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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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New indenyl nickel(II) complexes containing arsine or stibine ligands synthesised by a new methodology exhibit very high catalytic activities for the oligomerisation of styrene.

The use of nickel(II) complexes containing neutral alkene-, N-, O- or P-donor ligands as catalysts in oligo-/polymerisation of olefins has attracted great attention in the last twenty years.¹ Before this period, the classical work of Wilke and co-workers on the oligomerisation of olefins with neutral allyl nickel(II) complexes $[\text{Ni}(\eta^3\text{-allyl})(\text{L})\text{X}]$ (L=phosphines, phosphites; X= halides) was already well-established, leading to high activities when employed with aluminium-based cocatalysts, and selectivities depending upon the phosphorus ligands used.² The cationic allyl nickel complexes $[\text{Ni}(\eta^3\text{-2-R-allyl})\text{L}_2]^+$ (L= phosphines, phosphites, nitriles, ethers; L₂= 1,5-dienes; R= H, Me) were examples of very active homogeneous catalysts for the oligo-/polymerisation of olefins (namely, ethylene³ and styrene⁴) and conjugated dienes,⁵ eliminating the need for either aluminium or boron compounds as activators.

Indenyl nickel(II) complexes are thought to have chemical reactivities in between those of $\eta^3\text{-allyl}$ ($\eta^3\text{-CH}_2\text{CHCH}_2$) and $\eta^5\text{-cyclopentadienyl}$ ($\eta^5\text{-Cp} = \eta^5\text{-C}_5\text{H}_5$) nickel species,⁶ because the indenyl ligand ($\eta\text{-Ind} = \eta\text{-C}_9\text{H}_7$) can undergo $\eta^5\text{-}\eta^3$ ring slippage.⁷ The presence of the fused benzene ring in $\eta\text{-Ind}$ complexes facilitates this $\eta^5\text{-}\eta^3$ haptotropic shift, releasing an extra coordination position and helping the stabilisation of intermediates in various reactions (*indenyl effect*).⁸ Consequently, neutral and cationic indenyl nickel(II) complexes, $[\text{Ni}(\eta\text{-Ind})(\text{L})\text{X}]$ (L=phosphines; X= halides, triflate, amidates) and $[\text{Ni}(\eta\text{-Ind})(\text{L})\text{L}']^+$

(L=phosphines; L'= phosphines, nitriles, amines, alkenes), in the presence of halide abstractors (e.g. AgBF₄ or NaBPh₄) or *per se*, respectively, exhibit catalytic activity in reactions such as dimerisation of ethylene,⁹ oligo-/polymerisation of styrene^{4d,10,11} and polymerisation of norbornene.^{10a}

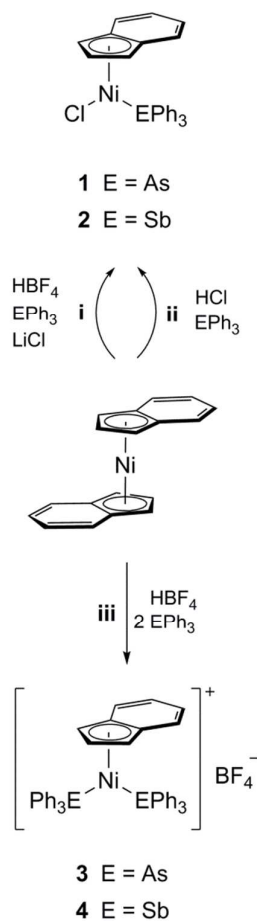
Although not as popular as their phosphine analogues, nickel(II) complexes containing arsine and stibine donor ligands and an η^3 -allyl fragment, [Ni(η^3 -2-R-allyl)(L)X] (L= AsPh₃, SbPh₃; X= halides; R= H, Me) and [Ni(η^3 -allyl)L_n]⁺ (L= AsPh₃ (n=2), SbPh₃ (n= 2 or 3); R= H, Me), have also been prepared, both neutral (in combination with AgBF₄) and cationic derivatives (*per se*) showing high catalytic activity in the polymerisation of butadiene,^{5a} oligomerisation of ethylene^{3b} and oligo-/polymerisation of styrenes.¹² In all cases, these complexes are more active than their phosphine analogues, which is attributed to the weaker donor ability and easier dissociation of arsine and stibine ligands.¹³

