

Synthesis and structural characterization of η^3 -allyl(α -diimine)nickel(II) complexes bearing trimethylsilyl groups

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Abstract

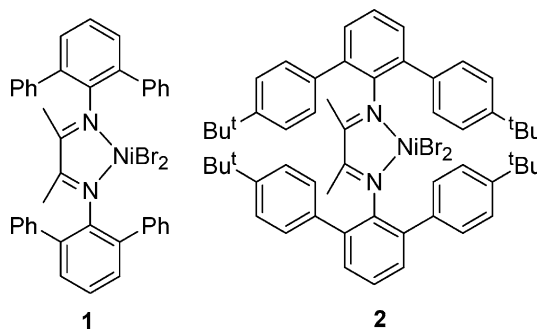
A set of isomeric *para*- and *meta*-trimethylsilylphenyl *ortho*-substituted *N,N*-phenyl α -diimine ligands [(Ar-N=C(Me)-(Me)C=N-Ar) Ar = 2,6-di(4-trimethylsilylphenyl)phenyl (**16**); Ar = 2,6-di(3-trimethylsilylphenyl)phenyl (**17**)] have been synthesized through a two-step procedure. The palladium-catalysed cross-coupling reaction between 2,6-dibromophenylamine (**7**) and 4-trimethylsilylphenylboronic acid (**8**), 3-trimethylsilylphenylboronic acid (**9**) was used to prepare 4,4'-bis(trimethylsilyl)-[1,1';3',1'']terphenyl-2'-ylamine (**10**) and 3,3'-bis(trimethylsilyl)-[1,1';3',1'']terphenyl-2'-ylamine (**11**). The di-1-adamantylphosphine oxide Ad₂P(O)H (**13**) and di-*tert*-butyl-trimethylsilylanyl methylphosphine *tert*-Bu₂P-CH₂-SiMe₃ (**14**) were used for the first time as ligands for the Suzuki coupling. The condensation of 2,2,3,3-tetramethoxybutane (**15**) with anilines **10** and **11** afforded α -diimines **16** and **17**. The reaction of π -allylnickel chloride dimer (**18**), α -diimines (**16**), (**17**) and sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (BAF) (**19**) or silver hexafluoroantimonate (**20**) led to two sets of isomeric complexes [η^3 -allyl(Ar-N=C(Me)-(Me)C=N-Ar)Ni]⁺ X⁻, [Ar = 2,6-di(4-trimethylsilylphenyl)phenyl, X = BAF (**3**), X = SbF₆ (**4**); Ar = 2,6-di(3-trimethylsilylphenyl)phenyl, X = BAF (**5**), X = SbF₆ (**6**)]. The steric repulsion of closely positioned trimethylsilyl groups in **4** caused the distortion of the nickel square planar coordination by 17.6° according to X-ray analysis.

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Keywords: Nickel; Palladium; Boron; Antimony; α -Diimine; X-ray analysis

1. Introduction

The easily varied steric and electronic properties of the α -diimine ligands are important features of nickel α -diimine catalyst systems (trademarked the Versipol® catalyst system by DuPont) for the polymerization of ethylene, α -olefins and the copolymerization of nonpolar olefins with a variety of functionalized olefins [1]. For example, the key to producing ultrahigh molecular weight polymers is the incorporation of phenyl substituents in the *ortho*-positions of aryl rings for the complex **1** [2,3] depicted below:



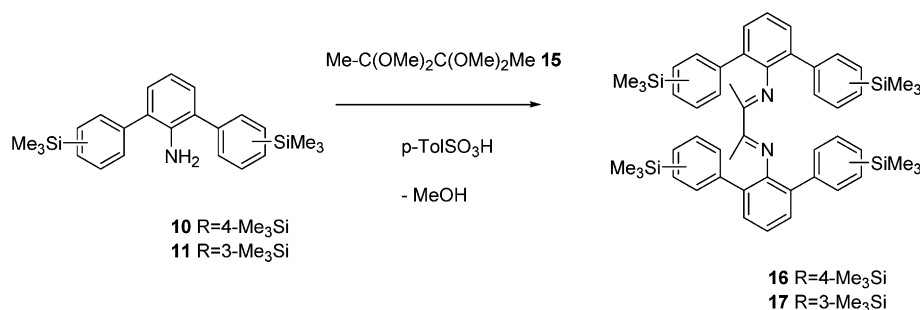
The corresponding nickel(II) dibromide complex **2** with *para-tert*-butylphenyl shows remarkably high polymerisation activity and affords high molecular weight polyethylene. Further substitution of *ortho*-phenyl groups with bulky substituents, e.g. trimethylsilyl, is expected to affect important catalyst properties such as catalyst lifetime.

