Binuclear Complexes of Ni(I) from a 4-Terphenyldithiophenol.

Felix Koch, Hartmut Schubert, Peter Sirsch, and Andreas Berkefeld*

Institut für Anorganische Chemie, Eberhard Karls Universität Tübingen, Tübingen, Germany

andreas.berkefeld@anorg.uni-tuebingen.de

Electronic Supplementary Information

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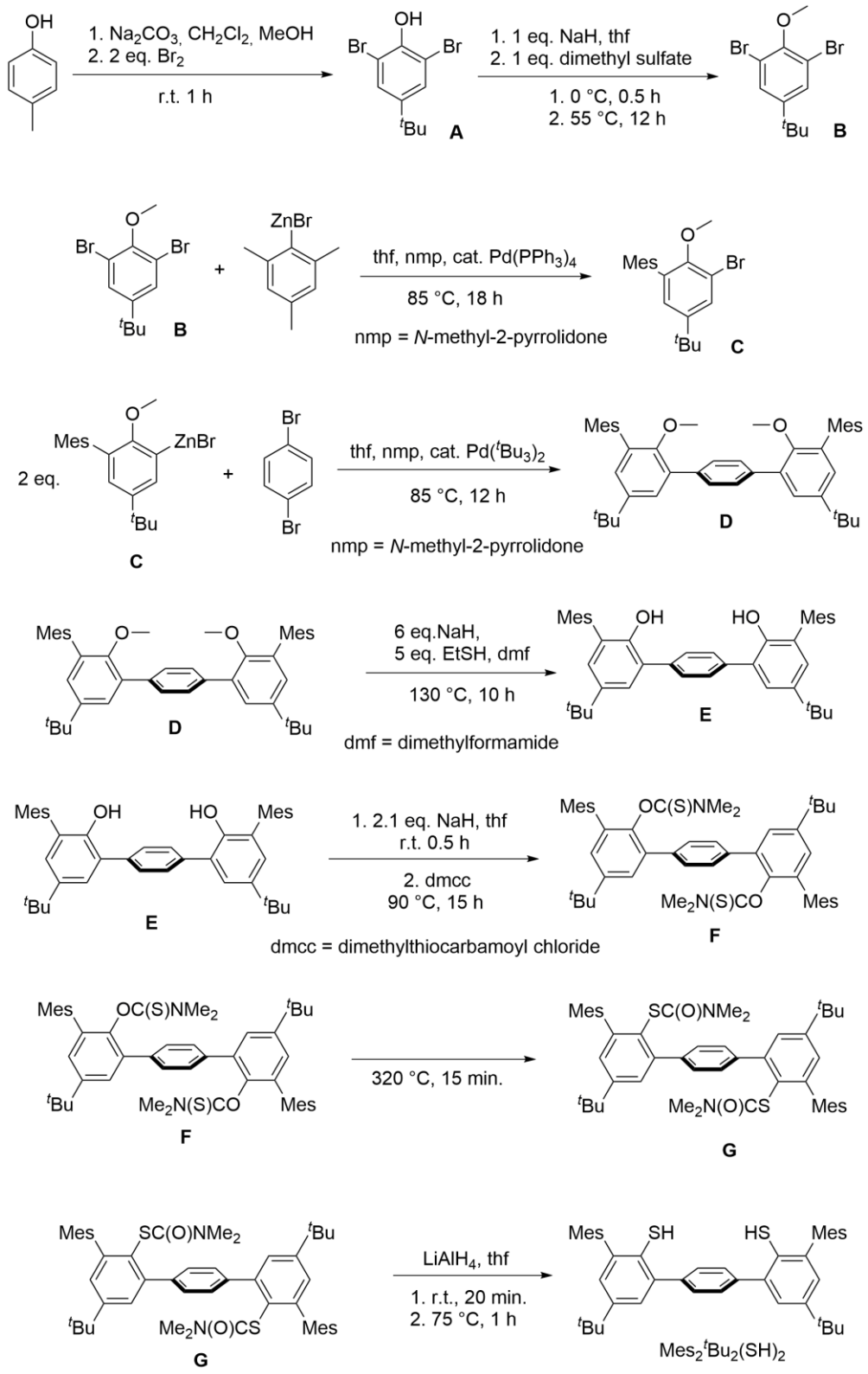
1 General considerations

All manipulations of air and moisture sensitive compounds were carried out under a dry argon atmosphere using standard Schlenk or glove box techniques (MBraun, MB 150-GI). Solvents were purified and dried prior to use. Dichloromethane and hexane were dried over Grubbs columns of an MBraun solvent purification system (SPS). Benzene, diethyl ether, pentane, tetrahydrofuran, and toluene were pre-dried over activated 3 Å molecular sieves and distilled from sodium benzophenone ketyl or potassium metal under argon. Methanol, N,N-dimethylformamide, and *N*-Methyl-2-pyrrolidone were dried by percolation through a column of activated neutral alumina. d_6-Benzene, d_8-toluene, and d_8-thf were dried over and distilled from NaK alloy whereas d-$CHCl_3$ and d_2-CH_2Cl_2 were dried over and vacuum transferred from 3 Å molecular sieves. All solvents were stored over 3 Å molecular sieves under argon. Molecular sieves and neutral alumina were activated by heating under dynamic vacuum (10^{-3} mbar) at 250 °C for 24-48 hours. NMR data were recorded on Bruker Avance II 400 and DRX 250 instruments. VT NMR spectra were collected on a Bruker AVII+500 spectrometer. δ values are given in ppm, *J* values in Hz. ^{1}H and $^{13}C\{^{1}H\}$ NMR chemical shifts are referenced to the residual proton and naturally abundant carbon resonances of the solvents: 7.16/128.06 (d_6-C_6H_6), 1.72/67.21 (d_8-thf), 5.32/53.84 (d_2-CH_2Cl_2), and 7.26/77.16 (d-$CHCl_3$) ppm. ^{31}P NMR chemical shifts are referenced to an external standard sample of 85% H_3PO_4 set to 0 ppm. IR data were collected on a Bruker Vertex 70 spectrometer equipped with a Harrik MVP 2 Series ATR module. Whenever applicable, reactions were monitored by GC-MS analysis on a HP 6890 instrument equipped with a DB-5MS capillary column (JW, 30m × 250µm × 0.25µm) and a MSD 5973 mass detector. Prior to GC analysis, aliquots were quenched appropriately using aqueous solutions of NH_4Cl or Na_2CO_3, the organic fractions extracted into diethyl ether or CH_2Cl_2, dried over Na_2SO_4, and filtered through alumina.

2 Ligand Synthesis

The ligand was prepared as schematised below.



2.1 Synthesis of phenol **A**

Bromine (30 mL, 0.58 mol) was added dropwise to a suspension of 4-(1,1-Dimethylethyl)-phenole (40 g, 0.26 mol), Na_2CO_3 (41 g, 0.39 mol), methanol (100 mL), and dichloromethane (DCM) (400 mL). The colour of the solution changed from white to orange and the reaction mixture was stirred for an additional 1 hour (h) at ambient temperature (r.t.). Water (200 mL) was added, the aqueous layer was separated and extracted with DCM (3 x 100 mL). The combined organic phases were washed with a saturated solution of $Na_2S_2O_3$, a saturated solution of NaCl, and finally dried over Na_2SO_4. The solvent was removed under reduced pressure and the brown residue was washed with hexane to yield phenol **A** as off-white solid (66.21 g, 83 %).

δ_H (400 MHz; d-$CHCl_3$; 298K) 7.44 (2 H, s), 5.73 (1 H, s), 1.27 (9 H, s).

δ_C (100 MHz, d-$CHCl_3$, 298K) 147.13, 146.18, 129.31, 109.58, 34.51, 31.37.

2.2 Synthesis of anisole **B**

NaH (5.90 g, 0.22 mol) was added in portions to a solution of **A** (66 g, 0.21 mol) in thf (250 mL) with cooling in an ice bath. Over the course of 20 minutes sodium phenolate precipitated as white solid. Dimethyl sulphate (dms) (21 mL, 0.24 mol) was added and the mixture stirred for 0.5 h at 0 °C and for an additional 12 h at 55 °C. A saturated NH_4Cl solution was added and the aqueous layer was extracted with ethyl acetate (3 x 100 mL). The combined organic phases were washed with a saturated solution of NaCl, dried over Na_2SO_4 and the solvent was removed under reduced pressure. The resulting brown oil was distilled under reduced pressure (85 °C, $6 \cdot 10^{-2}$ mbar) to give anisole **B** as colourless oil (62.30 g, 92 %).

δ_H (400 MHz; d-$CHCl_3$; 298K) 7.31 (2 H, s), 3.68 (3H, s), 1.10 (9H, s).

δ_C (100 MHz, d-$CHCl_3$, 298K) 151.68, 149.93, 129.68, 117.64, 60.58, 34.58, 31.16.

2.3 Synthesis of anisole **C**

Neat 2-Bromo-1,3,5-trimethyl-benzene (34 ml, 0.22 mol) was added dropwise to magnesium turnings (8.1 g, 0.33 mol) in thf (200 mL) and the reaction mixture was refluxed for 3 h. The Grignard solution (200 mL, 1 M in thf) was filtered and added to a suspension of $ZnCl_2$ (29 g, 0.21 mol) in thf (150 mL). The resulting mixture was stirred for 4 h at r.t. to produce a heavy precipitate that was dissolved by addition of *N*-Methyl-2-pyrrolidone (nmp) (10 mL). **B** (62 g, 0.19 mol) and tetrakis(triphenylphosphine)palladium(0) (1.1 g, 0.95 mmol) were added and the reaction mixture was refluxed for 2 days. The solvent was removed under reduced pressure and

the residue taken up in dcm and washed with aqueous HCl (6 M). The aqueous layer was separated and extracted with dcm (3 x 50 mL). The combined organic phases were washed with a saturated solution of NaCl, dried over Na_2SO_4 and the solvent removed under reduced pressure. Traces of palladium were removed by percolation of a dcm solution of the raw product through neutral alumina. Thorough washing of the raw product with methanol afforded **C** as a white solid (53 g, 76 %).

δ_H (400 MHz; d-$CHCl_3$; 298K) 7.52 (1 H, d, *J* 2.4), 7.01 (1H, d, *J* 2.4), 6.94 (2 H, s) 3.41 (3 H, s), 2.03 (6 H, s), 1.28 (9 H, s).

δ_C (100 MHz, d-$CHCl_3$, 298K) 152.05, 148.28, 137.01, 136.27, 135.08, 134.91, 129.12, 128.20, 128.11, 117.25, 60.01, 34.50, 31.40, 21.15, 20.69.