Neutral and cationic cyclopentadienyl nickel(II) complexes containing arsenic(III) or antimony(III) donor ligands, [Ni(η^5 -Cp)(EPh₃)X] and [Ni(η^5 -Cp)(EPh₃)₂]⁺ (E= As, Sb; X= halides), are known for several years¹⁴ but, to the best of our knowledge, no reports are found in the literature for analogous η -indenyl nickel(II) complexes. This gap is possibly due to the chemical inaccessibility of well-defined arsine and stibine adducts of nickel(II) halides, [NiX₂(EPh₃)₂] (E=As, Sb), whereas their phosphine analogues [NiX₂(PR₃)₂], easily accessible by the addition of PR₃ to NiX₂ salts, play a key role as starting materials in the synthesis of the great majority of the reported indenyl nickel(II) phosphine compounds, [Ni(η -Ind)(PR₃)X] and [Ni(η -Ind)(PR₃)L']⁺, through their reaction with M⁺Ind⁻ (M= Li, Na, K).

In view of our interest in the chemistry of η -indenyl nickel species, their structural relationship with allyl and cyclopentadienyl nickel(II) complexes, and their potential role as catalysts for multiple C-C bond formation,^{4,12,15} we report in this communication the synthesis and characterisation of the first examples of neutral and cationic indenyl nickel(II) complexes containing arsine or stibine ligands, and their application as efficient catalysts for the oligomerisation of styrene.

Inspired by the protonation reaction of nickelocene to generate the kinetically labile and elusive intermediate [Ni(η^5 -C₅H₅)(C₅H₆)]BF₄, described by Werner *et al.*,¹⁶ we developed herein new and efficient routes for the synthesis of neutral and cationic η -indenyl nickel complexes **1–4** containing AsPh₃ or SbPh₃ donor ligands (Scheme 1). These compounds were thus obtained from the protonation of [Ni(η -Ind)₂] with one equiv of HBF₄, followed by substitution of the possibly coordinated neutral indene ligand (in a possibly existing

intermediate $[\text{Ni}(\eta^5\text{-C}_9\text{H}_7)(\text{C}_9\text{H}_8)]\text{BF}_4^-$ by the corresponding neutral (AsPh_3 or SbPh_3) and anionic (Cl^-) ligands in the appropriate stoichiometries.



Scheme 1 New routes for the synthesis of neutral and cationic indenyl nickel(II) complexes **1–4** containing AsPh_3 or SbPh_3 donor ligands. Reagents: (i) HBF_4 soln. in Et_2O (1 equiv), then EPh_3 (1 equiv) and LiCl (excess), $-80\text{ }^\circ\text{C}$, in CH_2Cl_2 ; (ii) EPh_3 (1 equiv), then HCl soln. in Et_2O (1 equiv), $-80\text{ }^\circ\text{C}$, in CH_2Cl_2 or Et_2O ; (iii) EPh_3 (2 equiv), then HBF_4 soln. in Et_2O (1 equiv), $-80\text{ }^\circ\text{C}$, in CH_2Cl_2 .

The reaction of $[\text{Ni}(\eta\text{-Ind})_2]$ with one equiv of SbPh_3 and excess of LiCl , in the presence of a stoichiometric amount of HBF_4 (in Et_2O), at $-80\text{ }^\circ\text{C}$ (Scheme 1, route i), resulted in the formation of compound **2**, as dark red crystals, in 59% yield. The success obtained in the synthesis of this neutral compound prompted us to carry out the alternative protonation reaction with anhydrous HCl gas dissolved in Et_2O . The addition of a stoichiometric amount of this acid to $[\text{Ni}(\eta\text{-Ind})_2]$, at $-80\text{ }^\circ\text{C}$, in the presence of the suitable donor ligand EPh_3 ($\text{E} =$