We now report the synthesis of such complexes and have determined the structures of **3–6** below:

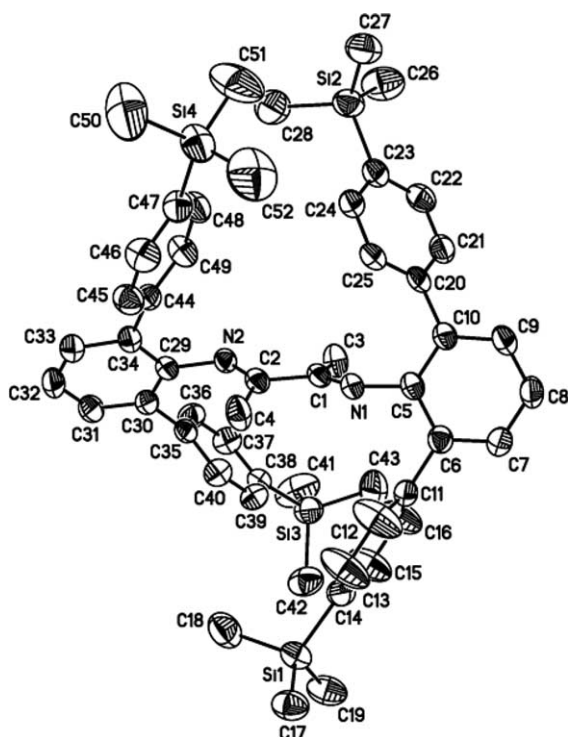
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¹ This is DuPont contribution #8415.

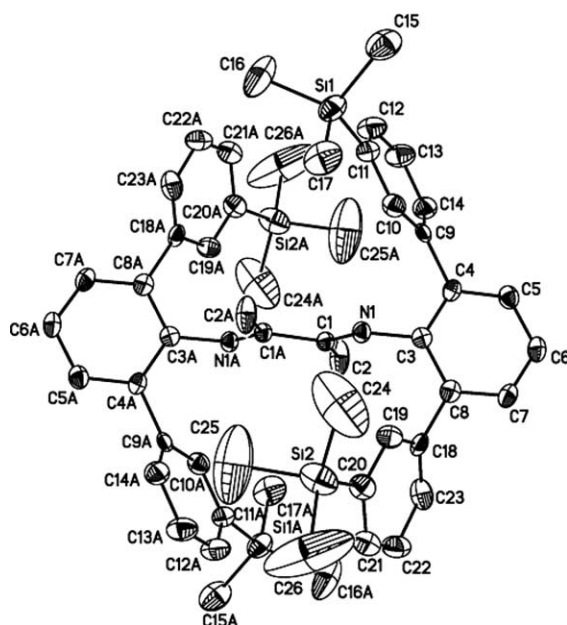


Scheme 2.

Fig. 1. ORTEP drawing of α -diimine ligand **16**. Thermal ellipsoids are drawn to the 50% probability level.

While the reaction of π -allylnickel chloride dimer **18** and sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate **19** or silver hexafluoroantimonate **20** afforded complexes **3–6**, we were unable to isolate the corresponding complexes from the reaction of bulky ligands **16**, **17** with (DME)NiBr₂. However, nickel(II) acetylacetonate reacts to give the corresponding diimine complexes **4** and **6** afforded single crystals suitable for X-ray analysis from toluene solutions (Tables 2 and 3).

X-ray analysis of the complexes **4** and **6** reveals that the central nickel atoms are four-coordinate with the bidentate α -diimine and π -allyl ligands. The position of the trimethylsilyl group on the *ortho*-phenyl moiety has a substantial effect on the metal coordination geometry. The ORTEP drawing of **4** (Fig. 3) clearly shows that the

Fig. 2. ORTEP drawing of α -diimine **17**. Thermal ellipsoids are drawn to the 50% probability level.

nickel square planar coordination has been distorted. This distortion can be measured by the dihedral angle Σ between the two sets of planes defined by N1–Ni–N2 and C–5–Ni–C7. The tetrahedral twist angle for **4** was 17.6° (Fig. 3).

The ORTEP drawing of the *meta*-isomer **6** revealed the usual square planar distortion of η^3 -allyl nickel fragments. In previous work, this has been shown to vary from 1.7° to 9.7° [10–12]. In contrast to complex **4**, the tetrahedral twist angle for **6** was 11.3°, which is only slightly greater than the usual range (Fig. 4).