2.4 Synthesis of terphenyldianisole **D**

C (53 g, 0.15 mol) dissolved in thf (150 mL) was added dropwise to magnesium turnings (6.00 g, 0.25 mol) in thf (250 mL) at r.t. After the exothermic reaction ceased, the reaction mixture was stirred for 12 h at r.t. The Grignard solution (400 mL, 0.37 M) was filtered and added to a suspension of $ZnCl_2$ (20 g, 0.15 mol) in thf (100 mL), and the resulting mixture stirred for 1.5 h at r.t. Addition of nmp (16 mL) redissolved any precipitate that had formed. 1,4-Dibromobenzene (16 g, 69 mmol) and bis(tri-*tert*-butylphosphine)palladium(0) (0.19 g, 0.34 mmol) were added and the mixture refluxed for 12 h. The solvents were removed under reduced pressure, and the residue was taken up in dcm (100 mL) and was washed with aqueous HCl (6 M). The aqueous layer was separated and extracted with dcm (3 x 50 mL). The combined organic phases were washed with saturated aqueous solutions of Na_2CO_3 and NaCl, dried over Na_2SO_4 and the solvent was removed under reduced pressure. Traces of palladium black were removed by percolation of a dcm solution of the raw product through neutral alumina. Washing of the raw product with cold diethyl ether yielded **D** as a white solid (34 g, 76 %).

δ_H (400 MHz; d-$CHCl_3$; 298K) 7.67 (4 H, s), 7.38 (2 H, d, *J* 2.5), 7.06 (2 H, d, *J* 2.5), 6.97 (4 H, s), 3.17 (6 H, s), 2.35 (6 H, s), 2.13 (12 H, s), 1.34 (18 H, s).

δ_C (100 MHz, d-$CHCl_3$, 298K) 152.88, 146.67, 138.15, 136.67, 136.56, 136.35, 134.12, 133.71, 129.13, 128.16, 128.00, 126.93, 60.15, 34.62, 31.68, 21.24, 20.96.

2.5 Synthesis of terphenyldiphenol **E**

Ethanethiole (21 g, 340 mmol) was added dropwise to a suspension of NaH (9.64 g, 402 mmol) in *N*,*N*-dimethylformamide (dmf) (550 mL) cooled in an ice bath. The resulting clear solution was stirred for 1 h at r.t. **D** was added as a solid and the heterogeneous mixture stirred for 10 h

at 130 °C to produce a bright yellow solution. Volatiles were removed under vacuum, and the residue was taken up in dcm (100 mL) and washed with aqueous HCl (6 M). The aqueous layer was separated, extracted with dcm (3 x 50 mL), and the combined organic phases were washed with saturated aqueous NaCl, dried over Na_2SO_4 and taken to dryness under reduced pressure. The raw product was repeatedly washed with methanol to yield **E** as white solid (37.6 g, 92 %).

δ_H (400 MHz; d-$CHCl_3$; 298K) 7.68 (4H, s), 7.33 (2 H, d, *J* 2.5), 7.06 (2 H, d, *J* 2.4), 6.99 (4 h, s), 5.28 (2 H, br), 2.32 (6 H, s), 2.07 (12 H, s), 1.31 (18 H, s).

δ_C (100 MHz, d-$CHCl_3$, 298K) 147.12, 143.40, 137.82, 137.74, 137.47, 133.05, 129.41, 128.70, 127.00, 126.76, 126.60, 126.58, 34.30, 31.66, 21.15, 20.47.

2.6 Synthesis of *N*,*N*-Dimethyl-*O*-thiocabamate ester **F**

A pressure stable reaction vessel was charged with a solution of **E** (20 g, 33 mmol) in thf (200 mL), and the solution was cooled in an ice bath. First, a suspension of NaH (1.7 g, 72 mmol) in thf was added, and the resulting mixture stirred for 30 minutes at r.t. after hydrogen evolution had ceased. Dimethylthiocarbamoyl chloride (dmcc) (10 g, 83 mmol) was added as a solid. The reaction vessel was degassed and heated to 90 °C for 15h to produce a clear pale yellow solution and a white precipitate of NaCl. Volatiles were removed under reduced pressure, and the residue was taken up in dcm and washed with aqueous HCl (6 M). The aqueous layer was separated and extracted with dcm (3 x 20 mL). The combined organic phases were washed with saturated aqueous NaCl, dried over Na_2SO_4, and the solvent was removed under reduced pressure. The raw product was washed with methanol to yield *N*,*N*-Dimethyl-*O*-thiocabamate ester **F** as a white solid (23 g, 89 %).

δ_H (250 MHz; d-$CHCl_3$; 298K) 7.55-7.50 (4 H, m), 7.40 (2 H, m), 7.19 (2 H, m), 6.91 (4 H, m), 3.00-2.91 (12 H, m), 2.30-2.09 (18 H, m), 1.37 (18 H, s).

IR (ATR): ν/cm^{-1} 1530 (C(S) stretch, very strong band).

2.7 Synthesis of *N*,*N*-Dimethyl-*S*-thiocabamate ester **G**

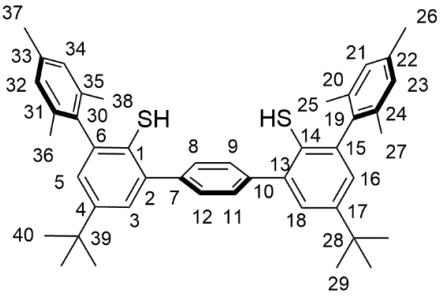
A Schlenk tube was charged with solid *N*,*N*-Dimethyl-*O*-thiocabamate ester **F** (2 x 11 g, 2 x 14 mmol). After the flask was evacuated and backfilled with argon three times the solids were molten at 320 °C in a metal bath to give a clear liquid that was kept for an additional 15 minutes at this temperature. After cooling to r.t. under argon the resulting pale brown solid was recovered and washed once with methanol to yield *N*,*N*-Dimethyl-*S*-thiocabamate ester **G** as a white solid (22 g, 95 %).

δ_H (400 MHz; d-$CHCl_3$; 298K) 7.47 (4 H, s), 7.40 (2 H, d, J 2.3), 7.20 (2 H, d, J 2.3), 6.93 (4 H, s), 2.63 (12 H, s), 2.34 (6 H, s), 2.03 (12 H, s), 1.34 (18 H, s).

δ_C (100 MHz, d-$CHCl_3$, 298K) 166.42, 152.57, 147.90, 146.44, 141.09, 139.05, 136.51, 136.42, 128.75, 127.75, 126.73, 126.70, 124.59, 34.83, 31.31, 21.15, 20.68.

IR (ATR): ν/cm^{-1} 1665 (C(O) stretch, very strong band).

2.8 Synthesis of 4-terphenyldithiophenol $Mes_2{}^tBu_2(SH)_2$



An ice cold solution of $LiAlH_4$ (6.43 g, 170 mmol) in thf (100 mL) was added slowly to a suspension of *N*,*N*-Dimethyl-*S*-thiocabamate ester **G** (22.2 g, 28.3 mmol) in thf (150 mL) at r.t. After stirring for 20 minutes at r.t. the reaction mixture was stirred at 75 °C for another 1 h. After cooling to 40 °C all volatiles were removed under reduced pressure and the resulting yellow residue was dissolved in diethyl ether and remaining $LiAlH_4$ was quenched by careful addition of ice water. The suspension was neutralised by aqueous HCl (6 M, 113 mL) and the aqueous layer was extracted with dcm. The combined organic layers were washed with saturated aqueous NaCl, dried over Na_2SO_4 and taken to dryness under reduced pressure. The ligand was obtained as a white solid after washing the raw product with methanol (16.22g, 89 %). In the following the neutral and doubly deprotonated form of the ligand are abbreviated as $Mes_2{}^tBu_2(SH)_2$ and $Mes_2{}^tBu_2S_2$.

δ_H (400 MHz; d-$CHCl_3$; 298K) 7.59 (4 H, s, 8-, 9-, 11-, 12-H), 7.30 (2 H, d, $J_{5\text{-}3}$ 2.3, 3-, 18-H), 7.10 (2 H, d, $J_{3\text{-}5}$ 2.6, 5-, 16-H), 7.02 (4 H, s, 21-, 23-, 32-, 34-H), 3.26 (2 H, s, S*H*), 2.37 (6 H, s, 26-, 37-H), 2.08 (12 H, s, 25-, 27-, 36-, 38-H), 1.34 (18 H, s, 4-, and 17-^{t}Bu).

δ_C (100 MHz, d-$CHCl_3$, 298K) 148.03 (C-4, -17), 141.04 (C-7, -10), 139.67 (C-2, -13), 138.67 (C-6, -15), 138.04 (C-19, -30), 137.38 (C-22, -33), 136.49 (C-20, -24, -31, -35), 129.33 (C-8, -9, -11, -12), 128.51 (C-21, -23, -32, -34), 127.62 (C-1, -14), 126.10 (C-3, -5, -16, -18), 34.48 (C-28, -40), 31.39 (C-29, -39), 21.15 (C-26, -37), 20.26 (C-25, -27, -36, -38).

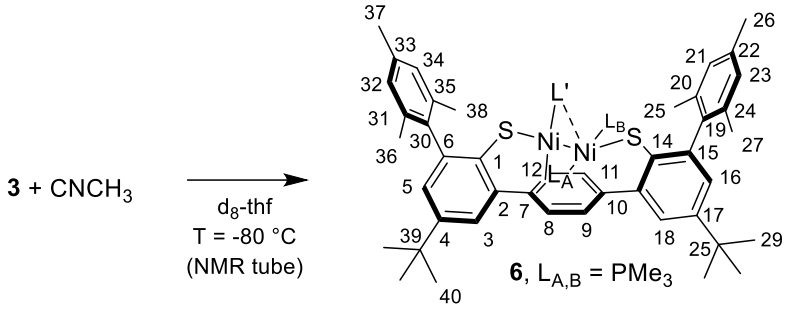
Elemental analysis found: C, 82.18; H, 7.78; S, 9.97. Calc. for $C_{44}H_{50}S_2$: C, 81.48; H, 7.93; S, 9.37%.