As or Sb), afforded the corresponding $[\text{Ni}(\eta\text{-C}_9\text{H}_7)(\text{EPh}_3)\text{Cl}]$, **1** and **2** (Scheme 1, route ii), as dark red crystals in 68 and 59%, respectively. The cationic compounds $[\text{Ni}(\eta\text{-C}_9\text{H}_7)(\text{EPh}_3)_2]\text{BF}_4$, **3** and **4**, were also prepared via the protonation method using HBF_4 , at -80°C , and subsequent addition of two equiv of the corresponding donor ligand (Scheme 1, route iii). The latter compounds were both obtained in 73% yield as mustard oily powders. Complexes **1–4** were fully characterised by NMR spectroscopy, elemental analysis, the structure of **1** being also determined by single-crystal X-ray diffraction.¹⁷

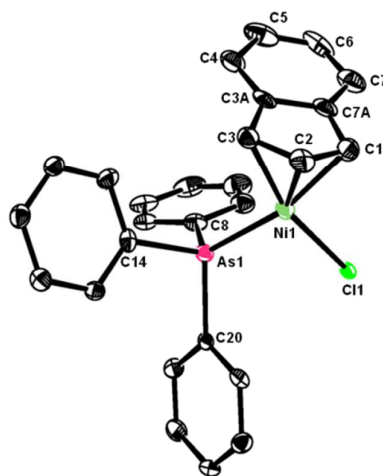


Fig. 1 ORTEP-III diagram for complex **1** (molecule 1) using 50% probability level ellipsoids. Selected bond lengths (Å), angles ($^\circ$) and typical indenyl structural parameters (see p. S6 in ESI): *Molecule 1* – Ni1-C1 2.052(6); Ni1-C2 2.024(5); Ni1-C3 2.058(5); Ni1-C3A 2.377(6); Ni1-C7A 2.352(6); Ni1-As1 2.2806(9); Ni1-Cl1 2.2093(14); C2-C1 1.397(8); C3-C2 1.409(8); C1-C7A 1.450(9); C3-C3A 1.456(8); C7A-C3A 1.412(8); C1-Ni1-C2 40.1(2); C3-Ni1-C2 40.4(2); C3-Ni1-C1 67.0(2); HA = 12.46° ; FA = 11.88° ; $\Delta_{\text{M-C}}$ = 0.395 Å. *Molecule 2* – Ni2-C1 2.062(6); Ni2-C2 2.049(5); Ni2-C3 2.040(6); Ni2-C3A 2.312(6); Ni2-C7A 2.305(6); Ni2-As2 2.2729(9); Ni2-Cl2 2.2357(13); C2-C1 1.386(9); C3-C2 1.402(8); C1-C7A 1.453(8); C3-C3A 1.463(8); C7A-C3A 1.408(8); C1-Ni2-C2 39.5(2); C3-Ni2-C2 40.1(2); C3-Ni2-C1 66.8(2); HA = 10.59° ; FA = 10.66° ; $\Delta_{\text{M-C}}$ = 0.253 Å.

The crystal structure of **1** shows two independent molecules in the asymmetric unit, revealing nickel complexes (Fig. 1) in which the geometries around the metal atom may be described as slightly distorted pseudo-square-planar, according to the description of Andersen *et al.*,¹⁸ considering C1 and C3 as the ‘terminal’ atoms of the pseudo-allylic moiety of the indenyl ligand, As1 and Cl1 occupying the remaining vertices of the pseudo-square-plane.

