

Supporting Information

16-electron Nickel(0)-Olefin Complexes in Low-Temperature C(sp²)-C(sp³) Kumada Cross-Couplings

Sigrid Lutz, Lukas Nattmann, Nils Nöthling and Josep Cornella*

Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, Mülheim an der Ruhr, 45470, Germany

cornella@kofo.mpg.de

Contents

General Experimental Notes	S3
According to Scheme 1	S4
<i>Stoichiometric experiments with compound 1</i>	S4
According to Scheme 2	S6
<i>Preparation of Ni-complexes 8</i>	S6
<i>Preparation of Ni-complexes 9</i>	S6
<i>Preparation of Ni-complexes 10</i>	S8
According to Scheme 3	S10
<i>Influence of the solvent in the catalytic reactions with compound 11</i>	S10
<i>With compound 8</i>	S10
<i>With compound 9</i>	S11
<i>With compound 10</i>	S11
According to Scheme 4	S13
<i>Control reaction</i>	S13
According to Figure 4	S14
<i>Stoichiometric reactions of Grignard and compound 10</i>	S14
According to Scheme 5	S17
<i>Preparation of Mg-Ni complexes</i>	S17
According to Scheme 6	S22
X-ray and TEM	S23
<i>Single crystal structure analysis of 13</i>	S23
<i>TEM EDX analysis of compound 13</i>	S30
References	S34

General Experimental Notes

Unless otherwise stated, all manipulations were performed using Schlenk techniques under dry argon in heat gun-dried glassware. Exceptionally rigorous technique was utilized when handling complex **1**, **9**, **10** and **13**. The respective Schlenk flasks containing the complexes were stored at $-78\text{ }^{\circ}\text{C}$ in a Dewar filled with dry ice. Rapid decomposition is observed when the complexes are subjected to elevated temperatures ($25\text{ }^{\circ}\text{C}$ and above). Measurements of pre-catalyst weight were undertaken as rapidly as possible to avoid unnecessary warming, and immediately returned to cold temperatures after recording the weight. Anhydrous solvents were distilled from appropriate drying agents and were transferred under Argon: THF, Et_2O (Mg/anthracene), toluene (Na/K), MTBE (CaH_2 + MS). Commercially available HexylMgBr solution 1.05 mol/l in THF (**3**) and MeMgBr solution 3 mol/L in Et_2O were obtained from Sigma-Aldrich. Flash chromatography: Merck silica gel 60 ($40\text{-}63\text{ }\mu\text{m}$). MS (EI): Finnigan MAT 8200 (70 eV), ESI-MS: ESQ 3000 (Bruker). Accurate mass determinations: Bruker APEX III FTMS (7 T magnet) or MAT 95 (Finnigan). NMR spectra were recorded using a Bruker Avance III HD 400 MHz spectrometer. ^1H NMR spectra (400 MHz) were referenced to the residual protons of the deuterated solvent used. ^{13}C NMR spectra (101 MHz) were referenced internally to the D-coupled ^{13}C resonances of the NMR solvent. Chemical shifts (δ) are given in ppm, relative to deuterated solvent residual peak, and coupling constants (J) are provided in Hz.

The preparation and use of (*E*)-1-(2-bromovinyl)-4-methoxybenzene (**2**), (*E*)-1-methoxy-4-(oct-1-en-1-yl)benzene (**4**), (*E*)-(2-bromovinyl)benzene (**5**) and compound **1** was described in the previous publication¹.

$\text{Ni}(\text{COD})_2$ was prepared according to literature procedure².

According to Scheme 1

Stoichiometric experiments with compound 1

Ni-Li-olefin complex **1** (20.9 mg, 0.0363 mmol) was dissolved at 0 °C in 1 mL THF- d_8 to obtain an orange solution. The solution was then cooled to -78 °C and styrenylbromide **5** (6.6 mg, 0.0363 mmol) was added via syringe. The mixture was quickly transferred to an NMR tube with a precooled pipette. A low temperature ^1H -NMR shows a mixture of compound **6** and Ni(COD) $_2$ (and free COD) with traces of polymeric aromatic material.

^1H NMR (227K, 400 MHz, THF- d_8):

Compound **6**: δ 7.47 (d, $J = 6.7$ Hz, 2H), 7.33 (t, $J = 6.7$ Hz, 2H), 7.25 (br, 1H), 6.78-6.69 (m, 1H), 5.84 (d, $J = 17.6$ Hz, 1H), 5.22 (d, $J = 10.6$ Hz, 1H).

COD: δ 5.51 (br, 4H), 2.35 (br, 8H).

Ni(COD) $_2$: δ 4.29 (br, 8H), 2.12 (br, 16H).

polymeric aromatic material: δ 7.5-6.5 (m).

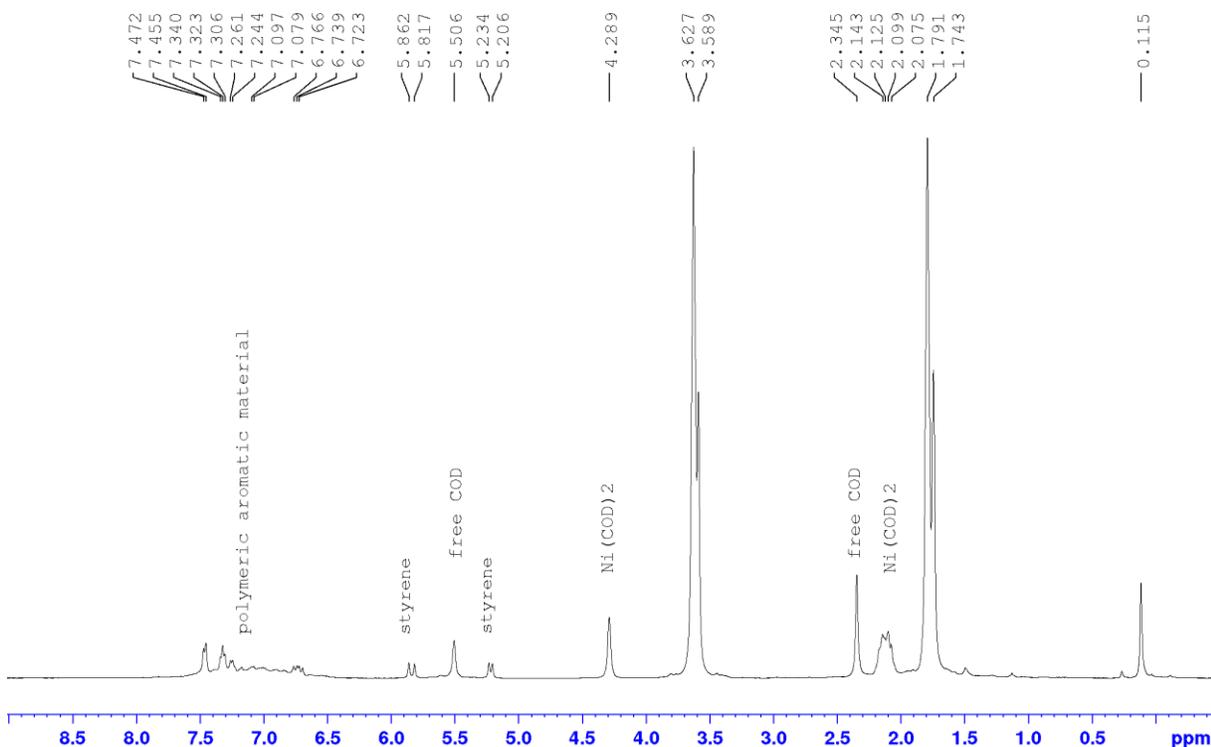


Fig. S1: ^1H NMR (400 MHz), of reaction **1** with **5**, in THF- d_8 at -46 °C.

After recording the ^1H NMR, the NMR tube was opened at 25 °C and quenched with water, washed with EtOAc and analyzed by GC/MS. A ratio of 2.2:1 for COD and styrene **6** was found.

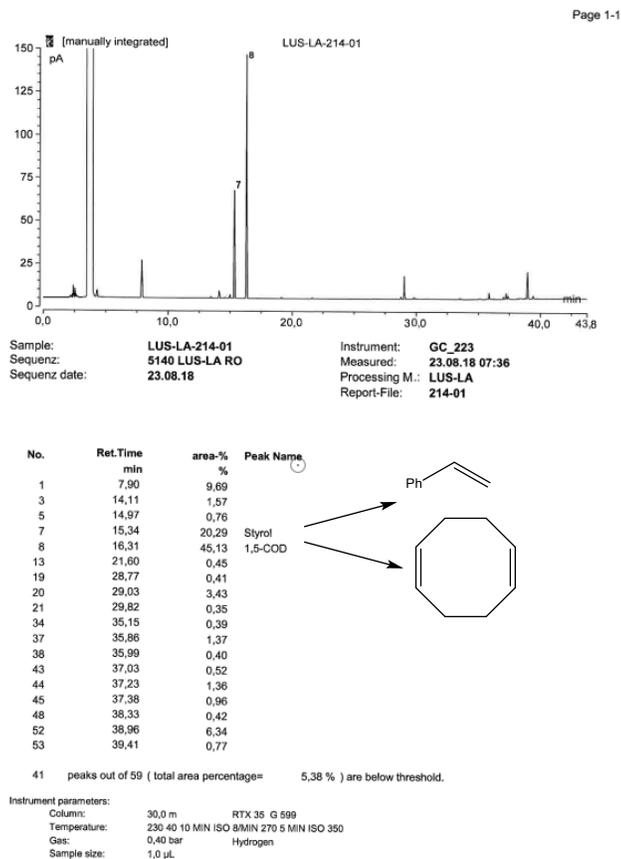
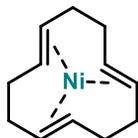


Fig. S2: GC column 30 m Rtx-35 (35% phenyl-65% methylpolysiloxane), inner diameter 0.25 mm, film thickness 0.25 µm, injector 230°C, detector (FID): 350°C. Program 10 min isotherm 40°C, 8°C/min toward 270°C, 5 min isotherm 270°C. 0.4 bar H₂.

According to Scheme 2

Preparation of Ni-complexes

Compound **8**

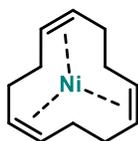


8

t-Ni(CDT) **8** was prepared according to literature procedure³.

A flask under argon was charged with *t*-CDT (10.56 g, 65.08 mmol, 1.35 equiv.). Anhydrous Ni(acac)₂ (12.41 g, 48.3 mmol, 1 equiv.) was added and the mixture was suspended in 100 mL Et₂O. The solution was cooled to 0 °C and AlEt₂(OEt) (16.65 mL, 14.32 g, 110 mmol, 2.3 equiv.) as a solution in 40 mL Et₂O was slowly added. The reaction was subsequently allowed to warm to 25 °C and stirred overnight. During this period, the solution turned red. The stirring was stopped and the precipitate was allowed to settle. The solution was transferred (without the precipitate) into a fresh Schlenk flask under argon, which was then put on dry ice for 2 days to crystallize the crude product. The mother liquor was removed and the remaining solids were sublimed under ultra-high vacuum (10⁻⁵ mbar). For around 12-48 hours the sublimation was conducted without cooling to remove excessive CDT. When no more CDT sublimed, the apparatus was cooled and the remaining solids were heated to 60 °C to sublime pure *t*-Ni(CDT). During this process, some of the crude product will decompose to Ni black and red needles will form on the cooled part of the apparatus (9.33 g, 23.67 mmol, 49% yield). Spectroscopic data matched those reported in the literature.

Compound **9**



9

c-Ni(CDT) **9** was prepared according to literature procedure⁴.

t-Ni(CDT) (**8**) (197 mg, 0.892 mmol) was dissolved in 4 mL Et₂O at -78 °C, resulting in a red solution. *c,c,c*-CDT (144.7 mg, 0.892 mmol) was added and stirring was continued. The temperature was slowly increased to 25 °C and the color changed from red to yellow. Due to the presence of some Ni black, the solution was filtered after 30 min. The now colorless solution was cooled to -78 °C and colorless needles formed. They were collected and dried at high-vacuum a 25 °C to give a beige powder (**9**, 150 mg, 0.679 mmol, 76% yield). Around 7% of *t*-CDT was still present in the Ni complex.

¹H NMR (247K, 400 MHz, THF-*d*₈):

t-CDT (7%): δ 4.78 (br, 6H), 2.38 (br, 12H).

c-CDT (23%): δ 5.62 (br 6H), 2.17 (br, 12H).

c-Ni(CDT) (**9**, 70%): δ 4.78 (br, 6H), 2.37(br, 12H).

¹³C NMR (247K, 101 MHz, THF-*d*₈):

t-CDT (7%): δ 132.5, 33.5.

c-CDT (23%): δ 131.7, 29.4.

c-Ni(CDT) (**9**, 70%): δ 89.8, 29.6.

