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η^6-Arene complexes of Ni(II), efficient catalysts for 1,3-butadiene and styrene polymerization†

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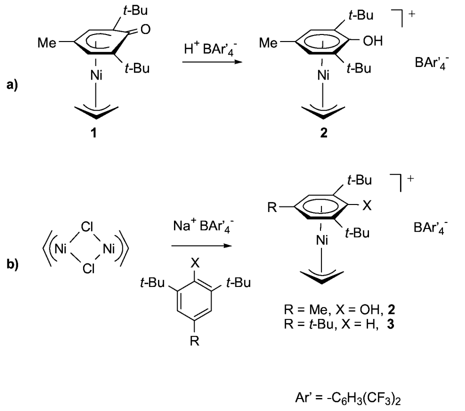
A simple procedure for the preparation of cationic arene complexes of Ni(II) of composition $[Ni(\eta^6\text{-}ArX)(\eta^3\text{-}C_3H_5)]^+[BAr'_4]^-$ (X = OH, H) is reported. These compounds are shown to behave as highly active catalysts for the polymerization of 1,3-butadiene and styrene.

In spite of the importance of transition metal arenes, the occurrence of Ni(II)–arene systems is rare.[1] Apart from the early works of Klabunde and co-workers,[2,3] only sporadic contributions have dealt with this kind of compounds.[4]

We[5] and others[6] have found recently that by placing *ortho*-substituents on aryloxide ligands their otherwise uncommon π-coordination to Ni(II) and Pd(II) centers becomes favoured over the usual sigma *O*-bonding. Thus, instead of a conventional dimeric formulation of the type $[Ni(\eta^3\text{-}C_3H_5)(\mu\text{-}OAr)]_2$, the sterically demanding 2,6-di-*tert*-butyl-4-methylphenolate gives rise to the monomeric structure $Ni(\eta^3\text{-allyl})(\eta^5\text{-}OAr)$ (**1**). In this paper we wish to report the facile formation of cationic Ni(II) organometallics that contain $Ni(\eta^6\text{-}ArOH)$ or $Ni(\eta^6\text{-}ArH)$ units (compounds **2** and **3**; see Scheme 1) and describe their use as active catalysts for 1,3-butadiene and styrene polymerization reactions.

As anticipated,[7] complex **1** reacts with the acid $H(OEt_2)_2(BAr'_4)$ [Ar′ = $(C_6H_3(CF_3)_2\text{-}3,5]$[8] to produce compound **2** which contains a neutral phenol ligand (Scheme 1(a)). Alternatively **2** may be obtained directly from $[Ni(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)]_2$ and $NaBAr'_4$ in the presence of 2,6-di-*tert*-butyl-4-methylphenol. This easier and more convenient route allows extension to the 1,3,5-tris(*tert*-butyl)benzene compound, **3** (Scheme 1(b)).



Scheme 1

The Ni–arenes **2** and **3** can be readily characterized by NMR spectroscopy.[9] Using the former as an example, and leaving aside the characteristic and easily identifiable signals of the $Ni(\eta^3\text{-}C_3H_5)$ fragment and ^{t}Bu and Me substituents of the phenol, this compound exhibits ^{1}H resonances (CD_2Cl_2, 20 °C) at δ 6.94 (2H) and 5.84 (1H). The latter is due to the phenol OH group, which is also responsible for an IR absorption at 3600 cm^{-1}, due to ν(O–H). In the $^{13}C\{^1H\}$ NMR spectrum, four aromatic resonances are identified at δ 140.2 (COH), 126.5 (*C*–^{t}Bu), 109.2 (*C*–Me) and 109.0 (C–H).

The structure of compound **2** has been additionally confirmed by an X-ray investigation (Fig. 1).‡ The Ni(II)–arene interaction is relatively strong (Ni to ring centre distance of 1.663(2) Å, the shortest hitherto observed for Ni(II)–arene complexes[2c,3c,4]) and is fairly symmetrical with the Ni–C distances varying between 2.126(4) and 2.248(4) Å. No significant C–C bond alternation is observed in the aromatic ring which is almost perfectly planar. The arene and allyl ligands have a relative orientation similar to that in complex **1**,[5a] with the allyl back-bone aligned approximately parallel to the axis defined by O, C(4), C(7) and C(14).