3 Additional NMR information of compound 2

δ_H (500 MHz; d_2-CH_2Cl_2; 193 K) 8.21 (2 H, s, 11-, 12-H), 7.44 (2 H, s, 8-, 9-H), 7.25 (2 H, s, 3-, 18H), 6.75 (6 H, br s, 5-, 16-, 21-, 23-, 32-, 34-H), 2.13 (6 H, s, 26-, 37-H), 1.83 (12 H, s, 25-, 27-, 36-, 38-H), 1.21 (18 H, s, 4-, and 17-^{t}Bu), 2.35-0.72 (m, P(C_6H_{11})$_3$).

δ_C (126 MHz; d_2-CH_2Cl_2; 193 K) 145.64, 140.28, 139.92, 137.65, 135.26, 134.24, 127.37 (C-8, -9), 126.94, 120.72, 108.35 (C-11, -12), 33.79, 30.57, 22.59, 20.46.

4 In-situ preparation and characterization of compound 6



A 0.5 mL sample of an 11 mM d_8-thf solution of **3** contained in a septum sealed NMR tube was cooled to -80 °C in a dry ice/ acetone bath. To this solution 11 µL of a 0.51 M methyl isocyanide solution in d_6-benzene were added and the tube inserted into the precooled NMR probe.

δ_H (500 MHz, d_8-thf, 178 K) 7.73 (1 H, d, $J_{12\text{-}11}$ 7.5, 12-H), 7.50 (1H, s, 18-H), 7.27 (1 H, br s, 3-H), 6.86 (br, 5-, 21-, 23-, 32-, 34-H), 6.77 (1 H, br s, 16-H), 6.53 (1 H, d, $J_{11\text{-}12}$ 7.5, 11-H), 6.47 (1 H, br s, 9-H), 6.18 (1 H, br s, 8-H), 3.32 (3 H, s, CNCH_3), 2.30 and 2.27 (s, 26-, 37-H), 2.15 (s, 36-H), 2.09 (s, 25-, 27-H), 2.07 (s, 38-H), 1.33 (s, 29-H), 1.30 (s, 40-H), 1.30 (d, PMe_3 = L_A), 1.05 (d, J_P = 10.6 Hz, PMe_3 = L_B).

δ_P (202 MHz, d_8-thf, 203K) -7.35 (d, $J_{P\text{-}P}$ 54, PMe_3 = L_A), -17.0 (d, $J_{P\text{-}P}$ 54, PMe_3 = L_B).

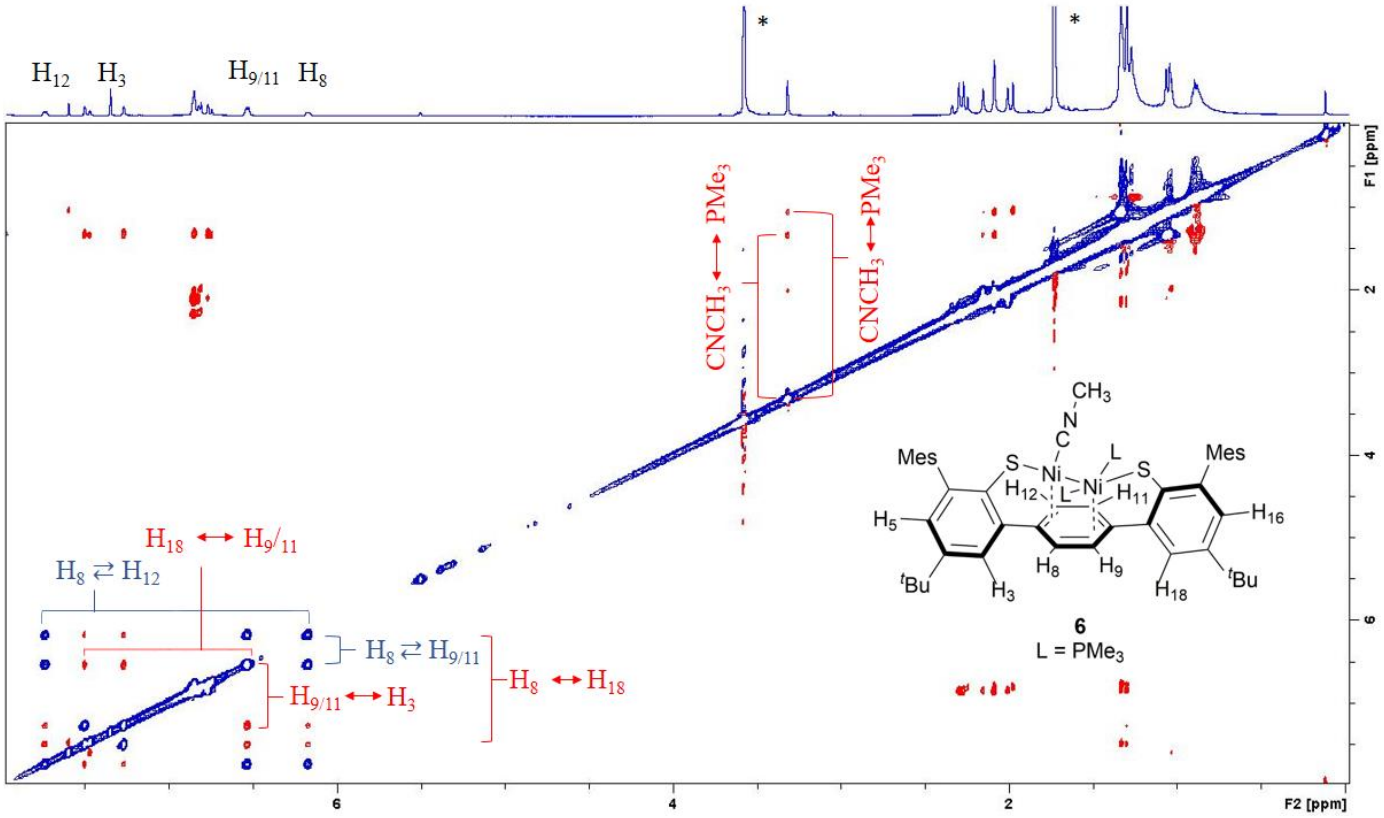


Figure S1. 500 MHz ^{1}H-^{1}H NOESY data (203 K, d_8-thf (*)) of compound **6** generated in-situ in an NMR tube. Chemical exchange is highlighted in blue (⇄), NOEs in red (↔).

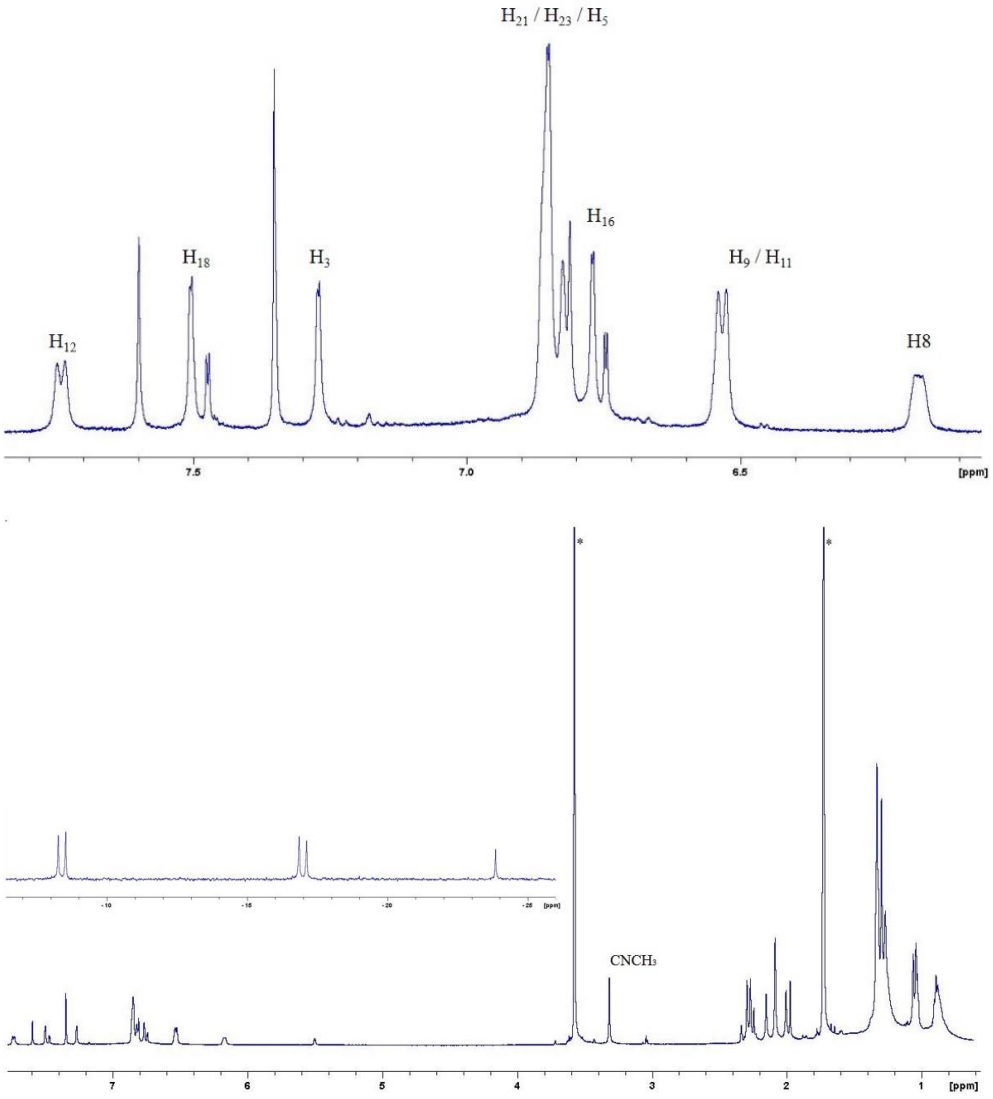


Figure S2. ^{1}H NMR spectra (500 MHz, d_8-thf (*), 173 K) of compound **3**. Bottom: Addition of $CNCH_3$. Top: Magnification of the low field region of the bottom spectrum. Characteristic signals of compound 6 are assigned. Inset: $^{31}P\{^{1}H\}$ spectrum (202 MHz, d_8-thf, 203K) of **3** after the addition of $CNCH_3$, showing the characteristic signals of **6** -7.35 (d, $J_{P\text{-}P}$ 54, $P_b(CH_3)_3$), -17.0 (d, $J_{P\text{-}P}$ 54, $P_a(CH_3)_3$), and residual **1**, at -24 ppm, from the synthesis of **3**.

