First examples of neutral and cationic indenyl nickel(II) complexes bearing arsine or stibine ligands: highly active catalysts for the oligomerisation of styrene

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Experimental Section

General considerations. All experiments dealing with air- and/or moisture-sensitive materials were carried out under inert atmosphere using a dual vacuum/nitrogen line and standard Schlenk techniques. Nitrogen gas was supplied in cylinders by Air Liquide and purified by passage through 4Å molecular sieves. Unless otherwise stated, all reagents were purchased from commercial suppliers (e.g. Acros, Aldrich, Fluka) and used without further purification. All solvents to be used under inert atmosphere were thoroughly deoxygenated and dehydrated before use. They were dried and purified by refluxing over a suitable drying agent followed by distillation under nitrogen. The following drying agents were used: sodium (for toluene and diethyl ether), calcium hydride (for n-hexane, dichloromethane and 1,2-dichloroethane). Deuterated solvents were dried by storage over 4Å molecular sieves (which were previously activated under vacuum and heat), and degassed by the freeze-pump-thaw method. Solvents and solutions were transferred using a positive pressure of nitrogen through stainless steel cannulae and mixtures were filtered in a similar way using modified cannulae that could be fitted with glass fiber filter disks.

Nuclear magnetic resonance (NMR) spectra were recorded on Varian Unity 300 (1H, 299.995 MHz; 13C, 75.4296 MHz), Bruker Avance III 300 (1H, 300.130 MHz; 13C, 75.4753 MHz) or Bruker Avance III 400 (1H, 400.132 MHz; 13C, 100.623 MHz) spectrometers. Spectra were referenced internally using the residual protio-solvent (1H) or solvent (13C) resonances relative to tetramethylsilane (δ=0). All chemical shifts are quoted in δ (ppm) and coupling constants (J) given in Hz. Multiplicities were abbreviated as follows: broad (br), singlet (s), doublet (d), double doublet (dd), triplet (t), quartet (q), and multiplet (m). For air- and/or moisture-sensitive materials, samples were prepared in J. Young tubes, using a glovebox. The NMR assignments of the indenyl ring were made according to the X-ray labelling. Elemental analyses were obtained from the IST elemental analysis services.

Molecular weights of the styrene oligomers were determined by Gel Permeation Chromatography/Size Exclusion Chromatography (GPC/SEC), in a GPC Waters 150-CV chromatograph, using THF as eluent, at a flow rate of 1.0 mL min⁻¹. The solvent was filtered through 0.50 μm Fluoropore (Millipore) membranes, and degassed by ultrasounds for 45 min. The polymer samples were always filtered through 0.22 μm Durapore filters (Millipore). The temperature of the various compartments was stabilized at 35, 35 and 30 ºC respectively for the injector, column and pump. The separation of oligomers was made with two MesoPore columns, protected by a MesoPore Guard column (Polymer Labs). The molecular weights were calibrated relative to polystyrene standards (TSK Tosoh Co.). The acquisition and data processing were performed with the program Millennium³² (version 3.05.01).

LiCl was dried under vacuum, at 100 ºC, for several hours and stored under nitrogen atmosphere. The salt TIBAr'[i.e. TIB[C₆H₃-3,5-(CF₃)₂]₄] was prepared following a method described in the
Indene (90%, stabilised with 4-tert-Butylcatechol (TBC)) and styrene (99%, stabilised with TBC) were purchased from Acrös, dried with calcium hydride (at room temperature), distilled trap-to-trap under vacuum (at room temperature), and stored under nitrogen at low temperature prior to use. The concentrations of the solutions of HBF₄ in Et₂O (Aldrich) and HCl in Et₂O (prepared in the laboratory) were determined by addition of a known excess of NaOH aqueous solution to a known volume of the corresponding acid and back-titrated with aqueous solutions of HCl, using an ethanolic solution of phenolphthalein (0.1%) as the indicator. [Na(η-Ind)]³, [NiBr₂(DME)]⁴ and [Ni(η-C₅H₇)₂]⁵ were synthesized following adaptations of methods described in the literature.