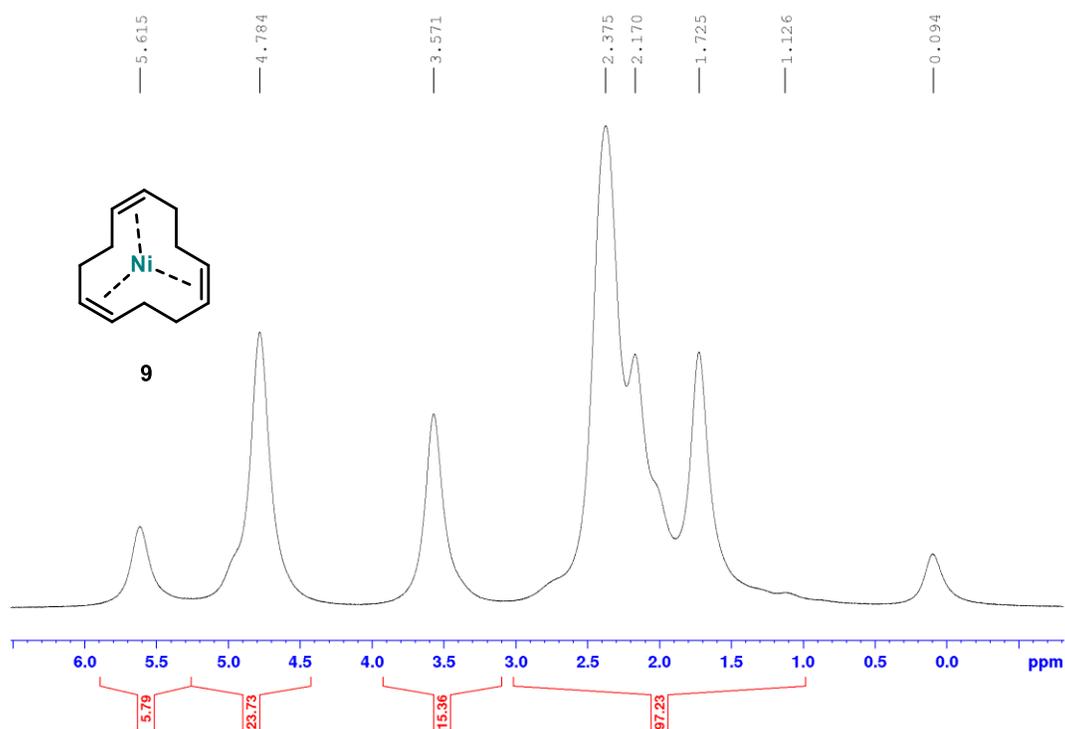


Fig. S3: ¹H NMR (400 MHz), of compound **9**, in THF-*d*₈ at -26 °C.

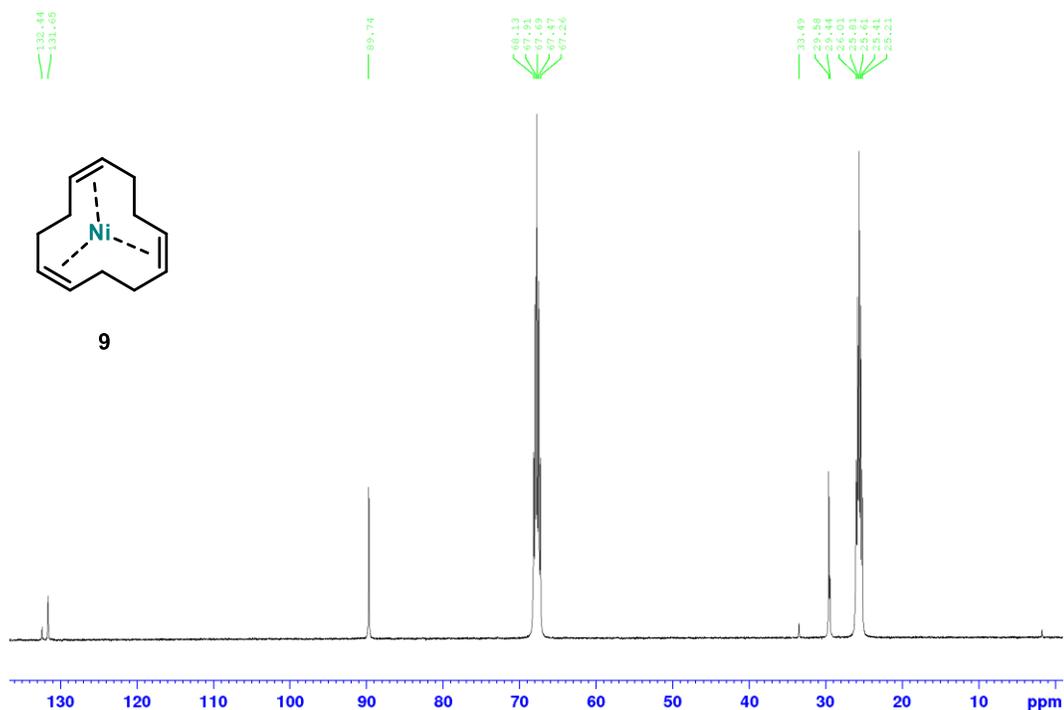
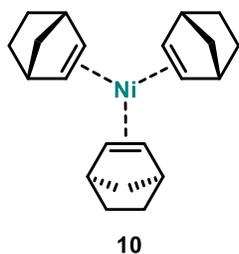


Fig. S4: ^{13}C NMR (101 MHz), of compound **9**, in $\text{THF-}d_8$ at $-26\text{ }^\circ\text{C}$.

Compound **10**



$\text{Ni}(\text{nor})_3$ **10** was prepared according to literature procedure⁵.

$t\text{-Ni}(\text{CDT})$ (**8**) (399.4 mg, 1.80 mmol) was suspended in 4 mL Et_2O at $-78\text{ }^\circ\text{C}$ and a solution of freshly sublimed norbornene (851.0 mg, 9.04 mmol) in 1 mL Et_2O was added. The mixture was stirred for 10 min at $-78\text{ }^\circ\text{C}$ and was then slowly warmed to $0\text{ }^\circ\text{C}$. After 2 h at this temperature, the reaction was filtered over a cooled argon frit at $0\text{ }^\circ\text{C}$. The collected solution was cooled to $-78\text{ }^\circ\text{C}$ and the product precipitated overnight. The mother liquor was removed with a cannula and the

remaining solids were washed with Et₂O (3 × 2 mL) at -78 °C. The colorless powder of Ni(nor)₃ (**10**) was dried under high vacuum at 0 °C (305.0 mg, 0.79 mmol, 44% yield).

¹H NMR (195K, 400 MHz, THF-*d*₈):

δ 3.48 (s, 2H), 3.04 (s, 2H), 2.94 (m, 4H), 2.82 (s, 4H), 1.59 (s, 6H), 1.51 – 1.09 (m, 6H), 0.43 – 0.21 (m, 3H), -0.50 – -0.63 (m, 2H), -0.69 (d, *J* = 8.2 Hz, 1H).

¹³C NMR (195K, 101 MHz, THF-*d*₈):

δ 77.4, 77.0, 74.1, 44.7, 44.6, 43.5, 40.9, 40.7, 29.0, 28.7 28.1.

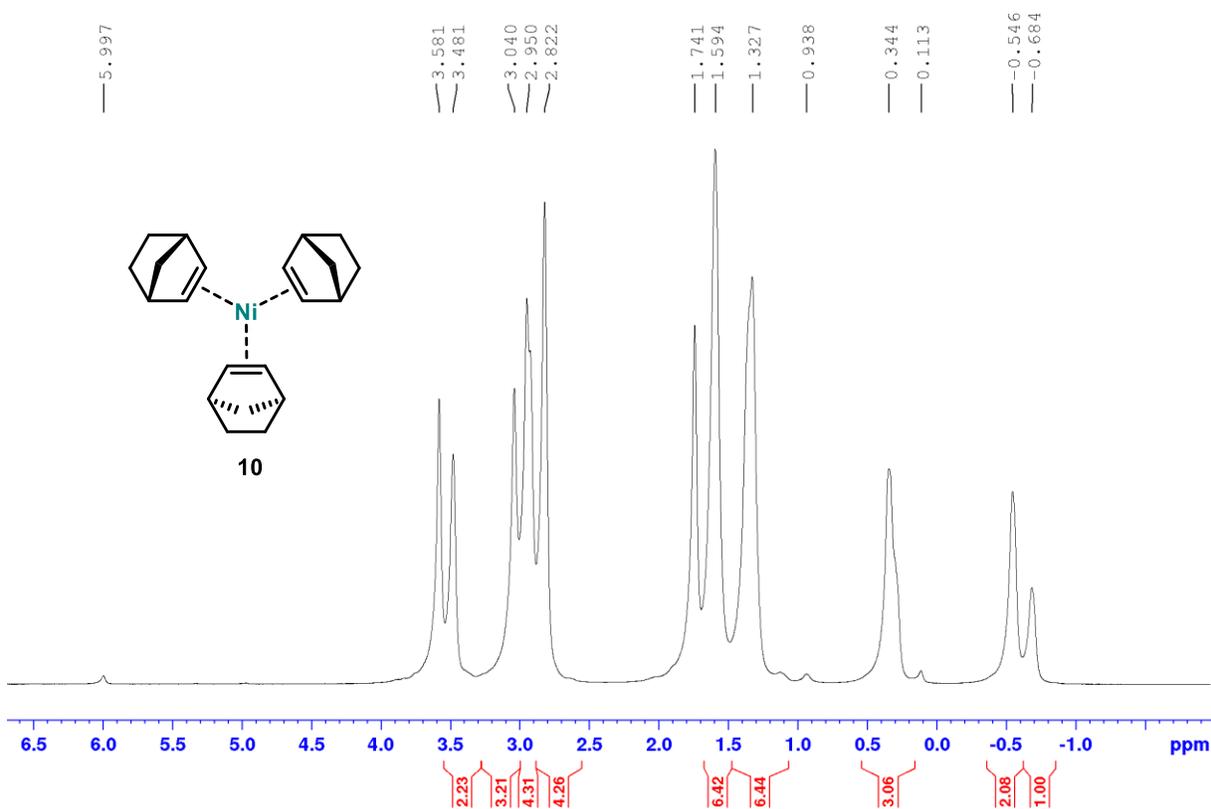


Fig. S5: ¹H NMR (400 MHz), of compound **10**, in THF-*d*₈ at -78 °C.

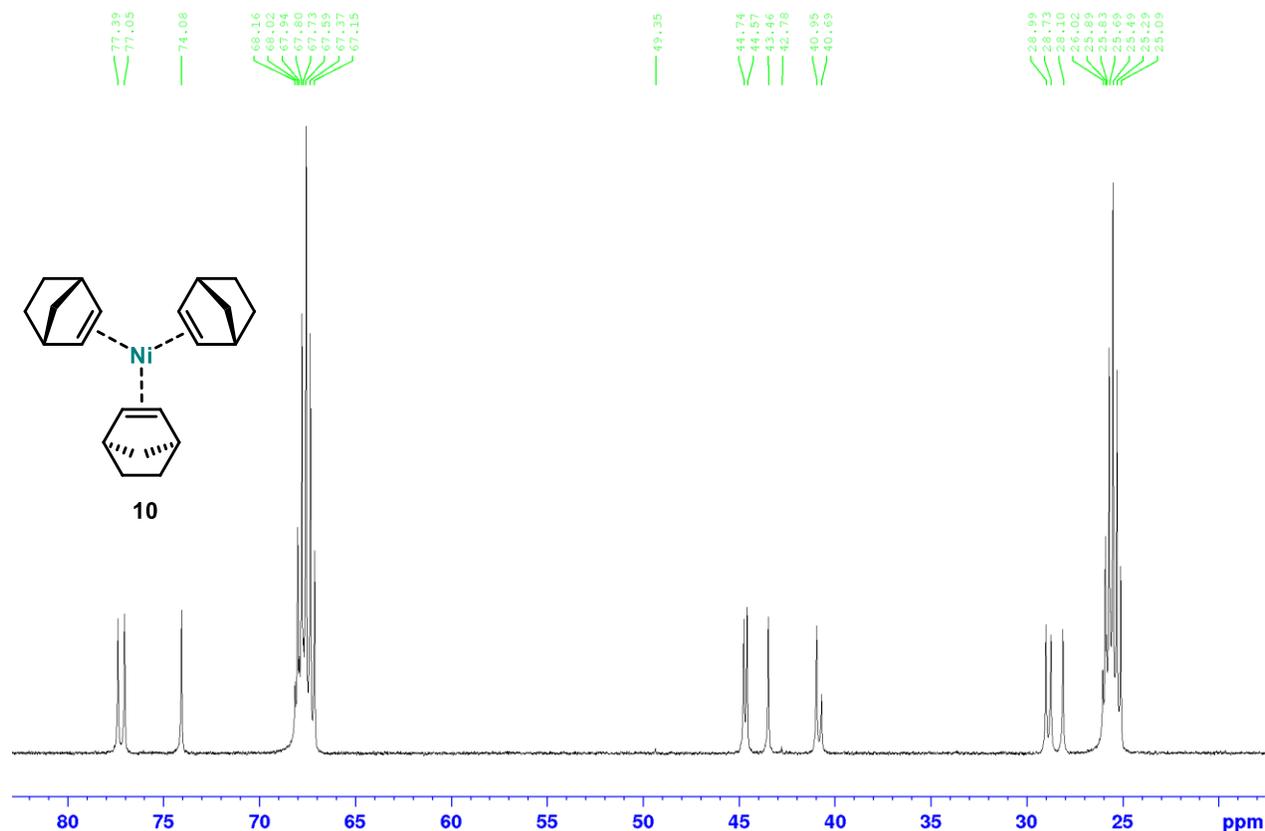


Fig. S6: ¹³C NMR (101 MHz), of compound **10**, in THF-*d*₈ at -78 °C.

