The novel \([\text{Ni}\{\text{Ph}_2\text{P}\}_2\text{N(CH}_3)_3\text{Si(OCH}_3)_3\text{-P,P}^-\text{I}_2]\) complex: Structural features and catalytic reactivity in the oligomerization of ethylene

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Abstract: The novel \([\text{Ni}\{\text{Ph}_2\text{P}\}_2\text{N(CH}_3)_3\text{Si(OCH}_3)_3\text{-P,P}^-\text{I}_2]\) complex (1) was synthesized and investigated by a variety of spectroscopic methods (IR, \(^1\)H and \(^31\)P NMR). The molecular structure of 1, determined by single crystal X-ray diffraction, was compared with those of the analogue \([\text{Ni}\{\text{Ph}_2\text{P}\}_2\text{N(CH}_3)_3\text{Si(OCH}_3)_3\text{-P,P}^-\text{Cl}_2]\) complex (2) and the recently reported \([\text{Ni}\{\text{Pr}_2\text{P}\}_2\text{NCH}_3\text{P,P}^-\text{I}_2]\) complex. Complexes 1 and 2 were tested as homogeneous catalysts for the oligomerization of ethylene, leading to the formation of \(C_6\) and, to a smaller extent, \(C_4\) products, in moderate yields.

Keywords: nickel, bis(phosphino)amine, ethylene oligomerization, homogeneous catalysis

1 Introduction

The preparation of linear olefins (up to \(C_{10}\)) is a field of significant interest, as these compounds are widely used in the chemical industry, for instance in the fabrication of various value-added chemical products by co-polymerization with ethylene [1]. Ethylene oligomerization affords a variety of up to \(C_{10}\) olefins, with 1-olefins being the most desirable ones [2]. A variety of metal complexes bearing various ligands have been extensively studied as catalysts for the oligomerization of ethylene, with chromium [2] and nickel [3] complexes being among the most common ones. Among various types of ligands employed for the synthesis of such catalysts, bis(phosphino)amines, \((R,P,R')\) in the following referred to as \((P,P)\), have been shown to afford a host of coordination compounds [4], the catalytic reactivity of which is under extensive investigation [5]. Among them, a large number of \(\text{Cr}(0)\) complexes bearing different \(N\)-substituent \(R'\) groups have been shown to be rather active catalysts for these reactions [6-10]. The nature of the \(R\) and \(R'\) group modifies the stereochemical and electronic properties of these catalysts, thus affecting their catalytic reactivity well [2]. On the other hand, complexes of \(\text{Ni}(II)\) bearing bis(phosphino)amine ligands have not been investigated as extensively. Up to now, complexes of the \([\text{Ni}(P,P)X_{2}]\), \(X = \text{Cl, Br, general type, have been shown to catalyze the polymerization of ethylene [11] or norbornene [12, 13], as well as the oligomerization of ethylene [14-16].}

With respect to the catalytic reactivity of such \(\text{Ni}(II)\) complexes in the oligomerization of ethylene, the reported studies have primarily probed the effects of i) the nature of the \(R'\) and \(R\) groups, ii) the size of the metal-ligand chelate ring by employing either \((P,P)\) or \((P,P=S)\) ligands [14-16]. These literature complexes contain either \(X = \text{Cl or Br and, to the best of our knowledge, no \([\text{Ni}(P,P)I_2]\) complexes have been investigated. For that reason, in the work presented herein, the synthesis and characterization of a \(\text{Ni}(II)\) complex of this type, namely \([\text{Ni}\{\text{Ph}_2\text{P}\}_2\text{N(CH}_3)_3\text{Si(OCH}_3)_3\text{-P,P}^-\text{I}_2]\) (1), is described. This compound bears the \(\text{Si}(\text{OCH}_3)_3\) group, via which it can be immobilized onto solid supports, as it has recently been shown for the structurally characterized analogous \(X = \text{Cl}\) (2) compound, which is an active heterogenized catalyst for the Kumada C–C coupling reaction [17, 18]. In an effort to probe the effects of the nature of the \(\text{Ni}(II)\)-coordinated halides \(X = \text{Cl, I, the structural and spectroscopic properties of complex 1 were determined by X-ray crystallography and IR/NMR spectroscopies and compared with those of complex 2 [17]. In addition, complexes 1 and 2 were investigated as homogeneous catalysts for the oligomerization of ethylene.}
2 Experimental

2.1 Synthesis

All synthetic experiments were carried out using standard Schlenk and vacuum line techniques, under an argon atmosphere. The solvents employed were dried and distilled according to published procedures [19]. The chemical reagents (3-aminopropyl)trimethoxysilane (97%) and chlorodiphenylphosphine (97%) were purchased from Alfa Aesar, whereas triethylamine (99%) from Merck. The bis(phosphino)amine ligand (Ph₂P)₃N(CH₂)₃Si(OCH₃)₃ [20] and complex 2 [17] were prepared according to published procedures.