**General procedures for the syntheses of neutral complexes 1 and 2:**

*Procedure i* – A solution of HBF₄ 5.8 M in Et₂O (0.17 mL, 1.0 mmol) was added to a cold solution (-80 °C) of [Ni(η-Ind)]₂ (0.30 g, 1.0 mmol) in dichloromethane (30 mL). After stirring for 5 min, a solution of SbPh₃ (0.37 g, 1.0 mmol) in CH₂Cl₂ (ca. 5 mL) was slowly added to the mixture, which was followed by the addition of a suspension of LiCl (0.17 g, 4.1 mmol) in Et₂O (30 mL). The reaction mixture was stirred for 30 min and the cold bath was removed, allowing the mixture to warm up for 25 min, while stirring. The solvent was removed under vacuum and the residue washed with n-hexane. A red solution was extracted with toluene, which was cooled to -80 °C, affording dark red crystals of 2.

*Procedure ii* – A solution of EPh₃ (1 mmol, E = As or Sb) in Et₂O or CH₂Cl₂ (ca. 5 mL) was added, under nitrogen atmosphere, to a red solution of [Ni(η-Ind)]₂ (0.29 g, 1 mmol) in the same solvent. The reaction mixture was stirred for further 10 minutes and cooled to -80 °C, using an ethanol/liquid nitrogen cold bath. A solution of HCl in Et₂O 3.6 M (0.28 mL, 1 mmol) was slowly added to the stirred mixture. The final solution was kept with continuous stirring for 3.5 h in the cold bath. After removal of the cold bath, the reaction was allowed to warm up and stir for another 30 minutes. The solvent was removed under vacuum and the residue washed with n-hexane. The residue was extracted with toluene, giving a dark red solution, and reprecipitated by dropwise addition of n-hexane with stirring. The solution was cooled to -80 °C and a red powder was separated by filtration. Further recrystallisation in cold toluene double layered with n-hexane (-20 °C), gave crystals of 1 and 2.

1: Yield: 0.35 g (68%). Calc. for C₂₇H₂₂AsClNi: C 62.90, H 4.30. Found: C 62.49, H 4.98. NMR [δH (300 MHz, C₆D₆, 298 K)]: 7.59 (m, 6H, Ph-H ortho), 6.99 (m, 10H, Ph-Hmeta+Ph-Hpara+H5 or H6), 6.87 (br, 1H, H6 or H5), 6.46 (t, 1H, H2), 6.15 (br, 1H, H4+H7), 5.85 (br, 1H, H1), 3.71 (br, 1H, H3).

NMR [δH (300 MHz, CDCl₃, 223 K)]: 7.44 – 7.33 (m, 15H, AsPh₃), 7.30 (d, 1H, 3JHH=7,8 Hz, H4 ou H7), 7.20 (t, 1H, 3JHH=7,5 Hz, H5 ou H6), 6.92 (t, 1H, 3JHH=7,5 Hz, H6 ou H5), 6.82 (t, 1H, 3JHH=3 Hz,

H2), 6.25 (d, 1H, 3\(J_HH=8.1\) Hz, H7 or H4), 5.88 (br, 1H, H1), 3.74 (br, 1H, H3). NMR [\(\delta_C\) (75 MHz, CD\(_2\)Cl\(_2\), 211 K)]: 133.0 (Ph-C ortho), 132.0 (Ph-C$_{ipso}$), 130.0 (Ph-C$_{para}$), 128.9 (C3A or C7A), 128.6 (Ph-C$_{meta}$), 127.2 (C5 or C6), 126.6 (C6 or C5), 126.2 (C7A or C3A), 119.0 (C4 or C7), 117.0 (C7 or C4), 103.4 (C2), 86.7 (C1 or C3), 66.1 (C3 or C1).

