

THE PREPARATION OF KEIM'S ETHYLENE OLIGOMERIZATION CATALYST.

An Introductory Experiment in Organometallic Chemistry

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ABSTRACT

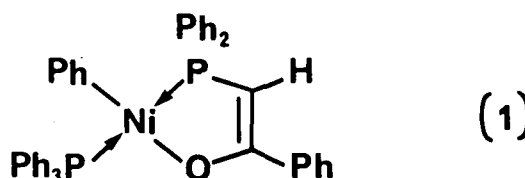
A conveniente sequence of reactions leading to Keim's ethylene polymerization catalyst $[Ni(Ph)(PPh_3)\{Ph_2PCHC(O)Ph\}]$ is proposed here as a practical exercise for undergraduate students. The reactions are straightforward and cover wide range of classical laboratory techniques. The synthesis is outlined in the following steps: 1) Nickel chloride hexahydrate is first reacted with pyridine (Py) to yield quantitatively $NiCl_2(Py)_4$. 2) Reduction of the latter with sodium in tetrahydrofuran in the presence of 1,5 - Cyclooctadiene (COD) gives the highly reactive $Ni(COD)_2$. 3) In the last step, the previously synthesized phosphonium ylide $Ph_3P = CHC(O)Ph$ is reacted with $Ni(COD)_2$ and triphenylphosphine (PPh_3) to give the desired product by rupture of a P-Ph bond. The Nickel (II) complex thus obtained polymerizes ethylene under very mild conditions and is presently used as an industrial catalyst for the preparation of linear α -olefins.

RESUMO

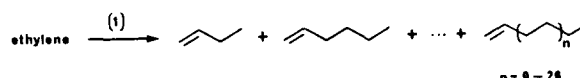
É proposta uma prática de laboratório de uma sequência de reações envolvendo a polimerização do etileno com o catalizador de Keim, $[Ni(Ph)(PPh_3)\{Ph_2PCHC(O)Ph\}]$. As reações são limpas e utilizam várias técnicas clássicas de laboratório. As sínteses estão resumidas nas seguintes etapas: 1) primeiramente reage-se cloreto de níquel hexaidratado com piridina (py) para produzir quantitativamente $NiCl_2(Py)_4$. 2) redução deste produto com sódio em tetraidrofurano na presença de 1,5-ciclooctadieno (COD), produzindo o altamente reativo $Ni(COD)_2$. 3) nesta última etapa reage-se a ilida de fosfônio $Ph_3P = CHC(O)Ph$, previamente sintetizada, com o $Ni(COD)_2$ e trifenilfosfina (PPh_3), dando o produto desejado pela quebra da ligação P-Ph. O complexo de Níquel (II) obtido polimeriza o etileno em condições brandas e é atualmente usado como um catalisador industrial para a preparação de α -olefinas lineares.

The Keim catalyst (1) is currently used by the Shell company for the industrial production of α -olefins by

the oligomerization of ethylene, in the so-called SHOP process, (Shell Higher Oligomerisation Process).

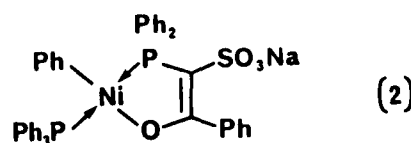


Operating in a homogeneous medium, and under mild conditions of temperature and pressure, (1) allows the conversion of ethylene to α -olefins, 99% of which are linear, with a high degree of selectivity (98%) (1).



Annual worldwide production of α -olefins is of the order of 800.000 tonnes and these α -olefins are widely used in the synthesis of a large number of organic products, especially detergents, fabric softeners, lubricants and oil additives.

The Gulf company has also patented (2) an ethylene oligomerization process using a similar nickel catalyst (2).



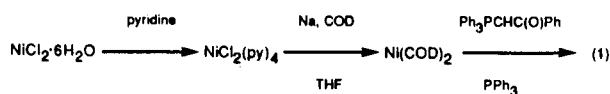
The presence of the sulfonate group in this catalyst induces solubility in polar solvents such as water or methanol. This allows the catalytic reaction to be performed in a two-phase system, thus facilitating the separation and removal of the products.

The sequence of reactions that we propose for the synthesis of (1) requires the normal laboratory equipment necessary to work under an inert gas atmosphere (vacuum line, dry argon, Schlenk tubes). The preliminary synthesis of $NiCl_2(py)_4$ (py = pyridine), obtained by the direct addition of pyridine to finely-ground, hydrated $NiCl_2$, can be performed in an open beaker without the necessity of an inert gas atmosphere (3). All solvents used, with the exception of pyridine, should be previously distilled under argon; toluene, pentane and hexane from Na wire; THF and diethylether from

Na-benzophenone; CH_2Cl_2 from P_2O_5 , and methanol from $\text{Mg}/\text{Mg}(\text{OCH}_3)_2$.

