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[Ni(η^3-CH$_2$C(CH$_3$)CH$_2$)(SbPh$_3$)$_3$][BAr′$_4$]: an extremely active cationic allyl nickel–stibine catalyst for the oligomerization of styrene

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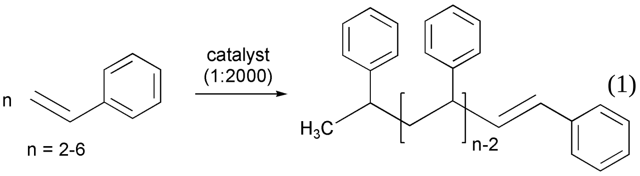
The pseudotetrahedral, formally 5-coordinate complex [Ni(η^3-CH$_2$C(CH$_3$)CH$_2$)(SbPh$_3$)$_3$][BAr′$_4$] (Ar′ = 3,5-C$_6$H$_3$(CF$_3$)$_2$) as well as the 4-coordinate derivative [Ni(η^3-CH$_2$C(CH$_3$)CH$_2$)(AsPh$_3$)$_2$][BAr′$_4$] act as extremely efficient catalysts for the oligomerization of styrene.

Cationic allyl complexes of nickel of the type [(η^3-allyl)-Ni(L)$_2$]$^+$ (L = N-, O- or P-donor group) have found considerable utility in recent years for olefin polymerisation reactions.[1,2] The complex [(η^3-2-methylallyl)Ni(η^4-COD)]$^+$ (COD = 1,5-cyclooctadiene)[3] is a very active homogeneous catalyst precursor for the low molecular weight polymerisation of styrene which does not require the use of either organoaluminium or organoboron compounds as activators. Addition of phosphine or phosphite ligands to this precursor causes in general an increase in the catalytic activity giving rise to regioregular head-to-tail low molecular weight polymers.[2] The most notorious case is met when one equivalent of PPh$_3$ is added, since the turnover frequency increases to a value above 1013 min^{-1} for a highly exothermic reaction which leads to a 100% conversion of oligo(styrene) in less than one minute (M_n = 740). This has been interpreted in terms of the *in situ* formation of the highly reactive 14-electron species [(η^3-2-methylallyl)Ni(PPh$_3$)]$^+$, since the complex [(η^3-2-methylallyl)Ni(PPh$_3$)$_2$]$^+$ has been shown to be much less active (turnover frequency 6.8 min^{-1}).[2] Whereas many types of N- and P-donor ligands in conjunction with [{(η^3-allyl)Ni(μ-Br)}$_2$]/NaBAr′$_4$ have been screened for olefin polymerisation,[1] Sb- or even As-donor ligands have never been evaluated for this purpose, as far as we are aware. Compared to their phosphine and arsine homologues, stibines in general are poorer donors, that tend to promote higher coordination numbers in their complexes and to reduce the tendency to dissociation,[4] leading to significant differences in reactivity.[5]

We have found that the reaction of [(η^3-2-methylallyl)Ni(η^4-COD)][BAr′$_4$] (**1**) with an excess of SbPh$_3$ in CH$_2$Cl$_2$ leads to the novel 5-coordinate complex [(η^3-2-methylallyl)Ni(SbPh$_3$)$_3$][BAr′$_4$] (**2**).† At variance with this, the reaction of **1** with AsPh$_3$ yielded under the same conditions the 4-coordinate [(η^3-2-methylallyl)Ni(AsPh$_3$)$_2$][BAr′$_4$] (**3**)† homologue of [(η^3-2-methylallyl)Ni(PPh$_3$)$_2$]$^+$, with no evidence for the formation of a 5-coordinate species. The crystal structure of **2** (Fig. 1)‡ revealed a rare distorted tetrahedral geometry around the Ni atom in the complex cation comprising the three Sb atoms and the central carbon atom of the 2-methylallyl unit C(2). The other only known case of a similar tetrahedral arrangement in an allyl-nickel derivative has been found very recently for the phosphine complex [(η^3-allyl)Ni(triphos)][BPh$_4$] (triphos = PPh(CH$_2$CH$_2$PPh$_2$)$_2$).[6] The most remarkable feature is the unsymmetrically bonded 2-methylallyl (Ni–C(1) 2.228(9) Å, Ni–C(3) 2.076(5) Å), whereas Ni–Sb separations are consistent with the scarce available data in the literature.[7] Both **2** and **3** are extremely active catalytic precursors for the oligomerization of styrene (eqn. 1).§