2: Yield: 0.33 g (58%). Calc. for C$_{27}$H$_{22}$ClNiSb: C 57.67, H 3.94. Found: C 57.32, H 3.61. NMR [\(\delta_H\) (300 MHz, CD$_2$Cl$_2$, 298 K)]: 7.48–7.40 (m, 16H, SbPh$_3$ + H7), 7.06–6.44 (m, 5H, H1+H2+H4+H5+H6), 4.37 (br, 1H, H3). NMR [\(\delta_H\) (300 MHz, CD$_2$Cl$_2$, 224K)]: 7.43–7.37 (m, 15H, SbPh$_3$), 7.30 (d, 1H, 3\(J_HH=7.8\) Hz, H7), 7.19 (t, 1H, 3\(J_HH=7.4\) Hz, H6), 6.92 (t, 1H, 3\(J_HH=7.4\) Hz, H5), 6.74 (br, 1H, H2), 6.55 (d, 1H, 3\(J_HH=7.2\) Hz, H4), 6.16 (br, 1H, H1), 4.10 (br, 1H, H3). NMR [\(\delta_C\) (75 MHz, CD$_2$Cl$_2$, 224 K)]: 135.8 (Ph-C ortho), 130.4 (Ph-C$_{para}$), 129.7 (Ph-C$_{ipso}$), 129.3 (Ph-C$_{meta}$+C7a or C3a), 127.6 (C6), 126.8 (C5+C3a or C7a), 119.2 (C7), 118.1 (C4), 102.6 (C2), 88.9 (C1), 59.8 (C3).

**General procedure for the synthesis of cationic complexes 3 and 4 (Procedure iii):** A solution of EPh$_3$ (2 mmol, E = As or Sb) in CH$_2$Cl$_2$ (ca. 10 mL) was added, under nitrogen atmosphere, to a red solution of [Ni(\(\eta_5\)-Ind)$_2$] (0.29 g, 1 mmol) in the same solvent, at -80 ºC. The reaction mixture was stirred for further 10 minutes, after which a solution of HBF$_4$ (0.17 mL, 1.1 mmol) in CH$_2$Cl$_2$ (10 mL) was slowly added to the mixture. The solution main tained the red colour, showing though dichroic yellowish features. The final solution was allowed to warm up to room temperature, and was further stirred for 30 minutes. The solvent was removed under vacuum and the oily residue was washed with n-hexane and Et$_2$O. The residue was extracted with dichloromethane and double-layered with n-hexane. The solution was cooled to -20 ºC, precipitating an oil, which was decanted. The precipitate was then dried under vacuum, giving mustard oily powders of 3 and 4.

3: Yield: 0.64 g (73%). Calc. for C$_{45}$H$_{37}$As$_2$BF$_4$Ni·0.25 CH$_2$Cl$_2$: C 60.77, H 4.23. Found: C 61.04, H 4.46. NMR [\(\delta_H\) (300 MHz, CD$_2$Cl$_2$, 298 K)]: 7.45 (t, 6H, 3\(J_HH=7.2\) Hz, Ph-H$_{para}$), 7.31 (t, 12H, 3\(J_HH=7.5\) Hz, Ph-H$_{meta}$), 7.21 (dd, 2H, 3\(J_HH=6\) Hz, 4\(J_HH=3\) Hz, H5+H6), 7.12 (d, 12H, 3\(J_HH=7.5\) Hz, Ph-H$_{ortho}$), 6.93 (t, 1H, 3\(J_HH=3\) Hz, H2), 6.18 (dd, 2H, 3\(J_HH=6\) Hz, 4\(J_HH=3\) Hz, H4+H7), 5.40 (d, 2H, 3\(J_HH=3\) Hz, H1+H3). NMR [\(\delta_C\) (75.45 MHz, CD$_2$Cl$_2$, 298 K)]: 133.2 (Ph-C$_{ortho}$), 131.7 (Ph-C$_{ipso}$), 131.3 (Ph-C$_{meta}$), 129.7 (Ph-C$_{para}$), 129.5 (C5+C6), 123.3 (C3a+C7a), 120.2 (C4+C7), 104.6 (C2), 84.0 (C1+C3).

