C(26)-C(25)-H(25) 119.4
Compound 4b crystallizes in the triclinic space group P-1 with one molecule in the asymmetric unit. The indenyl ligand and the solvent of crystallization (benzene) are both disordered over two sites. An anti-bumping restraint was included to keep the hydrogen atoms (H1T and H6T) on the minor component of the benzene molecule from colliding with the main molecule (H12b and H32C).

Table S30: Crystal data and structure refinement for 4b

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X-Ray Data for 4b (CCDC 939473)
F(000)           690
Crystal size     0.05 x 0.05 x 0.03 mm³
Theta range for data collection 2.79 to 62.39°.
Index ranges   -10<=h<=10,  -13<=k<=14,  -18<=l<=18
Reflections collected  59772
Independent reflections  5709 [R(int) = 0.1217]
Completeness to theta = 62.39°  99.0 %
Absorption correction Semi-empirical from equivalents
Max. and min. transmission  0.9711 and 0.9525
Refinement method Full-matrix least-squares on F²
Data / restraints / parameters  5709 / 779 / 551
Goodness-of-fit on F²  1.119
Final R indices [I>2σ(I)]  R1 = 0.0670, wR2 = 0.1913
R indices (all data)  R1 = 0.0821, wR2 = 0.2048
Largest diff. peak and hole  1.056 and -0.684 e.Å⁻³

Table S31: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å² x 10^3) for 4b. U(eq) is defined as one third of the trace of the orthogonalized U_ij tensor.

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Table S32: Anisotropic displacement parameters (Å² x 10³) for 4b. The anisotropic displacement factor exponent takes the form: -2π²[h² a*²U¹¹ + ... + 2 h k a* b* U¹²]

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C(1S)-C(6S) 1.408(9)
C(1S)-H(1S) 0.9500
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C(1T)-C(6T) 1.399(14)
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C(3A)-Ni(1)-C(8)  30.6(8)
C(8A)-Ni(1)-C(8)  7.0(7)
C(9)-C(1)-C(2)  108.3(9)
C(9)-C(1)-Ni(1)  74.1(6)
C(2)-C(1)-Ni(1)  70.8(5)
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C(2)-C(1)-H(1)  125.9
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C(1)-C(2)-C(3)  107.9(9)
C(1)-C(2)-Ni(1)  69.7(5)
C(3)-C(2)-Ni(1)  76.7(5)
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C(3)-C(2)-H(2)  126.1
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C(2)-C(3)-C(8)  107.7(8)
C(4)-C(3)-Ni(1)  126.6(11)
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C(8)-C(7)-H(7)  120.8
C(7)-C(8)-C(9)  131.9(9)
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C(2A)-C(1A)-Ni(1)  70.6(6)
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C(2A)-C(1A)-H(1A) 125.3
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C(1A)-C(2A)-Ni(1) 69.9(6)
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C(43)-C(42)-C(47)  121.7(3)
C(41)-C(42)-C(47)  121.1(3)
C(48)-C(47)-C(42)  111.5(3)
C(48)-C(47)-C(49)  110.1(3)
C(42)-C(47)-C(49)  113.0(3)
C(48)-C(47)-C(49)  113.0(3)
C(46)-C(41)-C(42)  122.3(3)
C(46)-C(41)-N(2)  119.2(3)
C(42)-C(41)-N(2)  118.4(3)
C(43)-C(42)-C(41)  117.2(3)
C(43)-C(42)-C(47)  121.7(3)
C(41)-C(42)-C(47)  121.1(3)
C(48)-C(47)-C(42)  111.5(3)
C(48)-C(47)-C(49)  110.1(3)
C(42)-C(47)-C(49)  113.0(3)
C(48)-C(47)-C(49)  113.0(3)
C(46)-C(41)-C(42)  122.3(3)
C(46)-C(41)-N(2)  119.2(3)
C(42)-C(41)-N(2)  118.4(3)
C(43)-C(42)-C(41)  117.2(3)
C(43)-C(42)-C(47)  121.7(3)
C(41)-C(42)-C(47)  121.1(3)
C(48)-C(47)-C(42)  111.5(3)
C(48)-C(47)-C(49)  110.1(3)
C(42)-C(47)-C(49)  113.0(3)
C(48)-C(47)-C(49)  113.0(3)
C(46)-C(41)-C(42)  122.3(3)
C(46)-C(41)-N(2)  119.2(3)
C(42)-C(41)-N(2)  118.4(3)
C(43)-C(42)-C(41)  117.2(3)
C(43)-C(42)-C(47)  121.7(3)
C(41)-C(42)-C(47)  121.1(3)
C(48)-C(47)-C(42)  111.5(3)
C(48)-C(47)-C(49)  110.1(3)
C(42)-C(47)-C(49)  113.0(3)
C(48)-C(47)-C(49)  113.0(3)
C(46)-C(41)-C(42)  122.3(3)
C(46)-C(41)-N(2)  119.2(3)
C(42)-C(41)-N(2)  118.4(3)
C(43)-C(42)-C(41)  117.2(3)
C(43)-C(42)-C(47)  121.7(3)
C(2S)-C(1S)-H(1S) 117.2
C(6S)-C(1S)-H(1S) 117.2
C(1S)-C(2S)-C(3S) 111.1(8)
C(1S)-C(2S)-H(2S) 124.4
C(3S)-C(2S)-H(2S) 124.4
C(4S)-C(3S)-C(2S) 124.1(8)
C(4S)-C(3S)-H(3S) 118.0
C(2S)-C(3S)-H(3S) 118.0
C(3S)-C(4S)-C(5S) 121.2(8)
C(3S)-C(4S)-H(4S) 119.4
C(5S)-C(4S)-H(4S) 119.4
C(6S)-C(5S)-C(4S) 115.7(8)
C(6S)-C(5S)-H(5S) 122.2
C(4S)-C(5S)-H(5S) 122.2
C(5S)-C(6S)-C(1S) 119.9(8)
C(5S)-C(6S)-H(6S) 120.0
C(1S)-C(6S)-H(6S) 120.0
C(2T)-C(1T)-C(6T) 122(2)
C(2T)-C(1T)-H(1T) 119.1
C(6T)-C(1T)-H(1T) 119.1
C(1T)-C(2T)-C(3T) 114.4(19)
C(1T)-C(2T)-H(2T) 122.8
C(3T)-C(2T)-H(2T) 122.8
C(4T)-C(3T)-C(2T) 113.6(18)
C(4T)-C(3T)-H(3T) 123.2
C(2T)-C(3T)-H(3T) 123.2
C(3T)-C(4T)-C(5T) 119(2)
C(3T)-C(4T)-H(4T) 120.3
C(5T)-C(4T)-H(4T) 120.3
C(6T)-C(5T)-C(4T) 114(2)
C(6T)-C(5T)-H(5T) 123.1
C(4T)-C(5T)-H(5T) 123.1
C(5T)-C(6T)-C(1T) 114.0(17)
C(5T)-C(6T)-H(6T) 123.0
C(1T)-C(6T)-H(6T) 123.0
References