5 In-situ preparation and characterization of compound 5*2L'.

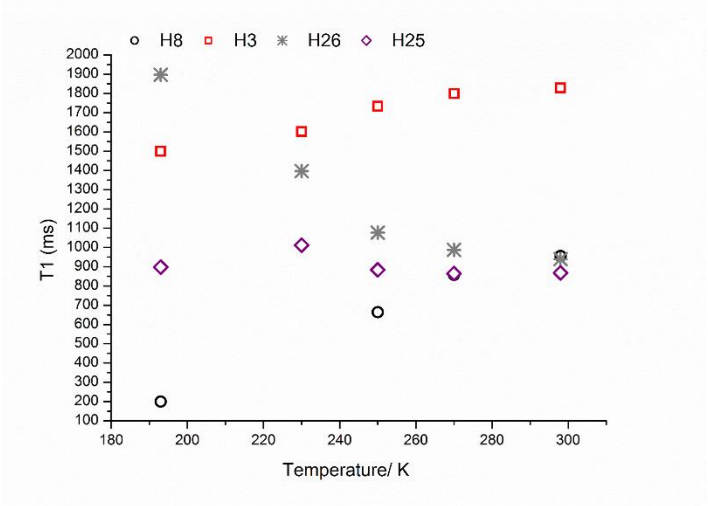
Compound **5***2L' (L' = $CNCH_3$): To a 30 mM sample of **5** in d_8-thf contained in a septum sealed NMR tube cooled to 193K in an dry ice/acetone bath was added a total of 2 equiv. of $CNCH_3$ in the form of a 0.51 M solution in d_6-benzene in 4 steps using a microliter syringe. Initial ^1H and $^{31}P\{^1H\}$ NMR spectra were taken at 213K but progressive precipitation of **5***2L' required warming the sample to 263K.

δ_H[δ_C from ^1H-^{13}C HSQC data] (500 MHz, d_8-thf, 263 K) 8.49[131.5] (2 H, d, *J* 8.0, 8-, 9-, 11-, 12-H), 7.59[124.2] (2 H, br s, 3-, 5-H), 7.53[127.6] (2 H, d, *J* 8.0, 8-, 9-, 11-, 12-H), 7.44[134.2] (12 H, *ortho*-H, PPh_3), 7.33[128.8] (6 H, *para*-H, PPh_3), 7.12[127.1] (12 H, *meta*-H, PPh_3), 6.76[124.5] (2 H, br s, 3-, 5-H), 6.96[127.1] and 6.88[127.0] (2 H each, 21-, 23-, 32-, 34-H), 2.35[20.3] (6 H, s, 26-, 37-H), 2.13[31.1] (6H, L'), 1.94[20.0] and 1.49[20.7] (6 H each, 25-, 27-, 36-, 38-H), 1.34[30.7] (18 H, s, ^{t}Bu).

δ_P (202 MHz, d_8-thf, 263K) 22.51 ($\nu_{1/2}$ = 24 Hz, **5***2L'), 33.2 ($\nu_{1/2}$ = 12 Hz, $(Ph_3P)_2(L')_2Ni(0)$).

6 Determination of ^{1}H NMR spin-lattice relaxation times, T_1

Measurement of ^1H spin-lattice relaxation time T_1 was performed on a Bruker AVII+500 spectrometer, using the inversion-recovery method. To determine the T_1-values Topspin 2.1 (Bruker) was used. Concentrations of the complex solutions are given with 20 mM for **2**, 21 mM for **3**, 15 mM for **4**, and 35 mM for **5.**



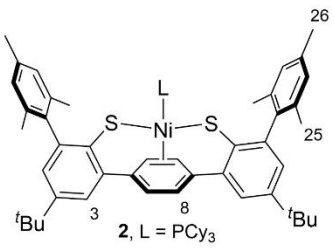
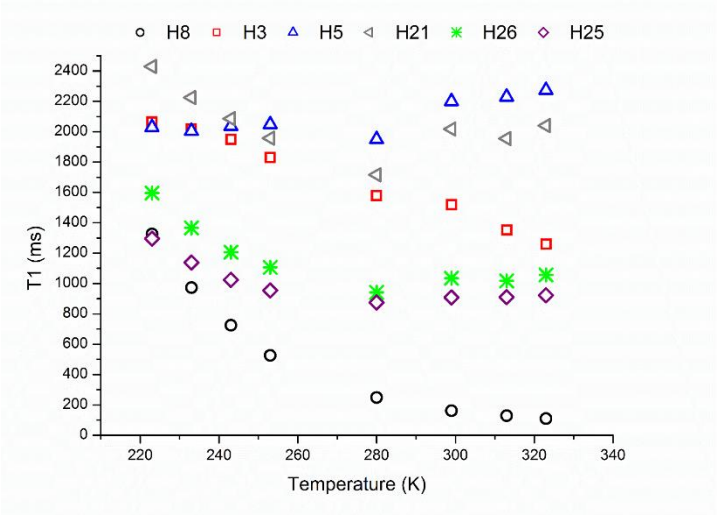
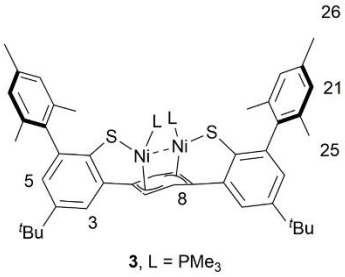


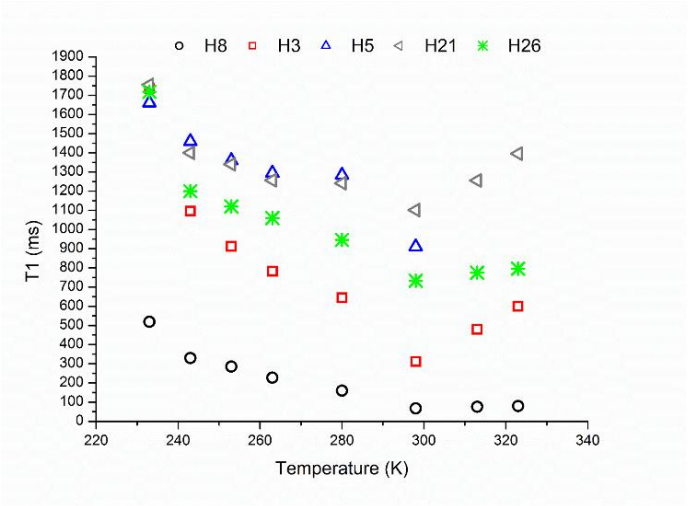
Figure S3. Temperature dependence of T_1 times for complex **2**, 20 mM in d_2-CH_2Cl_2.

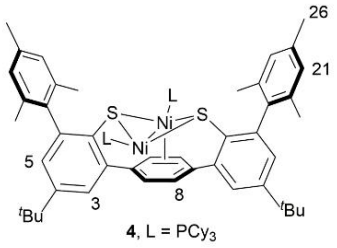




3, L = PMe_3

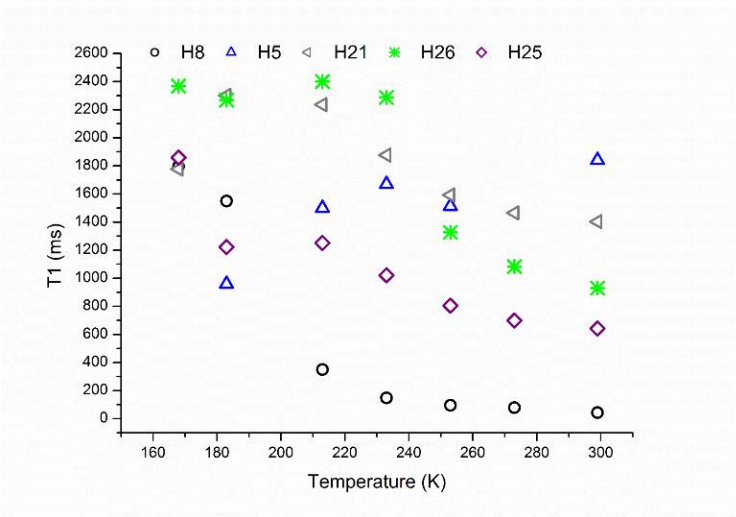
Figure S4. Temperature dependence of T_1 times for complex **3**, 21 mM in d_8-thf.

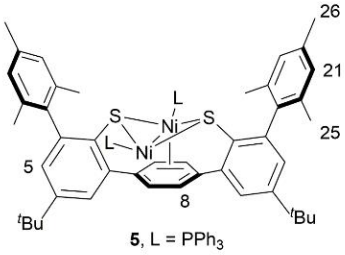




4, L = PCy_3

Figure S5. Temperature dependence of T_1 times for complex **4,** 15 mM in d_8-thf.





5, L = PPh_3

Figure S6. Temperature dependence of T_1 times for complex **5**, 35 mM in d_8-thf.

7 Temperature dependence of ^{1}H NMR chemical shifts

Concentrations in d_8-thf: 19 mM for **4**, and 35 mM for **5**.

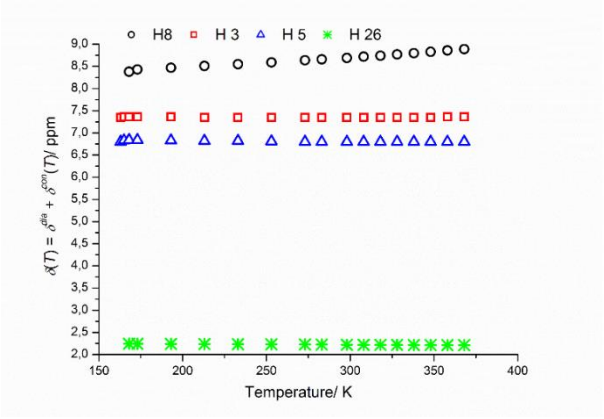


Figure S7. Temperature dependence of δ_H values of selected proton resonances of complex **4**, T range from 163 to 368 K.

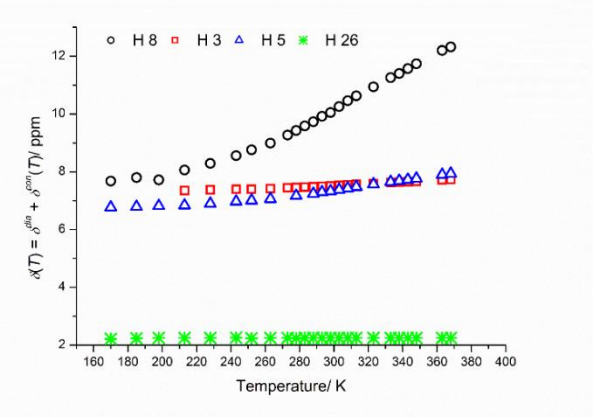


Figure S8. Temperature dependence of δ_H values of selected proton resonances of complex **5**, T range from 168 to 253 K.

