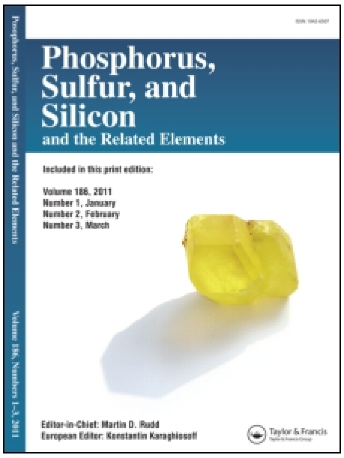
This article was downloaded by:
On: *29 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Phosphoranes Containing P-H Bonds

Richard A. Kemp[a]
[a] Catalysis Department, Westhollow Research Laboratory Shell Development Company, Houston, Texas

To cite this Article Kemp, Richard A.(1994) 'Phosphoranes Containing P-H Bonds', Phosphorus, Sulfur, and Silicon and the Related Elements, 87: 1, 83 — 92
To link to this Article: DOI: 10.1080/10426509408037442
URL: http://dx.doi.org/10.1080/10426509408037442

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Phosphorus, Sulfur, and Silicon, 1994, Vol. 87, pp. 83–92
Reprints available directly from the publisher
Photocopying permitted by license only

PHOSPHORANES CONTAINING P-H BONDS

RICHARD A. KEMP
Catalysis Department, Westhollow Research Laboratory
Shell Development Company, Houston, Texas 77251

(Dedicated to my Ph.D. Mentor, Professor Alan H. Cowley, on the Occasion of his 60th Birthday)

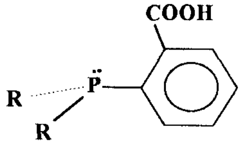
In an attempt to prepare *o*-dialkylphosphino-substituted benzoic acids we have discovered a unique cyclization process which affords phosphoranes containing P-H bonds. In this reaction the expected P(III) compound is not produced, but rather a phosphorane is formed by the internal oxidative addition of the carboxylic group to the substituted phosphine. Multi-nuclear NMR can yield a great deal of information about the exact structures of these compounds in solution. Characterization of the solid phase by DSC shows that the cyclic species formed can ring-open to yield the corresponding 8-P-3 phosphines. The P-H bond in these cyclic 10-P-5 complexes can be deprotonated using base to produce the *o*-dialkylphosphino-substituted benzoates rather than phosphoranides. These anions can chelate to metal ions, particularly nickel, to form highly active catalysts for the oligomerization of olefins. Use of these compounds as ligands to produce highly linear α-olefins will be discussed.

Key Words: phosphorane, oligomerization, apical P-H bond, catalysis, nickel chelate

INTRODUCTION

Although much of industrial chemistry is dominated by heterogeneous catalysis, several commercially important processes exist which utilize homogeneous catalysts.[1] Usually, the use of homogeneous catalysts indicate the inability of appropriate heterogeneous catalysts to perform the desired reaction with adequate selectivity, activity, and/or lifetime. Two commercially useful homogeneously-catalyzed reactions can be found in the Shell Higher Olefin Process, or SHOP. In the initial step of SHOP ethylene is oligomerized to high-purity, even-numbered linear α-olefins by use of an appropriate homogeneous catalyst, and in a later step of SHOP, internal olefins are isomerized and hydroformylated by a different homogeneous catalyst to produce primary alcohols. Commercial implementation of SHOP in 1977 has allowed Shell to become a dominant world-wide producer of α-olefins and internal olefins, producing approximately 2 billion pounds of these olefins annually. However, in order to provide customers with olefins of even higher purity, Shell is committed to continuously researching and developing new catalyst systems as well as process improvements.

There is much published work in the open and patent literature on the oligomerization of ethylene and other α-olefins using primarily nickel-based (Shell) or aluminum alkyl (Chevron, Ethyl) catalysts, and this area has recently been thoroughly reviewed.[2] Briefly, nickel-based catalyst systems discussed in the literature generally use ligands containing P~O or P~S moieties chelated to the metal.[3] As one would expect many chelating phosphorus compounds have been tried as ligands with various degrees of success in terms of catalyst activity and selectivity to α-olefins. Keim and co-workers have done a great deal of work to attempt to understand influences of the chelating ligand upon product quality.[4] We have been interested in preparing dialkyl-ligands of the type **1** to study as ligands for this reaction. Patented work by Shell[5] has shown that catalysts using ligands similar to **1** (R = Aryl) yield α-olefins with very high purities, and thus we were interested in preparing alkyl derivatives. However, upon attempted preparation of **1** (R = *c*-Hexyl) we discovered that this compound does not exist in the free phosphine-carboxylic acid form, but rather a rearrangement occurs to afford a cyclic phosphorane. We have further discovered that upon deprotonation these phosphoranes can function as effective ligands for the oligomerization of ethylene.