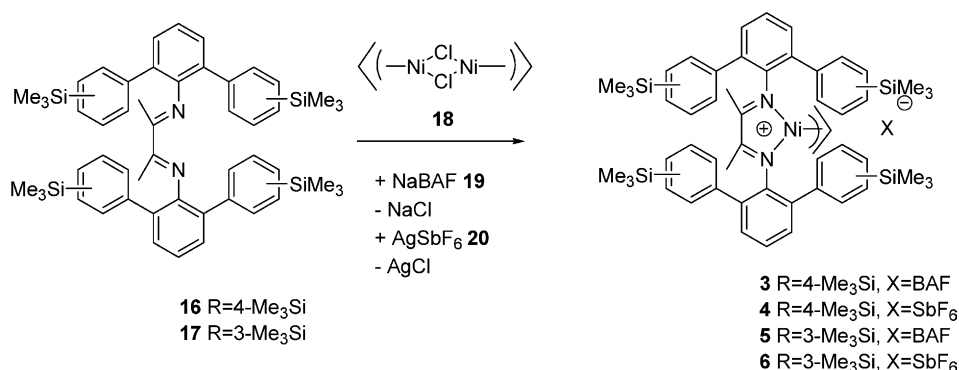
3. Summary

Sterically hindered η^3 -allyl(α -diimine)Ni complexes **3–6** with distorted configurations bearing 2,6-di(4-trimethylsilylphenyl)aniline fragments and 2,6-di(3-trimethylsilylphenyl)aniline fragments have been prepared. The repulsive interaction of trimethylsilyl groups in the *para*-position of *ortho*-substituted

Table 1
Selected bond lengths (Å), angles (°) and interplanar angles (°) for **16** and **17**

| 16 | | 17 | |
|----------------------|----------|--------------------|----------|
| N1–C1 | 1.268(3) | N1–C1 | 1.271(6) |
| N2–C2 | 1.272(3) | N1–C3 | 1.424(6) |
| N1–C5 | 1.415(3) | C1–C1a | 1.500(9) |
| N2–C29 | 1.418(3) | C1–C2 | 1.480(6) |
| C1–C2 | 1.503(3) | C3–N1–C1 | 119.1(4) |
| C1–C3 | 1.500(3) | N1–C1–C1a | 116.4(5) |
| C2–C4 | 1.497(3) | (C3–C8)–(N1,C1,C2) | 88.3 |
| C29–N2–C2 | 121.9(2) | (C3–C8)–(C9–C14) | 52.0 |
| N2–C2–C1 | 116.1(2) | (C3–C8)–(C18–C23) | 50.6 |
| C5–N1–C1 | 124.0(2) | | |
| N1–C1–C2 | 115.4(2) | | |
| (C5–C10)–(N1,C3,N2) | 62.4 | | |
| (C5–C10)–(C11–C16) | 82.6 | | |
| (C5–C10)–(C20–C25) | 47.9 | | |
| (C29–C34)–(N1,C3,N2) | 64.4 | | |
| (C29–C34)–(C35–C40) | 70.2 | | |
| (C29–C34)–(C44–C49) | 54.8 | | |

Symmetrically redundant values are not included for **17**.



Scheme 3.

Table 2
Selected bond lengths (Å) and angles (°) for **4** and **6**

| 4 | | 6 | |
|---------------------|-----------|-----------|------------|
| <i>Bond lengths</i> | | | |
| Ni1–N1 | 1.911(4) | Ni1–N1 | 1.949(2) |
| Ni1–N2 | 1.916(4) | Ni1–N2 | 1.949(2) |
| Ni1–C6 | 2.035(10) | Ni1–C3 | 2.031(3) |
| Ni1–C7 | 2.027(5) | Ni1–C5 | 2.006(3) |
| N1–C1 | 1.335(7) | N1–C1 | 1.299(3) |
| N2–C2 | 1.339(7) | N2–C2 | 1.297(3) |
| N1–C8 | 1.437(6) | N1–C6 | 1.444(3) |
| N2–C32 | 1.459(6) | N2–C30 | 1.448(3) |
| C1–C2 | 1.423(10) | C1–C2 | 1.506(3) |
| C1–C3 | 1.519(8) | C1–C1' | 1.495(3) |
| C2–C4 | 1.509(9) | C2–C2' | 1.484(3) |
| <i>Bond angles</i> | | | |
| N1–Ni1–N2 | 84.46(17) | N1–Ni1–N2 | 83.51(9) |
| N1–Ni1–C7 | 100.8(2) | N1–Ni1–C3 | 103.52(11) |
| N1–Ni1–C5 | 167.0(2) | N1–Ni1–C5 | 174.85(11) |
| N2–Ni1–C5 | 100.7(2) | N2–Ni1–C5 | 100.47(11) |
| N2–Ni1–C7 | 168.9(2) | N2–Ni1–C3 | 168.20(10) |
| C5–Ni1–C7 | 42.7(5) | C3–Ni1–C5 | 73.13(12) |

