

# The synthesis and X-ray structure of *trans*-NiCl<sub>2</sub>(1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene)<sub>2</sub>; attempts to polymerize olefins utilizing a nickel(II) complex of a sterically demanding *N*-heterocyclic carbene

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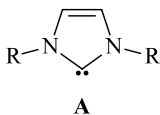
## Abstract

The compound *trans*-NiCl<sub>2</sub>(IPr)<sub>2</sub> (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) is synthesized and characterized crystallographically. In combination with MAO, it is converted to an intermediate which catalyses the dimerization of ethylene but which not the polymerization of ethylene, propylene or 1-hexene.

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**Keywords:** Nickel; *N*-Heterocyclic carbene ligands; Olefin polymers

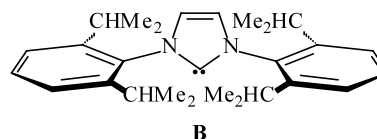
Recent years have seen a huge increase in interest in the coordination chemistry of unusually stable *N*-heterocyclic carbenes (NHCs) of the type **A** (R = bulky alkyl, aryl groups) [1]. Not only are complexes of virtually all transition metals known, but many of the complexes have been shown to exhibit a wide variety of interesting and useful catalytic properties [1,2].



A relatively small number of NHC nickel compounds has been reported, but these include nickel(II) complexes of the types NiX<sub>2</sub>(NHC)<sub>2</sub> (X = Cl, Br, I, Me) [3], [NiXL(NHC)<sub>2</sub>]<sup>+</sup> (L = tertiary phosphine) [4a], [Ni(bidentate chelating NHC)<sub>2</sub>]<sup>+</sup> [4a], η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>NiCl(NHC) [4b] and η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>NiCl(NHC) [4c], and nickel(0) complexes of the types Ni(NHC)<sub>2</sub> [5a,b] Ni(CO)<sub>3</sub>(NHC) [5c] and Ni(CO)<sub>2</sub>(NHC)<sub>2</sub> [5c]. In addition, some as yet incompletely characterized compounds are formed on

reaction of Ni(acac)<sub>2</sub> with NHCs [6] and are found to catalyse a variety of organic transformations, including cross-coupling of aryl chlorides with Grignard reagents [6a], amination of aryl chlorides [6b], reduction of aryl halides [6c] and coupling of 1,3-dienes with aldehydes [6d].

In view of the growing importance of nickel complexes as olefin polymerization catalysts [7], we have synthesized and investigated the possible utilization as an olefin polymerization catalyst of the compound NiCl<sub>2</sub>(1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene)<sub>2</sub>, henceforth NiCl<sub>2</sub>(IPr)<sub>2</sub> (IPr = **B**).



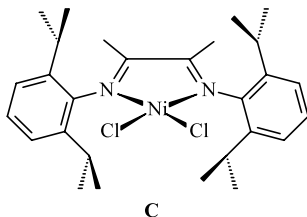
Only two nickel complexes of **B** are known, one a somewhat ill-defined catalyst for the coupling of 1,3-dienes with aldehydes [6d], the other being the above mentioned η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>NiCl(IPr) [4c]. In contrast, many IPr complexes of palladium [8] and ruthenium [9] are known and exhibit a variety of very interesting catalytic activities. Complexes of aluminum [10a], indium [10a], cobalt [10b], rhodium [10c] and iridium [10d] are also

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known and most exhibit interesting or unusual chemistry.

A key feature of many olefin polymerization catalysts based on square planar nickel compounds is the presence of ligands which provide considerable steric hindrance to access to the axial positions of the metal [7]. Examples of such ligands are  $\alpha$ -diimines such as  $\{2,6\text{-C}_6\text{H}_3(i\text{-Pr})_2\}N = \text{CMeCMe} = N\{2,6\text{-C}_6\text{H}_3(i\text{-Pr})_2\}$ , which coordinate in such a way that the bulky  $\{2,6\text{-C}_6\text{H}_3(i\text{-Pr})_2\}$  groups shield quite effectively the axial positions of the metal, as in C.