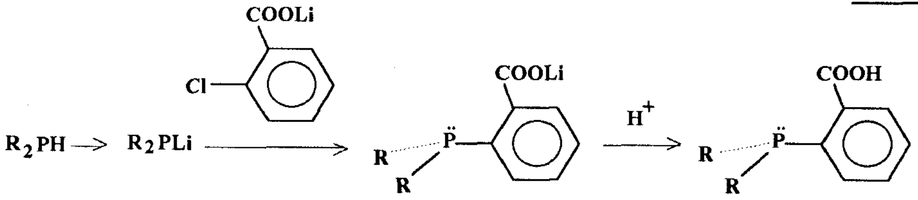
1

R = *c*-Hexyl

RESULTS AND DISCUSSION

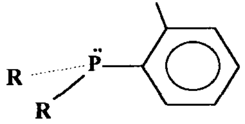
As mentioned in the Introduction we were originally interested in merely preparing dialkyl- derivatives of **1** to serve as chelating ligands for nickel in ethylene oligomerization studies. Our initial synthetic target was the dicyclohexyl-substituted **1**, primarily due to the relatively low cost and availability of dicyclohexylphosphine. Our strategy to prepare this compound is shown in **Scheme 1**.

Scheme 1



1

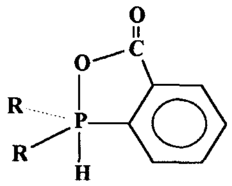
Conceptually, the phosphide anion attacks the Li salt of the *o*-chlorobenzoate in an ether solvent via a nucleophilic substitution in order to generate the desired *o*-dicyclohexylphosphinobenzoate. Extraction into water followed by protonation of this anion should yield the desired compound. Recovery of the acid complex would be by extraction with CH_2Cl_2 and recrystallization. However, as is the case with many synthetic schemes the final route varies from the designed route. It was originally intended that tetrahydrofuran would be the reaction solvent to allow for heating of the reaction mixture. However, despite some literature claims to the contrary, we found that dicyclohexylphosphide was not stable in THF. Switching to diethyl ether allowed the bright-yellow chemiluminescent phosphide to be prepared. When the *o*-chlorobenzoate salt was treated with the phosphide the major product obtained was tetracyclohexyldiphosphine (R_2P-PR_2). For reactions which occur by a S_{NRAD} mechanism [e.g., a soft nucleophile such as diphenylphosphide upon aryl halides] a possible by-product is a highly reactive $R_2P^{\cdot}$ radical which can couple to give R_2P-PR_2.[6] Issleib also notes the possibilities for lithium/halogen exchange in early work with lithium phosphides and aryl chlorides.[7] This could also lead to P-P coupling via elimination of LiCl. Fluoride is considered a better leaving group than chloride for aromatic nucleophilic substitution according to a recent textbook,[8] and the work of Issleib tended to confirm this. Switching to *o*-fluorobenzoate as the aryl halide gave significantly different results. Addition of the phosphide to the *o*-fluorobenzoate gave a colored solution after the addition was complete. The ^{31}P NMR spectrum of the rust-colored ether solution showed no evidence for R_2P-PR_2 formation. The only peaks present were a broad singlet at -8 ppm (discussed later) and dicyclohexylphosphine (roughly 80/20 ratio). The yield loss resulting in the presence of dicyclohexylphosphine most likely arises from attack on the aryl fluoride by the strongly basic phosphide to generate a benzyne and dicyclohexylphosphine. Addition of water to extract the desired anion followed by acidification to pH 2-3 gave a pale yellow solid in roughly 65-70% yield (after identification). Analytical data, discussed next, indicated that the compound isolated was clearly not the desired *o*-dicyclohexylphosphinobenzoic acid, at least not in the free acid form. In fact, it became clear that the resulting structure is the phosphorane **2** (five-coordinate phosphorus) rather than the desired phosphine **1**.