8 Additional crystallographic information

Colour code: C, black; H, light blue; O, red; Ni, plum; P, orange; S, yellow.

8.1 Single crystal molecular structure of **1**.

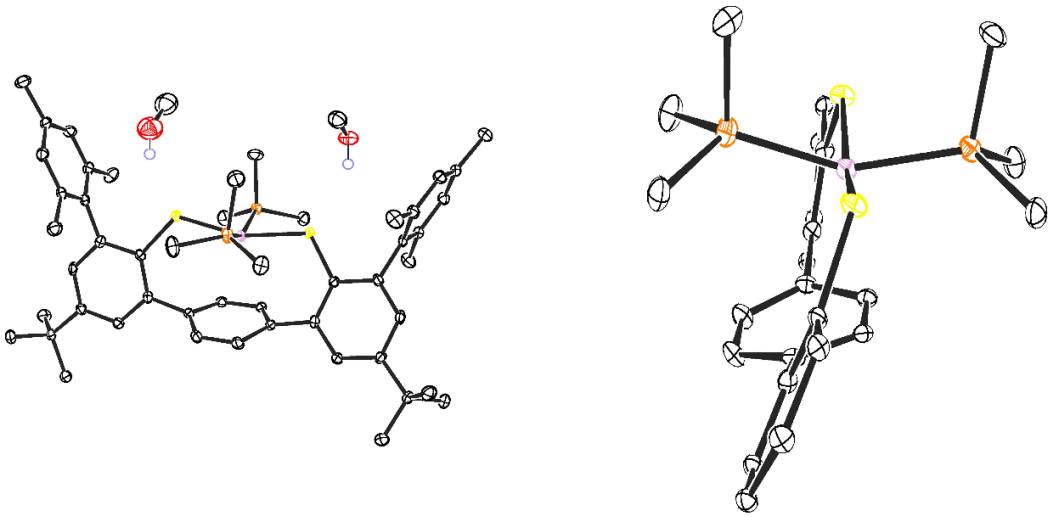


Figure S9. Left: ORTEP representation of **1**, 50% thermal probability ellipsoids; H-atoms omitted for clarity. Right: Side view on **1**, 50% thermal probability ellipsoids; H-atoms, lattice methanol, and peripheral ligand atoms omitted for clarity.

8.2 Structural details of **2**.

The asymmetric unit contains one molecule of tetrahydrofuran as a solvent of crystallization. The (Cy_3P)Ni(η^2-arene) moiety is disordered and was refined to a final ratio of 0.76/ 0.24. The remaining ligand backbone was found to be the same for both sites of the disorder.

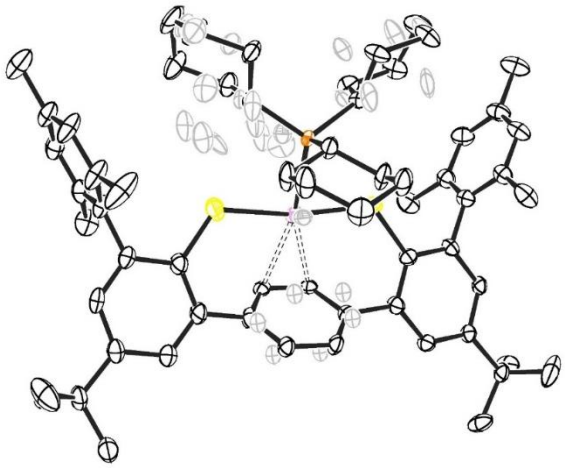


Figure S10. ORTEP representation of **2**; 50% thermal probability ellipsoids, H-atoms omitted for clarity.

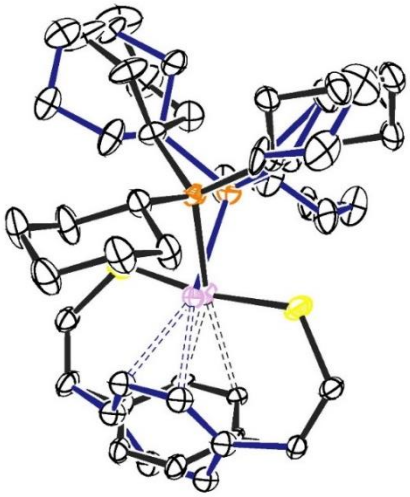


Figure S11. ORTEP representation showing the disordered part (black and purple) of **2**; 50% thermal probability ellipsoids; H-atoms, lattice thf, and peripheral substituent atoms omitted for clarity.

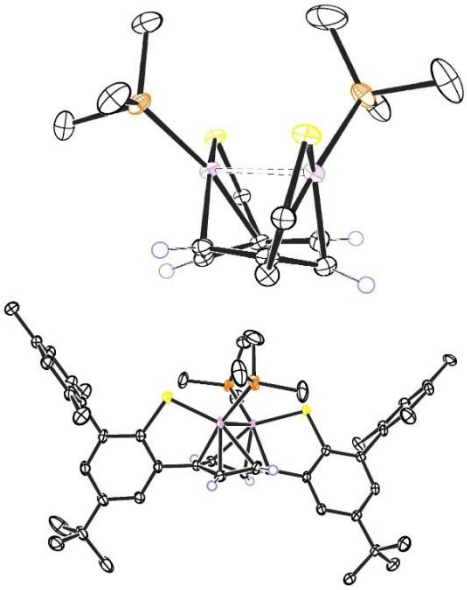


Figure S12. ORTEP representation of **3**; 50% thermal probability ellipsoids, H-atoms omitted for clarity. Top: Magnification of the *syn*-μ-η^3:η^3-arene-(κ^1-*S*-NiPMe$_3$)$_2$ moiety.

8.3 Structural details of **4**.

The crystals of **4** were mounted on the goniometer head under a nitrogen stream at 130 K. This procedure was necessary in order to minimize thermal stress on the crystals. The molecular structure revealed partial disorders of three C_6H_{11} substituents.

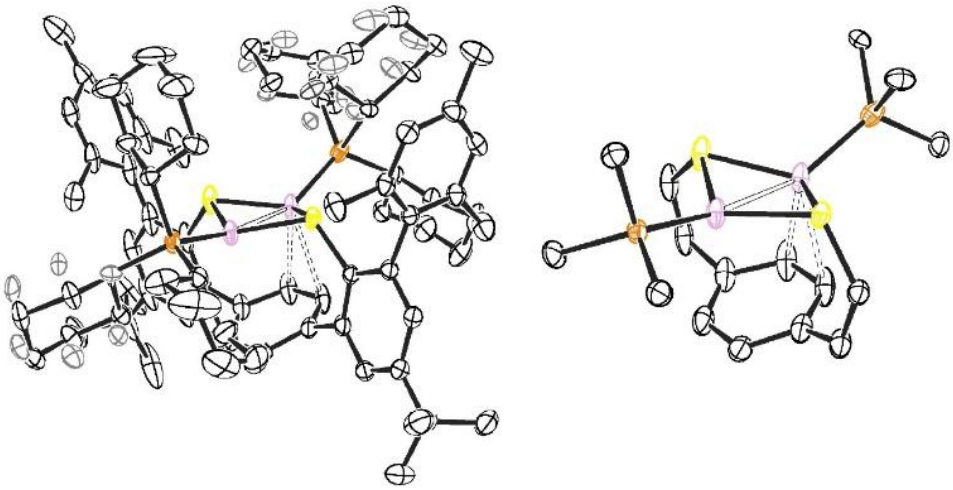


Figure S13. Left: ORTEP representation of **4**; 50% thermal probability ellipsoids. H-atoms omitted for clarity. Right: Detailed view of the $Ni_2(\mu\text{-}S)_2$ fragment, peripheral ligand substituents, H-atoms, and C_6H_{11} substituents not shown for clarity.

8.4 Structural details of **5**.

Residual electron density of a strongly disordered hexane molecule was excluded applying the program squeeze. Total potential solvent accessible volume (S.A.V.): 497.9 $Å^3$, and electrons found in S.A.V. = 112.3.

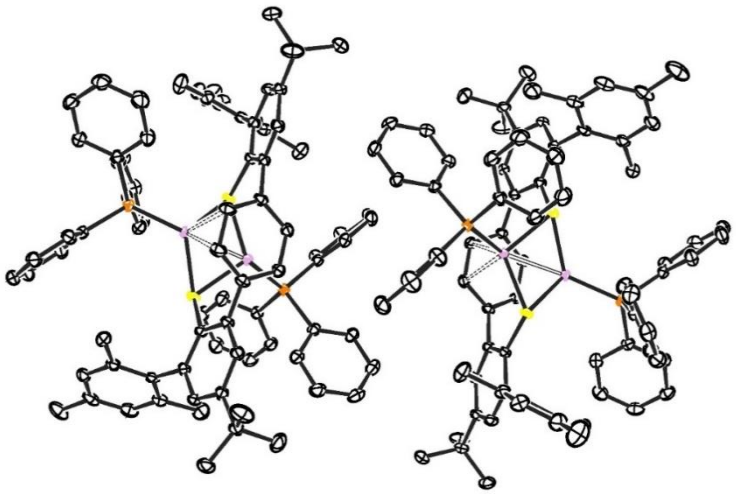


Figure S14. ORTEP representation of **5**; 50% thermal probability ellipsoids. H-atoms omitted for clarity.

Table S1. Crystal data for **1**, **2**, and **3**.

