The effects of metals and ligands on the oxidation of $n$-octane using iridium and rhodium “PNP” aminodiphosphine complexes

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Abstract
Ir and Rh “PNP” complexes with different ligands are utilized for the oxidation of $n$-octane. Based on the obtained conversion, selectivity, and the characterized recovered catalysts, it is found that the combination of Ir and the studied ligands do not promote the redox mechanism that is known to result in selective formation of oxo and peroxo compounds [desired species for C(1) activation]. Instead, they support a deeper oxidation mechanism, and thus higher selectivity for ketones and acids is obtained. In contrast, these ligands seem to tune the electron density around the Rh (in the Rh-PNP complexes), and thus result in a higher $n$-octane conversion and improved selectivity for the C(1) activated products, with minimized deeper oxidation, in comparison to Ir-PNP catalysts.

Keywords
Aminodiphosphine, iridium, $n$-octane, oxidation, rhodium

Introduction
The activation of alkanes is a desirable but challenging reaction due to the saturated carbon–hydrogen bonds having relatively inert character. In addition, the activated products are often more reactive than the alkane substrate, which may lead to over-oxidation of the products. There is a current need and economic urgency to replace current petrochemical feedstocks (olefins) with easily accessible alkanes, which can result in more proficient use of energy and efficient strategies for fine chemical synthesis.1–10

Terminally oxidized hydrocarbons are valuable starting materials in the pharmaceutical and chemical industries.11 However, one of the main challenges in the activation of alkane C–H bonds is the low selectivity in forming the desired products, that is, the preferential activation of sp$^2$ over sp$^3$ hybridized C–H bonds.12–14 Furthermore, the chemical inertness of alkanes, together with their high ionization energy, pK$_a$ values, and low electron affinity, makes activation of C–H bonds difficult.11,13,15–17

To overcome such problems, there has been a rapid development of catalytic systems inspired by the biological systems of cytochrome P450 and methane monooxygenase.16–27 These enzymes have the ability to efficiently catalyze a number of exogenous and endogenous organic compounds, such as medium chain alkanes, to large molecules including triterpenes, as well as steroidal, polyaromatic compounds, and, more importantly, oxygenates.28–36 Site selective C–H activation by iron complexes has been reported by White and co-workers in trying to mimic enzymes.37–41 These catalytic processes are carried out by a variety of oxidants, namely, PhIO, NaOCl, H$_2$O$_2$, alkyl hydroperoxides, percarboxylic acids, and molecular oxygen.29,34,42–49

The design of a suitable ligand system is one way of achieving selective activation of paraffins. These systems could include the aminodiphosphine or PNP ligand system.50–58 These hybrid ligands, which consist of both soft (N) and hard (P) donors, are of particular interest in that they are part of a system that can display high activity, stability, and variability.57–62 By modifying the ligand backbone through substitution of the donor atoms, the activity of the metal can be tailored.63,64 These ligands may bind to the metal centers as either monodentate, bidentate, or as bridged ligands, which allow the reactions of the...
metal ions to be selective due to the high demand the ligands place on the stereochemistry of the complex. In general, phosphine-based ligands are limited in their application in oxidation reactions due to ligand loss and degradation. Ruthenium-based phosphine complexes have been studied for the oxidation of n-octane; however, low conversions and over-oxidation are prevalent. The activation of alkane C–H bonds by rhodium and iridium complexes has not been thoroughly explored. However, Nomura and Uemura have used rhodium compounds such as Rh₃O, [Rh(acac)₃], [RhCl(CO)₂], [RhCl(PPh₃)₃], and [Rh₂(OAc)₄] for the oxidation of cyclohexane using peracetic acid, H₂O₂, TBHP (t-butyl hydroperoxide), and m-CPBA (meta-chloroperoxybenzoic acid).

