Cationic indenylnickel complexes bearing a 1,5-cyclooctadiene ligand: Synthesis and characterization

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The reaction of $[Ni(\eta\text{-}1\text{-}R\text{-}Ind)_2]$ (R = H, Me) with one equivalent of 1,5-cyclooctadiene (COD), in the presence of a stoichiometric amount of HBF_4 (in Et_2O), at low temperature, afforded the corresponding cationic $[Ni(\eta\text{-}1\text{-}R\text{-}Ind)(\eta^4\text{-}COD)]BF_4$ in high yields. In the solid state, these complexes showed a slightly distorted pseudo-square-planar geometry around the metal centre. In solution, ^{1}H NMR spectra showed the existence of a fluxional process involving the 1,5-cyclooctadiene ligand. This process was investigated by DFT calculations and the results exclude the possibility of η^5-indenyl rotation.

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1. Introduction

The synthesis of neutral and cationic nickel(II) complexes bearing alkene, N-, O-, and P-ligands and their application in catalysis, especially in the oligomerization and polymerization of olefins has been a focus of great interest in the last decades, both in academia and industry [1].

Neutral and cationic allyl nickel complexes of the type $[Ni(\eta^3\text{-allyl})(L)X]$ (L = phosphines, phosphites; X = halides) and $[Ni(\eta^3\text{-}2\text{-}R\text{-allyl})L_2]^+$ (L = phosphines, phosphites, nitriles, ethers; L_2 = 1,5-dienes; R = H, Me), respectively, are examples of very efficient homogeneous catalysts for the oligo-/polymerization of olefins that can be found in the literature [2,3]. On the other hand, indenyl ($\eta\text{-Ind} = \eta\text{-}C_9H_7$) nickel(II) complexes are known to undergo η^5–η^3 ring slippage, enabling the existence of an extra coordination position and stabilizing several reaction intermediates, due to the presence of the benzene fragment fused on the cyclopentadienyl ring [4]. This process is designated as the *indenyl effect* [5]. Therefore, indenyl nickel complexes are thought to have chemical reactivities in between η^3-allyl ($\eta^3\text{-}CH_2CHCH_2$) and η^5-cyclopentadienyl ($\eta^5\text{-}Cp = \eta^5\text{-}C_5H_5$) species, exhibiting catalytic activity in several homogeneous reactions [6].

The synthesis of neutral and cationic cyclopentadienyl nickel(II) complexes containing arsenic(III) or antimony(III) donor ligands, $[Ni(\eta^5\text{-}Cp)(EPh_3)X]$ and $[Ni(\eta^5\text{-}Cp)(EPh_3)_2]^+$ (E = As, Sb; X = halides), was reported several years ago [7], but no reports were found for their η-indenyl nickel(II) analogues until only very recently. Taking into account the work of Werner et al. [8] on the protonation of nickelocene with HBF_4, which generated the intermediate $[Ni(\eta^5\text{-}C_5H_5)(C_5H_6)]BF_4$, and due to our interest in the chemistry of nickel complexes bearing η-indenyl ligands and to their potential role as catalysts [3c–f,9,10], we developed a new and efficient method for the synthesis of neutral and cationic indenyl-nickel complexes containing arsine or stibine donor ligands (Chart 1, **A** and **B**, respectively). The method consisted in the protonation of bis(indenyl)nickel with one equivalent of HBF_4, in the presence of the appropriate ligands [11].

Similarly to what was observed by Werner et al. [8], one could envisage the formation of an intermediate of the type '$[Ni(\eta^5\text{-}C_9H_7)(C_9H_8)]BF_4$' in the reaction medium, followed by substitution of the possibly coordinated neutral indene ligand by the appropriate neutral and/or anionic ligands. This methodology enabled the preparation of the expected Ni(II) complexes in high yields, which acted as very efficient catalysts for the oligomerization of styrene [11].

The results obtained prompted us to investigate the versatility of this new synthetic method and, consequently, the possibility of its extension to the preparation of new indenyl-nickel derivatives

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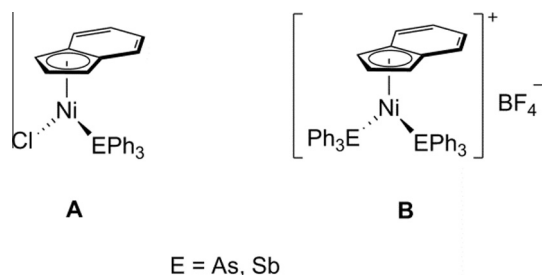 *E-mail address:* pedro.t.gomes@tecnico.ulisboa.pt (P.T. Gomes).

Chart 1. Indenylnickel complexes of arsine or stibine ligands reported previously [11].
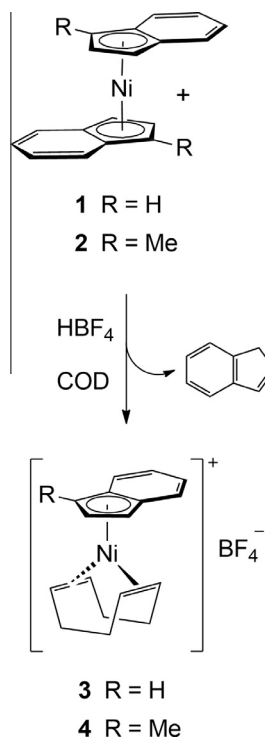
containing other type of ligands. One of such ligands is the neutral 1,5-cyclooctadiene (COD), which coordinates to metals in a bidentate fashion via both alkene groups. Metal-COD complexes are attractive because they are sufficiently stable to be isolated, and are often more robust than the related ethylene complexes, being their stability attributed to the chelate effect. Herein, we report the synthesis and full characterization of the new cationic 1-R-indenyl nickel complexes (R = H, Me), containing 1,5-cyclooctadiene as donor ligand and BF_4^- as counterion. DFT studies were also performed in order to investigate the dynamic behaviour observed by ^1H NMR spectroscopy.