According to Scheme 3

Influence of the solvent in the catalytic reactions with compound 11

With compound 8 at -60 °C in THF:

t-Ni(CDT) (**8**) (6.6 mg, 0.03 mmol, 5 mol%) was dissolved at -60 °C in 3 mL THF. Styrenylbromide **5** (109.3 mg, 0.597 mmol) was added to the solution at -60 °C, followed by 1.5 eq. hexylMgBr (**3**) (0.85 mL, 1.05 mol/L in THF, 0.896 mmol). After 36 h reaction time, the mixture was quenched with water, diluted with EtOAc, filtered through silica and analyzed by GC.

Yield based on C₁₀H₂₂ as internal standard: 36.4% compound **11** (40.9 mg, 0.217 mmol).

With compound 8 at –60 °C in MTBE:

t-Ni(CDT) (**8**) (10.0 mg, 0.045 mmol, 5 mol%) was dissolved at –60 °C in 5 mL MTBE. Styrenylbromide **5** (165.7 mg, 0.905 mmol) was added to the solution at –60 °C, followed by hexylMgBr (**3**) (1.29 mL, 1.05 mol/L in THF, 1.358 mmol). After 36 h reaction time, the mixture was quenched with water, diluted with EtOAc, filtered through silica and analyzed by GC.

Yield based on C₁₀H₂₂ as internal standard: 12.7% compound **11** (21.7 mg, 0.115 mmol).

With compound 8 at –60 °C in Et₂O:

t-Ni(CDT) (**8**) (6.3 mg, 0.029 mmol, 5 mol%) was dissolved at –60 °C in 3 mL Et₂O. Styrenylbromide **5** (104.4 mg, 0.570 mmol) was added to the solution at –60 °C, followed by hexylMgBr (**3**) (0.81 mL, 1.05 mol/L in THF, 0.855 mmol). After 36 h reaction time, the mixture was quenched with water, diluted with EtOAc, filtered through silica and analyzed by GC.

Yield based on C₁₀H₂₂ as internal standard: 18.7% compound **11** (20.1 mg, 0.107 mmol).

With compound 9 at –60 °C in THF:

c-Ni(CDT) **9** (7.6 mg, 0.0344 mmol, 5 mol%) (really sensitive to temperature and air; weight in at deep temperature.) was dissolved at –60 °C in 2.5 mL THF. A solution of styrenylbromide **5** (125.3 mg, 0.6848 mmol) in 0.5 mL THF was added to the Ni catalyst solution at –60 °C, followed by hexylMgBr (**3**) (0.97 mL, 1.05 mol/L in THF, 1.0185 mmol). After 36 h reaction time, the mixture was quenched with water, diluted with EtOAc, filtered through silica and analyzed by GC.

Yield based on C₁₀H₂₂ as internal standard: 9.3% compound **11** (12 mg, 0.064 mmol).

With compound 10 at –40 °C in THF:

Ni(nor)₃ (**10**) (6.9 mg, 0.02 mmol, 5 mol%) was dissolved in 2 mL THF at –78 °C (colorless solution). Styrenylbromide **5** (64.3 mg, 0.3512 mmol) was added, followed by hexylMgBr (**3**) (0.97 mL, 1.05 mol/L in THF, 1.0185 mmol). The light yellow mixture was stirred at –40 °C. After 36 h reaction time, the mixture was quenched with water, diluted with EtOAc, filtered through silica and analyzed by GC.

Yield based on C₁₀H₂₂ as internal standard: 74% compound **11** (48.9 mg, 0.260 mmol).

With compound 10 at –60 °C in THF:

Ni(nor)₃ (**10**) (8.0 mg, 0.021 mmol, 5 mol%) was dissolved in 4 mL THF at –78 °C (colorless solution). Styrenylbromide **5** (75.8 mg, 0.414 mmol) was added, followed by hexylMgBr (**3**) (0.59 mL, 1.05 mol/L in THF, 0.621 mmol). The light yellow mixture was stirred at –60 °C. After 36 h reaction time, the mixture was quenched with water, diluted with EtOAc, filtered through silica and analyzed by GC.

Yield based on C₁₀H₂₂ as internal standard: 57.7% compound **11** (45.0 mg, 0.239 mmol).

With compound 10 at –60 °C in MTBE:

Ni(nor)₃ (**10**) (6.6 mg, 0.017 mmol, 5 mol%) was dissolved in 3 mL MTBE at –78 °C (colorless solution). Styrenylbromide **5** (62.6 mg, 0.342 mmol) was added, followed by hexylMgBr (**3**) (0.49 mL, 1.05 mol/L in THF, 0.513 mmol). The light yellow mixture was stirred at –60 °C. After 36 h reaction time, the mixture was quenched with water, diluted with EtOAc, filtered through silica and analyzed by GC.

Yield based on C₁₀H₂₂ as internal standard: 47.9% compound **11** (30.8 mg, 0.164 mmol).

With compound 10 at –60 °C in Et₂O:

Ni(nor)₃ (**10**) (5.3 mg, 0.014 mmol, 5 mol%) was dissolved in 2.5 mL Et₂O at –78 °C (colorless solution). Styrenylbromide **5** (50.2 mg, 0.274 mmol) was added, followed by hexylMgBr (**3**) (0.39 mL, 1.05 mol/L in THF, 0.412 mmol). The light yellow mixture was stirred at –60 °C. After 36 h reaction time, the mixture was quenched with water, diluted with EtOAc, filtered through silica and analyzed by GC.

Yield based on C₁₀H₂₂ as internal standard: 38.5% compound **11** (19.9 mg, 0.274 mmol).

According to Scheme 4

Control reaction

An NMR tube was charged with styrenylbromide **5** (6.4 mg, 0.0351 mmol), Ni(nor)₃ **10** (13.1 mg, 0.0381 mmol) followed by 1 mL THF-*d*₈ at -78 °C. The ¹H NMR at -40 °C revealed that no reaction occurred and both **5** and **10** were present unreacted. (traces of free norbornene also detected).

¹H NMR (247K, 400 MHz, THF-*d*₈):

Styrenylbromide **5**: δ 7.40 (br, 2H), 7.31 (br, 3H), 7.16 (br, 2H).

Ni(nor)₃ (**10**): δ 2.83 (m, 12H), 1.57 (br, 6H), 1.32 (br, 6H), 0.31 (br, 3H), -0.56 (br, 3H).

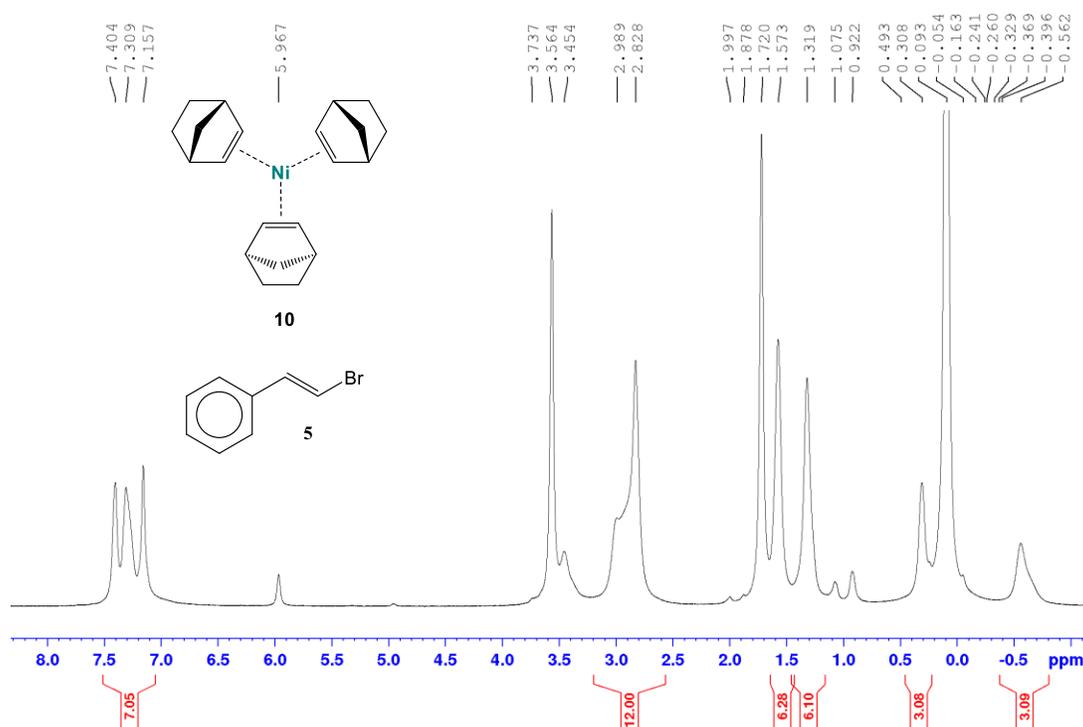


Fig. S7: ¹H NMR (400 MHz), of reaction **10** with **5**, in THF-*d*₈ at -26 °C.

Ni(nor)₃ (**10**) (12.1 mg, 0.0352 mmol) was dissolved in 1 mL THF at -78 °C and styrenylbromide **5** (5.8 mg, 0.0316 mmol) was then added. The light yellow mixture was stirred at -40 °C. After 36

h reaction time, the mixture was quenched with water, diluted with EtOAc, filtered through silica and analyzed by GC. No product **11** was detected. Mainly **5** recovered.

According to Figure 4

Stoichiometric reactions of Grignard and 10

HexylMgBr (**3**) (40 μ L, 1.05 mol/L in THF, 0.042 mmol) was dried at high vacuum and the solid organomagnesium was re-dissolved in 1 mL THF- d_8 . The solution was added to Ni(nor)₃ (**10**) (8.2 mg, 0.024 mmol) at -78 °C. ¹H NMR at both -40 °C and -10 °C show unreacted **3** and **10**.

¹H NMR (233K, 400 MHz, THF- d_8):

Grignard **3**: δ 1.26 (br, 10H), 0.88 (br, 3H).

Ni(nor)₃ **10**: δ 2.83 (m, 4H), 1.57 (br, 2H), 1.32 (br, 2H), 0.31 (br, 1H), -0.56 (br, 1H).

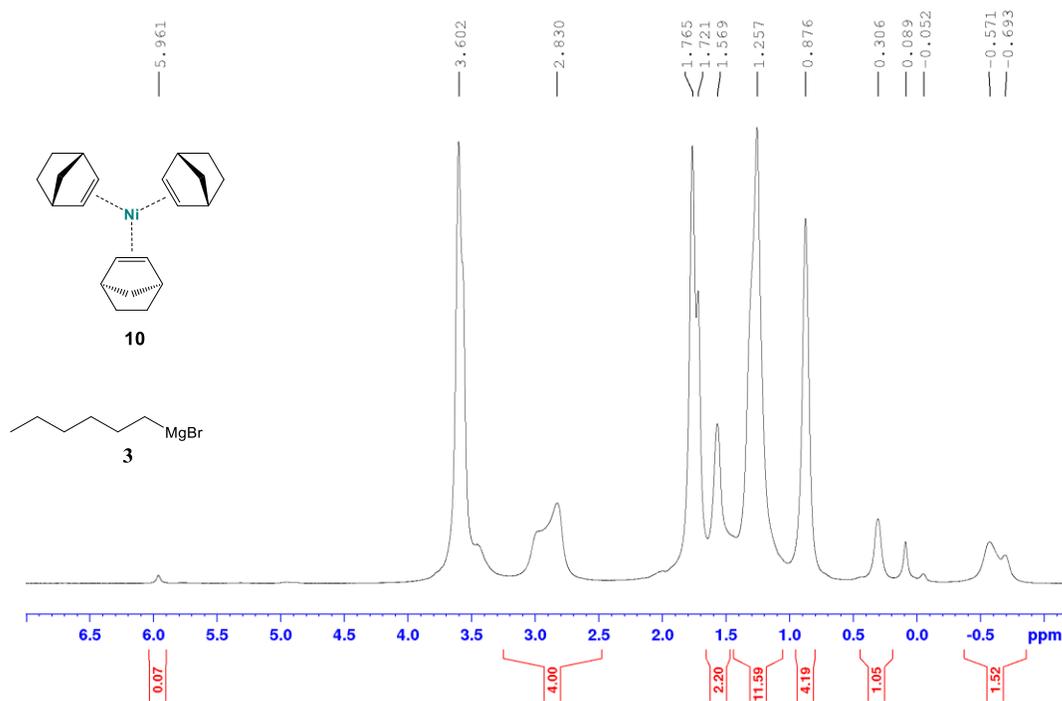


Fig. S8: ¹H NMR (400 MHz), of reaction **10** with **3**, in THF- d_8 at -40 °C.