Since the $Ni(\eta^3\text{-allyl})L_2^+$ and $[Ni(\eta^3\text{-allyl})(\mu\text{-}X)]_2$ compounds are good catalysts for the polymerization of 1,3-dienes[10] and styrene,[11] we have tested the catalytic activity of **1**–**3** in these reactions. While **1** is inactive in both cases, **2** and **3** exhibit remarkable activity toward 1,3-butadiene (Table 1) yielding stereoregular polymers of high molecular weight. ^{1}H and ^{13}C NMR spectroscopy reveals that they consist mostly of *cis*-1,4-polybutadiene (93%), accompanied by minor amounts of *trans*-1,4- and 1,2-units (5% and 2%, respectively).

Complex **2** also polymerizes styrene (entries 5–7). The molecular weights of the polymers are considerably lower than those observed for 1,3-butadiene. The polystyrenes display broad ^{1}H and complex ^{13}C NMR spectra,[12] which are consistent with a predominantly atactic structure. In addition, the carbon spectra indicate strict head-to-tail polymerization, since they lack methylene resonances within the region δ 25–35 (corresponding to $CHPhCH_2CH_2CHPh$ fragments) or methyne signals in the proximity of δ 48 (PhCHCHPh groups).[13] It is interesting that the catalytic activity of **2** is not affected by the

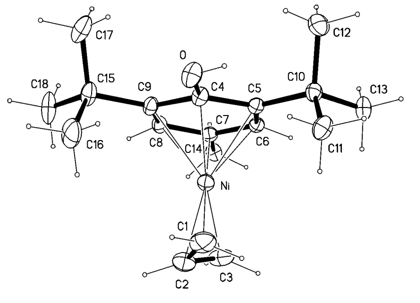


Fig. 1 ORTEP perspective of the cationic part of **2**.

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† Electronic supplementary information (ESI) available: synthetic procedures and analytical data for compounds **2** and **3**. ^{1}H and ^{13}C NMR spectra for polybutadiene and polystyrene. See http://www.rsc.org/suppdata/cc/b2/b209838e/

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Table 1 1,3-Butadiene and styrene polymerization with **2** and **3**

Entry	Catalyst	Monomer[a]/mol	Solvent[b]/mL	Yield (%)	TOF[c] ($\times 10^{-4}$)	Stereospecifity of polymers[d]	M_w	M_n	M_w/M_n
1	**2**	BN (0.44)	TOL (100)	63.0	8.03	93.5/4.3/2.2[e]	87,062	34,307	2.5
2	**2**	BN (0.24)	TOL (30)	98.7	6.78	93.6/4.7/1.7[e]	149,602	32,187	4.6
3	**3**	BN (0.24)	TOL (30)	76.4	5.56	94.0/4.2/1.8[e]	114,720	52,920	2.2
4	**2**	BN (0.24)	HEX (30)	48.2	3.35	92.9/4.9/2.2[e]	64,000	25,400	2.5
5	**2**	BN (0.24)	DCM (30)	22.3	1.55	92.4/5.5/2.1[e]	33,800	16,450	2.2
6	**2**	ST (0.12)	TOL (11)	56.3	1.95	44, 29, 27[f]	4,400	2,140	2.1
7	**2**	ST (0.12)	HEX (11)	66.4	2.31	41, 30, 29[f]	2,770	1,140	2.4
8	**2**	ST (0.12)	DCM (11)	76.9	2.67	40, 30, 30[f]	2,300	1,090	2.1

Polymerization conditions: 60 °C, 60 min., 3.45×10^{-6} mol of Ni complex.[a] BN: 1,3-butadiene; ST: styrene. [b] TOL: toluene; HEX: hexane; DCM: dichloromethane. [c] h^{-1}. [d] Determined from the ^{13}C NMR spectra. [e] *cis*/*trans*/1,2. [f] mm, mr, rr, approximate distribution from integration of the C_{ipso} signals.

presence of free 2,6-di-*tert*-butyl-4-methylphenol. Phenols, including the latter, are well known radical inhibitors,[14] and therefore a radical polymerization mechanism appears unlikely in this case.

