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SAND2005-6754

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Printed February 2006

LDRD Final Report on New Homogeneous Catalysts for Direct Olefin Epoxidation (LDRD 52591)

Richard A. Kemp, Karen I. Goldberg, Constantine A. Stewart, James E. Miller,
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National Nuclear Security Administration under Contract DE-AC04-94AL85000.

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Abstract

This report summarizes our findings during the study of a novel homogeneous epoxidation catalyst system that uses molecular oxygen as the oxidant, a “Holy Grail” in catalysis. While olefins (alkenes) that do not contain allylic hydrogens can be epoxidized directly using heterogeneous catalysts, most olefins cannot, and so a general, atom-efficient route is desired. While most of the work performed on this LDRD has been on pincer complexes of late transition metals, we also scouted out metal/ligand combinations that were significantly different, and unfortunately, less successful. Most of the work reported here deals with phosphorus-ligated Pd hydrides [(PCP)Pd-H]. We have demonstrated that molecular oxygen gas can insert into the Pd-H bond, giving a structurally characterized Pd-OOH species. This species reacts with oxygen acceptors such as olefins to donate an oxygen atom, although in various levels of selectivity, and to generate a [(PCP)Pd-OH] molecule. We discovered that the active [(PCP)Pd-H] active catalyst can be regenerated by addition of either CO or hydrogen. The demonstration of each step of the catalytic cycle is quite significant. Extensions to the pincer-Pd chemistry by attaching a fluorinated tail to the pincer designed to be used in solvents with higher oxygen solubilities are also presented.

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General Introduction / Executive Summary

The ability to selectively oxidize organic molecules directly using oxygen gas is one of the “Holy Grails” in catalytic chemistry (1). This is due to the huge energy savings possible if organic molecules can be converted directly and efficiently into other reactive molecules and intermediates used throughout the chemical industry. While a simple olefin like ethylene can be epoxidized selectively to ethylene oxide using heterogeneous silver catalysts, higher olefins such as propylene and cyclohexene containing allylic hydrogen atoms cannot be epoxidized at all using the same technology. These epoxides currently must be produced via multi-step synthetic routes (2). In this study we have been examining the production of higher olefin epoxides (oxiranes) using molecular oxygen as the oxidizing species, and homogenous, late transition metal – pincer complexes as possible catalysts. We have hypothesized a homogenous catalytic cycle beginning with a metal hydride that can react with oxygen to form a metal hydroperoxide. This hydroperoxide can donate an oxygen atom to generate the epoxide, and after reaction a metal-hydroxide species is formed. The rest of the proposed catalytic cycle involves regenerating the metal hydride by using either CO or hydrogen as a transforming agent. In order to fundamentally understand this cycle better, we have examined each proposed step in the cycle individually in stoichiometric reactions. We have demonstrated each individual step of this catalytic cycle in isolation, and have developed a single system (a phosphorus-pincer palladium complex) that can perform each of the steps.

During the course of this project we examined a large number of different organometallic ligand-metal combinations to attempt the direct conversion of higher olefins (such as propylene or cyclohexene) to their respective epoxides using molecular oxygen as the oxidant. If we are successful, this is breakthrough technology that can affect the study of all partial oxidation processes. While we have not solved this problem, we have made tremendous progress on the understanding and development of a homogeneous route to these epoxides. We believe that transition metals that appear early in the periodic chart are too oxophilic to complete the catalytic cycle. Therefore, we have concentrated our efforts on middle-late transition metal complexes. We spent a great deal of effort to use chelating, N,O- donating salen ligands with various metals such as Fe, Co, and the like; however, the complexes proved difficult to characterize and cleanly identify. Concurrent with this, we were also examining N or P-ligated pincer ligands to Pt and Pd (3). With a single PCP-pincer ligand complexed to Pd we were able to demonstrate individually all the steps of the proposed catalytic cycle. As well, we were able to characterize some of the intermediates explicitly using X-ray crystallography. Using the aforementioned PCP-Pd metal ligand combination we were able to synthesize and definitively characterize the (PCP)Pd-H complex, which is believed in our catalyst cycle to be the key intermediate. We demonstrated the insertion of oxygen gas into this species to form (PCP)Pd-OOH, which was identified by its X-ray structure. This is the first example of a well-characterized insertion of oxygen into a Pd-H bond. Further experiments demonstrated that the insertion of oxygen was not a radical process. The (PCP)Pd-OOH complex could donate an O atom to acceptors, some more cleanly than others. Reaction with propylene (the main target molecule) gave a mixture of products, but reaction with cyclohexene gave cyclohexene cleanly. As well, reaction with triphenylphosphine gave the triphenylphosphine oxide cleanly. After O atom transfer, a (PCP)Pd-OH species remained, which could be converted back to the (PCP)Pd-H starting material by reaction with CO, to form a well-characterized metal hydroxycarbonyl,