N,N-phenyl α -diimine ligands of nickel complexes distorts the square planar coordination of the metal center. Complexes **3–6** catalyze ethylene polymerization. The polymerization results will be published in due course.

4. Experimental

4.1. General procedures

All the operations related to catalysts were carried out under an argon atmosphere using standard Schlenk techniques. Anhydrous solvents were used in the reactions. Solvents were distilled from drying agents or passed through alumina columns under an argon or nitrogen atmosphere. 2,6-Dibromophenylamine, 4-trimethylsilylphenylboronic acid, 3-trimethylsilylphenylboronic acid, Pd₂dba₃, silver hexafluoroantimonate were purchased from Aldrich. Sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaBAF) was purchased from Boulder Scientific.

Table 3
Summary of crystal data, data collection, and structure refinement parameters

| | 4 | 6 | 16 | 17 |
|---|---|---|---|--|
| Empirical formula | C ₆₉ H ₈₅ F ₆ N ₂ NiSbSi ₄ | C ₆₂ H ₇₇ F ₆ N ₂ NiSbSi ₄ | C ₅₂ H ₆₄ N ₂ Si ₄ | C ₅₂ H ₆₄ N ₂ Si ₄ |
| Formula weight | 1349.21 | 1257.08 | 829.41 | 829.41 |
| Crystal color, form | Dark red prism | Red block | Colorless plate | Colorless prism |
| Crystal system | Triclinic | Monoclinic | Triclinic | Monoclinic |
| Space group | <i>P</i> $\bar{1}$ | <i>P</i> ₂ / <i>c</i> | <i>P</i> $\bar{1}$ | <i>P</i> ₂ / <i>n</i> |
| <i>a</i> (Å) | 11.220(3) | 17.623(5) | 11.760(6) | 10.3291(11) |
| <i>b</i> (Å) | 13.848(4) | 17.558(5) | 13.277(7) | 13.1990(12) |
| <i>c</i> (Å) | 24.210(7) | 20.688(5) | 16.711(8) | 18.924(2) |
| α (°) | 76.971(5) | | 79.783(9) | |
| β (°) | 78.851(5) | 101.39(4) | 88.419(10) | 98.899(3) |
| γ (°) | 78.395(6) | | 88.016(10) | |
| <i>V</i> (Å ³) | 3546.4(17) | 6275(3) | 2566(2) | 2548.9(4) |
| <i>Z</i> | 2 | 4 | 2 | 2 |
| Density (g/cm ³) | 1.263 | 1.331 | 1.074 | 1.081 mg |
| Absolute μ (mm ⁻¹) | 0.77(λ = Mo) | 0.81(λ = 0.7100) | 0.15(λ = Mo) | 0.15mm(λ = Mo) |
| <i>F</i> (000) | 1404 | 2608 | 892 | 892 |
| Crystal size (mm) | 0.34 × 0.07 × 0.07 | 0.03 × 0.03 × 0.01 | 0.42 × 0.37 × 0.06 | 0.16 × 0.16 × 0.14 |
| Scan mode | ω | ω | ω | ω |
| Detector | Bruker-CCD | Mar-CCD | Bruker-CCD | RaxisII-IP |
| θ_{\max} (°) | 52.74 | 59.16 | 52.74 | 46.50 |
| Number of unique reflections | 20817 | 16519 | 10395 | 3396 |
| Number of observed reflections | 14253 | 15609 | 5888 | 2502 |
| Number of parameters | 778 | 712 | 537 | 272 |
| <i>S</i> ^b | 1.012 | 1.00 | 1.019 | 1.066 |
| <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)] ^a | <i>R</i> ₁ = 0.0686, <i>wR</i> ₂ = 0.1715 | <i>R</i> ₁ = 0.0772, <i>wR</i> ₂ = 0.2095 | <i>R</i> ₁ = 0.0577, <i>wR</i> ₂ = 0.1366z | <i>R</i> ₁ = 0.0887, <i>wR</i> ₂ = 0.2386 |
| <i>R</i> indices (all data) ^a | <i>R</i> ₁ = 0.1266, <i>wR</i> ₂ = 0.2102 | <i>R</i> ₁ = 0.787, <i>wR</i> ₂ = 0.2122 | <i>R</i> ₁ = 0.1135, <i>wR</i> ₂ = 0.1654 | <i>R</i> ₁ = 0.1188, <i>wR</i> ₂ = 0.2602 |
| Maximum difference peak and hole (e Å ⁻³) | 1.070, -0.638 | 3.055, -1.047 | 0.351, -0.245 | 0.707, -0.591 |

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$ (sometimes denoted as R_w2).