Compound	**1**	**2**	**3**
Empirical formula	$C_{50}H_{66}P_2S_2 \cdot 2CH_3OH$	$C_{62}H_{81}NiPS_2 \cdot C_4H_8O$	$C_{50}H_{66}Ni_2P_2S_2 \cdot C_5H_{12}$
M_r/ g mol^{-1}	915.88	1052.17	982.65
Source	Mo K_α, 0.71073 Å	Mo K_α, 0.71073 Å	Mo K_α, 0.71073 Å
Temperature/ K	100(2)	100(2)	100(2)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	P 1 21/c	P 1 21/n	P 1 21/n
Z	4	4	4
a [Å]	13.5105(2)	9.7947(5)	15.8803(8)
b [Å]	12.1898(2)	31.5469(16)	20.1160(10)
c [Å]	29.9385(5)	19.7427(11)	17.6539(9)
α [°]	90.00	90	90
β [°]	91.7630(10)	94.199(3)	107.723(3)
γ [°]	90.00	90	90
V [Å^3]	4928.25(14)	6084.0(6)	5371.9(5)
Density ρ_{calc}/ g cm^{-3}	1.234	1.149	
Abs. coeff. μ/ mm^{-1}	0.581	0.453	0.872
F(000)	1968	2272	2104
Crystal size/ *mm^3*	0.231	0.200	0.380
Theta range [°]	1.36-27.50	1.22-26.37	1.51-30.10
Reflections collected	27715	81481	75839
Absorption correction	multi-scan	multi-scan	multi-scan
Parameters / restraints	554/ 0	869 / 370	571/ 29
R_1, wR_2 >2sigma(I)	0.0390/ 0.0996	0.0744/ 0.1898	0.0525/ 0.1302
R_1, wR_2 all data	0.0536/ 0.1114	0.1112/ 0.2111	0.0738/ 0.1389
Goodness-of-fit on F^2	1.069	1.070	1.038
Largest diff. peak/ hole/ e · Å^{-3}	-1.110/ 1.456	-0.570/ 1.097	-0.847/ 2.171
CCDC	1042645	1042646	1042647

Table S2. Crystal and refinement data for **4** and **5.**

Compound	**4**	**5**
Empirical formula	$C_{80}H_{114}Ni_2P_2S_2$	$C_{80}H_{78}Ni_2P_2S_2$,0.5(C_6H_{14})
M_r/ g mol^{-1}	1319.19	1282.9
Source	Mo K_α, 0.71073 Å	Mo K_α, 0.71073 Å
Temperature/ K	130.(2)	100(2)
Crystal system	triclinic	triclinic
Space group	P -1	P -1
Z	2	4
a [Å]	11.1421(4)	11.9127(3)
b [Å]	12.9165(5)	21.1860(5)
c [Å]	26.8959(10)	28.2328(7)
α [°]	95.2410(10)	77.6250(10)
β [°]	91.5290(10)	86.1850(10)
γ [°]	111.5980(10)	86.3060(10)
V [Å^3]	3576.3(2)	6935.3(3)
Density ρ_{calc}/ g cm^{-3}		1.270
Abs. coeff. μ/ mm^{-1}	0.672	0.692
F(000)	1424	2804
Crystal size/ mm^3	0.429	0.419
Theta range [°]	0.76- 28.33	0.985-27.103
Reflections collected	51911	30564
Absorption correction	multi-scan	multi-scan
Parameters/ restraints	949/ 420	1549/ 0
R_1, wR_2 >2sigma(I)	0.0392/ 0.0933	0.0308/ 0.0864
R_1, wR_2 all data	0.0535/ 0.1013	0.0371/ 0.0936
Goodness-of-fit on F^2	1.018	1.015
Largest diff. peak/ hole/ e · Å^{-3}	-0.699/ 0.725	-0.670/ 0.767
CCDC	1042648	1042649

9 Additional computational details

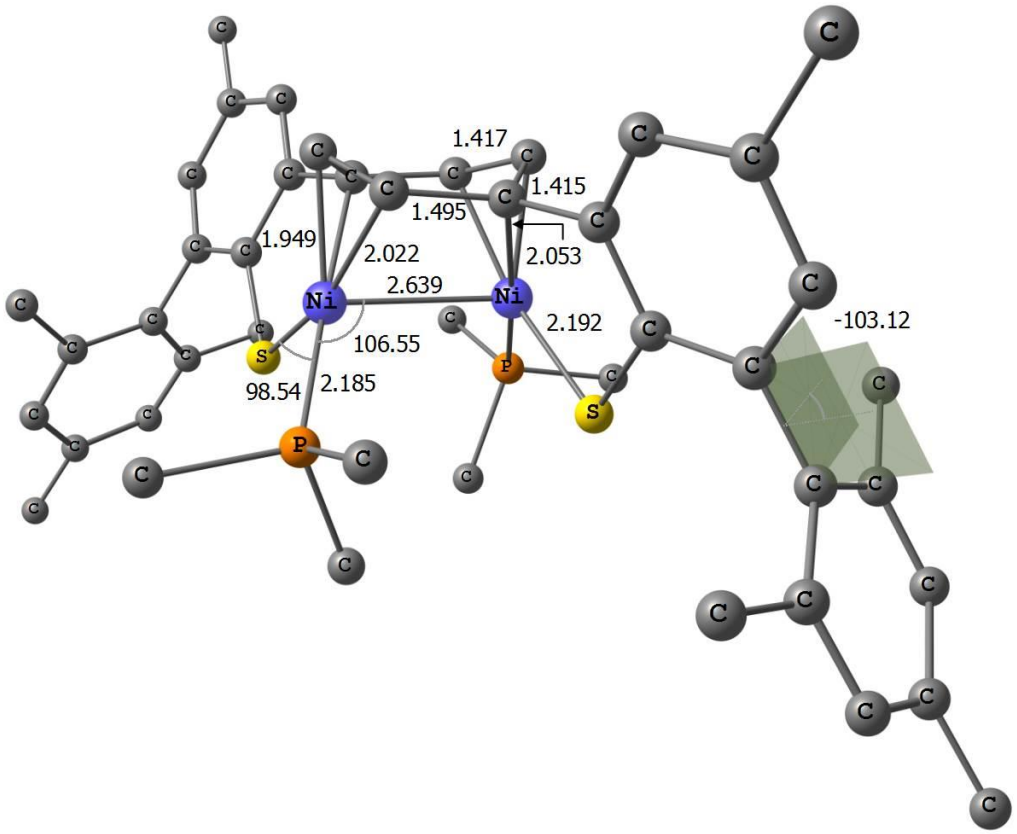


Figure S15. Optimised geometry (C_2 symmetry) and selected geometrical parameters (distances in Å, angles in °) for the theoretical model system of **3** (^{t}Bu substituents were replaced by methyl groups, H atoms are omitted for clarity).

Cartesian Coordinates for the model system of **3**:

6	1.100662000	4.980670000	2.967009000
6	0.774776000	5.589502000	1.752899000
6	0.882877000	3.606906000	3.087982000
6	-2.535548000	5.434710000	0.036284000
6	0.252957000	4.874584000	0.672967000
6	0.348272000	2.867883000	2.035615000
6	-1.432264000	5.868943000	-0.894213000
6	-0.088110000	5.584009000	-0.594460000
6	-1.735858000	6.544775000	-2.074411000
6	2.373592000	5.666446000	-1.190169000
6	0.925926000	5.976059000	-1.481787000
6	0.049902000	3.490160000	0.811612000
6	0.110808000	1.401471000	2.139702000
6	-0.742948000	6.944036000	-2.969373000
6	0.581556000	6.647267000	-2.656416000
6	-1.122867000	0.856755000	2.569464000
6	-1.095452000	7.697427000	-4.227730000
6	1.304087000	0.503351000	2.216464000
6	-1.304087000	-0.503351000	2.216464000
6	1.122867000	-0.856755000	2.569464000
6	-0.110808000	-1.401471000	2.139702000
6	-0.348272000	-2.867883000	2.035615000
6	-0.882877000	-3.606906000	3.087982000
6	-0.049902000	-3.490160000	0.811612000
6	-1.100662000	-4.980670000	2.967009000
6	-0.252957000	-4.874584000	0.672967000
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6	-2.373592000	-5.666446000	-1.190169000
6	2.535548000	-5.434710000	0.036284000
6	0.088110000	-5.584009000	-0.594460000
6	-0.925926000	-5.976059000	-1.481787000
6	1.432264000	-5.868943000	-0.894213000
6	-0.581556000	-6.647267000	-2.656416000
6	1.735858000	-6.544775000	-2.074411000
6	0.742948000	-6.944036000	-2.969373000
6	1.095452000	-7.697427000	-4.227730000
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1	-2.586309000	4.342792000	0.074137000
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1	2.999308000	5.886674000	-2.057122000
1	1.368800000	6.939370000	-3.344869000
1	2.505535000	4.615557000	-0.927536000
1	2.252419000	0.989023000	2.408337000
1	-0.309038000	7.604983000	-4.979954000
1	-2.027510000	7.329055000	-4.663550000
1	-2.252419000	-0.989023000	2.408337000
1	1.934444000	-1.481587000	2.923191000
1	-1.119487000	-3.102508000	4.019984000
1	-2.505535000	-4.615557000	-0.927536000
1	2.586309000	-4.342792000	0.074137000
1	-0.925438000	-6.658244000	1.635402000
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1	3.501537000	-5.816780000	-0.298816000
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1	1.230988000	-8.764941000	-4.022448000

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15	2.459089000	0.197760000	-0.814948000
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16	0.531693000	-2.488985000	-0.549798000
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28	1.100662000	-0.727791000	0.624862000
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1	-2.288918000	-6.593410000	3.776744000
1	-0.818333000	-6.257403000	4.688007000
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1	2.307290000	2.536230000	-0.270836000
1	3.720266000	1.795343000	0.503176000
6	1.817694000	0.399922000	-2.518909000
1	1.429545000	-0.555933000	-2.872818000
1	1.012494000	1.133327000	-2.495368000
1	2.605988000	0.743035000	-3.193340000
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1	3.656603000	-1.821823000	-1.396660000
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1	-2.307290000	-2.536230000	-0.270836000
6	-1.817694000	-0.399922000	-2.518909000
1	-1.012494000	-1.133327000	-2.495368000
1	-2.605988000	-0.743035000	-3.193340000
1	-1.429545000	0.555933000	-2.872818000