1

(not observed)

R = *c*-Hexyl



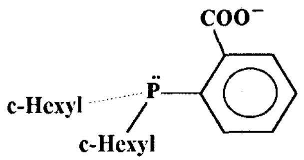
2

(observed)

The ^{31}P NMR spectrum of **2** (R = *c*-Hexyl) in CH_2Cl_2 showed only a single peak at +2.3 ppm ($J_{P\text{-}H}$ = 277 Hz), indicating a directly-bound hydrogen attached to phosphorus. The magnitude of this coupling is unusual and will be discussed momentarily. The isolated solid was further characterized by ^{13}C NMR. This spectrum indicated six peaks for the aromatic region and six peaks for the cyclohexyl region. A *J*-modulated spin-echo experiment indicated that in the phenyl region two carbons were not attached to hydrogen and four were attached to one hydrogen. Additionally, one quaternary carbon had a large J_{P-C} of 119.7 Hz, indicative of direct P-C bonding to a higher valent phosphorus (in Ph_3P, the J_{P-C} for the directly bound carbon is 11.9 Hz; for $Ph_3P{=}O$, the J_{P-C} for the directly bound carbon is 63.2 Hz). The cyclohexyl signals showed only one carbon with a single hydrogen attached - all others had two hydrogens. The carbon with the single hydrogen also had a large phosphorus coupling of 81 Hz. This is significantly larger than in (*c*-Hex)$_2$P-Ph ($J_{P-C(c\text{-Hex})}$ is 11.7 Hz), again indicating a higher valent phosphorus atom. The diastereotopic nature of the cyclohexyl groups has also been maintained, shown by the presence of six carbon signals. The ^1H NMR data were quite complex and difficult to interpret. However, the ^{31}P and ^{13}C NMR data allow the compound to be identified as **2** (R = *c*-Hexyl).

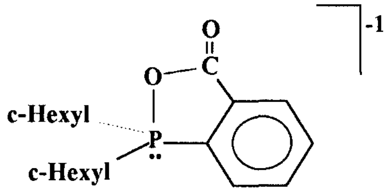
Phosphorane **2** can be assigned its structure with a great deal of certainty in accordance with the work of Martin, who has previously prepared a triarylalkoxy phosphorane which contained an apical P-H bond.[9] Other related apical P-H bonds can be found in charged compounds prepared by Verkade.[10] Martin's complex was synthesized by a different route, but the J_{P-H} measured was 266 Hz, similar to our value of 277 Hz. A P-H coupling from an equatorially substituted phosphorane would be expected to be in the range of 600-1100 Hz.[9] The apical nature of the P-H in a trigonal bipyramid geometry allows the dicyclohexyl- groups to maintain their diastereotopic nature, which is observed in the ^{13}C NMR. As noted above the magnitudes of the direct P-C couplings are indicative that phosphorus is in a higher valence state. A discussion of the influence of s character on the magnitude of P-C couplings can be found in a recent monograph.[11] Briefly, in the five-coordinate phosphorane **2** the directly-bound equatorial P-C couplings would be expected to be very large (sp^2 orbitals, 33% s); in a four-coordinate phosphonium salt or phosphine oxide (sp^3 orbitals, 25% s) the couplings would be large, but smaller than in the phosphorane; in a tri-coordinate phosphine (p^3 to sp^3 orbitals, <25% s) the P-C couplings would be small relative to the others. These differences will be very important when discussing the structures of the anion derived from the phosphorane (**3**) and the oxidized anion (**4**). The axial positions in the trigonal bipyramid can be assigned to the O- and H- ligands with the three C- ligands in the equatorial plane. To our knowledge **2** is thus the second compound to have the H- in an axial position rather than the equatorial plane, and using the nomenclature of Martin[12] this phosphorane is a 10-P-5 species (10 bonding electrons used in bonding 5 ligands to phosphorus). Additionally, infrared spectroscopy clearly identifies a P-H stretch at 2210 cm^{-1} as well as a C=O stretch at 1668 cm^{-1}. According to Martin this value for a P-H stretch is lower than is normally found, indicating the axial nature of the P-H bond.[9] No evidence of the "open" analog of our 10-P-5 phosphorane was seen. This would be the originally desired compound o-dicyclohexylphosphinobenzoic acid, an 8-P-3 phosphine (**1**).