According to the bond distances listed in Fig. 1's caption, molecule **1** is practically symmetrical in what the Ni-C bond lengths are concerned ($\text{Ni1-C2} < \text{Ni1-C3} \approx \text{Ni1-C1} \ll \text{Ni1-C3A} \approx \text{Ni1-C7A}$), virtually showing no hapticity distortions; within the five-membered indenyl ring this molecule shows C-C bond lengths ($\text{C1-C2} \approx \text{C2-C3} \approx \text{C3A-C7A} \ll \text{C3-C3A} \approx \text{C1-C7A}$) pointing to an *ene-allyl* type distortion.¹⁸ Molecule **2** shows a more unsymmetrical nature of the Ni-C bond lengths ($\text{Ni1-C3} < \text{Ni1-C2} < \text{Ni1-C1} \ll \text{Ni1-C3A} \approx \text{Ni1-C7A}$), more similar to the corresponding phosphine analogue $[\text{Ni}(\eta\text{-Ind})(\text{PPh}_3)\text{Cl}]$,¹⁹ in which the Ni-C1 bond length is noticeably longer than Ni-C3 ($\Delta = 0.052(2)$ Å). However, this asymmetry is less pronounced in molecule **2** of compound **1** ($\Delta = 0.022(6)$ Å), owing to a weaker basicity (lower *trans influence*) of AsPh_3 ligand in relation to PPh_3 ; although the bond length C1-C2 is shorter than C2-C3, molecule **2** also presents an *ene-allyl* type distortion within the five-membered indenyl ring.

Owing to the hindered rotation of the $\eta\text{-Ind}$ ligand around its coordination axis to the metal centre, the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of neutral $[\text{Ni}(\eta\text{-Ind})(\text{EPh}_3)\text{Cl}]$ ($\text{E} = \text{As}, \text{Sb}$) complexes **1** and **2**, at room temperature, exhibit a series of both sharp and broad resonances. However, a gradual temperature decrease converts the broad resonances into sharp peaks and modifies their chemical shifts (see Fig. S2 and S3 in ESI). Average $\Delta G^\ddagger_{T_c}$ values of 13.2 and 12.7 kcal mol⁻¹ for the ring rotation process were obtained²⁰ for complexes **1** and **2**, respectively, considerably below that determined by Zargarian and co-workers for the PPh_3 analogue (16 kcal mol⁻¹).^{19a} The order of magnitude of the rotation barriers for this series of complexes $[\text{Ni}(\eta\text{-Ind})(\text{L})\text{Cl}]$ is thus found to be $\text{SbPh}_3 < \text{AsPh}_3 < \text{PPh}_3$, in line with the increasing donor capacity of L and a decreasing Ni-L bond distance. According to the low temperature $^{13}\text{C}\{^1\text{H}\}$ NMR resonances data, all complexes showed intermediate η^5/η^3 hapticities, with a more pronounced η^3 character in the case of the neutral derivatives **1** and **2** (with $\Delta\delta_{\text{av}}^{13}\text{C}$ values of -3.2 and -2.7, respectively), whereas the cationic compounds **3** and **4** (with $\Delta\delta_{\text{av}}^{13}\text{C}$ values of -7.4 and -9.9, respectively) presented a higher tendency to a η^5 character.²¹

Both neutral and cationic nickel complexes are highly active as homogeneous catalysts for the oligomerisation of styrene, at room temperature (eqn 1 and Table 1). Complexes **1** and **2** are extremely active when *in situ* abstraction of the chloride ligand by TIBAr'_4 ($\text{Ar}' = 3,5\text{-}(\text{CF}_3)_2\text{C}_6\text{H}_3$) is performed (entries 1 and 2 in Table 1). In fact, the use of this thallium salt triggered quantitative conversions of styrene to low molecular weight oligomers in very short reaction times (≤ 10 minutes). Significantly, blank tests with complexes **1** and **2**, performed in

the absence of the chloride abstractor, revealed inactivity towards styrene oligomerisation. However, the use of an activator is not required for cationic compounds **3** and **4** (entries 3 and 4). These results suggest that the *in situ* generated cationic electron-deficient species $[\text{Ni}(\eta\text{-}1\text{-R-Ind})(\text{EPh}_3)]^+$ are considerably more active than the more saturated well-defined cations containing two EPh_3 ligands $[\text{Ni}(\eta\text{-}1\text{-R-Ind})(\text{EPh}_3)_2]^+$ (see Table 1). In fact, after chloride abstraction, a vacant position is created at the metal centre, which can be used for the straightforward coordination of styrene, whereas competitive coordination of the styrene with the second EPh_3 ligand shall take place at least in the initiation step of the oligomerisation.