The well known lability of η^6-arene–Ni(II) complexes[15] suggests that the polymerization reaction could be triggered by displacement of the η^6-arene by butadiene, to give the reactive intermediate $[Ni(\eta^3\text{-}C_3H_5)(\eta^4\text{-}C_4H_6)]^+$, able to undergo consecutive butadiene insertions and thereby following the stereoselective path described by Taube and Tobisch.[16,17] Notwithstanding this, the ready formation of compounds **2** and **3** also suggests that aromatic molecules exert a positive influence on the catalysis by stabilizing the Ni(II)–allyl species responsible for the polymerization process. This might be true particulary in aromatic solvents which are frequently used in this type of polymerization reactions,[10] and, moreover could account for the catalytic activities and molecular weights observed in toluene in the butadiene polymerization (Table 1, entries 2, 4, 5). On these grounds, the lower sensitivity of the styrene polymerization rates to the solvent effect (Table 1, entries 6–8) is not surprising, since this monomer already incorporates an aromatic fragment.

In summary, we have shown that $[Ni(\eta^3\text{-}C_3H_5)(\eta^6\text{-arene})]^+[BAr'_4]^-$ complexes, **2** and **3**, can be prepared by a very simple procedure, using readily available materials. They are single-component catalysts for the polymerization of butadiene and styrene. Their activity is comparable to those of the best Ni catalysts hitherto reported.[10a,11] Even if π-arene complexes of Ni have been known for many years, the ready complexation of the $Ni(\eta^3\text{-}C_3H_5)^+$ fragment by aromatic molecules has been unrecognized so far. We are currently examining the influence of aromatic solvents on these polymerization reactions, and studying the use of the new catalysts in the (co)polymerization of 1,3-butadiene, styrene and other monomers.

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Notes and references

‡ *Crystal data* for **2** (as dichloromethane solvate): $C_{50}H_{41}BF_{24}NiO$ (**2**·$1.5CH_2Cl_2$), M = 1310.74, triclinic, $P\bar{1}$ (no. 2), a = 13.807(9), b = 13.981(9), c = 17.466(11) Å, α = 95.84(2), β = 101.41(2), γ = 118.19(2)°, V = 2838(3) Å^3, Z = 2, D_c = 1.534 g cm^{-3}, T = 213(2) K, total reflections = 31705, unique reflections = 9971 (R_{int} = 0,043). Final R_1 = 0.0931, wR_2 = 0.1514 (all data). CCDC 195226. See http://www.rsc.org/suppdata/cc/b2/b209838e/ for crystallographic data in CIF or other electronic format.

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9 Selected spectroscopic data: **2**: ^1H NMR (CD_2Cl_2, 20 °C): δ 6.94 (s, 2H, CH arom.), 5.85 (m, 1 H, allyl H_c), 5.84 (s, 1H, OH), 3.61 (d, $^3J_{HH}$ 6.6 Hz, 2H, allyl H_{syn}), 2.46 (d, $^3J_{HH}$ 12.4 Hz, 2H, allyl H_{anti}). ^{13}C NMR (CD_2Cl_2, 20 °C): δ 140.2 (C_{arom}–OH), 126.5 (C_{arom}–^{t}Bu), 109.2 (C_{arom}–Me), 109.0 (C_{arom}–H), 106.5 (allyl CH), 58.7 (allyl CH_2). IR (Nujol mull): 3600 cm^{-1} (ν(OH)). **3**: ^1H NMR (CD_2Cl_2, 20 °C): δ 7.00 (s, 3H, CH arom.), 5.76 (m, 1 H, allyl H_C), 3.83 (d, $^3J_{HH}$ 6.5 Hz, 2H, allyl H_{syn}), 2.40 (d, $^3J_{HH}$ 12.4 Hz, 2H, allyl H_{anti}). ^{13}C NMR (CD_2Cl_2, 20 °C), δ 138.2 (C_{arom}–^{t}Bu), 105.3 (C_{arom}–H), 102.6 (allyl CH), 58.3 (allyl CH_2).

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