4: Yield: 0.71 g (73%). Calc. for C$_{45}$H$_{37}$BF$_4$NiSb$_2$·0.25 CH$_2$Cl$_2$: C 55.01, H 3.83. Found: C 54.77, H 3.96. NMR [\(\delta_H\) (300 MHz, CD$_2$Cl$_2$, 298 K)]: 7.46 (t, 6H, 3\(J_HH=7.2\) Hz, Ph-H$_{para}$), 7.32 (t, 12H, 3\(J_HH=7.2\) Hz, Ph-H$_{meta}$), 7.25 (dd, 2H, 3\(J_HH=6\) Hz, 4\(J_HH=3\) Hz, H5+H6), 7.12 (d, 12H, 3\(J_HH=7.2\) Hz, Ph-H$_{ortho}$), 6.88 (dd, 2H, 3\(J_HH=6\) Hz, 4\(J_HH=3\) Hz, H4+H7), 6.59 (t, 1H, 3\(J_HH=3\) Hz, H2), 5.95 (d, 2H, 3\(J_HH=3\) Hz, H1+H3). NMR [\(\delta_C\) (75.43 MHz, CD$_2$Cl$_2$, 298 K)]: 135.6 (Ph-C$_{ortho}$), 131.6 (Ph-C$_{para}$), 130.2 (Ph-C$_{meta}$), 129.3 (C5+C6), 128.3 (Ph-C$_{ipso}$), 120.8 (C3a+C7a), 120.4 (C4+C7), 101.5 (C2), 82.2 (C1+C3).
**General procedure for the oligomerisation of styrene:** In a typical experiment, a solution of the appropriate catalyst precursor (48 µmol) in 1,2-dichloroethane (2 mL) was prepared in a Schlenk tube, which was immersed in a thermostated water bath regulated to the desired temperature. This solution was allowed to equilibrate for 15 min and styrene (5.5 mL) was added with a degassed syringe, followed by the neutral ligand (when required), and TIB[C₆H₃-3,5-(CF₃)₂]₄ (1.05 equiv) as halide abstractor (in blank tests with complexes 1 and 2, the halide abstractor was not added). Aliquots of 1 mL were collected each 10 minutes and poured into a beaker containing methanol, which were kept stirring in order to quench the catalytic reaction. The product was dissolved in dichloromethane and the solution was filtered through a silica-gel 60 column (5 cm). The solvent was removed under vacuum and the obtained oligomers were dried under vacuum until reaching a stable mass. The ratios of the different oligomers present in the mixture were established by GPC/SEC.

**Crystal data for 1:** C₂₇H₂₂NiAsCl, FW = 515.53, triclinic, space group P-1 (no.2), Dₑ = 1.542 g cm⁻³, Z = 4, a = 10.0199(12), b = 14.4995(17), c = 16.754(2) Å, α = 66.647(2), β = 83.975(2), γ = 89.327(3) °, V = 2221.2(5) Å³, T = 100(2) K, Bruker AXS SMART platform 3-circle diffractometer with CCD area detector, λ (MoKα) = 0.71073 Å, μ = 2.484 mm⁻¹. Of 15658 reflections measured, 7713 were unique. Refinement on F² concluded with the values R₁ = 0.0577 and wR₂ = 0.1272 for 541 parameters and 7080 data with I > 2σI. The data were deposited in CCDC under the deposit number 734284.
Definitions of the typical structural parameters of an indenyl ligand coordinated to a metal atom

- **Hinge Angle** (HA)\(^{6-9}\)

\[ HA = \text{angle between the planes formed by the atoms [C1, C2, C3] and [C1, C3, C3a, C7a]} \]

- **Fold Angle** (FA)\(^{6-9}\)

\[ FA = \text{angle between the plane formed by the atoms [C1, C2, C3] and that containing the fused benzene ring} \]

- **Slip Parameter** \((\Delta_{M-C})^{6-9}\)

\[ \Delta_{M-C} = \frac{d(Ni-C7a) + d(Ni-C3a)}{2}, \frac{d(Ni-C1) + d(Ni-C3)}{2} \]

- **Slip Parameter in Solution** \((\Delta\delta_{av}^{13C})^{6,7,10}\)

\[ \Delta\delta_{av}^{13C} = \delta_{av}^{13C_{3a/7a}(M-Ind)} - \delta_{av}^{13C_{3a/7a}(NaInd)} \]

\[ \text{(with } \delta_{av}^{13C_{3a/7a}(NaInd)} = 130.7 \text{ ppm)} \]

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Variable temperature $^1$H NMR experiments

Fig. S2 VT-$^1$H NMR experiments for compound 1, in CD$_2$Cl$_2$.

Fig. S3 VT-$^1$H NMR experiments for compound 2, in CD$_2$Cl$_2$.