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2-Substituted 8-(2-benzhydrylarylimino)-5,6,7-trihydroquinoline-*N*,*N*′ nickel dichlorides: Synthesis, characterization and catalytic behavior towards ethylene

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ABSTRACT

A series of 2-substituted 8-(2-benzhydrylarylimino)-5,6,7-trihydroquinolines (**L**) was synthesized and fully characterized, and their nickel chloride complexes, namely 2-substituted 8-(2-benzhydrylarylimino)-5,6,7-trihydroquinoline-*N*,*N*′ nickel dichlorides (**L**NiCl$_2$), were prepared and characterized by FT-IR and elemental analysis. The structures of representative complexes were confirmed by single crystal X-ray crystallography, which revealed a distorted trigonal bipyramidal geometry at the metal for complexes **Ni3** and **Ni5** containing an additional solvent molecule, and a distorted tetrahedral geometry for the complex **Ni8**. Upon activation with methylaluminoxane (MAO), all nickel pre-catalysts showed good activity for ethylene polymerization and considerable activity for ethylene oligomerization.

1. Introduction

The impressive catalytic performances of diiminonickel halide complexes initiated the resurrection of interest in late-transition metal complexes, particularly their use in ethylene oligo- and polymerization [1]. Extensive studies have been conducted over the past two decades through the modification of the substituents present at the diimine ligand [2–7]. Sticking to the concept of using N^N bidentate ligands, some *N*-heterocyclic compounds have been designed and successfully used in nickel-based pre-catalysts for ethylene oligomerization and/or polymerization [8–18]. In addition, numerous alternative nickel pre-catalysts have been reported, which employ various ligand types such as bidentate N^P [19–21], N^O [22–30], P^O [31,32], or tridentate N^N^N [33–46], N^N^O [47,48], N^P^N [49–51]. Within the N^N bidentate nickel pre-catalyst family, those bearing iminopyridyl ligation showed high activities for ethylene polymerization [8,9]. Interestingly, bimetallic analogues produced both polyethylenes and oligomers [52]. Recently, nickel halide complexes bearing arylimino-5,6,7-trihydroquinoline derivatives performed impressively for either ethylene oligomerization [53,54] or polymerization [55–57]. Furthermore, benzhydryl-substituted anilines were successfully used in forming imino-based ligands, and their late-transition metal pre-catalysts possessed enhanced catalytic activities in ethylene polymerization [7,58,59]. On extending this research, 2-substituted 8-(2-benzhydrylarylimino)-5,6,7-trihydro-quinolines are now synthesized and used herein to prepare the corresponding nickel chloride complexes. Upon activation with MAO, these nickel pre-catalysts showed good activity in ethylene polymerization and considerable activity in ethylene oligomerization.

2. Results and discussion

2.1. Synthesis and characterization

The 2-substituted 8-(2-benzhydrylarylimino)-5,6,7-trihydroquinoline ligands (**L1**–**L8**) used in this work were prepared in reasonable yields according to our previous literature synthesis [55] by reaction of the respective 2-benzhydrylanilines (Scheme 1). The obtained compounds were confirmed to be two isomers of similar ratio comprising the forms enamine (**L**′) and Schiff-base (**L**); the two

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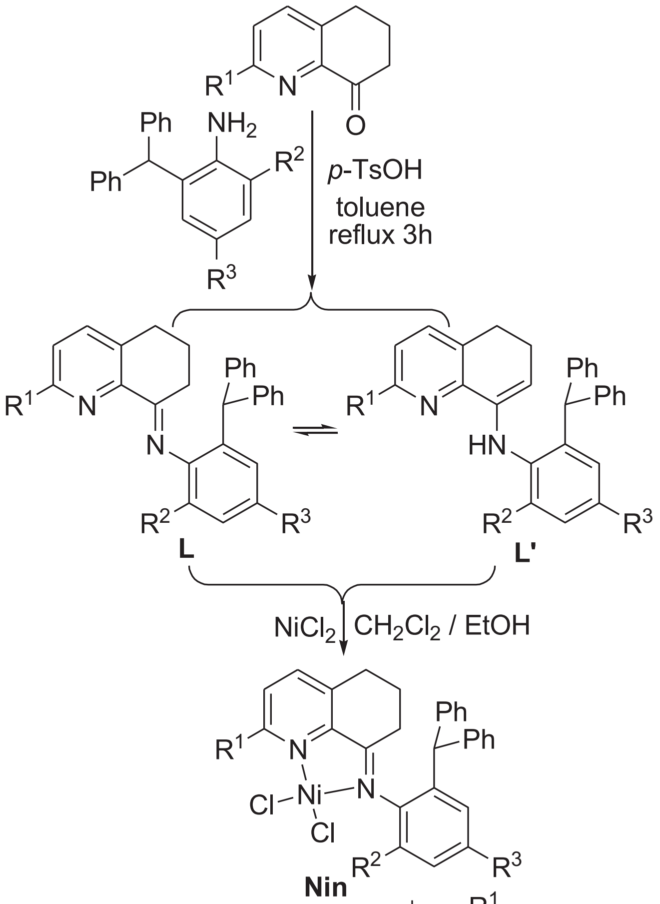

R^2	R^3	R^1	
		Ph	Cl
Me	-CH(Ph)$_2$	**Ni1**	**Ni5**
Me	Me	**Ni2**	**Ni6**
-CH(Ph)$_2$	Me	**Ni3**	**Ni7**
-CH(Ph)$_2$	*i*Pr	**Ni4**	**Ni8**

Scheme 1. Synthetic procedure.

isomers were quickly isomerised at room temperature as evidenced by the different fractions on column separation which showed the same ratio of isomers as monitored by NMR measurements. Two co-existing isomers for enamine and Schiff-base have been observed in our previous work [55,60].