^b Goodness-of-fit = $S = \{ \sum [w(F_o^2 - F_c^2)^2] / (n - p) \}^{1/2}$, where *n* is the number of reflections, and *p* is the total number of refined parameters.

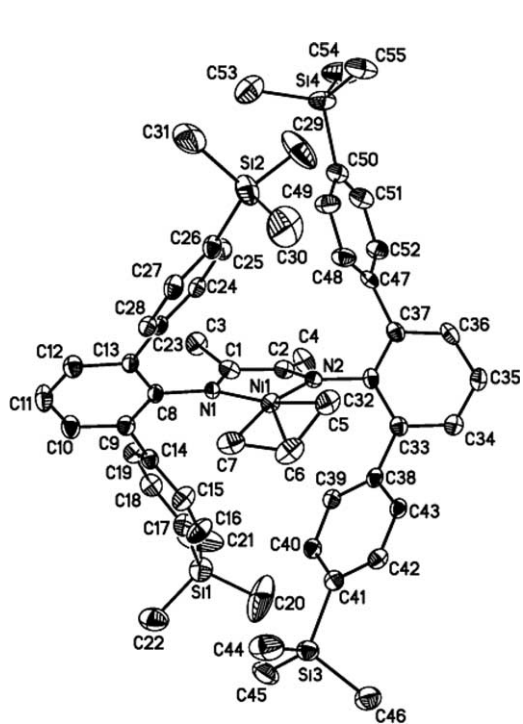


Fig. 3. ORTEP drawing of complex 4. Thermal ellipsoids are drawn to the 50% probability level. The tetrahedral twist angle for 4 was 17.6°.

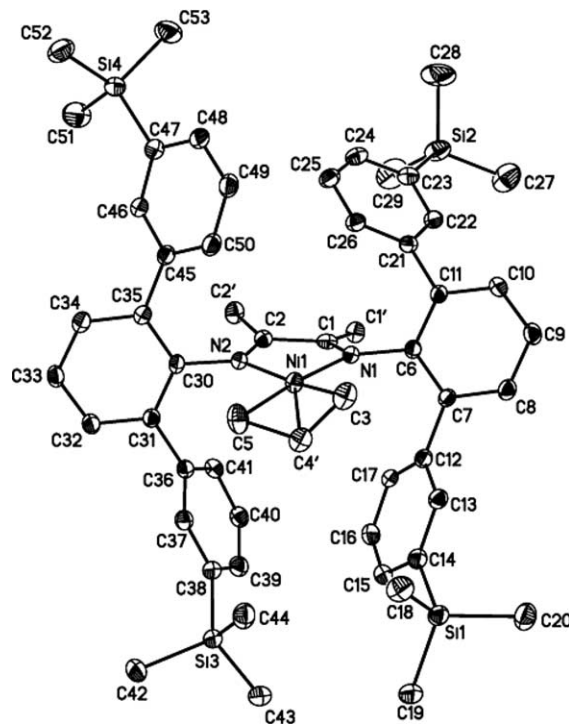


Fig. 4. ORTEP drawing of complex 6. Thermal ellipsoids are drawn to the 50% probability level. The tetrahedral twist angle for 6 was 11.3°.

4.2. 4,4''-Bis(trimethylsilyl)-[1,1';3',1'']terphenyl-2'-ylamine (10)

15.0 g (0.0773 mol) of 4-trimethylsilylphenylboronic acid (**8**), 6.46 g (0.026 mol) of 2,6-dibromophenylamine (**7**), 30.21 g (0.086 mol) of cesium carbonate, 0.37 g (0.00040 mol) of tris(dibenzylideneacetone)dipalladium, 0.37 g (0.00116 mol) di-1-adamantylphosphine oxide (**13**) and 125 ml of dioxane were refluxed for 1 h. The reaction mixture was cooled to room temperature, filtered and the solvent was removed under vacuum. The resulting mixture was purified by chromatography on silica gel with eluent petroleum ether/ethyl ether at 10/0.5. Yield of 4,4''-bis(trimethylsilyl)-[1,1';3',1'']terphenyl-2'-ylamine (**10**) was 4.79 g (48%) with m.p. 92.44 °C. ¹H NMR (CDCl₃) 0.10 (s, 18H, Me₃Si), 3.75 (s, 2H, NH₂), 6.66–7.45 (m, arom. 11H). Anal. Calc. for C₂₄H₃₁NSi₂: C, 73.97; H, 8.02; N, 3.59. Found: C, 74.18; H, 7.95; N, 3.50%. GC/MS MW is 389.