The phosphorane itself cannot chelate to metals without first removing the proton attached to phosphorus. This generates an anion which is presumably the same anion as is generated from the initial attack of phosphide upon the aryl halide. These 10-P-4 phosphoranides are known to exist in equilibria with their 8-P-3 anionic counterparts.[13] The position of the equilibria must be experimentally determined - compounds have been synthesized which favor essentially one isomer exclusively, or a mixture of both observable in the NMR spectrum. In our case deprotonation of the phosphorane with KOH generates a single species observable by NMR with a ^{31}P NMR shift of -8 ppm with no P-H coupling. Detailed analysis of the ^{13}C NMR spectrum shows that the cyclohexyl- groups are still diastereotopic; however, the directly bonded P-C couplings have decreased markedly in magnitude. The directly bound P-C$_{c\text{-Hex}}$ shows a coupling of only 9.9 Hz versus 81 Hz in the phosphorane. The aromatic carbon attached to phosphorus also shows a dramatic decrease in P-C coupling from 119.7 Hz in the phosphorane to 16.2 Hz in the anion. These values compare very favorably with the values seen for the model compound (c-Hex)$_2$P-Ph which has P-C couplings of 11.7 Hz and 18.8 Hz for the P-C$_{c\text{-Hex}}$ and P-C$_{\text{Phenyl}}$ carbons, respectively. The ^{31}P NMR shift of the anion (-8 ppm) is also very similar to the shift of (c-Hex)$_2$P-Ph (+1.5 ppm). Thus, the structure of the anion is clearly the desired form - an 8-P-3 form with a free carboxylate group. However, it should be pointed out that this shift is also in the region that Martin has attributed to 10-P-4 phosphoranides containing phenyl rather than alkyl substituents, showing that ^{31}P chemical shifts are not completely reliable in assigning structures.[9] However, infrared analysis of **3** (KBr pellet) shows the presence of an ionized carboxylate group by stretches at 1570 cm^{-1} and 1385 cm^{-1}. This indicates that the -COO anion is not tied back to the phosphorus, as would be required in a 10-P-4 phosphoranide. Also, the P-H stretch and the C=O stretch have disappeared. Interestingly, anion **3** appears to be air-stable; no evidence for an oxidized product is obtained upon exposure to ambient air over several days.



3

8-P-3 Anion



(not observed)

10-P-4 Phosphoranide

While the only observable product is the 8-P-3 anion it is possible that an equilibrium exists between the 8-P-3 form and the 10-P-4 form. The 10-P-4 structure may be present in such small quantities that it is undetectable, and so it cannot be said with certainty that the 8-P-3 form is the only species present. However, with only one electronegative group (benzoate) attached to the phosphorus in **3** there would be a large buildup of negative charge on the phosphorus in the 10-P-4 form that can be alleviated by opening up to the 8-P-3 structure. Thus, once opened, electron pair repulsions between the phosphine lone pair and the free carboxylate would also be expected to further stabilize the 8-P-3 form. When the anion is protonated in solution (as in the initial synthesis) the closed 10-P-5 structure of the phosphorane is formed. It may be surmised that initial attack of the proton is at the free carboxylate group, leading to **1** rather than **2**. In solution **1** will be partially ionized since it is a weak acid. Rearrangement of **1** into **2** follows, most likely due to an intermolecular proton transfer reaction. Once a proton has been shifted to phosphorus then no electron pair repulsions preclude closing the ring. Steric models of **1** reveal a crowded center phosphorus atom, not easily accessible to the -COOH group in an intramolecular process. In related compounds the favoring of an open structure of the anion and closed structure of the protonated compound has been previously seen, but the reasons for this are not known.[14]