followed by decarboxylation. We also discovered a new route to regenerate the desired(PCP)Pd-H complex – if hydrogen gas was used then water was eliminated from the presumed (PCP)Pd(H)₂-OH intermediate to give the Pd-H species. Thus, we can mimic Nature by capitalizing upon the elimination of water to regenerate our catalyst. We have also examined a number of other P-pincer-metal combinations, and also have examined pincers that contain other heteroatoms, such as N or S. These have not been as successful as the P-ligated pincers in our studies. We have also attempted to prepare new fluorinated pincer ligands for use with metal complexes in perfluorinated solvents. As the solubility of oxygen is significantly higher in fluorinated solvents versus hydrocarbon solvents, we had hoped that the increase in available oxygen in these systems would lead to more selective reactions. However, the synthetic chemistry to prepare these ligands without cleavage of the tails is difficult, and the status at the end of the project for the perfluorinated solvents is less certain than with the PCP-ligands.

Non-Pincer Metal-Ligand Complexes

Introduction

When we began this research project we were unsure of what ligand/metal combination would be functional for the epoxidation reaction. Our thought process, briefly outlined above in the *Executive Summary*, was that early transition metals (those on the left-hand side) would be too oxophilic to carry out an effective catalytic cycle, and so we scouted some middle-to-late transition metal-ligand combinations. This initial section is concerned with ligands that are not based on phosphorus-pincer ligands. This area did not prove to be as successful as the pincer chemistry, and so the coverage is more for archival purposes.

Discussion

The ligand system we chose to examine for middle-transition metals is the so-called salen ligand (4). The basic salen ligand, along with potential modifications, is shown in **Figure 1**. The chemistry of the salen ligand is dominated by its dianion, forming a chelating mixed O/N ligand to tightly coordinate to metals. As we were interested in preparing (salen)M-H species, we were interested in metals with at least an oxidation state of +3.

Figure 1. Various forms of the salen ligand, demonstrating possible variations on the basic structure.

Common metals with +3 oxidation states in the middle of the transition metal series are Co and Fe. It is known that FeCl_3 reacts with salenH_2 to yield a complex of Fe (Eq. 1) (5).

It should be pointed out that Fe^{3+} is a paramagnetic species, and as such, conventional methods of characterization such as NMR are not applicable. Being paramagnetic creates a much more difficult situation to try to identify the product(s). We attempted to prepare both hydride and hydroxide versions of this complex via the following reactions (Eq. 2 and 3).

These reactions were carried out in acetonitrile, and gave highly colored products. Efforts to grow single crystals in order to definitively characterize the solids formed were unsuccessful. It should also be pointed out that we did not see characteristic Fe-H or Fe-OH stretches in the infrared spectrum, thus indicating we may not have formed the desired Fe-H or Fe-OH species.

We also attempted related reactions with Co. Beginning with Co(salen) (a Co^{2+} paramagnetic species) we oxidized it to a stable, Co^{3+} diamagnetic salen salt (6). We are unsure whether the attempted replacement of the perchlorate anion with hydride in pyridine by use of a reducing agent went as planned to form a Co(H)salen complex. We did see a resonance in the ^1H NMR at -12.8 ppm, indicating a metal hydride, but no Co-H stretches were seen in the infrared spectrum. Although it is possible that reduction back to a paramagnetic Co^{2+} state might have occurred for the reaction, we tend to discount this as we could obtain a ^1H NMR signal (Eq. 4), indicating that the compound is diamagnetic.

We also examined the reactivity of later transition metal salen complexes. We attempted to prepare higher oxidation state derivatives of the known Pt(salen) and Pd(salen) complexes by oxidative addition reactions (7). The additions of various Lewis acids such as H^+ or CH_3^+ were not successful. No reaction was seen by NMR in any case. The Pd^{2+} and Pt^{2+} salen complexes appear to be extremely stable and unreactive for oxidative addition.

As the salen complexes were proving problematic, we decided to focus our efforts on the pincer ligand species with late transition metals, especially Pd. The next section will focus on those efforts.