Ni(nor)₃ (**10**) (9.7 mg, 0.0284 mmol) was dissolved in 1 mL toluene- d_8 and a solution of [Me₂Mg(TMEDA)] (**12**) (see page S17) (4.81 mg, 0.0282 mmol) in 0.5 mL toluene- d_8 was added

at $-78\text{ }^{\circ}\text{C}$. The mixture was stirred further at $-30\text{ }^{\circ}\text{C}$ for 16 h. The color of the solution did not change. NMR from $-40\text{ }^{\circ}\text{C}$ to $+10\text{ }^{\circ}\text{C}$ did not show any reactivity and both starting materials were present unreacted.

^1H NMR (247K, 400 MHz, toluene- d_6):

$[\text{Me}_2\text{Mg}(\text{TMEDA})]$ (**12**): δ 2.36 (br, 4H), 2.13 (br, 12H).

$\text{Ni}(\text{nor})_3$ (**10**): δ 2.87 (m, 4H), 1.63 (br, 2H), 1.44 (br, 2H), 0.32 (br, 1H), -0.52 (br, 1H).

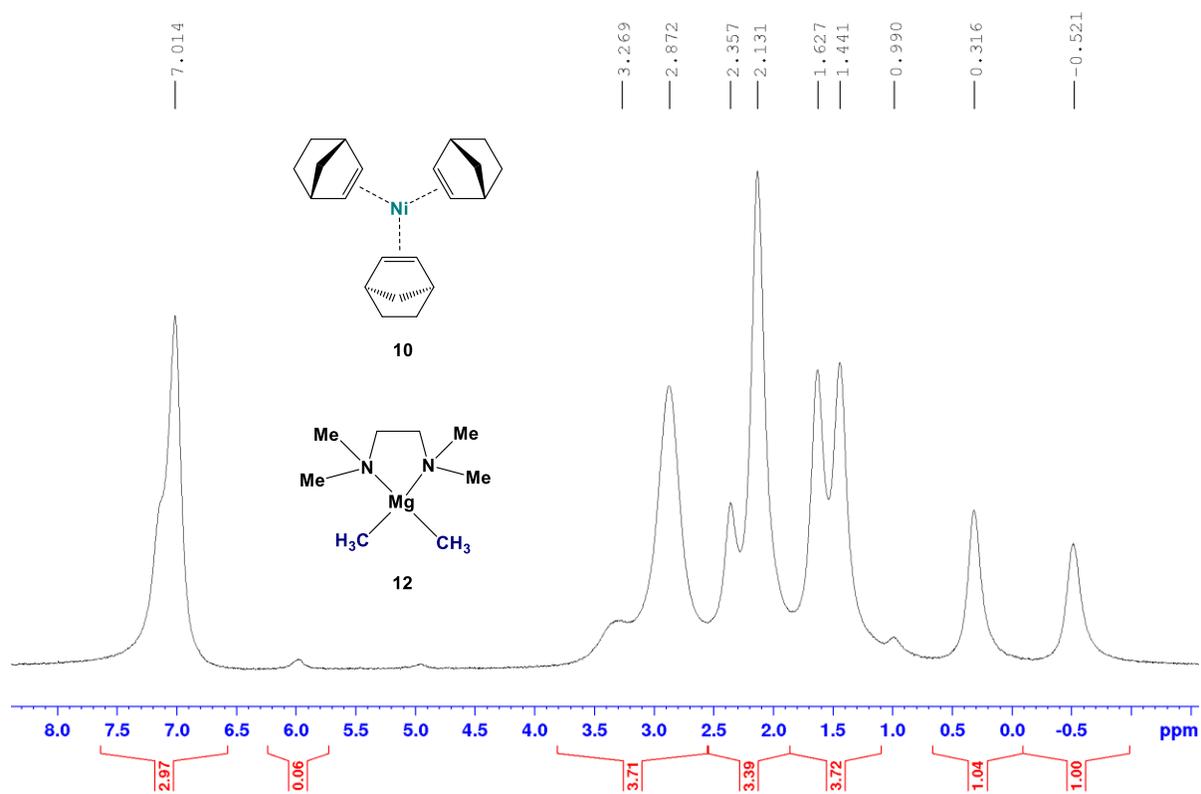


Fig. S9: ^1H NMR (400 MHz), of reaction **10** with **12**, in toluene- d_6 at $-26\text{ }^{\circ}\text{C}$.

Preparation of $[\text{Et}_2\text{Mg}(\text{THF})_2]$ **12b**, prepared according to literature procedure⁶, as an analog to $[\text{Me}_2\text{Mg}(\text{TMEDA})]$ (**12**).

EtMgBr 3.0 mol/L in Et_2O (15.0 mL, 45 mmol,) was diluted with 45 mL Et_2O to 1 mol/L. Heating to reflux, a mixture of 1,4-dioxane (5 mL, 58.5 mmol, 1.3 eq.) and 5 mL Et_2O was added with a

syringe. A white precipitate starts to form and the heating continued for 5 h, followed by cooling at 25 °C and stirred at this temperature for 16 h. The solid was filtered and washed with Et₂O until the solution is clear and colorless.

Note: Test on halides. An aliquot of the filtrate was quenched with water, acidified with HNO₃ and AgNO₃ was added. No precipitate formed.

The filtrate was concentrated to 15 mL with an argon flow over the solution and was then added dropwise via an additional funnel to a solution of 100 mL of toluene at reflux. After complete addition, the solution was allowed to cool to 25 °C and the reflux condenser was exchanged for a distillation apparatus. Et₂O, 1,4-dioxane and most of the toluene (until about 25 mL) was removed via distillation while Et₂Mg formed as precipitate. The suspension was allowed to cool to 25 °C for 16 h, and the precipitate was filtered, washed with pentane (2 × 15 ml) and dried under high vacuum. Et₂Mg (1.81g, 22.0 mmol, 97.8% yield).

Et₂Mg (1.075 g, 13.0 mmol,) was dissolved in 100 mL THF and stirred at 25 °C for 16 h. The suspension was added to a filtering frit and a titration of the solution with 0.1 N HCl gave a concentration of 0.086 mol/L of compound **12b**. This solution was directly used in the next reaction with **10**.

Ni(nor)₃ (**10**) (44.5 mg, 0.1304 mmol) was dissolved in 4 mL Et₂O at –10 °C and transferred to a cooling frit. A solution of [Et₂Mg(THF)₂] (**12b**) (1.3mL, 0.086 mol/L, 0.112 mmol) in THF was added and the temperature was allowed to reach 0 °C. The color of the solution changed from white to orange. Filtration of the mixture through the frit was collected in a Schlenk at –78 °C. Light yellow crystals formed in the Schlenk and the solvent was then separated via cannula. The solid was dried at –78 °C to –20 °C in high vacuum. The product of addition of **12b** to Ni(nor)₃ was not observed.

Ni(nor)₃ (**10**) (42.4 mg, 0.1243 mmol) was dissolved in 5 mL Et₂O and TMEDA (0.2 mL, 1.334 mmol) at –30 °C. A solution of EtLi in benzene/cyclohexane 1:1 (0.3 mL, 0.5 mol/L, 0.15 mmol) was added. The color of the solution changed to yellow and the mixture was stirred for 16 h at –20 °C. After this time, the solvent was evaporated in the high-vacuum at –20 °C and the remaining solids were washed with pentane at –78 °C. The yellow precipitate was dried under high-vacuum at –20 °C. ¹H NMR of the solids in THF-*d*₈ at –35 °C revealed the presence of **10**, traces of norbornene and a small amount of TMEDA.

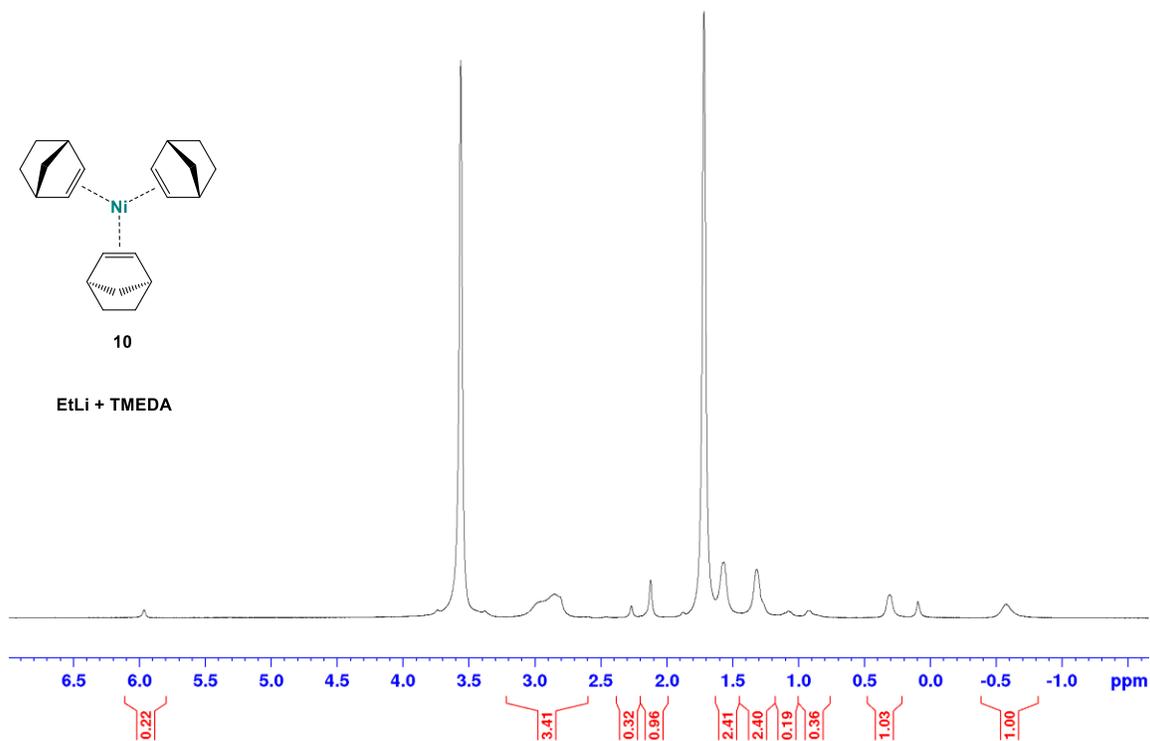
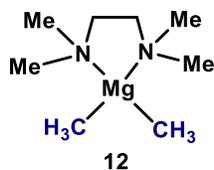


Fig. S10: ^1H NMR (400 MHz), of reaction **10** with EtLi/TMEDA, in $\text{THF-}d_8$ at $-26\text{ }^\circ\text{C}$.

According to Scheme 5

Preparation of Mg-Ni complexes

Compound **12** [$\text{Me}_2\text{Mg}(\text{TMEDA})$]



$[\text{Me}_2\text{Mg}(\text{TMEDA})]$ **12** was prepared according to literature procedure⁶.

MeMgBr 3.0 mol/L in diethylether (4.0 mL, 12 mmol,) was diluted with 8 mL Et_2O to 1 mol/L. Heating to reflux, a mixture of 1,4-dioxane (1.07 mL, 12 mmol, 1 eq.) and 1 mL Et_2O was added with a syringe. A white precipitate starts to form and the heating continued for 4 h followed by

cooling at 25 °C and stirred at this temperature for 16 h. The solid was filtered and washed with Et₂O until the solution is clear and colorless. To this solution, TMEDA (2.5 mL, 16.673 mmol, 1.4 eq.) is added slowly via syringe. The stirring continued for 30 min and the mixture was then cooled to -78 °C. White crystals of [Me₂Mg(TMEDA)] **12** (1g, 5.86 mmol, 97.7% yield) appeared, the solvent was removed via cannula at -78 °C and the solid dried at high vacuum from -78 °C to 25 °C.

¹H NMR (400 MHz, THF-*d*₈): δ 2.38 (s, 4H), 2.21 (s, 12H), -1.76 (s, 6H).

¹³C NMR (100 MHz, THF- *d*₈): δ 58.3, 46.4, -16.3.