Synthesis of complex 1. An amount of NaI (222 mg, 1.480 mmol) was added to an acetone solution of complex 2 (100 mg, 0.148 mmol) under argon. After the addition of NaI, the color of the solution changed from orange to purple. The reaction mixture was then stirred at room temperature for 2 h. The solvent was removed under vacuum and n-hexane (20 mL) was added to the filtrate, leading to the formation of a purple solid. The purple solid was collected by filtration and dried under vacuum. Yield: 112 mg, 88%.

2.2 IR and NMR spectroscopy

FT-IR spectra were recorded in an IRAffinity-1 SHIMADZU instrument using KBr pellets. ¹H-NMR spectra were recorded in a Varian 300 MHz instrument, at room temperature, in a CDCl₃ solution. A solution of H₃PO₄(aq) (85% w/w) was used as an external standard for the ³¹P(¹H) NMR spectra. ³¹P(¹H) NMR (121.4 MHz, CDCl₃, ppm): 61.6.

2.3 X-ray crystallography

The crystallographic data for compound 1 is listed in Table 1. A crystal of 1 (0.3× 0.4× 0.6 mm) was taken from the mother liquor and immediately cooled to -113 °C. Diffraction measurements were made on a Rigaku R-AXIS SPIDER Image Plate diffractometer, using graphite monochromated Cu Kα radiation. Data collection (ω-scans) and processing (cell refinement, data reduction and numerical absorption correction) were performed using the CrystalClear program package [21]. The structure was solved by direct methods using SHELXS-97 [22] and refined by full-matrix least-squares methods on F² using SHELXL2014/6 [23].

Further experimental crystallographic details: 2θ_max = 130.00 °; 251 parameters refined; (Δ/σ) max = 0.001; (Δρ) max/(Δρ) min = 1.09/-1.26 e/Å³. Two of the methyl groups of the ligand in structure 1 are in disordered positions and were refined with PART·1 instruction, considering 0.5 occupancies for both positions. The hydrogen atoms were refined isotropically at positions located either from difference Fourier Maps or at calculated ones using a riding model. All non-hydrogen atoms for both complexes were refined anisotropically.

2.4 Ethylene oligomerization

In a typical procedure, 10 µmol of the catalyst (complex 1 or 2) were transferred in a Young’s tube and 20 mL of toluene were added. After stirring for 15 min, methylluminoxane (MAO) (300 equivalents, 2.0 mL of 10% w/w solution in toluene) was added to the mixture. The flask was placed under vacuum for a short time and then it was filled with ethylene until the pressure reached 1 bar. The mixture was stirred for 1 h at 1 bar ethylene pressure, then cooled at 0 °C and the reaction was quenched by the addition of 5 mL of HCl(aq) 10%. Mesitylene (0.25 mL) was added as internal standard. The flask was then cooled to -20 ºC and an aliquote was taken from the organic layer, filtered and analyzed by gas chromatography (GC). Experiments employing higher ethylene pressure (10 bar) were performed in an autoclave reactor, under the experimental conditions described above. Ethylene oligomerization products were detected by GC-FID using a Varian L3800, fitted with a Varian WC07 fused silica capillary column, 25 m × 0.25 mm, i.d. coating CP-Sil 5CB, DF = 0.25. Ethylene oligomerization method: 40 to 80 ºC at 2 °C min⁻¹, then 80 to 250 ºC at 10 °C min⁻¹.

3 Results and Discussion

3.1 Synthesis and spectroscopic characterization of complex 1.

Complex 1 was prepared by adding an excess of NaI to an acetone solution of 2 [17], leading to the substitution of Cl⁻ by I⁻ (Scheme 1).
Complex 1 exhibits a very small $^{31}$P NMR chemical shift difference compared with the (Ph$_2$P)$_2$N(CH$_2$)$_3$Si(OCH$_3$)$_3$ ligand (61.6 versus 62.2 ppm [17], respectively). It should be noted that this difference is significantly larger for complex 2, which exhibits the corresponding peak at 42.8 ppm [17]. These observations would merit additional investigations. The synthesis and characterization of the [Ni{(Ph$_2$P)$_2$N(CH$_2$)$_3$Si(OCH$_3$)$_3$P,P'}Br$_2$] analogue, which is currently underway, will shed more light on this matter.