(1)

The highly exothermic reactions take place quantitatively in less than one minute, reaching a turnover frequency larger than 2000 min^{-1} (Table 1). If a co-ordinating solvent such as THF is used, the turnover frequency decreases dramatically, although the product distribution does not seems to be much affected. As occurred with PPh$_3$, addition of one equivalent of SbPh$_3$ or AsPh$_3$ to **1** also causes an increase in the turnover frequency, but never reaches the activity of neat **2** or **3** as catalysts. The analysis of the product distribution indicates that *ca.* 80% corresponds to the head-to-tail dimer when **2** is used as catalyst. In the case of **3**, the dimer accounts for *ca.* 50% of the total and higher oligomers are also present. When [(η^3-2-methylallyl)-Ni(PPh$_3$)$_2$]$^+$ is used as catalyst the mixture consists mainly of heptamer and higher oligomers. Thus, a trend is observed in the degree of oligomerization of styrene as a function of the co-ligand used: passing from PPh$_3$ to SbPh$_3$ through AsPh$_3$ causes

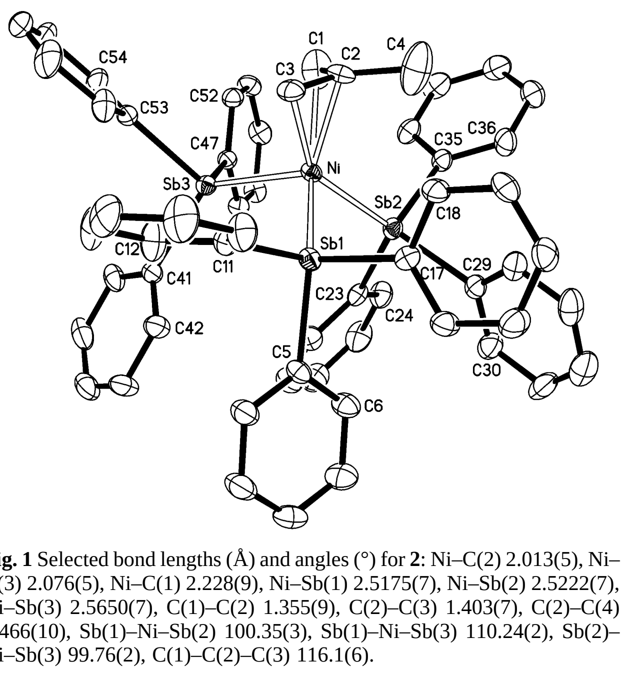


Fig. 1 Selected bond lengths (Å) and angles (°) for **2**: Ni–C(2) 2.013(5), Ni–C(3) 2.076(5), Ni–C(1) 2.228(9), Ni–Sb(1) 2.5175(7), Ni–Sb(2) 2.5222(7), Ni–Sb(3) 2.5650(7), C(1)–C(2) 1.355(9), C(2)–C(3) 1.403(7), C(2)–C(4) 1.466(10), Sb(1)–Ni–Sb(2) 100.35(3), Sb(1)–Ni–Sb(3) 110.24(2), Sb(2)–Ni–Sb(3) 99.76(2), C(1)–C(2)–C(3) 116.1(6).

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Table 1 Catalytic oligomerization of styrene

Entry	Catalyst	Conditions[a]	N_t[b]/min^{-1}	Total yield (%)	Product distribution (%)				
					Dimer	Trimer	Tetramer	Pentamer	Hexamer
1	**2**	CH_2Cl_2, 1 min	1965	100	78.7	17.1	4.2	—	—
2	**2**	THF, 2 h	10.7	66	83.0	14.4	2.0	0.5	—
3	**3**	CH_2Cl_2, 1 min	2052	100	52.6	26.6	11.8	5.2	3.7
4	**3**	THF, 2 h	8.1	48	59.3	27.0	9.0	4.6	—
5	**1** + $SbPh_3$	CH_2Cl_2, 45 min	43.8	100	86.5	12.1	1.4	—	—
6	**1** + 2 $SbPh_3$	CH_2Cl_2, 2 h	13.8	86	88.3	10.5	1.2	—	—
7	**1** + $AsPh_3$	CH_2Cl_2, 30 min	65.8	100	57.5	25.4	10.5	6.6	—

[a] Room temperature. Catalyst : styrene ratio 1 : 2000. [b] Turnover frequency.

an increase in the amount of dimer and a reduction in the amount of higher oligomers. A similar product distribution, but much lower activities, have been observed when the palladium compound [(η^3-2-methylallyl)Pd(η^4-COD)][BF_4] is used as catalyst precursor.[8] Complexes **2** and **3** are also active towards the oligomerization of dienes and other olefins, and the system is currently under study. From this work it becomes clear that stibine ligands may play an important role in the future development of highly active nickel catalysts for olefin oligomerization.

