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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 bearing 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) are 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. AgBF_4 or NaBPh_4) 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 $\eta^3\text{-allyl}$ fragment, $[\text{Ni}(\eta^3\text{-2-R-allyl})(\text{L})\text{X}]$ (L = AsPh_3 , SbPh_3 ; X = halides; R = H, Me) and $[\text{Ni}(\eta^3\text{-allyl})\text{L}_n]^+$ (L = AsPh_3 ($n = 2$), SbPh_3 ($n = 2$ or 3); R = H, Me), have also been prepared; both neutral (in combination with AgBF_4) and cationic derivatives (*per se*) show 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, $[\text{Ni}(\eta^5\text{-Cp})(\text{EPh}_3)\text{X}]$ and $[\text{Ni}(\eta^5\text{-Cp})(\text{EPh}_3)_2]^+$ (E = As, Sb; X = halides), have been known for several years¹⁴ but, to the best of our knowledge, no reports are found in the literature for analogous $\eta\text{-indenyl}$ nickel(II) complexes. This gap is possibly due to the chemical inaccessibility of well-defined arsine and stibine adducts of nickel(II) halides, $[\text{NiX}_2(\text{EPh}_3)_2]$ (E = As, Sb), whereas their phosphine analogues $[\text{NiX}_2(\text{PR}_3)_2]$, easily accessible by the addition of PR_3 to NiX_2 salts, play a key role as starting materials in the synthesis of the great majority of the reported indenyl nickel(II) phosphine compounds, $[\text{Ni}(\eta\text{-Ind})(\text{PR}_3)\text{X}]$ and $[\text{Ni}(\eta\text{-Ind})(\text{PR}_3)\text{L}]^+$, through their reaction with M^+Ind^- (M = Li, Na, K).

In view of our interest in the chemistry of $\eta\text{-indenyl}$ 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

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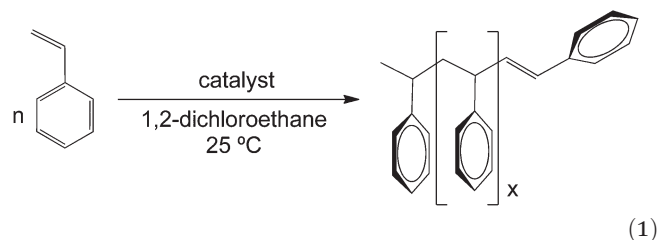
† Electronic supplementary information (ESI) available. CCDC 734284. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5dt02794b

distortion.¹⁸ Molecule 2 shows a more unsymmetrical nature of the Ni–C bond lengths (Ni1–C3 < Ni1–C2 < Ni1–C1 ≪ Ni1–C3A ≈ Ni1–C7A), more similar to the corresponding phosphine analogue [Ni(η-Ind)(PPh₃)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 AsPh₃ ligand in relation to PPh₃; 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 η-Ind ligand around its coordination axis to the metal centre, the ¹H and ¹³C{¹H} NMR spectra of neutral [Ni(η-Ind)(EPh₃)Cl] (E = As, 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 the ESI†). Average ΔG_{7c}^{\ddagger} 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 PPh₃ analogue (16 kcal mol⁻¹).^{19a} The order of magnitude of the rotation barriers for this series of complexes [Ni(η-Ind)(L)Cl] is thus found to be SbPh₃ < AsPh₃ < PPh₃, in line with the increasing donor capacity of L and a decreasing Ni–L bond distance. According to the low temperature ¹³C{¹H} NMR resonances data, all complexes showed intermediate η⁵/η³ hapticities, with a more pronounced η³ character in the case of the neutral derivatives 1 and 2 (with $\Delta\delta_{av}^{13C}$ values of –3.2 and –2.7, respectively), whereas the cationic compounds 3 and 4 (with $\Delta\delta_{av}^{13C}$ values of –7.4 and –9.9, respectively) presented a higher tendency to a η⁵ 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 TlBAR'₄ (Ar' = 3,5-(CF₃)₂C₆H₃) 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, 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 [Ni(η-Ind)(EPh₃)⁺] are considerably more active than the more saturated well-defined cations containing two EPh₃ ligands [Ni(η-Ind)(EPh₃)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 EPh₃ ligand shall take place at least in the initiation step of oligomerisation.



On the other hand, and accordingly, the addition of an equimolar amount of the required donor ligand EPh₃ to the catalyst system [Ni(η-Ind)(EPh₃)Cl]/TlBAR'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 abilities (AsPh₃, 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 [Ni(η-Ind)(EPh₃)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* gener-

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 (g mol ⁻¹)	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 TlBAR'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 = [Ni(η-Ind)(PPh₃)₂]BF₄.

ated 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 $\text{-CH=C}(\text{C}_6\text{H}_5)\text{H}$ 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 of 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/TIBAr₄ 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 equivalent 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 studies 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 = PMeiPr₂, PPhiPr₂).^{4d} However, the molecular weights obtained with 5 are much lower than those reported by some authors, though being higher than those obtained with 3 and 4.

In summary, we described herein the first examples 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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