N.B. All manipulations should be carried out under an effective fume hood.

Sequence of Reactions



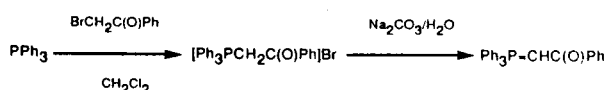
py = pyridine

COD = 1,5-cyclo-octadiene

THF = tetrahydrofuran

$\text{Ni}(\text{COD})_2$ is prepared by the sodium reduction of $\text{NiCl}_2(\text{py})_4$, in THF, in the presence of 1,5-cyclo-octadiene (COD) (4). For this reaction, the student is strongly advised to ensure that a sufficiently large volume of solvent is used, thus optimising the conditions for the conversion of $\text{NiCl}_2(\text{py})_4$ to $\text{Ni}(\text{COD})_2$: The latter complex, which is yellow in color, is unstable and highly reactive in air and, in order to avoid decomposition, $\text{Ni}(\text{COD})_2$ should be stored at low temperature, in a Schlenk tube, under an atmosphere of butadiene. ($\text{Ni}(\text{O})$ is capable of the dimerisation of butadiene to COD).

The synthesis of $\text{Ph}_3\text{PCH}_2\text{C}(\text{O})\text{Ph}$ proposed here is based upon the classic synthesis of phosphorus ylides (5). Initially, the phosphonium salt $[\text{Ph}_3\text{PCH}_2\text{C}(\text{O})\text{Ph}]\text{Br}$ is prepared by the quaternization of PPh_3 using $\text{BrCH}_2\text{C}(\text{O})\text{Ph}$. This reaction is both immediate and quantitative, and the product thus obtained is then deprotonated, using a saturated aqueous solution of $\text{Na}_2(\text{CO}_3)$, to give the desired ylide.



The final step is an oxidative addition reaction, ($\text{Ni}(\text{O}) \rightarrow \text{Ni}(\text{II})$), in which the addition of the phosphorus ylide proceeds *via* the rupture of a phenylphosphorus bond giving the two coordinating moieties, $[\text{C}_6\text{H}_5]^-$ and $[\text{Ph}_2\text{PCHC}(\text{O})\text{Ph}]^-$. The final complex, in which the nickel can be considered as a 16 electron center, can be easily characterized by infrared spectroscopy, (presence of an intense band at 1506 cm^{-1} due to a combination of $\nu(\text{C}=\text{O}) + \nu(\text{C}=\text{C})$), and by ^1H and $^{31}\text{P}\{^1\text{H}\}$ nuclear magnetic resonance spectroscopy (6).

As a teaching aid the student could carry out a literature survey on the chemistry of phosphorus ylides. These complexes constitute powerful tools for organic synthesis, (Wittig reaction (7), synthesis of Vitamin A, etc.), and equally find many applications in organometallic chemistry (formation of complexes with metal-car-

bon bonds, synthesis of Keim-type catalysts and catalysts for the synthesis of high molecular weight polymers (8)).

EXPERIMENTAL SECTION

Preparation of $\text{NiCl}_2(\text{py})_4$

In a 500 ml beaker were mixed $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (10.0g, 42.1 mmol), which had been previously ground to a fine powder using a mortar and pestle, and 200 ml of pyridine. In order to ensure complete conversion to the desired product the solution, which became blue upon addition of the pyridine, was stirred at room temperature for a period of 4 hours using a magnetic stirrer. The blue precipitate, thus obtained, was filtered using a No. 3 glass frit, washed with diethyl ether (2 x 50 ml), and dried *in vacuo* to yield $\text{NiCl}_2(\text{py})_4$, (17.8g, 39.9 mmol, 95%, $M = 446.02$).

Preparation of $\text{Ni}(\text{COD})_2$ (COD = 1,5-cyclo-octadiene).

It is imperative that this experiment is performed at room temperature under an argon atmosphere using dry distilled solvents. A 500 ml round-bottomed flask, equipped with a side-arm tap, was charged with $\text{NiCl}_2(\text{py})_4$ (10.0g, 22.4 mol) and a magnetic stirring bar. The flask and its contents were then placed under an argon atmosphere using a pump-fill technique. To the flask were then added THF (100 ml), and sodium wire (1.1g, 47.8 mmol). the 1,5-cyclo-octadiene, which had previously been degassed, (7.27g, *ca.* 8.3ml) was added and the mixture stirred for 4 hours. The resulting solution was then concentrated to approximately 50% of the original volume and the product precipitated by the addition of methanol (50ml). After allowing the precipitate to settle, the supernatant solution, which sometimes appears as a thickish suspension of $\text{NaO-Me}/\text{NaOH}$, was removed using a piston pipette. The remaining yellow precipitate was washed several times with small volumes of methanol and dried *in vacuo* to yield the pure $\text{Ni}(\text{COD})_2$, (2.75g, 10.0 mmol, 45%, $M = 265.08$). The product should be stored in a Schlenk tube under an atmosphere of argon/butadiene to reduce decomposition.