The appearance of only one $^{31}$P NMR peak for complex 1 signifies that, at room temperature, its two P atoms are magnetically equivalent. This is also confirmed by the crystal structure of complex 1, which is described in the following.

### 3.2 Structural features of complex 1.

Single crystals of complex 1 suitable for X-ray diffraction studies were obtained by the slow diffusion of n-hexane into a CH$_2$Cl$_2$ solution of complex 1 (layering method, CH$_2$Cl$_2$/n-hexane 1:3 v/v). The main crystallographic and structural data are listed in Tables 1 and 2, respectively.

The structure of complex 1 (Fig. 1) contains discrete molecules containing a NiP$_2$I$_2$ first coordination sphere of distorted square planar geometry. The metal center is coordinated by the (P,P) chelate, maintaining a four-member Ni-P-N-P ring of complex 2 used for its synthesis (Scheme 1).

The NiP$_2$I$_2$ core is almost planar, showing a small (0.007 Å) mean deviation from the best plane defined by the Ni, P and I atoms, with the I atom exhibiting the largest deviation (0.011 Å). Moreover, the four-member Ni-P-N-P ring is essentially planar, with the mean deviation from the best plane defined by these four atoms being 0.026(5) Å.

A search in the Cambridge Structural Database (CSD) [24] for deposited structures of [Ni(P,P)I$_2$] complexes, showed none. However, the structure of [Ni((Pr,P)$_2$)NH-353, OCH$_3$]-

Scheme 1: Synthesis of complex 1.

Table 1: Crystallographic data of complex 1.

| Parameter                  | Value          |
|----------------------------|----------------|
| Formula                    | C$_{30}$H$_{35}$I$_2$NO$_3$P$_2$NiSi |
| Fw                         | 860.13         |
| T (K)                      | 160            |
| radiation                  | Cu Kα          |
| Crystal system             | Orthorhombic   |
| Space group                | Pmcn           |
| a (Å)                      | 18.0618 (1)    |
| b (Å)                      | 8.7983 (1)     |
| c (Å)                      | 21.7705 (1)    |
| Volume (Å$^3$)             | 3459.62 (5)    |
| Z                          | 4              |
| D(calc), Mg m$^{-1}$       | 1.651          |
| Abs. coeff., μ mm$^{-1}$   | 16.27          |
| GOF on F$^2$               | 1.05           |
| Measured/ unique/          | 18390/2992/    |
| reflections with $I>2σ(I)$ | 2808           |
| $R_{int}$                  | 0.099          |
| R1 / wR2 (total)           | 0.0398/0.1020  |
| R1 / wR2 [for $I>2σ(I)$]   | 0.0382/0.1005  |
| CCDC deposition code       | 1517231        |

$R = \frac{\sum|\text{F}_o| - |\text{F}_c|}{\sum|\text{F}_o|}$ and $wR_2 = \frac{\sum w(\text{F}_o^2 - \text{F}_c^2)^2}{\sum w(\text{F}_o^2)^2})^{1/2}$

$w = \sqrt{\frac{1}{w(\text{F}_o^2)}}$ and $P = \frac{\text{F}_o^2 + 2\text{F}_c^2}}{3}$, $α = 0.0361$, $b = 5.4158$

The main bond lengths and angles of the later, along with those of complexes 1 and 2 [17], are listed in Table 2. It should be noted that the structure of one [Pd(P,P)I$_2$] complex (bearing one Me and three Ph as R groups and R’ = ’Pr) [26] and two [Pt(P,P)I$_2$] complexes (R = Ph, R’ = C$_6$H$_5$(CO$_2$CH$_3$) [27] or Ph[28]), have been reported and are available in the CSD.

By inspecting the structure of complex 1, the intermolecular interactions of the C–H⋯π type are
evident, involving the ligands’ CH$_3$ and Ph groups of neighboring molecules. A structural disorder involving two of the three –OCH$_3$ groups is observed in complex 1, and it has also been observed for complex 2 [17]. More significantly, complex 1 exhibits a mirror plane of symmetry (Fig. 1), unlike complex 2. The bond lengths in the two complexes exhibit certain differences, located mostly in the NiP$_2$X$_2$, X = Cl, I, coordination sphere. As expected, the Ni–I bond length is larger than the Ni–Cl one [2.501 and 2.192 Å (average), respectively]. In addition, the Ni–P bond lengths in complex 2 (average 2.128 Å) are slightly shorter compared with those of 1 (2.138 Å).