Considering the worldwide increase in gas to liquid plants, there is an increase in the production of medium- to long-chain paraffins, which increases the need to functionalize these hydrocarbons. In continuation of our previous work on metal complexes containing aminodiphosphine ligands for n-octane oxidation, this study focuses on the application of iridium (1) and rhodium (2) aminodiphos- phine “PNP” complexes (Figure 1) for the oxidation of n-octane. Optimization of the solvent, the temperature, and the oxidant was carried out. The substituents on the nitrogen atom were varied by making use of six functional groups (Figure 1), resulting in different properties such as basicity, steric hindrance, and various bite angles to see their effects on the catalytic performance and the reaction mechanisms of these catalysts during n-octane oxidation. Recycling studies and characterization of the used catalysts were performed, which provided some insights regarding the mechanism behind the relatively stable catalyst performances through three reaction cycles.

Catalyst preparation

The complexes 1 and 2 (Figure 1) were synthesized by the procedure reported elsewhere. The PNP ligands were added to methanol/acetone mixtures (2:1; v/v), to which the metal complex precursor and NH₄PF₆ salt were added. The complexes were characterized by NMR and infrared (IR) spectroscopy.

Results and discussion

Oxidation of n-octane

The optimization of the substrate to oxidant ratio. Our recent study on the application of these catalysts showed that these two families of complexes follow similar chemistry for styrene oxidation. Therefore, 1a was only chosen for the initial optimization studies. The reaction was initially carried out at 80 °C with tert-butyl hydroperoxide (TBHP) as the oxidant in acetonitrile using catalyst 1a (Figure 2). The catalyst/substrate molar ratio was maintained at 1:100, and then the substrate/oxidant molar ratio was varied (1:2.5; 1:5; 1:7.5; 1:10) (Figure 2). The ratio of 1:5 was found to be the optimum considering both highest conversion and lowest selectivity for the ketones (the over-oxidation products). The conversion at substrate/oxidant ratios greater than 1:5 showed negligible increases, suggesting that the quantity of the loaded catalyst to activate the oxo species was the limiting reagent at this substrate/oxidant ratio. Lowering the catalyst/substrate ratio to 1:50 at a 1:5 ratio of substrate/oxidant ratio did not change the conversion, but resulted in greater selectivity toward ketones that are of less interest in comparison to the aldehyde or alcohols.

Temperature optimization. Before optimizing the temperature for this reaction, another popular solvent [dichloroethane (DCE)] was tested for this reaction at the same temperature as for the optimized conditions in MeCN. Interestingly, a better catalytic performance was observed that might be linked to the better solubility of the substrates in this solvent in comparison to MeCN. Thereafter, the temperature optimization was performed using DCE at 25, 50, and 80 °C (Figure 3) with a catalyst/substrate molar ratio of 1:100 and a substrate/oxidant molar ratio of 1:5. At 25 °C, octanoic acid was the only product that formed with a 1% conversion of n-octane. At 50 °C, a 4% conversion of n-octane was noted. The highest conversion (9%) was obtained at 80 °C with good selectivity for the primary activation products (C1 activation). This also could be attributed to the solubility of the oxidant in the solvent. Similar studies carried out in alkene oxidation showed better conversion in chlorinated solvents. It has been shown that some catalytic reactions proceed more efficiently...
Oxidants. Hydrogen peroxide and m-CPBA (meta-chloroperoxycbenzoic acid) were also investigated for this reaction. However, the use of these two oxidants decomposed the catalyst, and hence poor catalytic performances were achieved. This finding is in agreement with reports that some catalysts are not able to activate certain peroxides, resulting in a low selectivity of the desired products. In a mixture of solvents, however, when a 1:1 ratio of DCE/MeCN was used, the reactions with and without the catalyst were comparable.

Figure 2. Optimization of the substrate/oxidant ratio in the oxidation of n-octane. Conditions: catalyst/substrate (1:100); temperature: 80 °C; solvent: MeCN; catalyst: 1a. In the case of the blank reaction, no catalyst was added.

Figure 3. Optimization of the temperature in the oxidation of n-octane. Conditions: catalyst/substrate (1:100); substrate/oxidant (1:5); solvent: DCE; catalyst: 1a. In the case of the blank reaction, no catalyst was added.