Chain transfer processes, which would result in lowered molecular weights, are made less competitive in these catalysts because the bulky *ortho* substituents block axial approach of monomer, thus retarding either the rate of displacement of polymer product or the rate of direct  $\beta$ -hydrogen elimination to coordinated monomer 7a. A compound such as  $\text{NiCl}_2(\text{IPr})_2$  thus seems particularly attractive because here also because the bulky *ortho*-isopropyl groups would be expected to result in similar effects.

## 1. Experimental

All operations were performed under purified argon using normal Schlenk techniques or an Mbraun glove box. Solvents were purified by standard methods, and distilled and degassed before use. All  $^1\text{H}$ - and  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra were recorded using Bruker Avance 300, 400 or 500 spectrometers, chemical shifts being referenced to residual  $^1\text{H}$  and  $^{13}\text{C}$  solvent peaks. Gel permeation chromatography experiments with the polymers were carried out at room temperature (r.t.) using a Waters Model 440 liquid chromatograph with THF as eluant and polystyrene standards. Elemental analyses were carried out by Canadian Microanalytical Services Ltd, Delta, BC.

### 1.1. Synthesis of 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr)

The ligand, IPr, was prepared in 90% yield via deprotonation 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride ( $\text{IPr}\cdot\text{HCl}$ ) by  $\text{KOBu}^t$  [9c].  $^1\text{H}$ -NMR (toluene- $d_8$ ):  $\delta$  1.13 (d,  $J$  7.0 Hz, 12H,  $\text{CH}(\text{CH}_3)_2$ ), 1.15 (d,  $J$  7.0 Hz, 12H,  $\text{CH}(\text{CH}_3)_2$ ), 2.91 (septet,  $J$  7.0 Hz, 4H,  $\text{CH}(\text{CH}_3)_2$ ), 6.56 (s, 4H,  $\text{N}(\text{CH})_2\text{N}$ ), 7.12 (m,

4H,  $m\text{-C}_6\text{H}_3$ ), 7.25 (2H,  $p\text{-C}_6\text{H}_3$ ); lit. ( $\text{C}_6\text{D}_6$ ):  $\delta$  1.13 (d,  $J$  9.2 Hz, 12H,  $\text{CH}(\text{CH}_3)_2$ ), 1.23 (d,  $J$  9.2 Hz, 12H,  $\text{CH}(\text{CH}_3)_2$ ), 2.91 (septet,  $J$  9.2 Hz, 4H,  $\text{CH}(\text{CH}_3)_2$ ), 6.57 (s, 4H,  $\text{N}(\text{CH})_2\text{N}$ ), 7.11 (m, 4H,  $m\text{-C}_6\text{H}_3$ ), 7.22 (2H,  $p\text{-C}_6\text{H}_3$ ) [9c].  $^{13}\text{C}\{^1\text{H}\}$ -NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  23.6 ( $\text{CH}(\text{CH}_3)_2$ ), 24.7 ( $\text{CH}(\text{CH}_3)_2$ ), 28.7 ( $\text{CH}(\text{CH}_3)_2$ ), 121.6 ( $\text{N}(\text{CH})_2\text{N}$ ), 123.6 ( $m\text{-C}_6\text{H}_3$ ), 129.0 ( $p\text{-C}_6\text{H}_3$ ), 139.0, 146.3 (*ipso*- $\text{C}_6\text{H}_3$ , *o*- $\text{C}_6\text{H}_3$ ), 220.7 (NCN); lit. ( $\text{C}_6\text{D}_6$ ):  $\delta$  23.6 ( $\text{CH}(\text{CH}_3)_2$ ), 24.8 ( $\text{CH}(\text{CH}_3)_2$ ), 28.7 ( $\text{CH}(\text{CH}_3)_2$ ), 121.5 ( $\text{N}(\text{CH})_2\text{N}$ ), 123.6 ( $m\text{-C}_6\text{H}_3$ ), 129.0 ( $p\text{-C}_6\text{H}_3$ ), 139.0 (*ipso*- $\text{C}_6\text{H}_3$ ), 146.2 (*o*- $\text{C}_6\text{H}_3$ ), 220.6 (NCN) [11]. The assignments were confirmed by HMQC experiments.