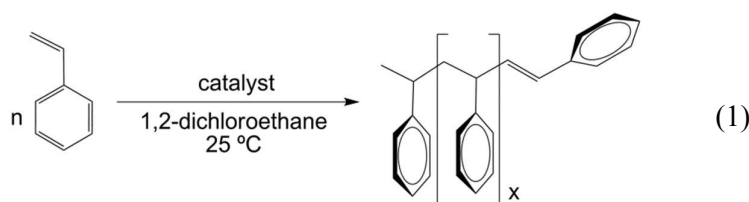


Table 1 Catalytic oligomerisation of styrene and mass characterisation of the styrene oligomers.^a

Entry	Catalyst	Yield (%)	N_t^b (min ⁻¹)	M_n^c	M_w/M_n^c	Product distribution ^c		
						Dimers (%)	Trimers (%)	Tetramers (%)
1 ^{d,e}	1	100	≥ 100	490	1.37	7	19	17
2 ^{d,e}	2	100	≥ 100	510	1.48	10	17	15
3 ^d	1 + AsPh_3 (1:1)	4	0.7	330	1.13	30	35	34
4 ^d	2 + SbPh_3 (1:1)	46	7.7	390	1.13	13	24	62
5	3	10	1.7	400	1.09	39	36	24
6	4	87	14.5	350	1.05	78	16	5
7 ^{f,g}	5 ^h	100	≥ 16.7	600	1.29	17	18	14

^a Conditions used: solvent (1,2-dichloroethane, 2 ml), catalyst (48 μmol), styrene (5.5 g), [catalyst]:[styrene] ratio = 1:1000, T = 25 °C, time = 60 min; ^b Turnover frequency (= moles_{sty}/(moles_{cat} × time)); ^c Determined by GPC/SEC; ^d For neutral complexes, abstraction of the Cl atom performed by *in situ* addition of 1.05 equiv of TIBAr_4' ; ^e Full conversion at $t \leq 10$ min; ^f T = 90 °C; ^g Traces of polystyrene at 25 and 50 °C after 2 h; ^h **5** = $[\text{Ni}(\eta\text{-Ind})(\text{PPh}_3)_2]\text{BF}_4$

On the other hand, and accordingly, the addition of an equimolar amount of the required donor ligand EPh_3 to the catalyst system $[\text{Ni}(\eta\text{-}1\text{-R-Ind})(\text{EPh}_3)\text{Cl}]/\text{TIBAr}'_4$ depresses dramatically the catalytic activity (entries 1 vs. 3 and 2 vs. 4). This fact is particularly relevant in the case of the complex containing ligands with greater donor ability (AsPh_3 , **1**; entry 3), which illustrates clearly the competition between the donor ligand and styrene molecules for the coordination to the metal centre. The observed trend in the activities of catalysts **1** and **2** is in agreement with that noticed for the corresponding cations $[\text{Ni}(\eta\text{-}1\text{-R-Ind})(\text{EPh}_3)_2]^+$ **3** and **4**, the compound containing the less donor stibine ligand being considerably more active than

the corresponding arsine analogue. However, the well-defined cations **3** and **4** (entries 5 and 6) produce higher activities when compared to the corresponding *in situ* generated species (entries 3 and 4, respectively), which may be related to a slow Cl abstraction owing to the quite non-polar nature of the reaction medium.