2. Results and discussion

The reaction of [Ni(η-Ind)$_2$] or [Ni(η-1-Me-Ind)$_2$] with one equivalent of 1,5-cyclooctadiene (COD), in the presence of a stoichiometric amount of HBF_4 (in Et$_2$O), at −80 °C, resulted in the formation of compounds **3** and **4** (Scheme 1), as brown crystals, in 86% and 94%, respectively. Both compounds show solubility features typical of cationic complexes since they are soluble in polar solvents (*e.g.* dichloromethane, THF) and insoluble in solvents such as *n*-hexane, toluene or diethyl ether. Complexes **3** and **4** were fully characterized by NMR spectroscopy, elemental analysis, and single-crystal X-ray diffraction.[1]

The crystal structures of both cationic complexes **3** and **4** show one molecule in the asymmetric unit. Their molecular structures are depicted in Fig. 1, whereas selected bond distances, angles and other relevant structural parameters are presented in Table 1. The cationic moieties of these nickel complexes (Fig. 1) display geometries around the metal centre that can be described as slightly distorted pseudo-square-planar, according to the description by Andersen et al. [12] considering C1 and C3 as the 'terminal' atoms of the pseudo-allylic part of the indenyl ligand, and the centroids of the two 1,5-cyclooctadiene double-bonds occupying the remaining vertices of the pseudo-square-planes (see dihedral angles α in Table 1).

According to the bond distances listed in Table 1, complexes **3** and **4** show hapticity distortions that correspond to the unsymmetrical nature of the Ni-C bond lengths (Ni1–C1 < Ni1–C2 < Ni1–C3 ≪ Ni1–C3A ≈ Ni1–C7A, for **3**, and Ni1–C3 ≈ Ni1–C2 ≪ Ni1–C1 ≪ Ni1–C3A ≈ Ni1–C7A, for **4**), the latter being similar to the cationic complex [Ni(η-1-Me-Ind)(PPh$_3$)(PMe$_3$)]BF$_4$ [13], in which the Ni–C1 bond length is noticeably longer than Ni–C3 (Δ = 0.052(2) Å). However, this asymmetry is more pronounced in the 1-Me-Ind derivative **4** (Δ = 0.078(10) Å), owing to the presence of the Me (methyl) substituent at C1, which increases the steric hindrance, preventing a closer approach between the Ind and the metal centre. Within the five-membered indenyl ring,

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[1] Experimental details about synthetic procedures, elemental analysis, NMR spectroscopy and X-ray crystal data are available in Section 4.

Scheme 1. Synthesis of complexes **3** and **4**.
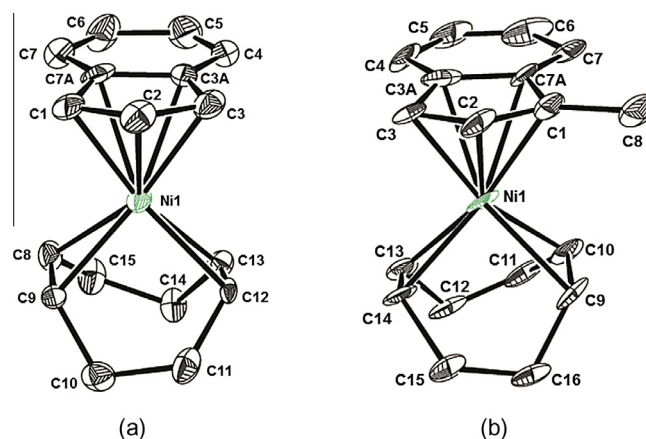

Fig. 1. Perspective views of the molecular structures of cationic 1-R-indenyl-nickel complexes (a) **3** and (b) **4**, with 50% probability level ellipsoids. All hydrogen atoms and the counteranions BF_4^- (in **3**) and $F_3BFBF_3^-$ (in **4**) were omitted for clarity.

these molecules show C–C bond lengths (C1–C2 ≈ C2–C3 < C3A–C7A ≪ C3–C3A ≈ C1–C7A for **3**, and C1–C2 < C3A–C7A < C2–C3 ≪ C3–C3A ≈ C1–C7A for **4**) pointing to an *ene-allyl* type distortion [12].

The Ind slip-fold distortion can be quantified, in the solid state, by calculating the *slip parameter*, Δ_{M-C}, the *hinge angle*, HA, and the *fold angle*, FA, from the crystal data [6,14–16]. The definition of these parameters is presented in Fig. S2 and Eq. S1 of Supplementary information. In general, values of Δ_{M-C} close to 0 Å correspond to a projection of the nickel atom almost coincident with the centroid of the five-membered ring, suggesting little distortion from a η^5 hapticity, whereas values above *ca.* 0.7 Å indicate that the projection shows the nickel atom closer to the allylic part formed by the carbon atoms C1, C2 and C3, pointing to a nearly η^3 coordination. Complexes **3** and **4** show *slip parameters*, Δ_{M-C}, of 0.192 and 0.084 Å, respectively, pointing to an hapticity between η^5 and