### 1.2. Synthesis of $\text{NiCl}_2(\text{IPr})_2$ (C)

Typically 0.169 g  $\text{NiCl}_2(\text{PPh}_3)_2$  (Strem) (0.258 mmol) was added in one portion to 200 mg of IPr (0.515 mmol) in 15 ml THF. The reaction mixture immediately turned red, and was stirred for 12 h. The solvent was then removed under reduced pressure, and the resulting residue was dissolved and eluted through a silica column using 1:3  $\text{CH}_2\text{Cl}_2$ -hexanes. The red band containing a mixture of  $\text{NiCl}_2(\text{IPr})_2$  and  $\text{PPh}_3$  was collected, the solvent was removed under reduced pressure and residual  $\text{PPh}_3$  contaminant was removed via sublimation at 70 °C under reduced pressure. The synthesis was carried out several times, yielding pure product in yields of 30–43%.  $^1\text{H}$ -NMR (toluene- $d_8$ ):  $\delta$  0.92 (d,  $J$  6.7 Hz, 24H,  $\text{CH}(\text{CH}_3)_2$ ), 1.15 (d,  $J$  6.7 Hz, 24H,  $\text{CH}(\text{CH}_3)_2$ ), 3.01 (septet,  $J$  6.7 Hz, 8H,  $\text{CH}(\text{CH}_3)_2$ ), 6.24 (s, 4H,  $\text{N}(\text{CH})_2\text{N}$ ), 7.15 (d,  $J$  7.7 Hz, 8H,  $m\text{-C}_6\text{H}_3$ ), 7.36 (t,  $J$  7.7 Hz, 4H,  $p\text{-C}_6\text{H}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$ -NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  23.3 ( $\text{CH}(\text{CH}_3)_2$ ), 26.3 ( $\text{CH}(\text{CH}_3)_2$ ), 28.6 ( $\text{CH}(\text{CH}_3)_2$ ), 124.3 ( $m\text{-C}_6\text{H}_3$  and  $\text{N}(\text{CH})_2\text{N}$ ), 129.7 ( $p\text{-C}_6\text{H}_3$ ), 137.3, 147.1 (*ipso*- $\text{C}_6\text{H}_3$ , *o*- $\text{C}_6\text{H}_3$ ), 168.9 (NCN). The assignments were confirmed by HMQC experiments.

Elemental analyses for  $\text{NiCl}_2(\text{IPr})_2$ : Calc. C 71.53, H 8.00, N 6.18; Found: C 70.89, H 7.72 N 6.14%. Allowing a red ether solution to evaporate slowly resulted in red crystals of  $\text{NiCl}_2(\text{IPr})_2$  suitable for crystallographic examination.

### 1.3. X-ray crystallography

A crystal of  $\text{NiCl}_2(\text{IPr})_2$  (red, block-shaped, size  $0.4 \times 0.3 \times 0.2$  mm) was mounted and sealed on a glass fiber with epoxy glue. Data collection was performed on a Bruker SMART CCD 1000 X-ray diffractometer with graphite-monochromated  $\text{Mo-K}_\alpha$  radiation ( $\lambda = 0.71073$  Å), operating at 50 kV and 35 mA at 23 °C over  $2\theta$  ranges of  $4.32^\circ$ – $57.26^\circ$ . No significant decay was observed during the data collection. Data were processed on a Pentium PC using the Bruker AXS WINDOWS NT SHELXTL software package (version 5.10) [12a]. Neutral atom scattering factors were taken from Cromer and Waber [12b]. The raw intensity data were

converted (including corrections for scan speed, background, and Lorentz and polarization effects) to structure amplitudes and their esd's using the program SAINT, which corrects for  $Lp$  and decay. Absorption corrections were applied using program SADABS. The crystal is orthorhombic space group  $P2_12_12_1$ , based on the systematic absences,  $E$  statistics and successful refinement of the structure. The structure was solved by direct methods. Full-matrix least-square refinements minimizing the function  $\sum w(F_o^2 - F_c^2)^2$  were applied to the compound. All non-hydrogen atoms were refined anisotropically. The positions for all hydrogen atoms were calculated, and their contributions were included in the structure factor calculations with isotropic thermal parameters 1.2 times that of the attached carbon atoms (1.5 times for methyl hydrogens).