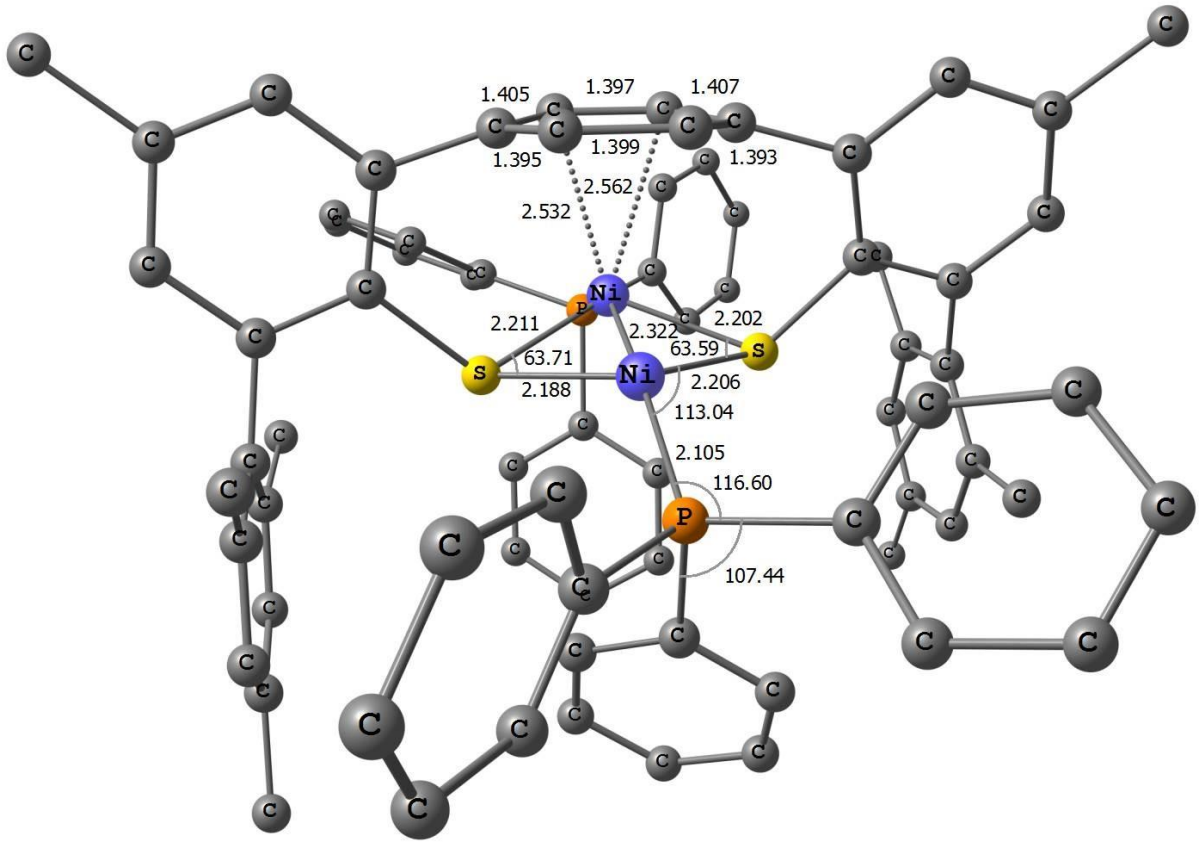

Figure S16. Optimised geometry (C_1 symmetry) and selected geometrical parameters (distances in Å, angles in °) for the theoretical model system of **5** (^{t}Bu substituents were replaced by methyl groups, H atoms are omitted for clarity).

Cartesian Coordinates for the model system of **5**:

1	-6.674383000	-2.805842000	-3.966389000
1	-5.565585000	-2.437465000	-5.295239000
1	-5.402926000	-3.947354000	-4.400820000
6	-5.637273000	-2.881808000	-4.299826000
6	-4.697905000	-2.211420000	-3.329224000
6	-5.033624000	-2.082603000	-1.978680000
6	-3.472847000	-1.693799000	-3.764639000
6	-4.372794000	4.636882000	-1.336116000
6	-5.189035000	4.819486000	-0.219591000
6	-5.213030000	1.089370000	-0.461599000
6	-4.156486000	-1.508501000	-1.059624000
6	-2.574216000	-1.113002000	-2.873953000
6	-5.013277000	0.082922000	0.641387000
6	-4.539327000	-1.210829000	0.355489000
6	-3.119037000	4.056336000	-1.191688000
6	-5.212628000	0.454303000	1.968931000
6	-3.683552000	-3.459393000	1.110216000
6	-4.288817000	-2.113472000	1.396057000
6	-2.894056000	-1.077945000	-1.500683000
6	-1.289270000	-0.488318000	-3.283981000
6	-4.949840000	-0.423194000	3.022284000
6	-4.502703000	-1.705754000	2.714508000
6	-4.741931000	4.417837000	1.035461000
6	-1.171288000	0.911380000	-3.209250000
6	-1.958331000	-5.203552000	-1.507712000
6	-5.117201000	0.026590000	4.452173000

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6	-2.662186000	3.653188000	0.069005000
6	-1.141557000	-4.140696000	-1.131509000
6	0.085740000	1.519817000	-3.223648000
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6	-0.340212000	5.709638000	0.323209000
6	0.446553000	6.825174000	0.059396000
6	1.116276000	-0.642271000	-3.508823000
6	-0.763821000	-6.648214000	0.014675000
6	1.245438000	0.731005000	-3.303271000
6	0.033092000	4.452828000	-0.166950000
6	1.609073000	6.698489000	-0.702454000
6	-0.132016000	-4.325124000	-0.185086000
6	0.062352000	-5.590745000	0.378298000
6	1.197253000	4.333890000	-0.929429000
6	1.982742000	5.452525000	-1.196787000
6	2.567185000	1.264526000	-2.878584000
6	-0.165114000	-3.179341000	2.809233000
6	3.516409000	1.776511000	-3.757818000
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6	0.811020000	-2.587073000	2.007089000
1	5.641435000	3.841473000	-4.363226000
6	0.546630000	-1.832070000	4.683490000
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6	2.883464000	1.154960000	-1.507120000
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6	0.455401000	2.845313000	4.028662000
1	6.811186000	2.594260000	-3.932224000
6	-0.266669000	1.789834000	4.576469000
6	4.172033000	-4.652436000	-1.558774000
6	3.442455000	-4.001372000	1.052135000
6	3.735221000	3.283496000	1.203619000
6	5.150256000	-1.209167000	-0.599824000
6	4.559240000	1.067070000	0.333291000
6	5.019551000	-4.975168000	-0.498541000
6	4.341866000	1.925317000	1.418146000
6	4.653089000	-4.646651000	0.803148000
6	5.009428000	-0.248081000	0.551469000
6	4.587228000	1.459635000	2.711646000
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6	5.031858000	0.161615000	2.951884000
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1	-6.006761000	-2.416141000	-1.632974000
1	-3.218909000	-1.726254000	-4.819081000
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1	-5.745427000	1.967060000	-0.098302000
1	-2.742957000	-5.040696000	-2.237296000
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1	-4.289077000	-2.402686000	3.519106000
1	-5.372383000	4.557220000	1.906487000
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1	-0.221635000	-2.328916000	-3.565442000
1	-4.991101000	-0.805159000	5.148228000
1	-1.296500000	-3.154715000	-1.546139000
1	-1.248652000	5.809459000	0.904846000
1	0.153319000	7.795401000	0.444081000
1	-4.377157000	0.792186000	4.707867000
1	0.171033000	2.595569000	-3.138816000
1	-0.617445000	-7.625735000	0.459905000
1	-3.137592000	3.531864000	2.160640000
1	2.009906000	-1.252364000	-3.560395000
1	2.218219000	7.570964000	-0.909564000
1	3.264402000	1.861261000	-4.809753000
1	-0.829987000	-3.924149000	2.392145000
1	-1.061560000	-3.258954000	4.759091000
1	1.494942000	3.361838000	-1.297372000
1	2.885016000	5.341870000	-1.786823000
1	0.861266000	-5.743287000	1.094494000
1	-2.160824000	0.965821000	1.889180000
1	0.437158000	-1.533181000	5.719800000
1	0.795405000	4.063462000	2.291811000
1	2.305227000	-3.756685000	-2.134879000
1	2.377664000	-1.097430000	1.926138000
1	2.157050000	-0.453340000	4.280711000
1	-1.770770000	0.287027000	4.209216000
1	4.218651000	3.827391000	0.389662000
1	4.170408000	-1.417314000	-1.036523000
1	4.453281000	-4.903379000	-2.575051000
1	3.160893000	-3.751105000	2.066351000
1	1.204354000	3.358590000	4.621154000
1	6.112492000	2.184889000	-1.619977000
1	2.683586000	3.167237000	0.931264000
1	5.574227000	-2.156297000	-0.270264000
1	-0.078856000	1.473640000	5.596204000
1	3.787319000	3.891353000	2.108591000
1	5.776412000	-0.800916000	-1.396283000
1	5.961082000	-5.477054000	-0.688826000
1	5.308200000	-4.894736000	1.630705000
1	4.400287000	2.122750000	3.550736000
1	5.565241000	-1.700935000	2.020487000
1	4.784571000	-1.295508000	4.525658000
1	4.903268000	0.373458000	5.097239000
1	6.346897000	-0.478505000	4.542911000
15	-0.969640000	2.950101000	0.156393000
15	0.944817000	-2.894291000	0.209499000
16	-1.738279000	-0.545666000	-0.255251000
16	1.689787000	0.684635000	-0.270139000
28	-0.415496000	1.136781000	-0.771255000
28	0.382539000	-1.037562000	-0.608244000

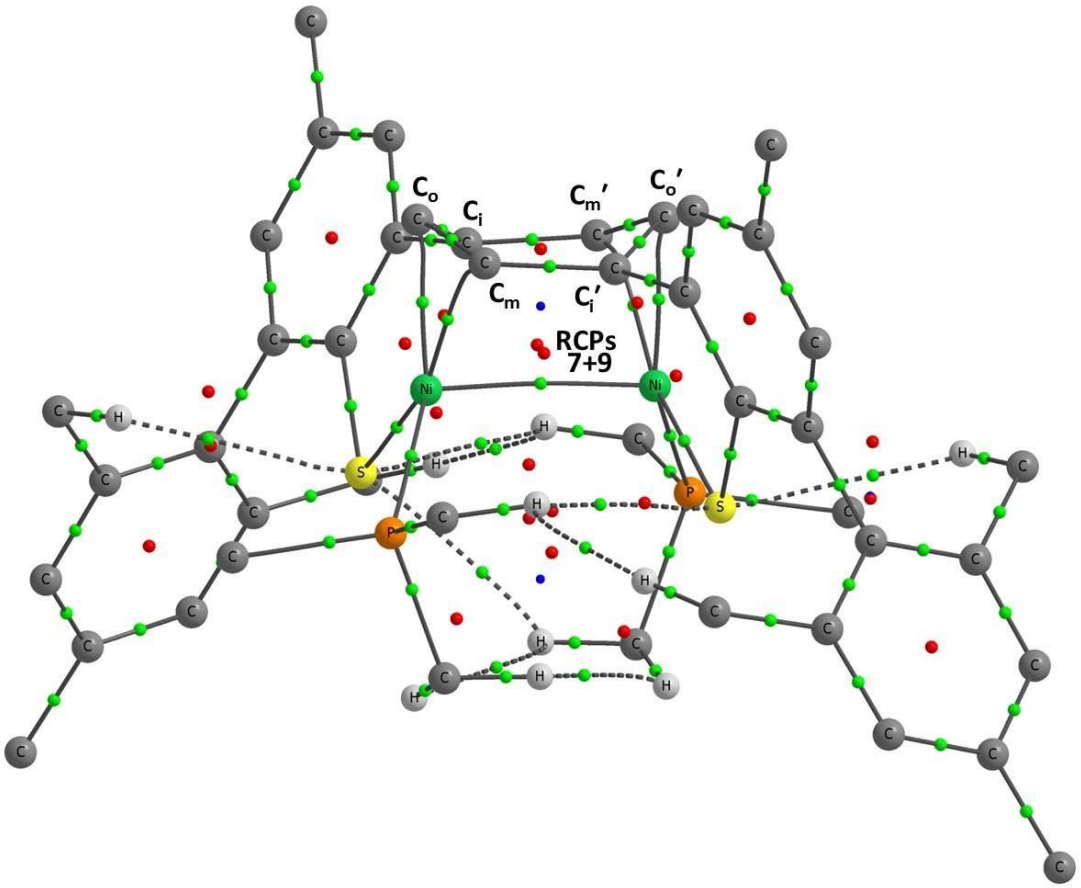

Figure S17. Molecular graph of the theoretical model system of **3**. The BCPs, RCPs (ring critical points) and CCPs (cage critical points) are represented by green, red and blue spheres, respectively. Dotted bond paths indicate weak interactions with $\rho(\mathbf{r}_b) \leq 0.025$ e bohr^{-3} (0.169 e Å^{-3}). Hydrogen atoms which are solely linked to their parent carbon atoms are omitted for clarity.