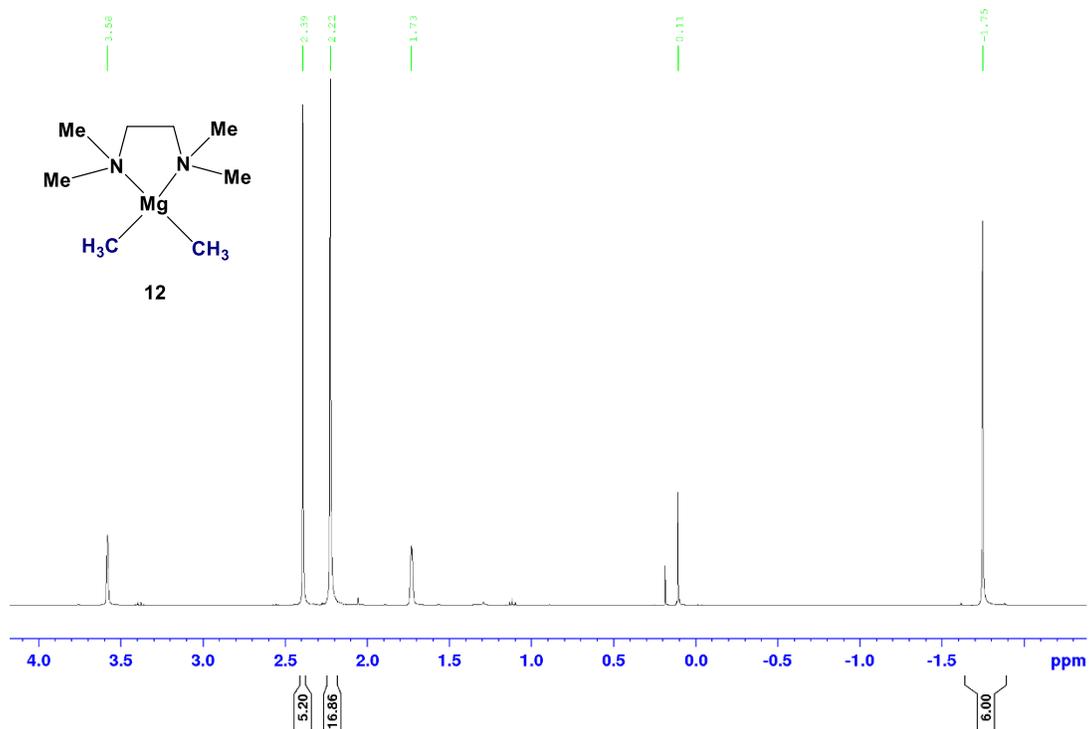


Fig. S11: ¹H NMR (400 MHz), of compound **12**, in THF-*d*₈.

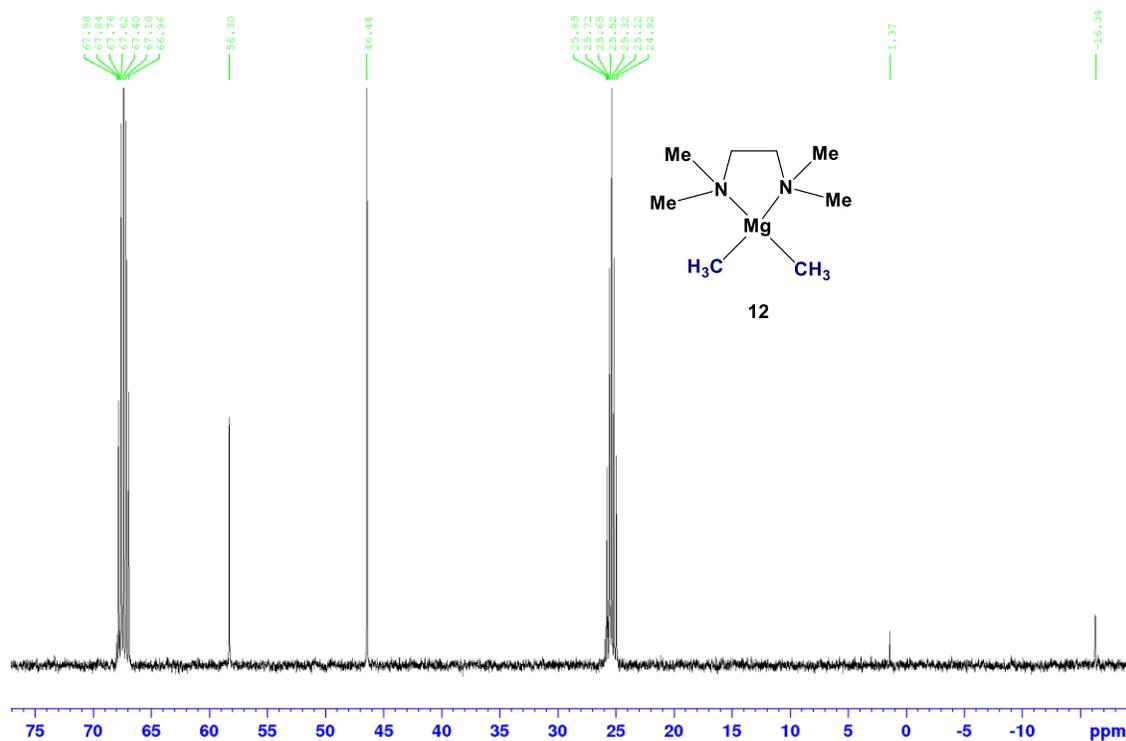
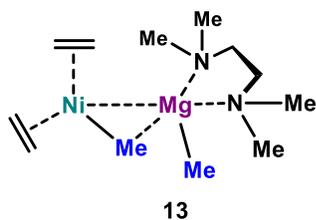


Fig. S12: ¹³C NMR (100 MHz), of compound **12**, in THF- *d*₈.

Compound 13



$[(\text{TMEDA})\text{MgCH}_3(-\text{CH}_3)\text{Ni}(\text{C}_2\text{H}_4)_2]$ **13** was prepared according to literature procedure⁶.

t-Ni(CDT) (**8**) (522 mg, 2.357 mmol) was dissolved at $-30\text{ }^\circ\text{C}$ in Et_2O (20 mL), and the solution was bubbled with ethylene. After 25 min the temperature was allowed to reach $-10\text{ }^\circ\text{C}$ and the stirring was continued for 20 min, until the red color of the solution disappeared. The $[\text{Me}_2\text{Mg}(\text{TMEDA})]$ (**12**) (402 mg, 2.357 mmol, 1 eq.) was dissolved in Et_2O (7 mL), and the solution

was added to the light brown solution of $\text{Ni}(\text{C}_2\text{H}_4)_3$. The mixture was then directly transferred to a cooling frit at $-20\text{ }^\circ\text{C}$, while having the collection Schlenk at $-78\text{ }^\circ\text{C}$. The mixture was filtered and the filtrate collected (at $-78\text{ }^\circ\text{C}$). Yellow crystals of **13** (360 mg, 1.047 mmol, 83%) appeared in the collected filtrate and the solvent was separated via canula. The solid was then isolated at $-78\text{ }^\circ\text{C}$, washed with pentane ($3 \times 10\text{ mL}$) and dried at $-30\text{ }^\circ\text{C}$. Yield 44.3% calculated to pure compound. NMR indicates the presence of 17 % *t*-CDT still present in the mixture.

^1H NMR (244 K, 500 MHz, toluene- d_8):

t-CDT (17%): δ 4.92 (s, 6H), 2.07 (s, 12 H).

Compound **13** (83%): δ 2.58 (s, 8H), 1.69 (s, 6H), 1.40 (s, 6H), 1.1 (m, br, 4H), 0.33 (s, 3H), -0.94 (s, 3H).

^{13}C NMR (244 K, 126 MHz, toluene- d_8): δ 55.4, 47.8, 46.6, 46.0, -10.8, -11.9.

Crystals for x-ray were isolated directly from Et_2O solution at $-78\text{ }^\circ\text{C}$. Showing a mixture of 81% compound **13** and 19% of the Br-compound **13b**. For more details on the structure of this mixture, see x-ray Section.

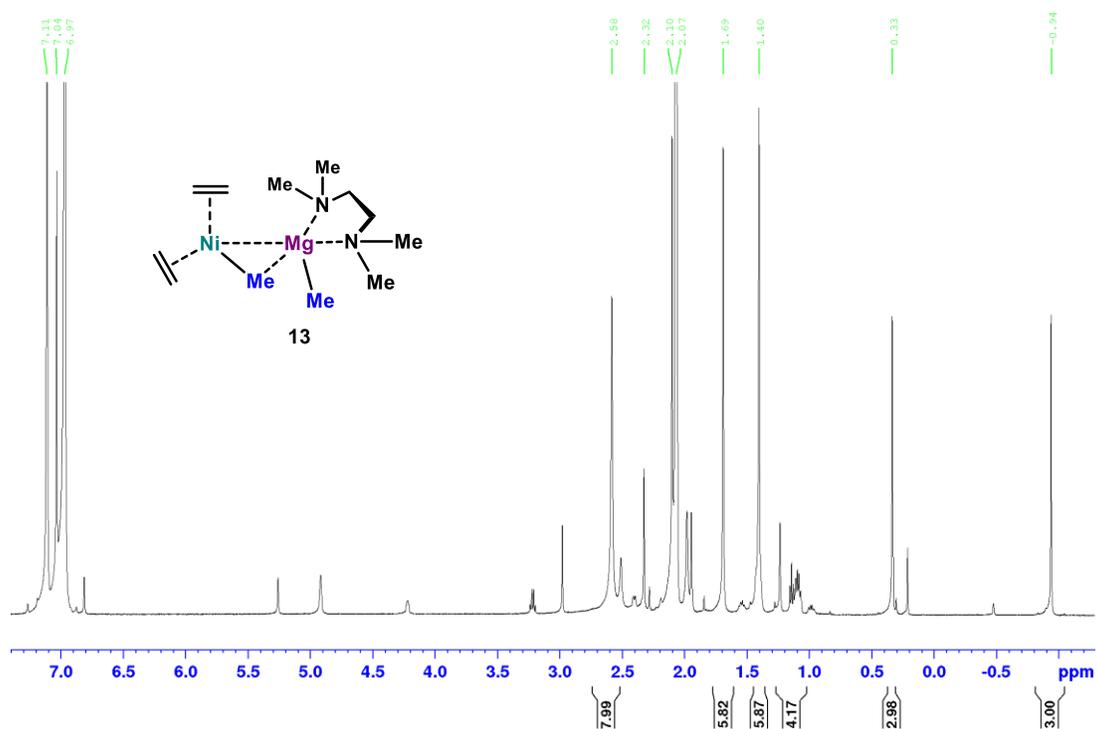


Fig. S13: ^1H NMR (500 MHz), of compound **13**, in toluene- d_8 at $-29\text{ }^\circ\text{C}$.

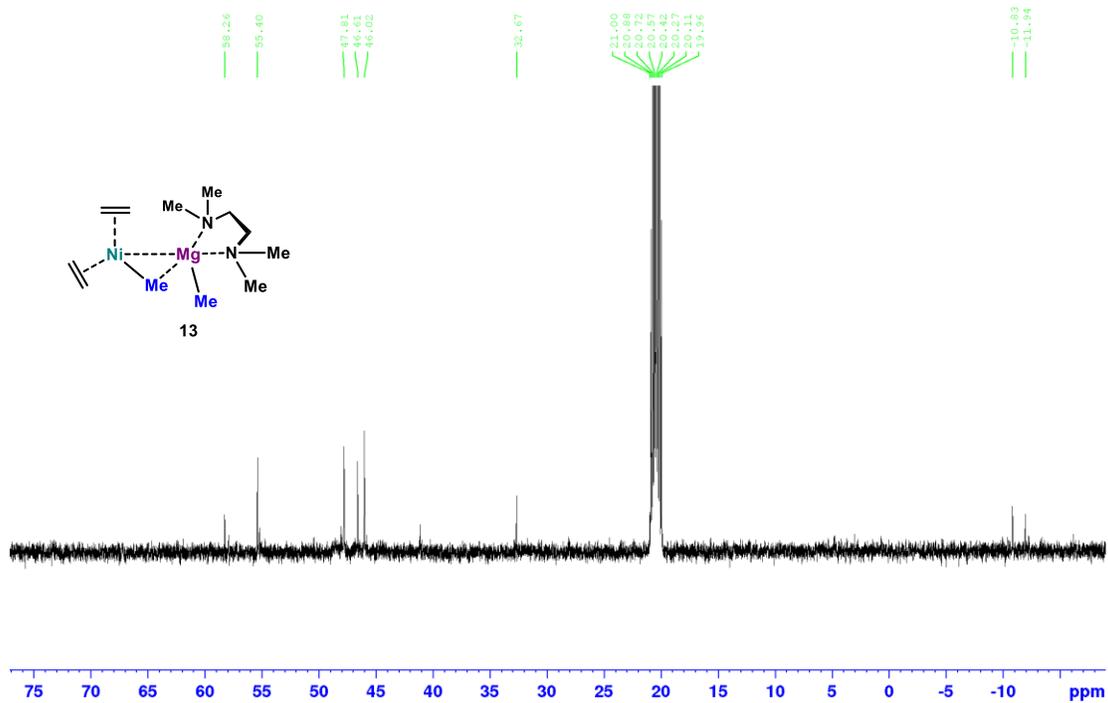


Fig. S14: ^{13}C NMR (126 MHz), of compound **13**, in toluene- d_8 at $-29\text{ }^\circ\text{C}$.

According to Scheme 6

Complex **13** (58.1 mg, 0.1629 mmol) was dissolved in 2 mL Et₂O at –40 °C and styrenylbromide **5** (14.5 mg, 0.079 mmol) was added at this temperature. After 3 h reaction time, the mixture was quenched with 2 mL water, diluted with EtOAc, filtered through silica and analyzed by GC.

Yield based on C₁₀H₂₂ as internal standard: 60 % compound **14** (5.6 mg, 0.047 mmol).

X-ray and TEM

Single crystal structure analysis of 13.