Convergence to final  $R_1 = 0.0436$  and  $wR_2 = 0.0780$  by using 6434 independent reflections and 304 parameters were achieved [12c], with the largest residual peak and hole to be 0.349 and  $-0.289 \text{ e } \text{Å}^{-3}$ , respectively. The full molecular structure is shown in Fig. 1, a structure with H atoms and isopropyl groups omitted but with important atom numberings included in Fig. 2. Crystallographic data are given in Table 1, bond lengths and angles in Table 2.

#### 1.4. General procedures for attempted polymerizations

Ethylene and propylene were purified by passing through columns containing 4A molecular sieves, while 1-hexene was dried over 4A molecular sieves. As a general polymerization procedure,  $\sim 0.8 \text{ ml}$  of a solution of MAO in toluene (10% MAO by weight) was added to a solution of 10 mg of  $\text{NiCl}_2(\text{IPr})_2$  in 10 ml

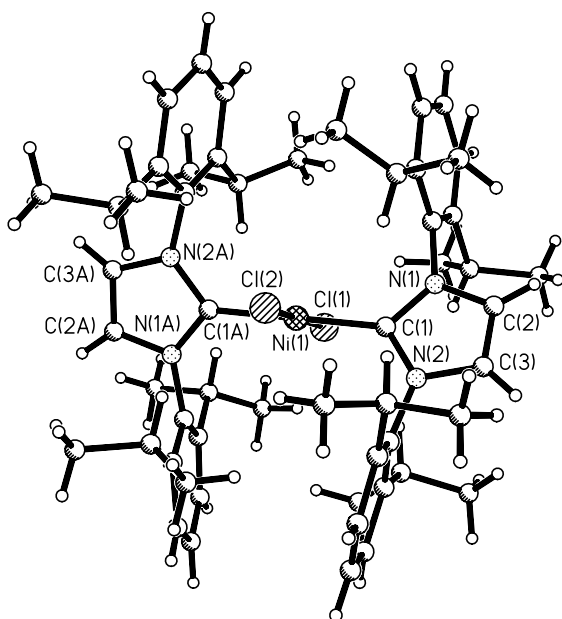


Fig. 1. Molecular structure of *trans*- $\text{NiCl}_2(\text{IPr})_2$ .

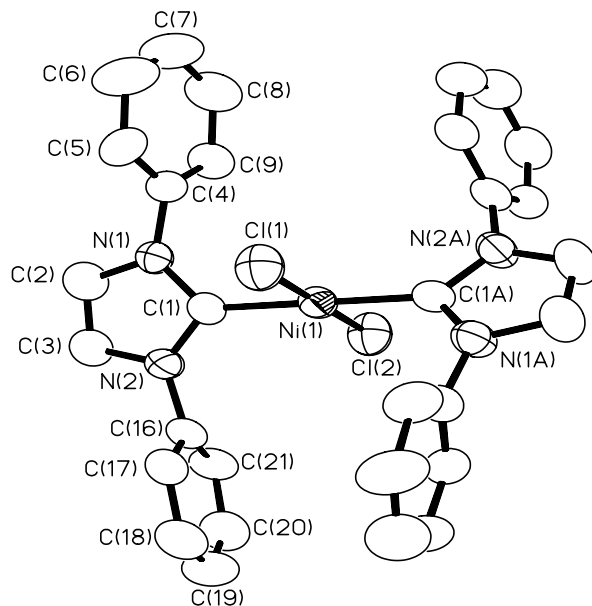


Fig. 2. Molecular structure of *trans*- $\text{NiCl}_2(\text{IPr})_2$  with H atoms and isopropyl groups removed and showing numbering scheme.

toluene containing a measured amount of 1-hexene or saturated with ethylene or propylene; the molar ratio of MAO:Ni was  $\sim 100:1$ . Ethylene or propylene continued to be bubbled through the reaction mixture while it was stirred at room temperature.