Table S3. Selected topological properties at bond critical points in the DFT-optimised model system of **3**.

Moiety	d^a	$\rho(\mathbf{r}_b)^b$	$\nabla^2\rho(\mathbf{r}_b)^c$	$\lambda_1{}^c$	$\lambda_2{}^c$	$\lambda_3{}^c$	ε	$G(\mathbf{r}_b)^d$	$G(\mathbf{r}_b)/\rho(\mathbf{r}_b)$	$H(\mathbf{r}_b)^d$	δ
Ni−Ni	2.639	0.194	1.856	−0.52	−0.51	+2.88	0.02	0.171	0.879	−0.041	0.23
Ni−S	2.192	0.617	4.824	−2.30	−2.25	+9.37	0.39	0.522	0.846	−0.184	0.76
Ni−P	2.185	0.658	4.049	−2.36	−2.20	+8.61	0.07	0.520	0.790	−0.237	0.73
Ni−C_o	1.949	0.689	7.642	−2.73	−1.28	+11.65	1.14	0.750	1.088	−0.215	0.44
Ni−C_m	2.022	0.644	7.229	−2.84	−0.26	+10.33	10.03	0.682	1.060	−0.176	0.57
Ni−C_i	2.053	–[e]									0.52
C_i−C_o	1.415	1.982	−17.879	−14.48	−11.36	+7.95	0.27	0.693	0.350	−1.945	1.23
C_o−C_m	1.417	1.977	−17.934	−14.42	−11.43	+7.92	0.26	0.681	0.344	−1.936	1.24
C_m−C_i'	1.495	1.710	−13.976	−11.88	−10.67	+8.58	0.11	0.453	0.265	−1.432	1.03
RCPs 7/9[f]		0.162									

[a]In units of Å. [b]In units of e Å^{-3}. [c]In units of e Å^{-5}. [d]In units of hartree Å^{-3}.[e]No bond path observed. [f]0.540 Å away from the Ni−Ni BCP.

Table S4. Selected atomic charges (AIM charges) in the DFT-optimised model system of **3**.[a]

Atom	Ni	S	P	C_i	C_o	C_m
$q(\Omega)$	+0.46	−0.34	+1.68	−0.09	−0.08	−0.12

[a]Obtained by integrating the electron density over the respective atomic basins.

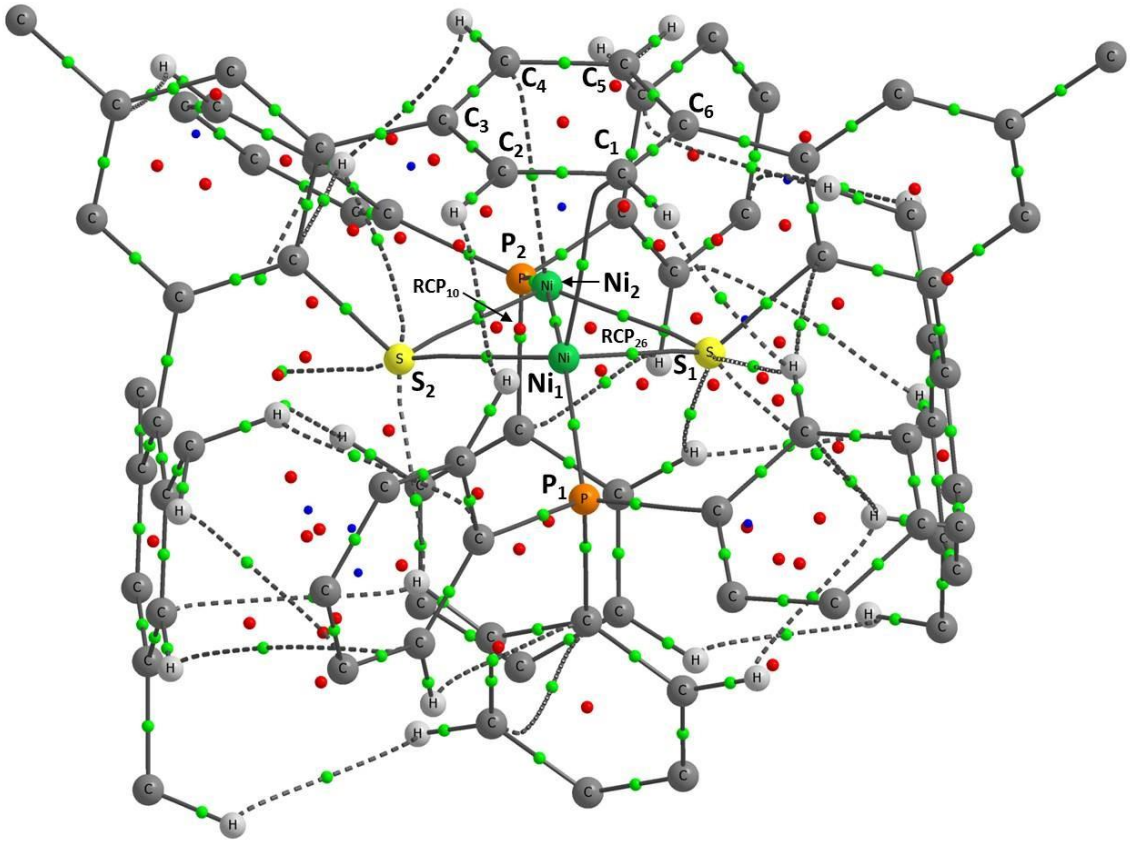

Figure S18. Molecular graph of the theoretical model system of **5**. The BCPs, RCPs (ring critical points) and CCPs (cage critical points) are represented by green, red and blue spheres, respectively. Dotted bond paths indicate weak interactions with $\rho(\mathbf{r}_b) \leq 0.025$ e bohr^{-3} (0.169 e Å^{-3}). Hydrogen atoms which are solely linked to their parent carbon atoms are omitted for clarity.

Table S5. Selected topological properties at bond critical points in the DFT-optimised model system of **5**.

Moiety	d^a	$\rho(\mathbf{r}_b)^b$	$\nabla^2\rho(\mathbf{r}_b)^c$	$\lambda_1{}^c$	$\lambda_2{}^c$	$\lambda_3{}^c$	ε	$G(\mathbf{r}_b)^d$	$G(\mathbf{r}_b)/\rho(\mathbf{r}_b)$	$H(\mathbf{r}_b)^d$	δ
Ni_1−Ni_2	2.322	0.407	1.686	−1.48	−1.09	+4.26	0.36	0.274	0.674	−0.156	0.55
Ni_1−S_1	2.211	0.581	5.529	−2.19	−2.00	+9.72	0.09	0.553	0.952	−0.166	0.70
Ni_1−S_2	2.202	0.591	5.623	−2.26	−2.08	+9.96	0.09	0.566	0.958	−0.173	0.69
Ni_2−S_1	2.188	0.602	5.689	−2.33	−2.15	+10.17	0.08	0.577	0.958	−0.179	0.71
Ni_2−S_2	2.206	0.585	5.501	−2.23	−2.05	+9.78	0.09	0.554	0.947	−0.169	0.72
Ni_1−P_1	2.111	0.729	4.499	−2.60	−2.41	+9.51	0.08	0.615	0.845	−0.300	0.84
Ni_2−P_2	2.105	0.736	4.624	−2.62	−2.37	+9.62	0.11	0.628	0.854	−0.305	0.86
Ni_1−C_1	2.532	0.215	2.227	−0.68	−0.19	+3.10	2.50	0.185	0.863	−0.029	0.16
Ni_1−C_2	2.562	−[e]									0.15
C_1−C_2	1.397	2.067	−20.367	−15.37	−12,81	+7.81	0.20	0.672	0.325	−2.098	1.34
C_2−C_3	1.407	2.038	−19.801	−15.12	−12,66	+7.97	0.19	0.647	0.318	−2.034	1.30
C_3−C_4	1.393	2.082	−20.552	−15.57	−12,78	+7.80	0.22	0.690	0.331	−2.128	1.35
C_4−C_5	1.399	2.058	−20.290	−15.30	−12,83	+7.84	0.19	0.659	0.320	−2.080	1.34
C_5−C_6	1.395	2.080	−20.479	−15.55	−12,75	+7.82	0.22	0.689	0.331	−2.122	1.35
C_6−C_1	1.405	2.042	−19.902	−15.16	−12,70	+7.95	0.19	0.650	0.319	−2.044	1.30
RCP_{10}[f]		0.362									
RCP_{26}[g]		0.364									

[a]In units of Å. [b]In units of e Å^{-3}. [c]In units of e Å^{-5}. [d]In units of hartree Å^{-3}.[e]No bond path observed. [f]0.425 Å away from the Ni−Ni BCP. [g]0.420 Å away from the Ni−Ni BCP.

Table S6. Selected atomic charges (AIM charges) in the DFT-optimised model system of **5**.[a]

Atom	Ni_1	Ni_2	P_1	P_2	S_1	S_2
$q(\Omega)$	+0.31	−0.31	+1.66	+1.67	−0.27	−0.27

[a]Obtained by integrating the electron density over the respective atomic basins.