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Notes and references

† Selected spectroscopic data: All new compounds gave satisfactory analytical data.

2: [NMR, CD_2Cl_2, δ] ^{1}H, 2.04 (s, 3H, $CH_2C(CH_3)CH_2$), 2.94 (s, 2H, $\mathrm{CH}^{syn}H^{anti}\mathrm{C(CH_3)CH}^{syn}H^{anti}$), 4.31 (s, 2H, $\mathrm{C}H^{syn}\mathrm{H}^{anti}\mathrm{C(CH_3)C}H^{syn}\mathrm{H}^{anti}$), 7.27, 7.28, 7.33, 7.44 (m, 45H, $Sb(C_6H_5)_3$). $^{13}C\{^1H\}$ 23.94 (s, $CH_2C(CH_3)CH_2$), 65.21 (s, $CH_2C(CH_3)CH_2$), 126.79 (s, $CH_2C(CH_3)CH_2$), 129.84, 130.32, 136.09 ($Sb(C_6H_5)_3$). **3**: [NMR, $CDCl_3$, δ] ^{1}H, 2.01 (s, 3H, $CH_2C(CH_3)CH_2$), 2.80 (s, 2H, $\mathrm{CH}^{syn}H^{anti}\mathrm{C(CH_3)CH}^{syn}H^{anti}$), 3.69 (s, 2H, $\mathrm{C}H^{syn}\mathrm{H}^{anti}\mathrm{C(CH_3)C}H^{syn}\mathrm{H}^{anti}$), 7.20, 7.28, 7.40 (m, 30H, $As(C_6H_5)_3$). $^{13}C\{^1H\}$ 23.13 (s, $CH_2C(CH_3)CH_2$), 70.07 (s, $CH_2C(CH_3)CH_2$), 125.92 (s, $CH_2C(CH_3)CH_2$), 129.64, 131.14, 132.66 ($As(C_6H_5)_3$).

‡ Crystal data for **2**: $C_{90}H_{64}BF_{24}NiSb_3$, FW = 2036.18, triclinic, space group $P1$ (no. 2), D_c = 1.553 g cm^{-3}, Z = 2, a = 14.075(3), b = 17.525(3), c = 18.742(3) Å, α = 93.20(1), β = 106.50(1), γ = 98.89(1)°, V = 4355.1(14) Å^3, T = 297(2) K, Bruker AXS SMART platform 3-circle diffractometer with CCD area detector, $\lambda(MoK_\alpha)$ = 0.71073 Å, μ = 1.228 mm^{-1}. Of 50300 reflections measured, 18811 were unique. Refinement on F^2 concluded with the values R_1 = 0.0480 and wR_2 = 0.0894 for 1144 parameters and 14082 data with $I > 2\sigma_I$. 7 of the 8 CF_3 groups of the BAr'_4 anion showed orientation disorder and were refined as pairs of CF_3 with complementary orientations (dominant orientation with anisotropic displacement parameters, subordinate orientation with isotropic displacement parameters). CCDC 205627. See http://www.rsc.org/suppdata/cc/b3/b302553e/ for crystallographic data in CIF or other electronic format.

§ General procedure: A Schlenk tube was loaded with 0.0005 equivalents of the catalyst (**2**, **3**, or **1** + $SbPh_3$/**1** + $AsPh_3$ in the appropriate ratios) and dichloromethane (2 mL). Then, 1 equivalent of neat styrene was added. When **2** or **3** are used, a violent, exothermic reaction takes place in a few seconds, causing the mixture to boil. After stirring for the corresponding period of time (Table 1) at room temperature, MeOH (5 ml) was added and the mixture exposed to air. The volatiles were removed *in vacuo*. Then, the residue was extracted with dichloromethane and filtered through a plug of silica gel. The silica gel was washed with several portions of dichloromethane, and the washings combined with the filtrate. Removal of the solvent using a rotary evaporator first, and a vacuum pump afterwards afforded an oily mixture of styrene oligomers in quantitative yield. The ratios of the different oligomers present in the mixture were established by gel permeation chromatography (GPC) and by integration of the relevant signals in the ^{1}H NMR spectrum.

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