## 2. Results and discussion

The original objective of this research was to synthesize a compound of the type  $\text{NiCl}_2(\text{NHC})_2$  and test it as an olefin polymerization catalyst on activation with MAO. For reasons of convenience, therefore, we decided to begin with the known compound  $\text{NiCl}_2(1,3\text{-dicyclohexylimidazol-2-ylidene})_2$  [3a]. Unfortunately, we could not reproduce the synthesis of the required 1,3-dicyclohexylimidazol-2-ylidene (A: R = cyclohexyl), and we next tried the procedure of Nolan and co-workers for the synthesis of IPr (A: R = isopropyl) [9c]. The ligand synthesis was now accomplished in excellent yield (see also [13]). We next turned our attention to the synthesis of  $\text{NiCl}_2(\text{IPr})_2$ , obtaining this new compound via the reaction of  $\text{NiCl}_2(\text{PPh}_3)_2$  with two equivalents of IPr in reasonably good yields. We note that displacement of the phosphine ligands of  $\text{NiCl}_2(\text{PPh}_3)_2$  by other NHCs is reported to give yields varying between 0 and  $\sim 80\%$ , although there is no obvious reason for the apparent discrepancies [3a,b].

The compound  $\text{NiCl}_2(\text{IPr})_2$  is bright red and was characterized satisfactorily by elemental analyses,  $^1\text{H}$ - and  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectroscopy and X-ray crystallography. The molecular structure is shown in Figs. 1 and 2; the crystal and structure refinement data are

Table 1  
Crystal data and structure refinement for *trans*-NiCl<sub>2</sub>(IPr)<sub>2</sub>

Empirical formula	C <sub>54</sub> H <sub>72</sub> Cl <sub>2</sub> N <sub>4</sub> Ni·(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O
Formula weight	980.89
Temperature (K)	296(2)
Wavelength (Å)	0.71073
Crystal system	orthorhombic
Space group	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2
Unit cell dimensions	
<i>a</i> (Å)	12.924(5)
<i>b</i> (Å)	20.464(7)
<i>c</i> (Å)	10.598(4)
$\alpha$ (°)	90
$\beta$ (°)	90
$\gamma$ (°)	90
<i>V</i> (Å <sup>3</sup> )	2802.8(17)
<i>Z</i>	2
<i>D</i> <sub>calc</sub> Mg m <sup>-3</sup>	1.162
Absorption coefficient (mm <sup>-1</sup> )	0.482
<i>F</i> (0 0 0)	1056
Crystal size (mm <sup>3</sup> )	0.4 × 0.3 × 0.2
Theta range for data collection (°)	2.16–28.63
Index ranges	−16 ≤ <i>h</i> ≤ 16, −26 ≤ <i>k</i> ≤ 27, −13 ≤ <i>l</i> ≤ 12
Reflections collected	19 803
Independent reflections	6434 [ <i>R</i> <sub>int</sub> = 0.0659]
Completeness to $\theta$ (°)	28.63 (95.0%)
Absorption correction	Empirical (Bruker SADABS)
Max and min transmission	1.0000 and 0.7807
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	6434/2/304
Goodness-of-fit on <i>F</i> <sup>2</sup>	0.768
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0436, <i>wR</i> <sub>2</sub> = 0.0780
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.1422, <i>wR</i> <sub>2</sub> = 0.0921
Absolute structure parameter	0.061(17)
Largest difference peak and hole (e Å <sup>-3</sup> )	0.349 and −0.289