Pd-Based Complexes with Pincer Ligands

Introduction

Pincer ligands are an emerging class of chelating ligands that have seen explosive growth and interest over the past several years (see, *e.g.*, 3). One reason for their intense interest is the fact that they can be so easily modified and derivatized to form a wide range of ligands that differ in steric and electronic requirements (**Figure 2**). Pincer ligands can be prepared with donor atoms that range from hard ligands (O, N) to softer ligands (P, As, S). Thus, the ligand interactions with the metals that are “encapsulated” by these multi-dentate ligands can often be fine-tuned by synthetic chemists to yield the desired properties of the complex. An additional benefit to these ligands is that they can form very stable complexes with metals. The complexes are not only stable in terms of not dissociating from the metal easily, they are also stable complexes to the environment, such as oxygen and water. As we propose a catalytic cycle that has at its heart a direct reaction with oxygen, and a possible water molecule being formed as a side product, it is imperative that the organometallic complexes we make be stable to oxygen and water.

Figure 2. Different carbon-based pincer ligand types. The metal sits directly bonded to the carbon atom on the ring, as well as to the heteroatom arms. Other derivatives can incorporate N in place of the coordinating ring carbon (thus changing the charge on the ring from -1 to neutral) or tails hanging off the back end of the aromatic ring.

Discussion

Insertion of Molecular Oxygen into a Palladium(II)-Hydride Bond

While still a relatively rare transformation, the direct reaction with molecular oxygen to form a hydroperoxide has been observed for a few different transition metal hydrides (8). However, similar reactions in model palladium systems have remained elusive. This was particularly surprising since just such a transformation has been repeatedly offered as a proposal for the mode of oxygen activation in various palladium catalyzed oxidation reactions (9). In the course of our research toward the development of a catalyst for propylene oxidation using molecular oxygen as the oxidant, we have observed the first example of this reaction for Pd—insertion of molecular oxygen into a palladium(II) hydride bond to form an (η^1 -hydroperoxo)palladium(II) complex.

Upon exposure to O_2 (0.8 – 10 atm), solutions of (^{tBu}PCP)PdH (**1**) (ref. 10) (^{tBu}PCP = [1,3-($CH_2P^tBu_2$) C_6H_3]) in benzene- d_6 react cleanly to form (^{tBu}PCP)Pd(OOH) (**2**) and

(^{*i*}BuPCP)Pd(OH) (**3**) in variable ratios (Eq. 10). While the initial ratio of **2**:**3** can be up to 25:1, over time **2** is observed to convert to **3** and, ultimately, **3** is obtained in high yield (90%).

Complex **3** was also synthesized independently by the addition of KOH to (^{*i*}BuPCP)Pd(ONO₂), similar to the reported preparation of the closely related hydroxide complex, (^{*i*}PrPCP)Pd(OH) (**11**).

There are only a small number of structurally characterized transition metal η^1 -hydroperoxide species (**12**). X-ray quality crystals of **2** were obtained from the reaction of **1** with O₂ (10 atm) in pentane at -10 °C. The ORTEP is shown in **Figure 3** (13). The unit cell is comprised of two molecules of **2**. Hydrogen bonding occurs between neighboring hydroperoxyl moieties, forming a six-membered, radially symmetric ring (Figure 1). A similar arrangement was reported for the platinum(IV) hydroperoxo species, (Tp^{Me2})PtMe₂(OOH) (Tp^{Me2} = hydridotris(-3,5-dimethylpyrazolyl)borate) (**12a**).

Figure 3. Molecular structure of **3**. Ellipsoids are shown at 50% probability and non-located hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Pd(1) – O(1) 2.074(3); Pd(1) – C(1) 2.022(3); O(1) – O(2) 1.470(4); O(2) – H(2) 1.10(4); C(1) – Pd(1) – P(2) 84.34(10); C(1) – Pd(1) – O(1) 175.27(11); P(1) – Pd(1) – P(2) 167.68; Pd(1) – O(1) – O(2) 108.53(19); O(1) – O(2) – H(2) 99(2).

The reaction of **1** with O₂ to form **2** and **3** was conveniently monitored by ¹H{³¹P} NMR spectroscopy. The reactions of **1** with O₂ were first order with respect to **1**, as shown by the exponential decay in **Figure 4a**, and the linear fits for the first order plots of ln[**1**] versus time in **Figure 4b**. The doubling of the rate constant from 5.6(8) × 10⁻⁴ s⁻¹ under 5 atm O₂ to 1.13(3) × 10⁻³ s⁻¹ under 10 atm O₂ clearly indicates that there is also a first-order dependence on O₂ (**14**).