4.3. 3,3''-Bis(trimethylsilyl)-[1,1';3',1'']terphenyl-2'-ylamine (11)

15.0 g (0.0773 mol) of 3-trimethylsilylphenylboronic acid (**9**), 8.24 g (0.033 mol) of 2,6-dibromophenylamine (**7**), 30.21 g (0.086 mol) of cesium carbonate, 1.06 g (0.0012 mol) of tris(dibenzylideneacetone)dipalladium, 0.65 g (0.0028 mol) di-*tert*-butyltrimethylsilyltrimethylphosphane (**14**) and 100 ml of dioxane were stirred at room temperature for 12 h. The reaction mixture was filtered and the solvent was removed under vacuum. The resulting viscous liquid was purified by chromatography on silica gel with eluent petroleum ether/ethyl ether at 10/0.5. Yield of 3,3''-bis(trimethylsilyl)-[1,1';3',1'']terphenyl-2'-ylamine (**11**) was 4.73 g (37%) with m.p. 38.47 °C. ¹H NMR (CDCl₃) 0.05 (s, 18H, Me₃Si), 3.80 (s, broad, 2H, NH₂), 6.70–7.55 (m, arom. 11H). Anal. Calc. for C₂₄H₃₁NSi₂: C, 73.97; H, 8.02; N, 3.59. Found: C, 73.89; H, 7.92; N, 3.54%. GC/MS MW is 389.

4.4. 2,3-Butanedione-bis(4,4''-bis(trimethylsilyl)-[1,1';3',1'']terphenyl-2'-ylimine) (16)

3.63 g (0.0093 mol) of 4,4''-Bis(trimethylsilyl)-[1,1';3',1'']terphenyl-2'-ylamine (**10**), 0.75 g (0.0042 mol) of 2,2,3,3-tetramethoxybutane (**15**), 50 mg of *para*-toluenesulfonic acid and 50 ml of toluene were refluxed under argon for 5 h. The reaction mixture was allowed to cool off to RT and the formed methanol and toluene were removed under vacuum. The product was purified by chromatography on silica gel with eluent petroleum ether/ethyl ether at 10/2. Yield of 2,3-butanedione-bis(4,4''-bis(trimethylsilyl)-[1,1';3',1'']terphenyl-2'-ylimine) (**16**) was 0.54 g (16%) with m.p. 207.05 °C. ¹H NMR (CDCl₃) 0.12 (s, 36H, Me₃Si), 1.02 (s, 6H, CH₃), 6.95–7.43 (m, arom. 22H). ¹³C NMR (CDCl₃) 0.0, 18.7,

125.1, 129.4, 130.6, 132.8, 133.8, 139.5, 141.7, 146.3, 168.8. Anal. Calc. for C₅₂H₆₄N₂Si₄: C, 75.30; H, 7.78; N, 3.38. Found: C, 75.04; H, 7.76; N, 3.35%. LC/MS MW is 828. The structure was proved by X-ray analysis.

4.5. 2,3-Butanedione-bis(3,3''-bis(trimethylsilyl)-[1,1';3',1'']terphenyl-2'-ylimine) (17)

6.75 g (0.0173 mol) of 3,3''-Bis(trimethylsilyl)-[1,1';3',1'']terphenyl-2'-ylamine (**11**), 1.38 g (0.0077 mol) of 2,2,3,3-tetramethoxybutane (**15**), 50 mg of *para*-toluenesulfonic acid and 50 ml of xylenes were refluxed under argon for 5 h. The reaction mixture was allowed to cool off to RT and the formed methanol and xylenes were removed under vacuum. The product was purified by chromatography on silica gel with eluent petroleum ether/ethyl ether at 10/2. Yield of 2,3-butanedione-bis(3,3''-bis(trimethylsilyl)-[1,1';3',1'']terphenyl-2'-ylimine) **17** was 0.62 g (9.66%) with m.p. 219.96 °C. ¹H NMR (CDCl₃) 0.10 (s, 36H, Me₃Si), 1.26 (s, 6H, CH₃), 6.78–7.40 (m, arom. 22H). ¹³C NMR (CDCl₃) 0.2, 17.3, 125.0, 128.0, 130.6, 130.7, 132.6, 135.2, 140.3, 140.7, 147.1, 167.9. Anal. Calc. for C₅₂H₆₄N₂Si₄: C, 75.30; H, 7.78; N, 3.38. Found: C, 75.10; H, 7.74; N, 3.37%. LC/MS MW is 828. The structure was proved by X-ray analysis.