listed in Table 1, important bond lengths and angles in Table 2. As can be seen, the compound assumes a *trans* square planar structure very similar to those of the previously reported *trans*-NiCl<sub>2</sub>(1,3-dicyclohexylimidazol-2-ylidene)<sub>2</sub>, which occurs in two crystallographically independent forms [3a]. In these and in NiCl<sub>2</sub>(IPr)<sub>2</sub>, the carbene ligands are mutually *trans* and at angles very close to 90° to the halide ligands. It is interesting to note that the metal–ligand bond distances of *trans*-NiCl<sub>2</sub>(1,3-dicyclohexylimidazol-2-ylidene)<sub>2</sub> are slightly longer than those of *trans*-NiCl<sub>2</sub>(IPr)<sub>2</sub>, although it is not clear whether this reflects electronic or steric differences. In addition, as anticipated, the planes of the carbene ligands are perpendicular to those of the metal centers and hence provide apparently significant steric hindrance to the axial sites as may be necessary for compounds of this type to behave as olefin polymerization catalysts (see above).

As indicated above, the yields of NiCl<sub>2</sub>(IPr)<sub>2</sub> isolated were routinely less than 50%. The major product in all cases was an insoluble, off-white compound which could

Table 2  
Comparison of Bond Lengths (Å) and Bond Angles (°) of NiCl<sub>2</sub>(IPr)<sub>2</sub> and of the two crystallographically independent molecules of NiCl<sub>2</sub>(1,3-dicyclohexylimidazol-2-ylidene)<sub>2</sub>.<sup>3a</sup>

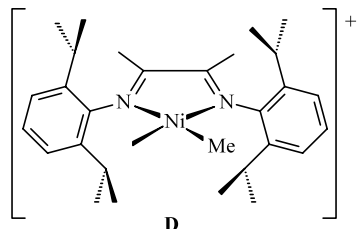
	NiCl <sub>2</sub> (IPr) <sub>2</sub>		NiCl <sub>2</sub> (1,3-dicyclohexylimidazol-2-ylidene) <sub>2</sub>	
			Molecule A	Molecule B
<i>Bond lengths</i>				
Ni(1)–C(1)	1.933(3)	1.911(2)	1.912(2)	1.912(2)
Ni(1)–C(1)#1	1.933(3)	1.911(2)	1.912(2)	1.912(2)
Ni(1)–Cl(1)	2.1586(17)	2.1818(8)	2.1858(8)	2.1858(8)
Ni(1)–C(2)	2.1588(17)	2.1818(8)	2.1858(8)	2.1858(8)
N(1)–C(1)	1.365(4)	1.354(3)	1.356(3)	1.356(3)
N(1)–C(2)	1.367(4)	1.390(3)	1.382(3)	1.382(3)
N(1)–C(4)	1.435(4)	1.475(3)	1.473(3)	1.473(3)
N(2)–C(1)	1.366(4)	1.357(3)	1.356(3)	1.356(3)
N(2)–C(3)	1.370(4)	1.387(4)	1.386(4)	1.386(4)
N(2)–C(16)	1.440(4)	1.472(3)	1.472(3)	1.472(3)
C(2)–C(3)	1.356(5)	1.333(5)	1.339(3)	1.339(3)
<i>Bond angles</i>				
C(1)–Ni(1)–C(1)#1	179.8(2)	180.00	180.00	180.00
C(1)–Ni(1)–Cl(1)	90.11(11)	90.75(7)	90.83(7)	90.83(7)
C(1)#1–Ni(1)–Cl(1)	90.11(11)	89.25(7)	89.17(7)	89.17(7)
C(1)–Ni(1)–Cl(2)	89.89(11)	89.25(7)	89.17(7)	89.17(7)
C(1)#1–Ni(1)–Cl(2)	89.89(11)	90.75(7)	90.83(7)	90.83(7)
Cl(1)–Ni(1)–Cl(2)	180.0	180.00	180.00	180.00
C(1)–N(1)–C(2)	111.3(3)	110.9(2)	110.8(2)	110.8(2)
C(1)–N(1)–C(4)	129.7(3)	124.6(2)	123.4(2)	123.4(2)
C(2)–N(1)–C(4)	118.8(3)	124.4(2)	125.5(2)	125.5(2)
C(1)–N(2)–C(3)	111.8(3)	110.6(2)	111.1(2)	111.1(2)
C(1)–N(2)–C(16)	128.9(3)	124.6(2)	124.1(2)	124.1(2)
C(3)–N(2)–C(16)	119.2(3)	124.8(2)	124.6(2)	124.6(2)
N(1)–C(1)–N(2)	103.4(3)	104.5(2)	104.3(2)	104.3(2)
N(1)–C(1)–Ni(1)	127.9(2)	127.81(17)	129.47(18)	129.47(18)
N(2)–C(1)–Ni(1)	128.7(2)	127.56(18)	126.12(17)	126.12(17)
C(3)–C(2)–N(1)	107.2(3)	106.7(3)	107.3(2)	107.3(2)
C(2)–C(3)–N(2)	106.2(3)	107.3(2)	106.4(2)	106.4(2)