The reaction of the deuteride analog **1-d₁** with O₂ (to form **2-d₁** and **3-d₁**) resulted in a significant retardation in the observed reaction rate (10 atm O₂; *k*_{obs} = 1.95(11) × 10⁻⁴ s⁻¹). This

corresponds to a kinetic isotope effect ($k_{\text{H}}/k_{\text{D}}$) of 5.8(5) for the insertion of O_2 into the Pd-H(D) bond. A similar KIE value was recorded when the measurement was repeated under 5 atm of oxygen. Based on the Pd-H(D) stretching frequencies for **1** (1717.8 cm^{-1}) and **1-*d*₁** (1227.5 cm^{-1}), a maximum theoretical kinetic isotope effect for direct homolytic cleavage of 3.3 can be calculated (15). While it is not obvious why the observed KIE is significantly greater than this value, the large magnitude of the observed KIE strongly implicates the involvement of Pd-H bond cleavage in the rate-determining step.

Figure 4. (a) Reaction of **1** with O_2 (5 atm) over time. The concentrations of **1** (●), **2** (●) and **3** (■) are shown. (b) Linear relationship between $\ln[\mathbf{1}]$ and time. Kinetic plots for reactions of **1** with 10 atm (■) and 5atm (●) O_2 are shown.

The reaction of **1** with O_2 to form **2** is similar to the reported reaction of $(\text{Tp}^{\text{Me}_2})\text{PtMe}_2(\text{H})$ with O_2 to form the corresponding platinum(IV) hydroperoxide complex (**12a**). The platinum reaction was proposed to proceed via a radical chain pathway. This mechanistic proposal was based on the dramatic difference in reaction rates between reactions carried out in the light and in the dark, and between reactions with added radical initiator or radical inhibitor. Involvement of radical mechanisms have also been implicated in other reported reactions of metal hydrides and oxygen (**12a**, **16**). In contrast to these reactions, the insertion of molecular oxygen into the Pd-H bond of **1** was found to proceed at reproducible rates that were relatively insensitive to the presence of radical inhibitors or light. When the reaction of **1** with O_2 (10 atm) was carried out in the presence of radical inhibitors 2,6-di-*tert*-butyl-4-hydroxytoluene (BHT; $k_{\text{obs}} = \text{ca. } 1.4\text{ s}^{-1}$) and 2,2,6,6-tetramethyl-1-piperidinyloxy free radical (TEMPO; $k_{\text{obs}} = 1.16\text{ s}^{-1}$), no significant effect on the reaction rate was observed (17). Furthermore, parallel reactions carried out under ambient light and in the dark showed highly comparable rates for the consumption of **1**. These results strongly suggest that the insertion of O_2 into the Pd-H bond of **1** to form **2** occurs via a non-radical pathway.

In summary, direct insertion of molecular oxygen into a palladium hydride bond has been observed for the first time, and the palladium hydroperoxide product has been structurally characterized. Preliminary mechanistic studies indicated a non-radical pathway with second order rate law (first order in palladium and first order in oxygen) and significant Pd-H bond cleavage in the rate-determining step. A mechanism involving the direct reaction of the oxygen with the Pd-H bond or, alternatively, coordination of oxygen to the palladium(II) center followed by migratory insertion into the Pd-H bond would be consistent with the data. The apparent absence of radical involvement in this insertion is of particular interest since the selectivity of oxidation reactions can be compromised by the propensity of

O₂ to participate in radical pathways. This identification of a clean, well-characterized and non-radical activation of dioxygen by an isolable palladium(II) complex should have significant impact on the development of palladium catalyzed selective aerobic oxidation reactions.

Reactivity of a Palladium(II)-Hydroperoxide Complex

The hydroperoxo species, **2**, is relatively stable as a solid at ambient temperature. However, solutions of **2** in benzene-*d*₆ were observed to form **3**. Other metal hydroperoxide complexes have been observed disproportionate to form their corresponding hydroxide complexes and O₂ (18). In contrast to the reaction of **1** with O₂ to generate **2** and **3**, the rate of conversion of **2** to **3** was variable and appeared sensitive to light. For reactions of **1** and O₂ carried out in ambient light, **3** was present at higher concentrations than **2** throughout the reaction, while in the dark the ratio of **2** to **3** was substantially higher. This is suggestive of the involvement of a radical mechanism for the conversion of **2** to **3**, perhaps similar to the decomposition of organic analogs like *tert*-butyl hydroperoxide, which decomposes to form *tert*-butyl alcohol and O₂ (19). Further investigations into the mechanism of the conversion reaction of **2** to **3** are underway.