In comparing the structural features of complexes 1 and 3 [25], it is of interest to note that the atoms of the NiP$_2$I$_2$ core in complex 3 are not located in the same plane. More specifically, the mean deviation from the best plane defined by the Ni, P, I atoms is 0.1458 Å, with the P atom showing the largest deviation (0.458 Å). The Ni–I and Ni–P bond lengths of complex 3 are slightly larger and shorter, respectively, than those of complex 1.

A comparison of the bond angles of complexes 1, 2 and 3, show a larger I-Ni-I value in complex 3, and the X = I complexes 1 and 3 exhibit slightly larger P-N-P angles compared with that of complex 2. The three complexes exhibit similar P-Ni-P angles (Table 2), the magnitude of which seems to be controlled by the formation of the four-member Ni-P-N-P ring.

### 3.3 Ethylene oligomerization.

Complexes 1 and 2 were tested as catalysts for the oligomerization of ethylene (Table 3). The experiments were carried out in the presence of methylaluminoxane (MAO), under an ethylene pressure of either 1 or 10 bar. The reactions lead, in moderate yields, to primarily C$_4$ products (dimerization of ethylene) and only small amounts of the C$_6$ oligomers (Table 3). At low ethylene pressure (1 bar), complex 1 exhibits a larger selectivity for 1-C$_6$ products compared with that of complex 2, whereas at 10 bar the two complexes exhibit similar selectivity. It should be stressed that due to the moderate activity of complexes 1 and 2, there are significant differences in the data obtained from experiments performed under the same conditions (entries a and b, Table 3). The observed differences between the catalytic activity of complexes 1 and 2 may be explained by their main structural difference, namely the large difference in their Ni–X bond length, X = I, Cl, (2.501 and 2.196 Å, respectively, Table 2). This difference, may lead to diverse ways of substrate coordination and activation in the first coordination.
sphere of the catalyst. Ongoing investigations on the catalytic activity and sensitivity of the X = Br analogue, under similar experimental conditions, are expected to shed more light concerning this matter.

The ethylene pressure affects the catalytic activity. Catalytic reactions performed at a higher ethylene pressure (10 bar), provided higher yields and improved catalytic activities. Increased pressure increases the yield in C₄ products, but the selectivity in C₅ products remains moderate (Table 3). The relatively low selectivity of both complexes in producing 1-C₅, at 10 bar of ethylene pressure, is compatible with a co-dimerization process of the C₄ products and unreacted ethylene, leading to branched C₅ products, as previously suggested in the literature [15].

4 Conclusions

The novel \([\text{Ni}((\text{Ph})\text{P})_2\text{N(CH}_3)_2\text{Si(OCH}_3)_2\text{P}^-\text{P}^-]_2\text{I}_2\) complex (1) was synthesized and structurally characterized by X-ray crystallography. The structural features of this compound were compared with those of the recently reported complexes \([\text{Ni}((\text{Pr})\text{P})_2\text{N(CH}_3)_2\text{Si(OCH}_3)_2\text{P}^-\text{P}^-]_2\text{I}_2\) (3) and \([\text{Ni}((\text{Ph})\text{P})_2\text{N(CH}_3)_2\text{Si(OCH}_3)_2\text{P}^-\text{P}^-]_2\text{Cl}_2\) (2). Complexes 1 and 2 were tested as homogeneous catalysts for the oligomerization of ethylene, leading to the formation of C₄ and, to a smaller extent, C₅ products, both in moderate yield. The catalytic reactivity of immobilized complexes 1 and 2, as well as that of the \([\text{Ni}((\text{Ph})\text{P})_2\text{N(CH}_3)_2\text{Si(OCH}_3)_2\text{P}^-\text{P}^-]\text{Br}_2\) analogue complex, is currently under investigation and will be reported at a later date.

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Table 3. Catalytic ethylene oligomerization by complexes 1 and 2.

| Complex | 1   | 2   |
|---------|-----|-----|
| Activity g (g₄₅h)⁻¹ | a   | 145 | 388 |
|          | b   | 220 | 350 |
|          | c   | 600 | 800 |
| C₄ %    | a   | 87  | 91  |
|          | b   | 85  | 92  |
|          | c   | 92  | 90  |
| C₅ %    | a   | 13  | 9   |
|          | b   | 13  | 6   |
|          | c   | 8   | 10  |
| 1-C₅ %  | a   | 57  | 5   |
|          | b   | 23  | 10  |
|          | c   | 25  | 30  |

All percentages are by mass. The fraction 1-C₅ is given as a percentage of the C₄ total fraction. Experiments a and b were performed under low ethylene pressure (1 bar), whereas experiments c under 10 bar of ethylene pressure.
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