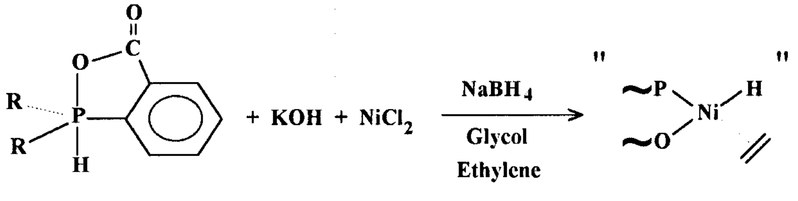
To further characterize **3** we attempted to oxidize it with hydrogen peroxide to a phosphine oxide anion. Addition of 30% hydrogen peroxide to **3** in water immediately causes a precipitate to form which quickly redissolves. The ^{31}P NMR spectrum shows a large downfield shift from -8 ppm in **3** to +59 ppm (singlet) in the product **4**. This large downfield shift is also observed in the oxidation of (c-Hex)$_2$P-Ph (+1.5 ppm) to (c-Hex)$_2$P(O)Ph (+40.1 ppm), thus indicating that the lone pair on the phosphorus has been converted to a P=O moiety. Once again ^{13}C NMR data for the oxidation product of **3** prove useful. Diastereotopic carbons are seen for the cyclohexyl-groups, indicating that both are still attached to the phosphorus. The magnitudes of the directly-bound phosphorus-carbon couplings have also increased, as would be expected upon oxidation of the phosphorus. The J_{P-C} for the P-aryl carbon has increased to 85.0 Hz and the J_{P-C} for the P-cyclohexyl carbon has increased to 65.4 Hz. These values are between the phosphorane and phosphine values mentioned earlier. In addition the ^{13}C chemical shift for the carbonyl carbon is unchanged from **3** (176.4 ppm), indicating very similar structures for **3** and the oxidized anion **4**, differing only in the conversion of the phosphine to a phosphine oxide.

We have also briefly examined the solid phase behavior of **2** by differential scanning calorimetry (DSC). Species **2** precipitates from acidic solution as a glass. When dried at elevated temperatures (~90°C) the phosphorane melts during this drying step and recrystallizes to give a solid which has a sharp melting point at 153°C. Upon continued heating in the DSC cell above 153°C the molten compound undergoes exothermic ring-opening at 227°C to afford the originally desired compound **1**. Cooling to room temperature does not convert **1** back into **2**; rather **1** solidifies as a glass with a T_g of 50°C. The conversion of **2** into **1** can easily be shown by infrared spectroscopy - the P-H stretch and the C=O stretch have disappeared and bands consistent with a carboxylic acid functionality are now present. These include an O-H stretch at 3415 cm^{-1}, a C=O stretch at 1692 cm^{-1}, and a C-O stretch at 1150 cm^{-1}. **1** cannot convert back to **2** in the melt whether for steric reasons (e.g., a solution is needed for intermolecular transfer of protons to form **2**), or electronic reasons (e.g., intermolecular hydrogen bonding when free -COOH groups are present). A more detailed analysis of the characterization of **2** as well as syntheses and characterization of related phosphoranes and zwitterions with alkyl groups other than cyclohexyl will be forthcoming.[15]

CATALYTIC RESULTS

The phosphorane **2** can be easily deprotonated using KOH to give the anion **3**. We were interested in using this anion **3** as a component in ethylene oligomerization studies. Briefly, the active catalyst is prepared by combining **2**, KOH, $NiCl_2 \cdot 6H_2O$, and $NaBH_4$ in a glycol solvent in the reactor under ethylene pressure for several minutes as shown in **Scheme 2**. The reactor is then brought to the desired conditions of temperature and pressure and the reaction begins. Exact quantities of each component used can be varied over a wide range, affecting the final α-olefin product distribution or quality slightly differently. Typical values are given in the Experimental section.

Scheme 2



2

Active Catalyst

Since Shell is a commercial supplier of olefins we have product specifications on the minimum α-olefin content of each cut (or, alternatively, the maximum level of internal and branched olefins allowed as impurities). We have found that use of **3** as a ligand in ethylene oligomerization yields catalysts which exceed our product specifications for α-olefin purities. Data shown in **Table I** compare measured levels of internal and branched olefin impurities at one specific cut, 1-dodecene; however, the advantages seen for the new catalyst system are also seen for the other α-olefin product cuts. Also seen are the advantages in product quality obtained by running at higher partial pressures of ethylene as well as by operating at lower reaction temperatures. **Table I** shows a wide range of conditions in which olefins meeting product specifications can be produced.