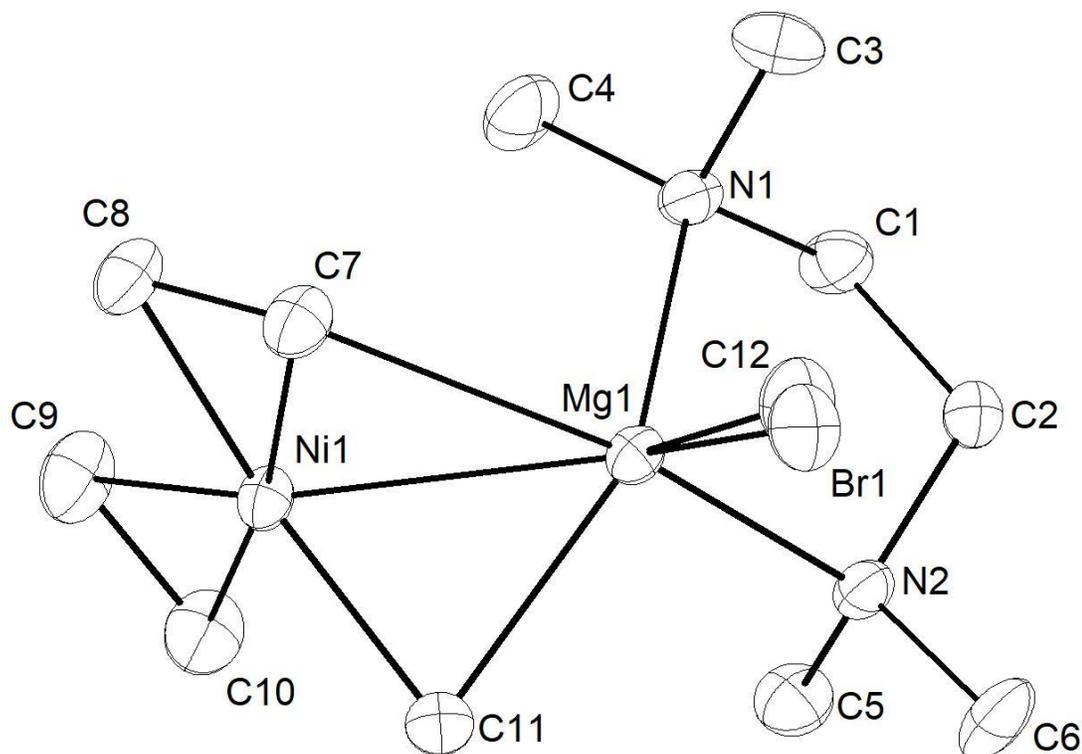
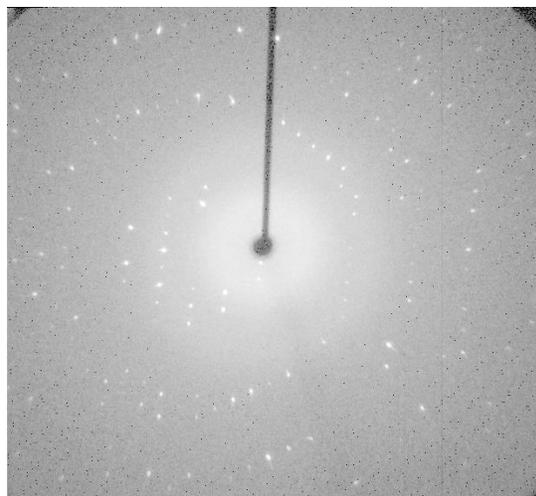


Fig. S15: The molecular structure of complex **13**. H atoms have been removed for clarity.

X-ray Crystal Structure Analysis of complex 13: $C_{11.81} H_{29.43} Br_{0.19} Mg N_2 Ni$, $M_r = 297.72$ g mol⁻¹, yellow block, crystal size 0.18 x 0.16 x 0.10 mm³, monoclinic, $P 2_1/c$ [14], $a = 14.8670(9)$ Å, $b = 8.3234(9)$ Å, $c = 14.2697(11)$ Å, $\beta = 114.739(5)^\circ$, $V = 1603.7(2)$ Å³, $T = 100(2)$ K, $Z = 4$, $D_{calc} = 1.233$ g·cm³, $\lambda = 0.71073$ Å, $\mu(Mo-K\alpha) = 1.703$ mm⁻¹, Gaussian absorption correction ($T_{min} = 0.83779$, $T_{max} = 0.89385$), Bruker AXS Enraf-Nonius KappaCCD diffractometer with a FR591 rotating Mo-anode X-ray source, $2.861 < \theta < 33.154^\circ$, 34079 measured reflections, 6100 independent reflections, 5145 reflections with $I > 2\sigma(I)$, $R_{int} = 0.0374$. The structure was solved by *SHELXS* and refined by full-matrix least-squares (*SHELXL*) against F^2 to $R_1 = 0.0342$ [$I > 2\sigma(I)$], $wR_2 = 0.0666$, 212 parameters.



	h	k	l	distance (mm)
1.	0	1	0	0.05
2.	0	-1	0	0.06
3.	-1	-1	3	0.09
4.	-1	1	3	0.07
5.	1	1	-3	0.09
6.	1	-1	-3	0.09
7.	-1	0	0	0.05
8.	1	0	0	0.05

The automatic indexing gave these results:

```
{Input cell : a=14.2814 b=8.3365 c=14.8750 alpha=89.990 beta=114.762 gamma=90.008 P
Reduced cell : a=8.3365 b=14.2814 c=14.8750 alpha=65.238 beta=89.990 gamma=89.992
Conventional : a=14.2814 b=8.3365 c=14.8750 alpha=89.990 beta=114.762 gamma=90.008 P
Volume : 1608.13; System: monoclinic; Point group: 2/m}
```

78 reflections from the peaklist fit this lattice, 1 do not
If this is not correct, please run dirax and find the cell manually.

Fig. S16: Crystal faces, diffraction pattern, indexation and unit cell determination of complex 13.

INTENSITY STATISTICS FOR DATASET

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	Rmerge	Rsigma
Inf - 2.70	99	109	90.8	9.50	108.73	71.50	0.0319	0.0129
2.70 - 1.80	232	233	99.6	8.40	103.80	66.74	0.0287	0.0118
1.80 - 1.42	319	320	99.7	7.68	72.78	60.89	0.0268	0.0122
1.42 - 1.24	318	318	100.0	7.41	42.86	49.26	0.0284	0.0143
1.24 - 1.12	343	343	100.0	6.91	35.47	43.86	0.0261	0.0159
1.12 - 1.04	307	307	100.0	6.67	27.11	38.51	0.0317	0.0184
1.04 - 0.98	321	322	99.7	6.32	23.42	33.91	0.0342	0.0217
0.98 - 0.92	382	382	100.0	5.96	19.05	28.09	0.0375	0.0250
0.92 - 0.88	329	330	99.7	5.74	16.74	26.21	0.0423	0.0282
0.88 - 0.85	282	282	100.0	5.55	13.41	22.33	0.0489	0.0338
0.85 - 0.82	330	330	100.0	5.20	11.76	19.98	0.0544	0.0388
0.82 - 0.79	383	383	100.0	5.01	9.90	17.63	0.0630	0.0461
0.79 - 0.77	276	276	100.0	4.87	8.63	15.19	0.0761	0.0530
0.77 - 0.75	314	314	100.0	4.55	7.11	12.84	0.0903	0.0662
0.75 - 0.73	372	372	100.0	4.41	6.60	11.52	0.0917	0.0731
0.73 - 0.71	376	376	100.0	4.28	6.01	10.65	0.1096	0.0824
0.71 - 0.70	223	223	100.0	4.03	5.66	9.56	0.1125	0.0916
0.70 - 0.68	448	448	100.0	3.92	4.85	8.23	0.1303	0.1060
0.68 - 0.67	260	261	99.6	3.67	4.71	7.59	0.1352	0.1163
0.67 - 0.66	264	264	100.0	3.64	3.84	6.37	0.1612	0.1424
0.66 - 0.65	281	292	96.2	3.39	3.95	6.70	0.1509	0.1389
0.75 - 0.65	2224	2236	99.5	3.94	5.17	8.83	0.1193	0.1003
Inf - 0.65	6459	6485	99.6	5.43	21.68	25.12	0.0370	0.0259

The structure contains a substitutional disorder of a methyl- and a bromide-entity at the Mg1 atom with a respective occupancy of 81:19. The presence of a bromine atom was confirmed by EDX in

a TEM (see TEM part of SI). Complete .cif-data of the compound are available under the CCDC number **CCDC-2047047**.

Table S1: Crystal data and structure refinement.

Identification code	13098	
Empirical formula	$C_{11.81} H_{29.43} Br_{0.19} Mg N_2 Ni$	
Color	yellow	
Formula weight	297.72 g·mol ⁻¹	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$, (No. 14)	
Unit cell dimensions	$a = 14.8670(9)$ Å	$\alpha = 90^\circ$.
	$b = 8.3234(9)$ Å	$\beta = 114.739(5)^\circ$
	$c = 14.2697(11)$ Å	$\gamma = 90^\circ$.
Volume	1603.7(2) Å ³	
Z	4	
Density (calculated)	1.233 Mg·m ⁻³	
Absorption coefficient	1.703 mm ⁻¹	
F(000)	644 e	
Crystal size	0.18 x 0.16 x 0.10 mm ³	
θ range for data collection	2.861 to 33.154°.	
Index ranges	$-22 \leq h \leq 22$, $-12 \leq k \leq 12$, $-21 \leq l \leq 21$	
Reflections collected	34079	
Independent reflections	6100 [$R_{int} = 0.0374$]	
Reflections with $I > 2\sigma(I)$	5145	
Completeness to $\theta = 25.242^\circ$	99.8 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.89385 and 0.83779	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6100 / 0 / 212	
Goodness-of-fit on F^2	1.249	
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0342$	$wR^2 = 0.0666$
R indices (all data)	$R_1 = 0.0467$	$wR^2 = 0.0700$
Extinction coefficient	n/a	
Largest diff. peak and hole	0.363 and -0.608 e·Å ⁻³	

Table S2: Bond lengths [Å] and angles [°].

C(1)-C(2)	1.519(2)	C(1)-H(1A)	0.981(18)
C(1)-H(1B)	0.93(2)	C(1)-N(1)	1.4845(18)
C(2)-H(2A)	0.9900	C(2)-H(2B)	0.9900
C(2)-N(2)	1.4767(18)	C(3)-H(3A)	0.9800
C(3)-H(3B)	0.9800	C(3)-H(3C)	0.9800
C(3)-N(1)	1.4822(18)	C(4)-H(4A)	0.9800
C(4)-H(4B)	0.9800	C(4)-H(4C)	0.9800
C(4)-N(1)	1.4790(18)	C(5)-H(5A)	0.9800
C(5)-H(5B)	0.9800	C(5)-H(5C)	0.9800
C(5)-N(2)	1.4778(18)	C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800	C(6)-H(6C)	0.9800
C(6)-N(2)	1.4785(17)	C(7)-C(8)	1.412(2)
C(7)-H(7A)	0.984(19)	C(7)-H(7B)	0.979(19)
C(7)-Ni(1)	1.9963(14)	C(7)-Mg(1)	2.7151(15)
C(8)-H(8A)	0.98(2)	C(8)-H(8B)	0.99(2)
C(8)-Ni(1)	1.9730(15)	C(9)-C(10)	1.389(2)
C(9)-H(9A)	0.96(2)	C(9)-H(9B)	0.96(2)
C(9)-Ni(1)	1.9992(15)	C(10)-H(10A)	0.95(2)
C(10)-H(10B)	0.97(2)	C(10)-Ni(1)	2.0011(15)
N(1)-Mg(1)	2.2425(12)	N(2)-Mg(1)	2.2481(12)
Ni(1)-Mg(1)	2.5960(5)	Ni(1)-C(11)	2.0294(15)
Br(1)-Mg(1)	2.363(3)	Mg(1)-C(12)	2.179(7)
Mg(1)-C(11)	2.2786(16)	Mg(1)-H(11C)	2.23(2)
C(12)-H(12A)	0.9800	C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800	C(11)-H(11A)	0.96(2)
C(11)-H(11B)	0.97(2)	C(11)-H(11C)	0.92(2)
C(2)-C(1)-H(1A)	110.1(11)	C(2)-C(1)-H(1B)	109.1(12)
H(1A)-C(1)-H(1B)	108.7(15)	N(1)-C(1)-C(2)	111.02(11)
N(1)-C(1)-H(1A)	107.8(11)	N(1)-C(1)-H(1B)	110.1(12)
C(1)-C(2)-H(2A)	109.4	C(1)-C(2)-H(2B)	109.4
H(2A)-C(2)-H(2B)	108.0	N(2)-C(2)-C(1)	111.09(11)
N(2)-C(2)-H(2A)	109.4	N(2)-C(2)-H(2B)	109.4
H(3A)-C(3)-H(3B)	109.5	H(3A)-C(3)-H(3C)	109.5