not be identified. After exhaustive Soxhlet extraction by benzene, followed by drying under reduced pressure, elemental analyses of the compound resulted in the following data: C 36.3, H 4.2, N 3.0, Cl 27.4. Assuming the remaining 29.1% is nickel, then the data correspond to no obviously reasonable stoichiometry. The lack of NMR data because of the insolubility of the compound, in addition to the observation that it is colorless rather than the blue or green expected of nickel(II) complexes, leave us with no reasonable suggestion for structure.

### 2.1. Attempted polymerizations utilizing NiCl<sub>2</sub>(IPr)<sub>2</sub>

Polymerizations of e.g. ethylene by  $\alpha$ -diimine complexes such as **C** generally require the intermediacy of cationic alkyl complexes of the type **D**, with a vacant site *cis* to the alkyl group and to which the monomer can coordinate [7].





While simple substitution of the chloride ligands on the *trans* structure of  $\text{NiCl}_2(\text{IPr})_2$  does not naturally lend itself to the necessary *cis* isomer of a presumed intermediate such as  $[\text{Ni}(\text{Me})(\text{IPr})_2]^+$ , we anticipated that dimethylation of  $\text{NiCl}_2(\text{IPr})_2$  would result because of the high *trans* influence of the methyl ligand [14] in formation of the *cis* isomer which should form the desired cationic catalyst on treatment with a co-catalyst such as  $\text{B}(\text{C}_6\text{F}_5)_3$  [15]. To our surprise, however, several attempts to substitute the chloride ligands of  $\text{NiCl}_2(\text{IPr})_2$  using methyl lithium failed; only  $\text{NiCl}_2(\text{IPr})_2$  was recovered. This rather surprising finding may be a result of the steric hindrance to axial attack, as discussed above. Certainly nickel complexes of *cis* chelating NHCs do react with methyl lithium to form unstable methyl complexes [3c].

We therefore attempted to use  $\text{NiCl}_2(\text{IPr})_2$  as an olefin polymerization catalyst using MAO [15] as an activator. As a general procedure,  $\sim 0.8$  ml of a solution of MAO in toluene (10% MAO by weight) was added to a solution of 10 mg of  $\text{NiCl}_2(\text{IPr})_2$  in 10 ml toluene saturated with ethylene or propylene; the molar ratio of MAO:Ni was  $\sim 100:1$ . Ethylene or propylene continued to be bubbled through the reaction mixture while it was stirred at room temperature. The procedure for 1-hexene was similar except that 0.9 ml of 1-hexene was added to the solution prior to the addition of MAO. In the case of ethylene, the reaction mixture turned yellow on the addition of MAO and a small amount of yellow precipitate appeared. In contrast, the propylene and 1-hexene reaction mixtures both turned bright blue, and a small amount of a dark precipitate formed. In all cases, any reactions were stopped after 30 min by the addition of 5 ml of a methanol–HCl solution. At this time the reaction mixtures became colourless. Work-up in all cases involved removal of volatiles under reduced pressure followed by extraction of the solid residue with hexanes. The resulting hexanes solutions were then filtered through silica and solvent was removed from the eluants under reduced pressure. In no case was any polymeric material obtained!