TABLE I

Catalytic Results Using **2** as Ligand Precursor

Run	Temp (°C)	Pressure (bar)	Reactor Testing, % C_{12} (internal)	Reactor Testing, % C_{12} (branched)	Commercial Specs, % C_{12} (internal)	Commercial Specs, % C_{12} (branched)
1	93	90	0.5	1.6	2.0	2.5
2	93	120	<0.4	1.2	2.0	2.5
3	80	90	<0.4	1.3	2.0	2.5
4	83	120	<0.4	0.8	2.0	2.5

As expected, raising the partial pressure of ethylene from 90 to 120 bar further enhances the insertion of ethylene over re-insertion of higher olefins. Re-insertion of these higher olefins is one route leading to increased branching (Run 1 versus Run 2). Lowering the temperature also disfavors re-insertion of higher olefins, as can be seen in **Table I** (Run 1 versus Run 3). Combining both approaches of high pressure and low temperature as shown in Run 4 can lead to catalyst systems which give α-olefins which easily meet and significantly exceed commercial quality specifications.

EXPERIMENTAL

All manipulations were carried out in an inert atmosphere using standard air-sensitive techniques. Reagents were procured commercially and used without further purification. Solvents were dried and distilled prior to use when appropriate. All ^{1}H, ^{13}C, and ^{31}P NMR spectra were obtained on a Bruker AMX-400 spectrometer. Chemical shifts are reported in ppm (δ) with positive values downfield of the reference (^{1}H, ^{13}C: $Si(CH_3)_4$; ^{31}P: external 85% H_3PO_4). Differential scanning calorimetry data were generated under a nitrogen atmosphere using a Perkin-Elmer Model 7 Thermal Analysis System.

Preparation of **2** *(1,1-Dicyclohexyl-3-oxo[3H-2,1-benzoxaphosphole]):*

In a nitrogen-purged 500 ml flask *o*-fluorobenzoic acid (7.01 g, 50 mmoles) was added along with 100 ml of anhydrous diethyl ether. The flask was cooled to -78°C and n-butyllithium (34 ml/1.6M in hexanes, 54.4 mmoles) was slowly added to form the lithium *o*-fluorobenzoate. The white precipitate was allowed to warm to room temperature (Slurry 1). In a separate 250 ml flask purged with nitrogen was added dicyclohexylphosphine (9.91 g, 50 mmoles) along with 100 ml of anhydrous diethyl ether. This solution was cooled to -78°C and n-butyllithium (36 ml/1.6M in hexanes, 57.6 mmoles) was added dropwise. The solution was allowed to warm slowly to room temperature, whereupon it turned bright yellow near 0-10°C (Slurry 2). The yellow chemiluminescent phosphide was allowed to stir at room temperature for approximately 1-2 hours. Slurry 1 was recooled to -78°C and Slurry 2 was added via cannulus over 8-10 minutes. The solution was allowed to warm to room temperature overnight whereupon it assumed a dark red/rust color. The solution was then filtered and then 250 ml of degassed deionized water was added to extract the anion. Initially upon water addition the solution became greenish, then more yellow as more water is added. The layers were separated in a separatory funnel and the organic phase was back-extracted with two 75 ml portions of water. The water layers were combined and acidified to pH 3 with diluted hydrochloric acid. An off-white precipitate forms which can be isolated by filtration, water-washing, and drying at 30-90°C for several hours. Isolated yield of air-and water-stable phosphorane **2** was 10.8 g, or 68% yield. Anal. Calculated: C: 71.6%, H: 8.5%; Found: C: 71.1%, H: 8.6%. ^{31}P (CD_2Cl_2): +2.3 ppm ($J_{P\text{-}H}$ 277 Hz); ^{13}C (CD_2Cl_2): *Phenyl Carbons:* 126 ppm ($J_{P\text{-}C}$ 119.7 Hz), 130.9 ppm ($J_{P\text{-}C}$ 14.3 Hz), 140.2 ppm ($J_{P\text{-}C}$ 10.5 Hz), 134.1 ppm ($J_{P\text{-}C}$ 12.4 Hz), 126.9 ppm ($J_{P\text{-}C}$ 11.4 Hz), 134.4 ppm ($J_{P\text{-}C}$ 2.0 Hz); *Cyclohexyl Carbons:* 36.7 ppm ($J_{P\text{-}C}$ 81.0 Hz), 30.0 ppm, 28.2 ppm ($J_{P\text{-}C}$ 3.8 Hz), 26.1 ppm ($J_{P\text{-}C}$ 16.7 Hz), 25.9 ppm ($J_{P\text{-}C}$ 17.8 Hz), 25.3 ppm; *C=O:* 166.7 ppm.

