η⁶-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(η⁶) of composition [Ni(η⁶-ArX)(η⁵-C₃H₅)][BAR₄]⁻ (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(n)-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 We5 and others6 have found recently that by placing ortho-substituents on aryloxide ligands their otherwise uncommon π-coordination to Ni(n) and Pd(n) centers becomes favoured over the usual sigma bonding. Thus, instead of a conventional dimeric formulation of the type [Ni(η⁵-C₃H₅)(μ-OAr)]₂, the sterically demanding 2,6-di-tert-butyl-4-methylphenolate gives rise to the monomeric structure Ni(η⁶-allyl)(η⁵-OAr) (1). In this paper we wish to report the facile formation of cationic Ni(η⁶) organometallics that contain Ni(η⁶-ArOH) or Ni(η⁶-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(OEt₂)₂ (BAR₄) [Ar'X = (C₆H₅)(CF₃)₂]-3,5]b to produce compound 2 which contains a neutral phenol ligand (Scheme 1(a)). Alternatively 2 may be obtained directly from [Ni(η⁵-C₃H₅)(μ-Cl)]₂ and NaBAR₄ 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)).

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(η⁶-C₃H₅) fragment and 'Bu and Me substituents of the phenol, this compound exhibits 1H resonances (CD₂Cl₂, 20 °C) at 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 13C[1H] NMR spectrum, four aromatic resonances are identified at δ 140.2 (COH), 126.5 (C–'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(n)-arene interaction is relatively strong (Ni to ring centre distance of 1.663(2) Å, the shortest hitherto observed for Ni(η⁶-C₃H₅) fragment and 'Bu and Me substituents of the phenol, this compound exhibits 1H resonances (CD₂Cl₂, 20 °C) at 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 13C[1H] NMR spectrum, four aromatic resonances are identified at δ 140.2 (COH), 126.5 (C–'Bu), 109.2 (C–Me) and 109.0 (C–H).

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Since the Ni(η⁶-allyl)L₅¹ and [Ni(η⁶-allyl)(μ-X)]₂ compounds are good catalysts for the polymerization of 1,3-dienes 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. H and 13C 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 H and complex 13C 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 CH₂Ph₂CH₂CH₂CH₂Ph fragments) or methyne signals in the proximity of δ 48 (PhCH₂CH₂Ph groups).13 It is interesting that the catalytic activity of 2 is not affected by the

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

Fig. 1 ORTEP perspective of the cationic part of 2.
presence of free 2,6-di-tert-butyl-4-methylphenol. Phenols, including the latter, are well known radical inhibitors, and therefore a radical polymerization mechanism appears unlikely in this case.

The well known lability of \(\eta^2\)-arene–Ni(n) complexes\(^{15}\) suggests that the polymerization reaction could be triggered by displacement of the \(\eta^2\)-arene by butadiene, to give the reactive intermediate \([\text{Ni}(\eta^2\text{-C}_2\text{H}_4)(\eta^2\text{-C}_6\text{H}_{10})]^{+}\), 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 catalysts by stabilizing the Ni(n)-allyl species responsible for the polymerization process. This might be true particularity 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 towards the butadiene polymerization (Table 1, entries 2, 4, 5). On these grounds, the lower sensitivity of the styrene polymerization compared to those of the best Ni catalysts hitherto reported.\(^{10,11}\) Even if \(\eta^2\)-arene complexes of Ni have been known for many years, the ready complexation of Ni have been known for many years, the ready complexation of aromatic solvents on these polymerization reactions, and 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 copolymerization of 1,3-butadiene, styrene and other monomers.

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Notes and references

9. Selected spectroscopic data: 2: \(\text{H NMR (CD}_2\text{Cl}_2, 20\text{°C)}: \delta 6.94 (s, 2H, CH arom.)}, 5.85 (m, 1H, allyl H), 5.84 (s, 1H, OH), 3.61 (d, \({\text{J}}_{\text{HH}}\) 6.2 Hz, 2H, allyl H), 2.46 (d, \({\text{J}}_{\text{HH}}\) 12.4 Hz, 2H, allyl H), \(\text{^13C NMR (CD}_2\text{Cl}_2, 20\text{°C)}: \delta 140.2 (\text{C arom}), 126.5 (\text{C aliph-B}), 109.2 (\text{C aliph-Me}), 109.0 (\text{C aliph-H}), 106.5 (\text{aliph CH}), 58.7 (\text{aliph CH})\)). IR (Nujol mull): 3600 cm\(^{-1}\) (OH), 3460 cm\(^{-1}\) (Ni-C), 2400 cm\(^{-1}\) (C-C). 3: \(\text{H NMR (CD}_2\text{Cl}_2, 20\text{°C)}: \delta 7.00 (s, 3H, CH arom.), 7.56 (m, 1H, allyl H), 6.33 (d, \({\text{J}}_{\text{HH}}\) 6.5 Hz, 2H, allyl H), 2.40 (d, \({\text{J}}_{\text{HH}}\) 12.4 Hz, 2H, allyl H), \(\text{^13C NMR (CD}_2\text{Cl}_2, 20\text{°C)}: \delta 138.2 (\text{C aliph-B}), 105.3 (\text{C aliph-H}), 80.6 (\text{aliph CH})\)).
15. Both 2 and 3 undergo ready arene displacement and exchange reactions. See also ref. 2b.