Preliminary experiments to examine the potential of the hydroperoxide species, **2**, to act as a selective oxidizing reagent were also carried out. Reaction of **2** with triphenyl phosphine leads to oxidation to triphenyl phosphine oxide with concomitant formation of **3** (Eq. 11). This establishes the viability of the PdOOH group to transfer an oxygen atom. Preliminary results also suggest that under suitable conditions, **2** reacts with cyclohexene to produce cyclohexene oxide. Experiments are planned to expand and confirm this chemistry with respect to other olefins and to optimize this reaction over the disproportionation reaction of **2** noted above. Mechanistic experiments on both the disproportionation and the olefin epoxidation will be carried out to provide insight into the optimization of the epoxidation reaction.

Regeneration of Palladium(II) Hydride from Palladium(II) Hydroxide

One of our proposed methods of regenerating the metal hydride from the metal hydroxide was reaction of the metal hydroxide with carbon-monoxide followed by release of carbon dioxide. Literature precedent exists for carbon monoxide insertion into palladium hydroxide bonds, including into the palladium-hydroxide bond of a complex closely related to hydroxide complex **3** (20). It was recently reported that in the presence of a large excess of carbon monoxide, (ⁱPrPCP)Pd(OH) reacts by CO insertion into the Pd-OH bond to form the palladium(II) hydroxycarbonyl complex, (ⁱPrPCP)Pd(COOH) (**4**). Under lower pressures of CO, a binuclear species with a bridging CO₂ group is produced with an equivalent of water. This same species is formed when the mononuclear (ⁱPrPCP)Pd(COOH) is deprived of a CO atmosphere. Thus, rather than loss of CO₂, the hydroxycarbonyl compound loses carbon monoxide and water, to reform the binuclear species (12).

We anticipated that the introduction of increased steric bulk on the tridentate ligand (*i.e.* the use of *tert*-butyl in place of *iso*-propyl groups) might prevent the formation of binuclear complexes. Indeed, exposure of **3** to 5 atm of carbon monoxide led to the formation of a single species with NMR signals consistent with that expected for the hydroxycarbonyl species ($^{t\text{Bu}}\text{PCP}$)Pd(COOH) (**4**). No evidence for a dinuclear complex was observed. When the CO atmosphere was removed and the solution of **4** heated in a closed system to 80 °C, several products are observed, including **1**, **3**, and a new species, ($^{t\text{Bu}}\text{PCP}$)Pd(O₂CH). This reactivity illustrates the viability of the desired palladium hydride regeneration but also points to the reversibility of the CO insertion and a potentially limiting competitive reaction of the (PCP)PdH with carbon dioxide to form a formate complex. Further investigations of this reaction are needed to understand the reactivity and learn how to control the selectivity for the hydride product.

The potential of regenerating **1** by the reaction of **3** with hydrogen gas was also explored. Oxidative addition of H₂ to **3** would be expected to produce a Pd(IV) intermediate which could reductively eliminate water resulting in the formation of **1**. Preliminary results on this regeneration pathway are promising. Heating a C₆D₆ solution of **3** at 50 °C for several hours in the presence of hydrogen gas, results in the appearance of **1**. No Pd(IV) intermediates are observed.

Putting a Fluorous Tail on the Pincer Ligand

Ideally we would like to conduct the partial oxidation of propylene to produce propylene oxide in fluorous solvents for three reasons; 1) fluorous solvents are non-flammable and heat stable (21), 2) the oxygen solubility of fluoroalkyl solvents is slightly higher than other conventional solvents, and 3) the ability to separate a fluorous soluble catalyst from an alkyl phase soluble product can be done more easily.

The solubility of oxygen in fluoroalkyl solvents is known. For example, the oxygen solubility in perfluoro methylcyclohexane vs. tetrahydrofuran (O₂ solubility, mole fraction) is roughly a factor of 5 (22).