4.6. Nickel(1+), [N,N'-(1,2-dimethyl-1,2-ethanediylidene)bis(4,4''-bis(trimethylsilyl)-[1,1';3',1'']terphenyl-2'-ylamine)](η³-2-propenyl)-, tetrakis[3,5-bis(trifluoromethyl)phenyl] borate (1-)(3)

0.175 g (0.00021 mol) of 2,3-Butanedionebis(4,4''-bis(trimethylsilyl)-[1,1';3',1'']terphenyl-2'-ylimine) (**16**), 0.0285 g (0.000105 mol) of nickel allyl chloride dimer (**18**), 0.187 g (0.00021 mol) of sodium tetrakis[3,5-bis(trifluoromethyl)phenyl] borate (**19**) and 5 ml of ethyl ether were stirred at RT for 12 h. The resulting reaction mixture was filtered through Celite®, and the solvent was evaporated in vacuum. The residue was washed with 10 ml of pentane and dried affording 0.31 g (82%) yield of above nickel compound **3**. ¹H NMR (CD₂Cl₂) 0.19 (s, 36H, Me₃Si), 1.25 (s, 6H, CH₃), 1.65 (s, b, 2-allyl-H), 2.55 (s, b, 2-allyl-H), 5.14 (s, 1H central allyl-H), 6.95–7.43 (m, arom. 34 H). ¹³C NMR (CDCl₃), (selected signals) 180.2 (s, C=N). Anal. Calc. for C₈₇H₈₁BF₂₄N₂NiSi₄: C, 58.30; H, 4.55; N, 1.56. Found: C, 58.27; H, 4.54; N, 1.41%.

4.7. Nickel(1+), [N,N'-(1,2-dimethyl-1,2-ethanediylidene)bis(3,3''-bis(trimethylsilyl)-[1,1';3',1'']terphenyl-2'-ylamine)](η³-2-propenyl)-, tetrakis[3,5-bis(trifluoromethyl)phenyl] borate (1-)(5)

0.20 g (0.00024 mol) of 2,3-Butanedionebis(3,3''-bis(trimethylsilyl)-[1,1';3',1'']terphenyl-2'-ylimine) (**17**),

0.033 g (0.00012 mol) of nickel allyl chloride dimer (**18**), 0.214 g (0.00024 mol) of sodium tetrakis[3,5-bis(trifluoromethyl)phenyl] borate (**19**) and 5 ml of ethyl ether were stirred at RT for 12 h. The resulting reaction mixture was filtered through Celite®, and the solvent was evaporated in vacuum. The residue was washed with 10 ml of pentane and dried affording 0.31 g (82%) yield of above nickel compound **5**. ¹H NMR (CD₂Cl₂) 0.20 (s, 36H, Me₃Si), 1.40 (s, 6H, CH₃), 1.80 (s, b, 2-allyl-H), 2.65 (s, b, 2-allyl-H), 5.20 (s, 1H central allyl-H) 6.70–7.60 (m, arom. 34H). ¹³C NMR (CDCl₃), (selected signals) 177.9 (s, C=N). Anal. Calc. for C₈₇H₈₁BF₂₄N₂NiSi₄: C, 58.30; H, 4.55; N, 1.56. Found: C, 58.20; H, 4.49; N, 1.55%.