The mixture of each ligand (0.5 mmol) was reacted with an equivalent amount of $NiCl_2 \cdot 6H_2O$ in 5 mL ethanol and 2 mL dichloromethane at room temperature. After being stirred for 3 h, the resultant solution was mixed with 20 mL ether and further stirred to precipitate the yellow nickel complex. According to their FT-IR spectra, the peaks around 3350 cm^{-1} for the N–H and 1564 cm^{-1} for the C=C bond of enamine of free ligands disappeared from the FT-IR spectra of their nickel complexes, indicating the isomer transformation of enamine (**L**′) into Schiff-base derivatives occurred during coordination with the nickel centre. Checking their data of elemental analysis, most showed relative lower values of nitrogen contents than the theoretic data; and that could be due to problems with combustion in the series of ligands used, previously being observed in our research [61]. One, the molecular structures of the nickel complexes **Ni3**, **Ni5** and **Ni8** were further confirmed by single crystal X-ray diffraction studies.

2.2. Molecular structures

Single crystals of complex **Ni3** suitable for X-ray diffraction were obtained by re-crystallization from a saturated dichloromethane solution, and the molecular structure revealed the distorted trigonal bipyramidal geometry around the five-coordinated nickel atom; there is an additional water molecule of solvation (Fig. 1). Unlike their iminopyridylnickel chloride complexes which exist as dimers [53,54,62,63], a mono-ligated mononuclear nickel complex was observed due to the presence of the bulky benzhydryl substituents on the $\text{aryl}_{\text{imino}}$ group. The N2–C8 bond at 1.294 Å clearly showed double bond characteristics, consistent with coordination of the ligand as the Schiff-base form. The atoms Ni1, N1, C9, C8 and N2 formed a planar metallocycle with a slight deviation of 0.0555 Å for C8 and 0.0461 Å for C9 out of the plane. The phenyl plane linked on the imine was perpendicular to the fused pyridyl ring; selected bond lengths and angles are tabulated in Table 1.

Single crystals of complex **Ni5** were obtained by laying diethyl ether on to a DMF solution. The molecular geometry is very similar to that of **Ni3**, but with an additional DMF molecule present, which in this case is ligated to the nickel centre via its oxygen (Fig. 2). As shown for **Ni3**, the bond N2–C8 of **Ni5** at 1.280(5) Å was consistent with a double bond. Within the five-membered metallocyclic plane of Ni1, N1, C9, C8 and N2, the deviations were for C8 0.0740 Å and C9 0.0862 Å out of the plane. Again, the phenyl plane is almost perpendicular (99.1°) to the fused pyridinyl ring. Selected bond lengths and angles are listed in Table 1.

Single crystals of complex **Ni8** were grown by the slow diffusion of diethyl ester into a dichloromethane solution under nitrogen atmosphere. The molecular structure in this case revealed a distorted tetrahedral geometry around the nickel (Fig. 3). As shown for the above two complexes **Ni3** and **Ni5**, the bond N2–C8 of **Ni8** was 1.291(5) consistent with a coordinated C=N bond. The five-membered metallocycle comprising atoms Ni1, N1, C9, C8 and N2 is almost co-planar with the deviations of C8 of 0.0057 Å and C9 of 0.0023 Å, respectively. The dihedral angle between the phenyl and fused pyridinyl planes is 92.5°, indicating their near perpendicular feature. Selected bond lengths and angles are collected in Table 1.

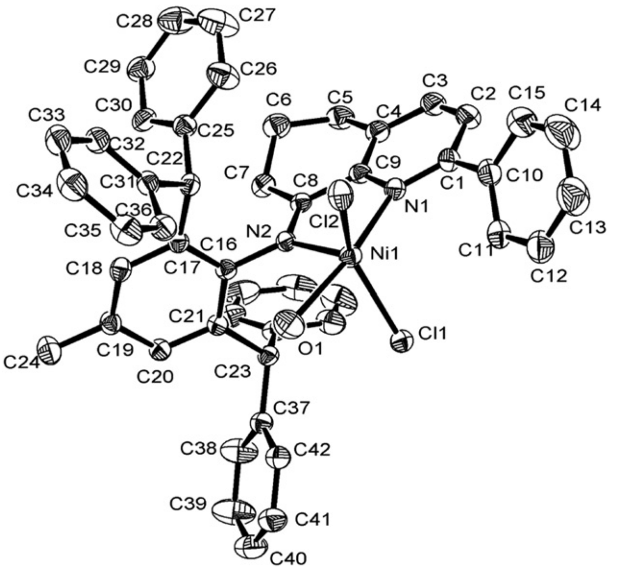

Fig. 1. ORTEP drawing of complex **Ni3**·H$_2$O. Thermal ellipsoids are shown at 30% probability. Hydrogen atoms have been omitted for clarity.