H(3B)-C(3)-H(3C)	109.5	N(1)-C(3)-H(3A)	109.5
N(1)-C(3)-H(3B)	109.5	N(1)-C(3)-H(3C)	109.5
H(4A)-C(4)-H(4B)	109.5	H(4A)-C(4)-H(4C)	109.5
H(4B)-C(4)-H(4C)	109.5	N(1)-C(4)-H(4A)	109.5
N(1)-C(4)-H(4B)	109.5	N(1)-C(4)-H(4C)	109.5
H(5A)-C(5)-H(5B)	109.5	H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5	N(2)-C(5)-H(5A)	109.5
N(2)-C(5)-H(5B)	109.5	N(2)-C(5)-H(5C)	109.5
H(6A)-C(6)-H(6B)	109.5	H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5	N(2)-C(6)-H(6A)	109.5
N(2)-C(6)-H(6B)	109.5	N(2)-C(6)-H(6C)	109.5
C(8)-C(7)-H(7A)	118.2(11)	C(8)-C(7)-H(7B)	120.6(11)
C(8)-C(7)-Ni(1)	68.28(8)	C(8)-C(7)-Mg(1)	124.42(10)
H(7A)-C(7)-H(7B)	113.4(15)	Ni(1)-C(7)-H(7A)	119.0(11)
Ni(1)-C(7)-H(7B)	109.7(11)	Ni(1)-C(7)-Mg(1)	64.79(4)
Mg(1)-C(7)-H(7A)	65.4(10)	Mg(1)-C(7)-H(7B)	102.2(11)
C(7)-C(8)-H(8A)	120.0(11)	C(7)-C(8)-H(8B)	118.6(12)
C(7)-C(8)-Ni(1)	70.05(8)	H(8A)-C(8)-H(8B)	116.8(16)
Ni(1)-C(8)-H(8A)	107.6(11)	Ni(1)-C(8)-H(8B)	112.4(12)
C(10)-C(9)-H(9A)	122.0(12)	C(10)-C(9)-H(9B)	120.6(13)
C(10)-C(9)-Ni(1)	69.76(9)	H(9A)-C(9)-H(9B)	114.4(18)
Ni(1)-C(9)-H(9A)	110.0(11)	Ni(1)-C(9)-H(9B)	107.6(13)
C(9)-C(10)-H(10A)	120.0(13)	C(9)-C(10)-H(10B)	119.6(13)
C(9)-C(10)-Ni(1)	69.61(9)	H(10A)-C(10)-H(10B)	117.3(17)
Ni(1)-C(10)-H(10A)	107.1(12)	Ni(1)-C(10)-H(10B)	109.9(12)
C(1)-N(1)-Mg(1)	106.40(8)	C(3)-N(1)-C(1)	109.25(12)
C(3)-N(1)-Mg(1)	106.79(9)	C(4)-N(1)-C(1)	108.68(11)
C(4)-N(1)-C(3)	108.22(12)	C(4)-N(1)-Mg(1)	117.30(9)
C(2)-N(2)-C(5)	110.08(11)	C(2)-N(2)-C(6)	108.85(11)
C(2)-N(2)-Mg(1)	101.05(8)	C(5)-N(2)-C(6)	107.94(12)
C(5)-N(2)-Mg(1)	117.01(9)	C(6)-N(2)-Mg(1)	111.57(9)
C(7)-Ni(1)-C(9)	128.72(6)	C(7)-Ni(1)-C(10)	168.80(7)
C(7)-Ni(1)-Mg(1)	71.13(4)	C(7)-Ni(1)-C(11)	99.95(6)
C(8)-Ni(1)-C(7)	41.67(6)	C(8)-Ni(1)-C(9)	87.50(6)
C(8)-Ni(1)-C(10)	128.10(7)	C(8)-Ni(1)-Mg(1)	107.43(5)
C(8)-Ni(1)-C(11)	138.19(7)	C(9)-Ni(1)-C(10)	40.63(7)

C(9)-Ni(1)-Mg(1)	139.69(6)	C(9)-Ni(1)-C(11)	130.48(7)
C(10)-Ni(1)-Mg(1)	114.66(5)	C(10)-Ni(1)-C(11)	91.18(7)
C(11)-Ni(1)-Mg(1)	57.47(4)	C(7)-Mg(1)-H(11C)	78.3(5)
N(1)-Mg(1)-C(7)	96.74(5)	N(1)-Mg(1)-N(2)	81.66(4)
N(1)-Mg(1)-Ni(1)	98.37(3)	N(1)-Mg(1)-Br(1)	111.69(9)
N(1)-Mg(1)-C(11)	139.38(5)	N(1)-Mg(1)-H(11C)	162.8(6)
N(2)-Mg(1)-C(7)	165.31(5)	N(2)-Mg(1)-Ni(1)	121.49(3)
N(2)-Mg(1)-Br(1)	101.84(10)	N(2)-Mg(1)-C(11)	95.95(5)
N(2)-Mg(1)-H(11C)	98.9(5)	Ni(1)-Mg(1)-C(7)	44.09(3)
Ni(1)-Mg(1)-H(11C)	66.6(6)	Br(1)-Mg(1)-C(7)	92.35(10)
Br(1)-Mg(1)-Ni(1)	130.35(10)	Br(1)-Mg(1)-H(11C)	85.1(6)
C(12)-Mg(1)-C(7)	92.2(3)	C(12)-Mg(1)-N(1)	106.7(2)
C(12)-Mg(1)-N(2)	102.3(3)	C(12)-Mg(1)-Ni(1)	132.2(3)
C(11)-Mg(1)-C(7)	75.68(5)	C(11)-Mg(1)-Ni(1)	48.67(4)
C(11)-Mg(1)-Br(1)	108.50(10)	C(11)-Mg(1)-H(11C)	23.5(6)
Mg(1)-C(12)-H(12A)	109.5	Mg(1)-C(12)-H(12B)	109.5
Mg(1)-C(12)-H(12C)	109.5	H(12A)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12C)	109.5	H(12B)-C(12)-H(12C)	109.5
Ni(1)-C(11)-Mg(1)	73.86(5)	Ni(1)-C(11)-H(11A)	121.6(12)
Ni(1)-C(11)-H(11B)	88.8(12)	Ni(1)-C(11)-H(11C)	125.0(13)
Mg(1)-C(11)-H(11A)	99.0(12)	Mg(1)-C(11)-H(11B)	157.0(12)
Mg(1)-C(11)-H(11C)	75.2(13)	H(11A)-C(11)-H(11B)	103.0(16)
H(11A)-C(11)-H(11C)	107.3(17)	H(11B)-C(11)-H(11C)	104.1(17)

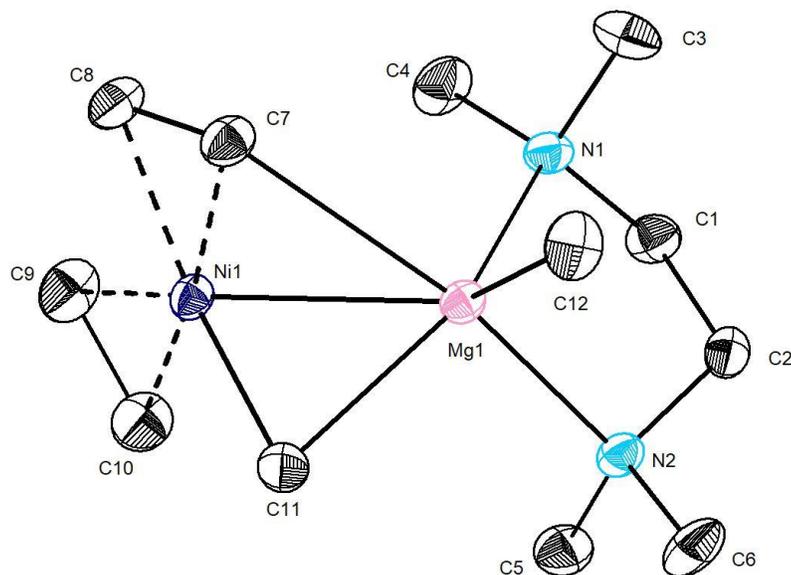


Fig. S17: ORTEP of the molecular structure of methyl component (81%) of complex **13a**. H atoms have been removed for clarity.

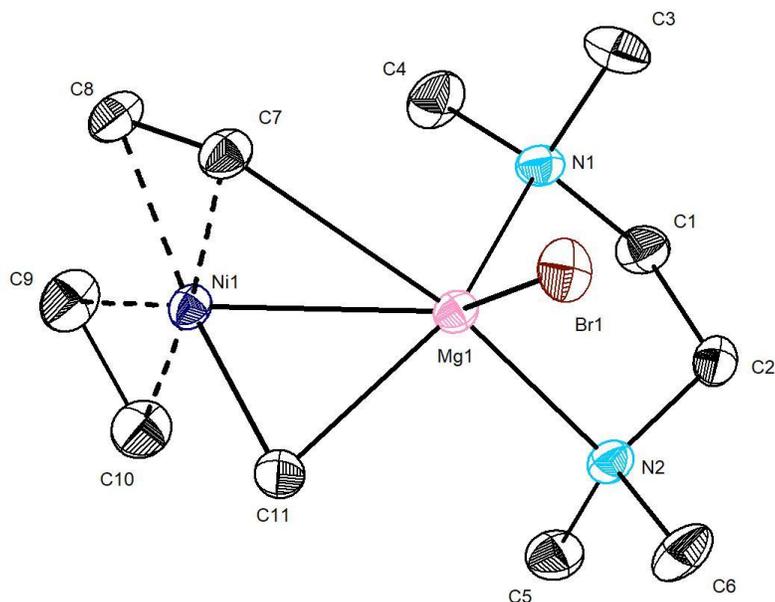
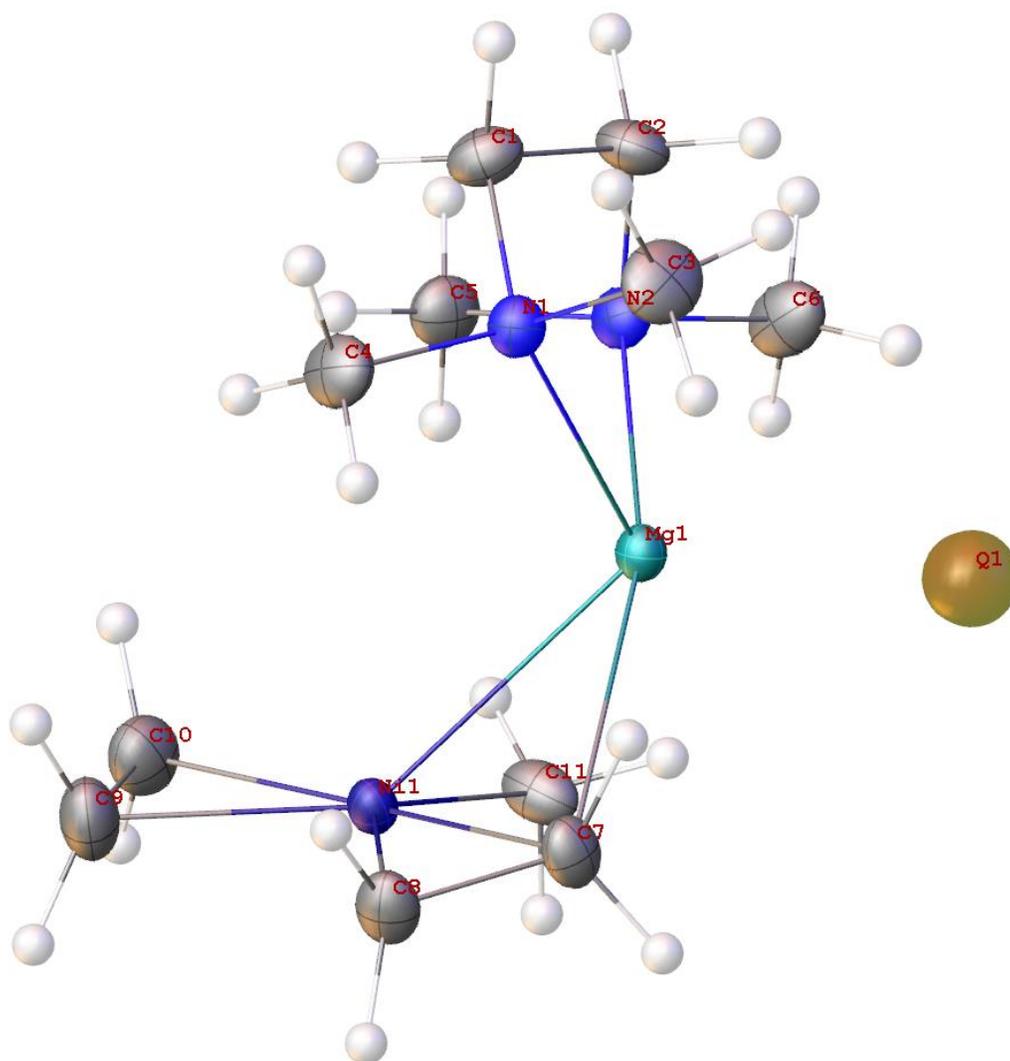


Fig. S18: ORTEP of the molecular structure of bromine component (19%) of complex **13b**. H atoms have been removed for clarity.

TEM EDX analysis of Complex 13b.

During structure solution and refinement, a high residual electron density peak appeared at a distance of 2.334 Å from the Mg1 atom. This distance and the unusually high residual density of 25.1 eÅ⁻³ indicates that a more electron-rich substituent than just a methyl group must be located at this position.