In general, the neutral and cationic η -Ind nickel catalysts **1–4** gave rise to very low average molecular weight *head-to-tail* styrene oligomers (with saturated $\text{CH}_3\text{--CH}(\text{C}_6\text{H}_5)\text{--}$ and vinyl $\text{--CH}=\text{C}(\text{C}_6\text{H}_5)\text{H}$ end groups), which are characterised by low dispersity indices ($D = M_w/M_n$), containing high percentages of dimers, trimers and tetramers (Table 1). In fact, the well-defined cationic compounds **3** and **4** (entries 5 and 6) generate oligostyrenes with dispersities close to unity, almost exclusively consisting of dimers, trimers and tetramers of styrene. The bis-SbPh₃ cationic derivative **4** originates mixtures in which the selectivity in dimer is very high (78%), whereas the bis-AsPh₃ cationic catalyst **3** generates more balanced amounts of the 3 components, its average molecular weight being higher than that obtained with **4**. On the other hand, in a less controlled process, catalyst systems **1** and **2**/TIBAr'₄ produce styrene oligomers with higher average molecular weights and dispersities, the fractions of dimers, trimers and tetramers amounting only to 42–43%. Thus, the absence of a second equiv of EPh₃ ligand in the catalyst coordination sphere seems to reduce the frequency of β -hydrogen elimination reaction.

For comparison with the new As and Sb catalysts, catalytic tests using complex $[\text{Ni}(\eta\text{-Ind})(\text{PPh}_3)_2]\text{BF}_4$ (**5**)²² were carried out at 50 and 90 °C, for 2 h, resulting in traces and 100% yield, respectively (see Table 1, entry 7). These results demonstrate the much stronger donor character of PPh₃ in relation to AsPh₃ or SbPh₃. Therefore, the phosphine complexes only become active at a very high temperature, presumably upon significant dissociation of the PPh₃ ligand. This is in agreement with the works of Zargarian *et al.*^{10b,d} and Shen *et al.*,¹¹ for systems of the type $[\text{Ni}(\eta\text{-1-R-Ind})(\text{PPh}_3)\text{X}]/\text{PPh}_3/\text{AgBF}_4$ or AgBPh_4 (R= Si(Me)₂allyl, X= Cl;^{10d} R= (CH₂)₂NMe₂, X= Cl;^{10b} R= cyclopentyl, benzyl, Me, X= Cl;^{11a} R= Et, X= Cl, Br, I^{11b}), or of Jiménez-Tenorio *et al.* for $\text{Ni}(\eta\text{-2-Me-Ind})(\text{PR}_3)_2]\text{BPh}_4$ (PR₃= P*Me*iPr₂, P*Ph*iPr₂).^{4d} However, the molecular weights obtained with **5** are much lower than those reports by those authors, though being higher than those obtained with **3** and **4**.

In summary, we described herein the first cases of neutral and cationic indenyl nickel(II) complexes (**1–4**); these compounds clearly exhibit efficient catalytic reactivities towards the oligomerisation of styrene, similar to those previously reported for the analogous allyl nickel(II) complexes of AsPh₃ and SbPh₃.¹² The new synthetic methods employed in this

work will be soon extended to other neutral and cationic compounds of the types $[\text{Ni}(\eta\text{-Indenyl})(\text{L})\text{X}]$ and $[\text{Ni}(\eta\text{-Indenyl})(\text{L})\text{L}']^+$.

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 $\Delta G_{T_c}^\ddagger = 19.14 T_c [10.32 + \log_{10}(T_c/k_c)]$ (in kcal mol⁻¹) and $k_c = (\pi/\sqrt{2})\Delta\nu$ (in s⁻¹); k_c is the rate constant for the exchange process occurring between H1 and H3, at the coalescence temperature T_c (in K); $\Delta\nu$ (in Hz) is the difference between the two resonances H1 and H3 in the “static” spectrum. (a) H. Friebolin, *Basic One- and Two-Dimensional NMR Spectroscopy*, VCH Publishers, New York, 1991; Chapter 11; (b) G. Binsch, in L. M. Jackman, F. A. Cotton, Eds., *Dynamic Nuclear Magnetic Resonance Spectroscopy*, Academic Press, New York, 1975.
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Graphical Abstract

New indenyl nickel(II) complexes bearing arsine or stibine ligands synthesised by a new methodology exhibit very high catalytic activities in the oligomerisation of styrene