Preparation of Anion **3***:*

Anion **3** can be prepared simply by adding equimolar KOH to **2** in CH_2Cl_2 and isolating the insoluble product **3**, or in solution by using a mixed solvent of CH_2Cl_2 in water with KOH. In this case **3** is in the aqueous layer, and can be clearly identified by NMR. The NMR spectrum does not change upon exposure to air (several hours). ^{31}P (CD_2Cl_2): -8.0 ppm; ^{13}C (CD_2Cl_2): *Phenyl Carbons:* 128.9 ppm ($J_{P\text{-}C}$ 16.2 Hz), 130.7 ppm, 148 ppm ($J_{P\text{-}C}$ 31.4 Hz), 125.6 ppm, 125.3 ppm ($J_{P\text{-}C}$ 7.2 Hz), 127.6 ppm); *Cyclohexyl Carbons:* 32.7 ppm ($J_{P\text{-}C}$ 9.9 Hz), 28.7 ppm ($J_{P\text{-}C}$ 14.4 Hz), 26.0 ppm, 28.2 ppm ($J_{P\text{-}C}$ 9.9 Hz), 25.9 ppm, 25.1 ppm; *C=O:* 176.4 ppm.

Preparation of Oxidized Anion 4:

To a solution of **3** in CH_2Cl_2/H_2O is added H_2O_2 dropwise, giving a white precipitate which immediately goes back into the aqueous solution. The oxidized product **4** can be positively identified by NMR. ^{31}P (CD_2Cl_2): +59.0 ppm; ^{13}C (CD_2Cl_2): *Phenyl Carbons:* 125.9 ppm ($J_{P\text{-}C}$ 85.0 Hz), 128.0 ppm ($J_{P\text{-}C}$ 9.5 Hz), 142.4 ppm ($J_{P\text{-}C}$ 9.5 Hz), 128.7 ppm (9.5 Hz), 132.9 ppm ($J_{P\text{-}C}$ 6.7 Hz), 131.9 ppm; *Cyclohexyl Carbons:* 37.1 ppm ($J_{P\text{-}C}$ 65.0 Hz), 26.1 ppm ($J_{P\text{-}C}$ 25.1 Hz), 26.2 ppm, 26.4 ppm ($J_{P\text{-}C}$ 3.6 Hz), 26.5 ppm ($J_{P\text{-}C}$ 2.7 Hz), 25.6 ppm; *$C=O$:* 176.4 ppm.

Preparation of Dicyclohexylphenylphosphonium Tetrafluoroborate 5:

Dicyclohexylphenylphosphine (1.00 g, 3.7 mmoles) was added to a nitrogen-purged flask along with 15 ml of THF. A solution of HBF_4 in diethyl ether (0.60 g, 3.7 mmoles) was added slowly via syringe. A precipitate formed after approximately 1-2 minutes. CH_2Cl_2 was added to redissolve the precipitate. The presence of a phosphonium salt was shown by NMR. ^{31}P (CD_2Cl_2): +26.0 ppm ($J_{P\text{-}H}$ 486 Hz).

Catalytic Experiments:

All laboratory-scaled catalytic experiments were performed in a 4-unit, batch autoclave system under complete computer control. The 500-cc Zipperclave® reactors were obtained from Autoclave Engineers, Inc. The in-house design for the reactors allowed for ethylene to be fed on demand as the pressure dropped in each individual unit during the conversion of ethylene to the less-volatile higher olefins. The reactors were capable of operating at pressures up to 140 bar and temperatures from 60°C to 250°C. All four units were capable of independent operation. Analysis of the product olefin stream was by a Hewlett-Packard Model 5880A gas chromatograph using a DB-1 capillary column. Laboratory reactor results were further validated on a significantly larger scale in a developmental pilot plant unit.

A typical catalyst preparation is described next. The catalyst solution was prepared by adding **2** (0.159 g, 0.50 mmoles), $NiCl_2.6H_2O$ (0.261 g, 1.10 mmoles), and KOH (0.028 g, 0.50 mmoles) in 175 grams of a glycol solvent. This solution was stirred for approximately 15 minutes under 30 bar ethylene pressure. The catalyst is activated by adding a solution of $NaBH_4$ (0.053 g, 1.40 mmoles) in 25 grams of glycol. The reactor is then raised to the desired temperature and pressure. Ethylene is fed on demand as the pressure in the reactor decreases from conversion of the gaseous ethylene into less volatile olefins. The resulting olefin stream is immiscible with the glycol solvent and can be separated and analyzed by gas chromatography. Levels of α-olefins, internal olefin impurities, and branched olefin impurities at each specific olefin fraction can be determined by GC. Product distributions followed a geometric, Schulz-Flory distribution. The amount of each individual oligomer is related to the amount of the preceding oligomer by a constant amount. In order to compare product qualities it is necessary to run all experiments at the same constant factor.