Figure 4. Screening of the iridium (Ir) and rhodium (Rh) catalysts in n-octane oxidation with the different substituents on the nitrogen atom (a–f). Conditions: catalyst/substrate (1:100); substrate/oxidant (1:5); solvent: DCE; temperature: 80 °C. R = cyclohexyl (a); isopropyl (b); pentyl (c); phenyl (d); o-chlorophenyl (e); m-methoxyphenyl (f); Cp^* = η^5-pentamethylcyclopentadienyl.

Comparing the catalysts with the alkyl substituents on the nitrogen atom (a–c) (Figure 1), the longer alkyl chains render the complexes more basic, as in catalysts 1e and 1f. In theory, the more basic nature of an organometallic catalyst, the stronger is its electron-donating ability that results in a greater electron density located on the metal center. As discussed in a previous study, this renders it easier to go from the M^I to M^III states (oxidation) upon activation by the oxidant. However, the formation of the active tert-butoxy radical becomes more difficult, since the highly basic nature of the complex stabilizes the M^III oxidation state. It was noted that electron-donating substituents decrease the reactivity of the oxo species. Catalysts 2a and 2b are comparable in terms of their activity, which is also observed with Cr complexes bearing the same ligand backbone in ethylene oligomerization. The Rh catalyst with the phenyl substituent (2d) gives the highest conversion (13%). Comparing the catalysts with the substituted phenyl rings, it was observed that the chloro (e) or the methoxyphenyl (f) group has very little effect in changing the catalytic activity (Figure 4).

The selectivity for the products of oxidation by the Ir catalysts is shown in Figure 5. Deeper oxidation to the ketonic product is prevalent, as seen by the high selectivity for the octanones (59%–77%) for all the Ir-based catalysts. The extent of the oxidation is referred to as depth here. So, deep oxidation refers to the catalyzed reactions that yield highly oxidized products like the acid. Secondary or moderate oxidation (deeper oxidation) is a relative term, meaning if it is used in the case of alcohols, it refers to ketones (deeper oxidation products). When applied to ketones, it refers to acids (deeper oxidation).

However, the octanols are the second major products with selectivities of 18%–26%. The C(1) position of the n-octane chain is the least activated, with the C(2) and (C3) positions being the most activated carbons. For the catalysts with ligand backbones containing substituted phenyl groups (1e and 1f), over-oxidation of 1-octanol to octanal, and thereafter octanoic acid is much slower in comparison to the catalysts with alkyl substituents. This might be due to

Metal. Using the optimum conditions (catalyst/substrate molar ratio of 1:00, substrate/oxidant molar ratio of 1:5 at 80 °C in DCE), screening of the iridium (1) and rhodium (2) catalysts (Figure 1) bearing different substituents on the nitrogen atom of the ligand backbone was undertaken. Interestingly, both the Rh and Ir–based catalysts showed relatively high conversion of n-octane. In general, the Rh catalysts were found to be more active than the corresponding Ir catalysts with the same substituents (Figure 4). This may be due to the rhodium complexes having a greater ability to coordinate to larger hydrocarbons than the iridium catalysts. Periana and Bergman have shown that the relative rate constants for rhodium catalysts are almost double those of the iridium catalysts in reactions involving n-hexane and n-pentane.
the conjugation effect of the phenyl ring via resonance that decreases the charge density around the metal center, and therefore decreases the formation of over-oxidation products. For both catalysts 1e and 1f, a 3% selectivity for 1-octanol was observed with 7% and 5% selectivities for octanals, respectively. However, for the catalysts with alkyl substituents, 1a and 1b, 17% and 11% selectivities for octanols and octanoic acid are observed, with no selectivity to octanal (indicating that these ligands with Ir cannot perform the mild activation of the terminal C of n-octane). This suggests that catalysts 1a and 1b are well capable of oxidizing the aldehydes to acids. In contrast, catalyst 1d, that contains an unsubstituted phenyl ring in its structure, did not result in the formation of 1-octanol, octanal, and octanoic acid, which suggests that this catalyst cannot activate the n-octane at its α position [C(1)]. Thus, it seems that substitution of the aromatic ring and changing the electronic structure of the complexes containing phenyl rings easily modifies the reaction selectivity with these catalysts. This clearly confirms the contribution of the nitrogen atoms of the ligands in these complexes in tuning the selectivity to certain products, besides the already discussed role in improving the catalyst basicity that was discussed in a previous study using these catalysts.