Preparation of phenacyltriphenylphosphonium bromide $[\text{Ph}_3\text{PCH}_2\text{C}(\text{O})\text{Ph}]\text{Br}$.

The experiment was carried out at room temperature under an argon atmosphere. A 500 ml round-bottomed flask, equipped with a side-arm tap and magnetic stirring bar, was charged with PPh_3 (10.0g, 38.1 mmol). The flask was then placed under an argon atmosphere, using a pump-fill technique, and dry, degassed CH_2Cl_2 (60 ml) added. To this stirred solution solid $\text{BrCH}_2\text{C}(\text{O})\text{Ph}$ (7.6g, 38.2 mmol) was added in small portions. Precipitation occurred rapidly to yield the product in the form of white crystals. (At this stage 30-50 ml of diethyl ether can be added to ensure the

complete precipitation of the product). The product was then filtered, using a No. 3 glass frit, washed with diethyl ether (2 x 30 ml), and dried *in vacuo* to yield $[\text{Ph}_3\text{PCH}_2\text{C}(\text{O})\text{Ph}]\text{Br}$, (16.3g, 35.3 mmol, 93%, $M = 461.34$). M.P. 268-270°C. I.R. (KBr): 1645 cm^{-1} , s, (ν C=O).

Preparation of $[\text{Ph}_3\text{PCH}_2\text{C}(\text{O})\text{Ph}]$.

This experiment was carried out at room temperature under an air atmosphere. A mixture of 10% aqueous Na_2CO_3 (250 ml) and $[\text{Ph}_3\text{PCH}_2\text{C}(\text{O})\text{Ph}]\text{Br}$ (10.0g, 21.7 mmol) were stirred overnight in a 500 ml round-bottomed flask. The resulting suspension was filtered through a No. 3 glass frit to leave a white solid on the frit. This solid was dissolved directly into another 500 ml round-bottomed flask by washing with hot toluene (150 mL). Addition of pentane to this resulting solution afforded the ylide as a white precipitate which was filtered, washed with pentane (2 x 30 ml) and dried *in vacuo*. The yield was approximately 90%, (7.4g, 19.4 mmol, $M = 380.43$). M.P. 178-180°C. I.R. (KBr): 1515 cm^{-1} , s, (ν C=O). $^{31}\text{P}\{^1\text{H}\}$ (toluene-benzene d_6), δ 17.7, singlet.

Preparation of $[\text{Ni}(\text{Ph})\{\text{Ph}_2\text{PCHC}(\text{O})\text{Ph}\}(\text{PPh}_3)]$ (I)

This section of the experiment should also be performed under an argon atmosphere and all solvents should be dried and distilled prior to use. Using a 250 ml round-bottomed flask, equipped with a side-arm tap and magnetic stirring bar, PPh_3 , (5.0 g, 19.1 mmol) and $[\text{Ph}_3\text{PCHC}(\text{O})\text{Ph}]$, (7.3g, 19.1 mmol) were dissolved in toluene (150 ml). This solution was then added dropwise to a solution of $\text{Ni}(\text{COD})_2$ (5.3g, 19.1 mmol), in toluene (80 ml), in a 500 ml round-bottomed flask maintained at 0°C in an ice bath. This mixture was then stirred at room temperature for 24 hours and then for a further 2 hours at 50°C. The red-brown solution obtained was then evaporated to dryness in order to remove the liberated COD. The residue was redissolved in 40-50 ml of toluene, filtered and hexane (50 ml) added slowly to the

filtrate. Upon storage at 0°C, the product precipitated in the form of yellow-green crystals, which were washed with hexane (2 x 30 mmol) and dried *in vacuo*, to yield $[\text{Ni}(\text{Ph})\{\text{Ph}_2\text{PCHC}(\text{O})\text{Ph}\}(\text{PPh}_3)]$, (9.1g, 13.8 mmol, 68%, $M = 701.43$). M.P. = 268-270°C dec. I.R. (KBr): 1506 cm^{-1} , s, (ν (C—O) + ν (C=C)). ^1H NMR (CDCl_3): δ 5.0 (s, ^1H , PCH), 6.4-8.0 (35H, H aromatic). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): δ 20.8 and 22.3 (4 line AB spin system, $^2J_{\text{A-B}} = 272$ Hz).

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EDUCAÇÃO

“REAVIAÇÃO DE UM CONHECIDO MODELO PARA DETERMINAR A GEOMETRIA MOLECULAR. O EXEMPLO DA H_2O ”.

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ABSTRACT

The directional character of p atomic orbitals has

been used, in qualitative model, to justify the bent geometry of molecular systems such as H_2O . In this work calculations (ab-initio with STO-3G basis set) were ma-