The reaction(s) with MAO were studied further by NMR spectroscopy. Dry, solvent free MAO was obtained by removing the toluene from the commercial, 10% solution under reduced pressure. A part of the resulting white solid was used to make a stock solution of 0.495 M MAO in toluene- $d_8$ .

Under argon, 9.6 mg  $\text{NiCl}_2(\text{IPr})_2$  ( $1.05 \times 10^{-5}$  mol) and 4.5 mg MAO ( $7.75 \times 10^{-5}$  mol of ‘MeAlO’) were placed in an NMR tube to which 0.5 ml toluene- $d_8$  was added. Although the resulting solution turned blue and a small amount of blue solid slowly formed, a  $^1\text{H-NMR}$  spectrum exhibited only the resonances of  $\text{NiCl}_2(\text{IPr})_2$  and MAO. The blue solid was isolated and dried, but a  $^1\text{H-NMR}$  spectrum in  $\text{CD}_2\text{Cl}_2$  was uninformative.

In a complementary experiment, 5.1 mg  $\text{NiCl}_2(\text{IPr})_2$  ( $0.56 \times 10^{-5}$  mol) were dissolved in 0.5 ml toluene- $d_8$  under argon. Saturation of the resulting pink solution with ethylene resulted in neither a colour change nor a shift in the resonances of ethylene ( $\delta$  5.35) or  $\text{NiCl}_2(\text{IPr})_2$ . Subsequent addition of 0.2 ml of 0.495 M solution of MAO ( $9.9 \times 10^{-5}$  mol of ‘MeAlO’) resulted in a yellow solution, the  $^1\text{H-NMR}$  spectrum of which exhibited resonances of ethylene,  $\text{NiCl}_2(\text{IPr})_2$  and 1-butene at  $\delta$  0.90 (t, Me), 1.93 (m,  $\text{CH}_2$ ), 4.92, 5.79 (m,  $\text{CH}_2=\text{CH}-$ ). Integration after 1 and 2 h showed that the ratio of 1-butene: $\text{NiCl}_2(\text{IPr})_2$  was  $\sim 1:1$  and  $\sim 2:1$ , respectively. After 24 h, the spectrum also exhibited the resonances of *cis*- and *trans*-2-butene, but partial decomposition of the catalyst had resulted in a rather complicated NMR spectrum and useful integrations could not be obtained. However, the total amount of butenes present certainly exceeded the amount of  $\text{NiCl}_2(\text{IPr})_2$  in solution, and since  $\text{NiCl}_2(\text{IPr})_2$  seems to be essentially unreactive with MeLi and MAO, it seems likely that the actual catalyst is some other species, present in very low concentrations. Thus the resultant ethylene dimerization was catalytic.

Catalytic ethylene dimerization by nickel compounds has been known for many years [16], and played a special role in the original discovery of Ziegler catalysts 16a. While this work was in progress Cavell and co-workers [3d] reported similar olefin dimerizations catalyzed by nickel(II) complexes of NHCs in ionic liquid solvents. From our results, however, it is clear that an ionic solvent medium is not necessary for catalysis by NHC complexes of nickel(II). It is, however, not clear why  $\text{NiCl}_2(\text{IPr})_2$  is a poor catalyst for ethylene oligomerization or polymerization. Given its inertness with respect to alkylation reactions, it seems possible that the 2,6-diisopropylphenyl groups of the IPr ligands are too sterically demanding.

### 3. Supplemental material

Crystallographic data for *trans*- $\text{NiCl}_2(\text{IPr})_2$  have been deposited with the Cambridge Crystallographic Data Centre. Copies of these data may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://>

[www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)). The deposition number is CCDC 205515.

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