A search in the CSD database (performed on 22nd of May 2020; using ConQuest 2020.1; CSD version 5.41 (November 2019) + 1 update) with chemical meaningful substituents identifies two potential possibilities.

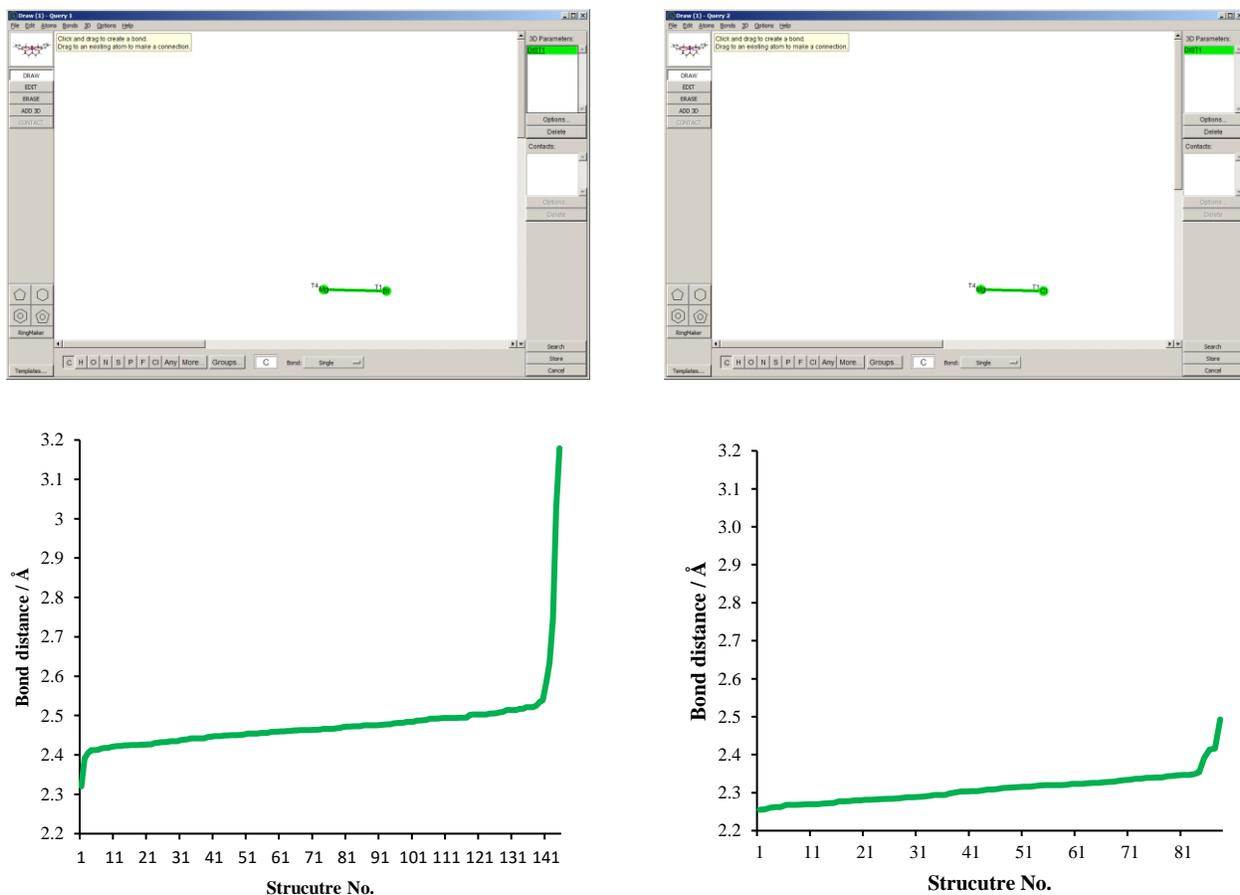


Fig. S19: Analysis of Mg-Br and Mg-Cl distances. Input structures and predefined 3D parameter (top) and graphical plot of resulting bond distances (bottom).

Substituent	Mg-Br	Mg-Cl
No. of structures	145	88
Average bond distance / Å	2.477(86)	2.303(26)

The statistical analysis does not give a fully conclusive answer to the question of which type of atom (Cl versus Br) is attached to the Mg1 atom in addition to methyl. During refinement using freely refined occupancies (FVAR, with C12 and Br1 or Cl1), both structure models converge satisfactorily.

Therefore the sample was investigated with EDX analysis. For these experiments, a TEM vacuum transfer holder (Gatan Model 647) was transferred into a glove box. Inside the glove box, a tiny amount of crystalline sample of Complex 1 was placed on lacey carbon film supported by a copper TEM grid and the sample holder was sealed under inert

conditions. After extracting from glove box, the device was inserted into the high vacuum column of a 100 kV TEM (Hitachi H-7500) equipped with a BRUKER (X Flash 6 TI 30) EDX detector. In order to have a statistically meaningful result, three different positions (25, 26 and 27) were analyzed.

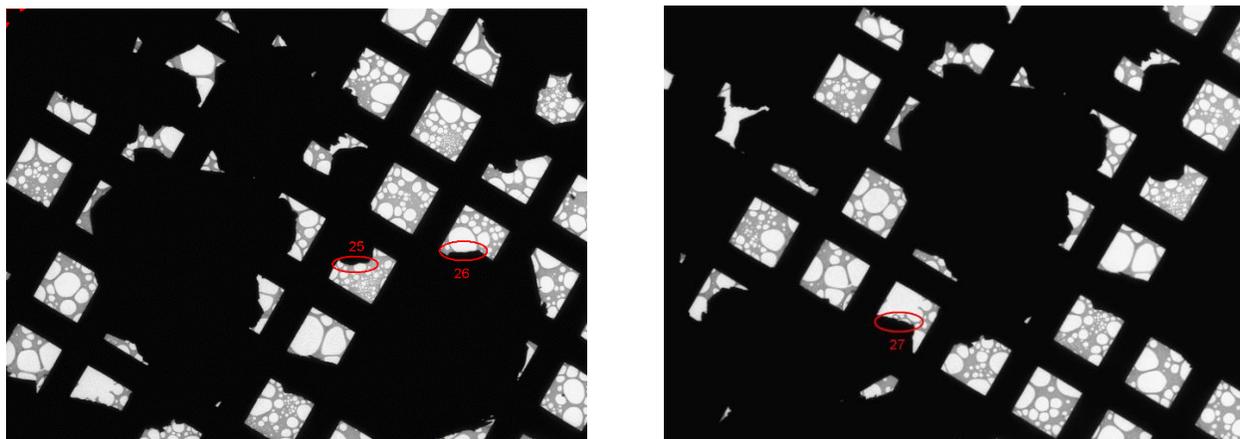


Fig. S20: TEM images of the crystalline sample on the carbonated copper grid.

TEM Parameter		EDX Parameter	
HV	100 kV	Range	40 keV
Magnification	30 000 x	Dead time	22 %
Tilt	20,0 °	Live time	---- s
		Temperature	-39,9 °C
		Max. throughput	600 kcps
		Incomming count rate	2,81 kcps

The EDX analysis clearly shows that only bromine is present in the crystalline sample. Therefore the structural model using a Mg-Br entity instead of a Mg-Cl entity was chosen for the single crystal structure refinement.

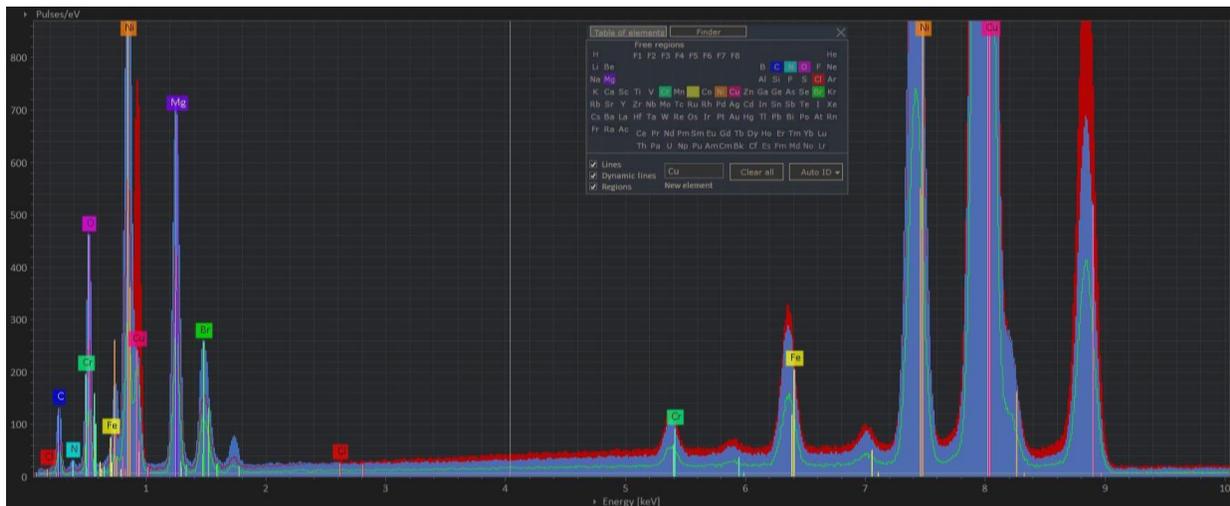
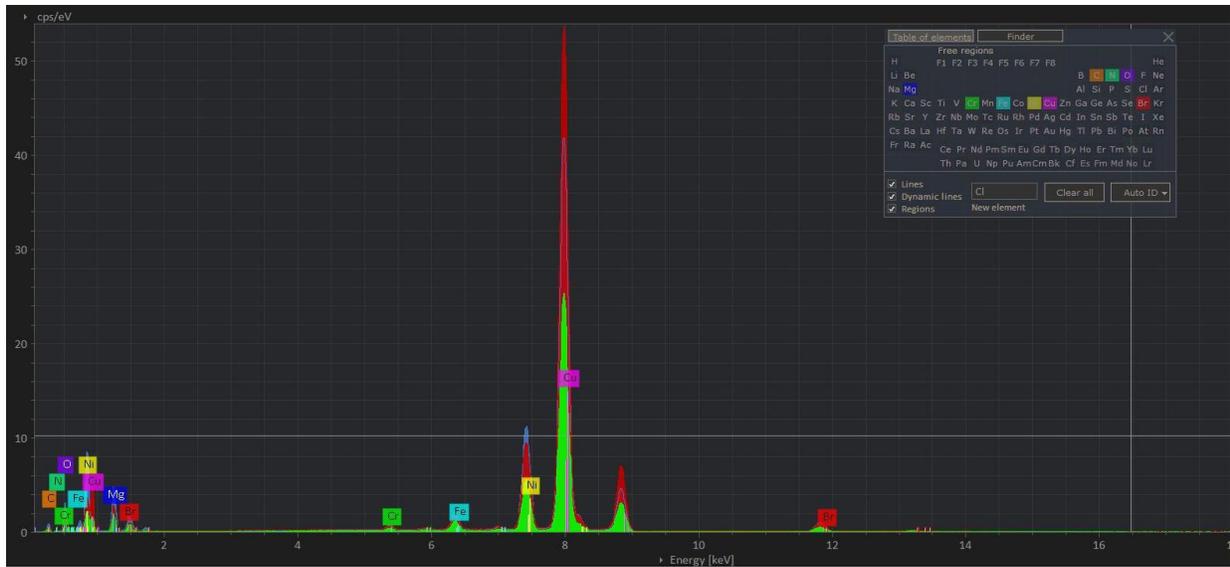


Fig. S21: Overlay of EDX spectra (position 25, 26, 27) with automated element search (top) and a partial view of all three spectra showing the absence of characteristic Cl lines (bottom).

References:

- (1) Nattmann, L.; Lutz, S.; Ortsack, P.; Goddard, R.; Cornella, J.; *J. Am. Chem. Soc.* **2018**, *140*, 13628-13633.
- (2) Bogdanović, B.; Kröner, M.; Wilke, G.; Olefin-komplexe des Nickel(0), *Liebigs Ann. Chem.* **1966**, *699*, 1
- (3) Wilke, G. Neues über cyclische Butadien-Oligomers. *Angew. Chem.* **1960**, *72*, 581.
- (4) Chernyshova, E. S.; Goddard, R.; Pörschke, K. –R. *cis,cis,cis-1,5,9-Cyclododecatriene-Metal complexes.* *Organometallics* **2007**, *26*, 4872.
- (5) Über die katalytische Umwandlung von Olefinen, VIII, „Nacktes“ Nickel als Katalysator bei der Umalkylierung von Aluminiumtrialkylen mit α -Olefinen. Fischer, K.; Jonas, K.; Mollbach, A. Wilke, G. *Z. Naturforsch. B* **1984**, *39b*, 1011.
- (6) Kaschube, W.; Pörschke, K. –R.; Angermund, K.; Krüger, C.; Wilke, G. Diorganylmagnesium-Komplexe von Nickel(0): $(\text{TMEDA})\text{MgCH}_3(\mu\text{-CH}_3)\text{Ni}(\text{C}_2\text{H}_4)_2$. *Chem. Ber.* **1988**, *121*, 1921.