The other foreseen advantage of using a fluoroalkyl soluble catalyst comes during the process of separating the product from the catalyst. Horváth, Gladysz and others have been very active in the area of fluorous biphasic chemistry (22-28). The concept is one of designing a catalyst (perfluoro-substituted) that will locate in the fluoroalkyl phase and the reactants and products in the alkyl phase. At an elevated temperature the fluoroalkyl and alkyl phases will be soluble and allow for the chemistry to take place. Upon lowering the

temperature the two solvents will partition with the catalyst going back into the fluorous phase and the product into the alkyl phase. Liquid-liquid counter flow extraction could then be used to separate the product from the catalyst.

The synthetic approach for this project targeted the preparation of a number of fluoroaryl-substituted thiopincer and perfluoroalkyl-substituted phosphinepincer complexes.

In addition to preparing the ligands mentioned above we also investigated the preparation of the SCSPd-H, which could be a necessary precursor catalyst for the oxidation of propylene to propylene oxide.

Fluoroaryl substituted thiopincer ligands

Bis-(perfluoroaryl thiomethyl)benzene (29) reported by Arroyo and coworkers was prepared along with two new fluoroaryl substituted thiopincer ligands, these are shown below.

reported by Arroyo, *et al.*
Synthesis, 10, pp.
1565 - 1568, 2003.

This route involves the preparation of an intermediate bis(fluorosubstitutedaryl phenyl thiolate) lead compound (30) followed by reaction with 3,5-di(bromomethyl) benzene. In most cases the yields were good (57- 97%) and the purity was high for the bis(fluoroaryl thiomethyl)benzene ligands. The general reaction scheme is shown below.

These three bis(fluoroaryl thiomethyl) benzene ligands were reacted with bis(acetonitrile) palladium dichloride. The $\text{ArF}_5\text{SCSArF}_5$ and the ArFSCSArF did not react and gave back only starting material. The $\text{ArF}_2\text{SCSArF}_2$ reacted with bis(acetonitrile) palladium dichloride to give $[\text{ArF}_2\text{SCSArF}_2]\text{PdCl}$. See the reaction scheme next.

Initial attempts to reduce $[\text{ArF}_2\text{SCSArF}_2]\text{PdCl}$ to the hydride were unsuccessful as was the case when trying to reduce SCSPdCl to the hydride (reducing agents; NaBH_4 , LiAlH_4 , and $n\text{-Bu}_3\text{SnH}$).

Preparation of 4-fluoroalkyl-2,6-Bis[(di-*t*-butylphosphino)methyl]phenyl ligands

Several routes were investigated in an effort to prepare fluoroalkyl substituted 2,6-bis[(dialkylphosphino)methyl]phenyl ligands. For the most part these routes were unsuccessful for one reason or another.

For instance, it was found that putting the fluoroalkyl tail at the 1-position of the 3,5-dimethylbenzene prior to brominating the methyl groups the tail cleaved off and 1-bromo-3,5-dibromomethyl benzene was isolated in good yield. Also, the yield was rather low when using the Grignard route to attaching the perfluoroalkyl ethyl tails to these *m*-xylenes. In the end, the method to preparing a perfluoroalkyl tail to a bis(phosphino)benzene ligand is shown below and involved the use of a silyl group as a linker.

The complexation of 1-heptafluoro-(1,1,2,2-tetrahydrodecyl) dimethylsilyl-3,5-bis-[(*t*-butyl)phosphinomethyl]benzene with palladium is shown below. This is a modified route from that reported by Shaw and Moulton (10).

The use of an excess of triethylamine is necessary to neutralize the hydrogen chloride that is produced as the palladium inserts into the C-H bond. Without the base the free HCl will attack the silicon at the 1-position and cleave the tail off giving heptafluoro-(1,1,2,2-tetrahydrodecyl) dimethylsilylchloride and PCP-PdCl complex.

A comparison of the ^{31}P chemical shifts and melting points between PCP-PdCl and $\text{CF}_3(\text{CF}_2)_5\text{CH}_2\text{CH}_2(\text{Me}_2)\text{Si-PCP-PdCl}$ is shown below. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ spectra indicate that the perfluoroalkyl-PCP-PdCl complex was made.

$\delta^{31}\text{P} = 72.5 \text{ ppm}$
 $\text{mp} = 270 - 294 \text{ deg C}$
 C.J. Moulton & B.L. Shaw
JCS Dalton, pp. 1020-1-24, 1976

$\delta^{31}\text{P} = 73.0 \text{ ppm}$
 $\text{mp} = 205 \text{ deg C, dec.}$
 This work.

Acknowledgements

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the U.S. Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94-AL85000. This project was funded under LDRD 52591.

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