The deep oxidation process (ketone formation) is much slower with the rhodium catalysts in comparison to the Ir catalysts (Figure 6), which is noted by the higher selectivity for the octanols (11%-41%), with catalyst 2b being the most selective (41%) and 2c being the least selective toward these octanols. As also noted with the iridium catalysts, the C(1) position is the least active, with the C(2) and C(3) positions being the most active carbons (Table 1). The higher activity of internal carbons is also observed in other oxidation systems. Research has been quite limited using Ir and Rh catalysts for the oxidation of alkanes. Nomura and Uemura reported a TON (turnover number) of 93 for the oxidation of n-octane using Rh catalysts. In other reported studies, the regioselectivity parameters at the C(2), C(3), and C(4) positions of the alkane chain are much higher, due to the primary selectivity being substantially lower, whereas in this system, the primary selectivity, the C(1) position, is high, accounting for the lower internal regioselectivity parameters. Unlike the system reported in this study, other studies report no selectivity for the products with an activated terminal carbon, with only the ketones being obtained. Therefore, Ir-based catalysts followed the expected pathways and resulted in the activation of internal carbons within octane, but Rh with the studied ligands seems to switch the reaction from the oxidation of the internal to terminal carbons, that are indeed more interesting for industry since C(1) activated alkanes can be easily transformed into α-olefins that are in high demand by polymer industries.

According to the recent work by Chepaikin et al., oxidative homogeneous catalysis of alkanes can follow two mechanisms. Mechanism A is referred to as an outer-sphere mechanism (A), where the reaction takes place using the in situ generated oxo and peroxo metal complexes. This reaction mechanism is known to yield alcohols (Scheme 1). In contrast, the inner-sphere mechanism (B) happens mainly with catalysts that contain Cl with M-alkyl radical intermediate formation, and results in the deep oxidation of alkanes to ketone and acids. Also, the free-radical mechanism (C) is known to result in deep oxidation and forms products such as ketones and acids as discussed for mechanism (B). It is important to note that in the majority of cases, the latter two mechanisms dominate. However, generally, and considering the selectivity for different products observed over the Rh-based catalysts (except for 2c), the data support the slight involvement of mechanism A during oxidation using these catalysts, which is in agreement with the findings of Chepaikin et al. In contrast, Ir-based catalysts very dominantly follow mechanisms B and C.

Catalyst recovery

It is known that catalysts following mechanism A are highly sensitive toward the metals and ligands that are used to synthesize the catalysts. Therefore, we focused on the recyclability of catalysts 1c and 2c, that were recovered and re-used over two more cycles (Figure 7), since we were interested in examining whether the structure of the catalyst was important.
The amounts of catalyst recovered were low due to mechanical loss during sampling and the small amounts of catalysts used. The selectivity profiles toward alcohols, ketones, aldehydes, and acids are shown in Figures 8 and 9 for both series of catalysts. For catalyst 1c, the fresh and cycle 2 provided comparable n-octane conversions; however, only octanones were detected during cycle 1. The $^{31}$P NMR spectra imply slight differences in the catalyst structure with the appearance of a new peak (for catalyst 2c) (Figure 10). It can be

During the radical pathways (mechanisms B and C) or not. The amounts of catalyst recovered were low due to mechanical loss during sampling and the small amounts of catalysts used. The selectivity profiles toward alcohols, ketones, aldehydes, and acid are shown in Figures 8 and 9 for both series of catalysts. For catalyst 1c, the fresh and cycle 2 provided comparable n-octane conversions; however, only octanones were detected during cycle 1. The $^{31}$P NMR spectra imply slight differences in the catalyst structure with the appearance of a new peak (for catalyst 2c) (Figure 10). It can be