4.8. Nickel(1+), [N,N'-(1,2-dimethyl-1,2-ethanediylidene)bis(4,4'-bis(trimethylsilyl)-[1,1';3',1'']terphenyl-2'-ylamine)](η³-2-propenyl)-, hexafluoroantimonate (1-) (**4**)

0.19 g (0.00029 mol) of 2,3-Butanedionebis(4,4''-bis(trimethylsilyl)-[1,1';3',1'']terphenyl-2'-ylimine) (**16**), 0.031 g (0.00046 mol) of nickel allyl chloride dimer (**18**), 0.079 g (0.00023 mol) of silver hexafluoroantimonate (**20**) and 40 ml of ethyl ether were stirred at RT for 12 h. The resulting reaction mixture was filtered through Celite®, and the solvent was evaporated in vacuum. The residue was recrystallized from benzene affording 0.24 g (75%) yield of above nickel compound **4** with m.p. 271.02 °C. ¹H NMR (CD₂Cl₂) 0.21 (s, 36H, Me₃Si), 1.34 (s, 6H, CH₃), 1.40 (s, b, 2-allyl-H), 2.50 (s, b, 2-allyl-H), 5.20 (s, 1H central allyl-H), 7.10–7.70 (m, arom. 22H). ¹³C NMR (CDCl₃), (selected signals) 180.5 (s, C=N). Anal. Calc. for C₅₅H₆₉F₆N₂NiSbSi₄: C, 56.71; H, 5.97; N, 2.40. Found: C, 56.83; H, 6.09; N, 2.41%.

4.9. Nickel(1+), [N,N'-(1,2-dimethyl-1,2-ethanediylidene)bis(3,3'-bis(trimethylsilyl)-[1,1';3',1'']terphenyl-2'-ylamine)](η³-2-propenyl)-, hexafluoroantimonate (1-) (**6**)

0.20 g (0.00024 mol) of 2,3-Butanedionebis(3,3''-bis(trimethylsilyl)-[1,1';3',1'']terphenyl-2'-ylimine) (**17**), 0.033 g (0.00012 mol) of nickel allyl chloride dimer (**18**), 0.083 g (0.00024 mol) of silver hexafluoroantimonate (**20**) and 30 ml of ethyl ether were stirred at RT for 12 h. The resulting reaction mixture was filtered through Celite®, and the solvent was evaporated in vacuum. The residue was recrystallized from toluene affording 0.27 g (81%) yield of above nickel compound **6** with m.p. 228.63 °C. ¹H NMR (CD₂Cl₂) 0.22 (s, 36H, Me₃Si), 1.23 (s, 6H, CH₃), 1.50 (s, b, 2-allyl-H), 2.60 (s, b, 2-allyl-H), 5.21 (s, 1H central allyl-H), 6.70–7.65 (m, arom. 22H). ¹³C NMR (CDCl₃), (selected signals) 179.5 (s, C=N). Anal. Calc. for C₅₅H₆₉F₆N₂NiSbSi₄: C, 56.71; H, 5.97; N, 2.40. Found: C, 56.97; H, 6.18; N, 2.28%.

5. Supplementary material

CCDC contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk). The deposition numbers are CCDC 210401–210404 for the compounds **4**, **6**, **16**, **17** correspondingly.

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References

- [1] S.D. Ittel, L.K. Johnson, M. Brookhart, Chem. Rev. 100 (2000) 1169.
- [2] M. Schmid, R. Eberhardt, M. Klinga, M. Leskela, B. Rieger, Organometallics 20 (2001) 2321.
- [3] L.S. Moody, P.B. MacKenzie, C.M. Killian, G.G. Lavoie, J.A. Ponasik, T.W. Smith, J.C. Pearson, A.G.M. Barrett, US Pat. Appl., US 2002/0049135 A1.
- [4] L.K. Johnson, C.K. Killian, M. Brookhart, J. Am. Chem. Soc. 117 (1995) 6414.
- [5] J.R. Goerlich, R. Schmutzler, Phosphorus Sulfur Silicon Related Elements 81 (1993) 141.
- [6] H. Gruetzmacher, H. Pritzkow, Angew. Chem., Int. Ed. Engl. 30 (1991) 709.
- [7] J.-L. Montchamp, F. Tian, M.E. Hart, J.W. Frost, J. Org. Chem. 61 (1996) 3897.
- [8] A.S. Ionkin, US Pat. Appl. Publ. US 2003/130514.
- [9] G. Wilke, B. Bogdanovic, P. Hardt, P. Heimbach, W. Keim, M. Kroner, W. Oberkirch, K. Tanaka, E. Steinbrucke, D. Walter, H. Zimmerman, Angew. Chem., Int. Ed. 5 (1966) 151.
- [10] D. Walther, T. Dohler, N. Theyssen, H. Gorls, Eur. J. Inorg. Chem. (2001) 2049.
- [11] J. Sinnema, H. tom Dieck, G. Fendesak, J. Organomet. Chem. 397 (1990) 261.
- [12] B.Y. Lee, G.C. Bazan, J. Vela, Z.J.A. Komon, X. Bu, J. Am. Chem. Soc. 123 (2001) 5352.