ACKNOWLEDGMENTS

I wish to acknowledge the assistance of several staff members at Westhollow for useful discussions, particularly Dr. J.H. Worstell, Dr. P.A. Kibala, and Dr. W.M. Skiff. Thermal analysis data were obtained by Dr. J.S. Grebowicz, all NMR spectra were acquired by Ms. D.D. Cansler, and infrared spectra were obtained by Ms. V.J. Spence. Catalyst preparations and reactor runs were ably performed by Mr. J.E. Brixey and Mr. L.L. Marshall. Useful discussions with Professor M. Lattman at Southern Methodist University in Dallas are also acknowledged. I thank the Detergents and EO/EG Business Center of Shell Chemical Company for project funding and permission to publish. Lastly, I thank Professor Alan H. Cowley of The University of Texas for providing a tremendously stimulating, educational, and entertaining environment during the three years I spent in his group as a graduate student. His intense enthusiasm for discovery is a trait which he fortunately has passed on to many of his former graduate and post-doctoral students.

REFERENCES

1. G.W. Parshall and S.D. Ittel, *Homogeneous Catalysis* (John Wiley, New York, 1992), 2nd ed.
2. A.M. Al-Jarallah, J.A. Anabtawi, M.A.B. Siddiqui, A.M. Aitani, and A.W. Al-Sa'doun, *Catal. Today* **14**, 1 (1992).
3. G. Braca, M. Di Girolamo, A.M. Raspolli Galleti, G. Sbrana, M. Brunelli, and G. Bertolini, *J. Mol. Cat.* **74**, 421 (1992).
4. K. Hirose and W. Keim, *J. Mol. Cat.* **73**, 271 (1992), and references therein.
5. See, for example, E.F. Lutz, U.S. Patent No. 4,528,416 (1985).
6. This speculation in based on work done by J.A van Doorn at Royal Dutch/Shell's laboratory in Amsterdam.
7. K. Issleib, A. Tzschach, and H. Block, *Chem. Ber.* **101**, 2931 (1968).
8. J. March, *Advanced Organic Chemistry : Reactions, Mechanisms, and Structure* (John Wiley, New York, 1985), 3rd ed., Chap. 13, p. 587.
9. M.R. Ross and J.C. Martin, *J. Am. Chem. Soc.* **103**, 1234 (1981); M.R. Ross and J.C. Martin, *Phosphorus Chemistry* (ACS Symposium Series, Washington, D.C., 1981), L.D. Quin and J.G. Verkade, Eds., Volume **171**, pp. 429-433.
10. J.C. Clardy, D.S. Milbrath, J.P. Springer, and J.G. Verkade, *J. Am. Chem. Soc.* **98**, 623 (1976); C. Lensink, S.K. Xi, L.M. Daniels, and J.G. Verkade, *J. Am. Chem. Soc.* **111**, 3478 (1989); M.A.H. Laramay and J.G. Verkade, *J. Am. Chem. Soc.* **112**, 9421 (1990).
11. L.D. Quin, *Methods in Stereochemical Analysis* (VCH, New York, 1987), Volume **8**, pp. 398-401.
12. C.W. Perkins, J.C. Martin, A.J. Arduengo, W. Lau, A. Alegria, and J.K. Kochi, *J. Am. Chem. Soc.* **102**, 7753 (1980).
13. There are several references to this phenomenon - for example, see I. Granoth and J.C. Martin, *J. Am. Chem. Soc.* **100**, 7434 (1978); I. Granoth and J.C. Martin, *J. Am. Chem. Soc.* **101**, 4623 (1979); or B. Garrigues, M. Koenig, and A. Munoz, *Tet. Lett.* **43**, 4205 (1979).
14. Professor M. Lattman, Southern Methodist University, private communication.
15. R.A. Kemp and P.A. Kibala, manuscript in preparation.