**Table 1.** Selectivity parameters for the Ir and Rh catalysts in the oxidation of n-octane.$^a$

| Catalyst | Alcohol$^{b,c}$ C(1):C(2):C(3):C(4) | Ketone$^{b,c}$ C(2):C(3):C(4) | Total$^d$ C(1):C(2):C(3):C(4) |
|----------|----------------------------------|----------------------------|--------------------------|
| Ir       | 1a 1:9:12:9                      | 1:1:1                     | 1:2:2:2                  |
|          | 1b 1:5:6:4                       | 1:1:1                     | 1:3:3:3                  |
|          | 1c 1:4:5:3                       | 1:1:1                     | 1:1:7:16:16              |
|          | 1d 0:1:2:1                       | 1:2:2                     | 0:1:2:2                  |
|          | 1e 1:4:0:4                       | 1:1:1                     | 1:2:1:2                  |
|          | 1f 1:3:3:4                       | 1:1:1                     | 1:2:2:2                  |
| Rh       | 2a 1:4:5:4                       | 1:1:1                     | 1:2:2:3                  |
|          | 2b 0:1:1:1                       | 1:1:2                     | 1:2:2:3                  |
|          | 2c 1:2:1:2                       | 1:2:1                     | 1:3:3:3                  |
|          | 2d 1:1:6:4                       | 1:1:2                     | 1:3:5:5                  |
|          | 2e 1:2:4:2                       | 1:1:1                     | 1:1:2:2                  |
|          | 2f 1:3:6:5                       | 1:1:2                     | 1:1:1:2                  |

$^a$Conditions: catalyst/substrate (1:100); substrate/oxidant (1:5); solvent: DCE; temperature: 80 °C.

$^b$Parameters C(1):C(2):C(3):C(4) are the relative reactivities of the hydrogen atoms at carbons 1, 2, 3, and 4 of the n-octane chain.

$^c$The calculated reactivities from the % selectivity are normalized, that is, calculated taking into account the number of hydrogen atoms at each carbon.

$^d$It includes the % selectivity of octanoic acid, octanal, alcohols, and ketones and the values are normalized.

**Scheme 1.** Outer-sphere (A) and inner-sphere (B) and free-radical (C) mechanisms of C–H bond activation in alkanes.$^{85,86}$
postulated that the ligand backbone remains unchanged since the characteristic phosphorous peak for both the fresh and recovered catalysts is observed. However, the appearance of a phosphorous peak (2.04 parts per million (ppm)) in the $^{31}$P NMR spectrum of the recovered catalyst $2c$ may indicate the formation of a new intermediate species during the catalytic cycle that promotes ketone formation. The melting points of the recovered catalyst $1c$ (166–168 °C) and used catalyst mixture (262–263 °C) are also different, which can explain the difference in the selectivity. For catalyst $2c$, the fresh run and recovered cycles are comparable, with only cycle 1 being slightly different in the octanone selectivity. These tests showed that the mechanism was not highly dependent on the structures of the catalysts, suggesting the involvement of mechanism B.

Ketone formation, due to deeper oxidation, is common when TBHP ($t$-BuOOH) is used as an oxidant,\textsuperscript{20,87} It can be postulated that the reaction mainly proceeds through the formation of hydroxyl or free radicals (mechanisms B and C), especially in the case of the Ir catalysts.\textsuperscript{84,88}

**Conclusion**

Five different aminodiphosphine ligands were complexed with Ir and Rh as the metals, and were applied for the oxidation of $n$-octane using TBHP as the oxidant. The ligands were selected based on their chain length/steric hindrance, electron density, and their ability to yield different bite angles. Both catalysts gave relatively good $n$-octane conversion. In general, Ir-based complexes catalyze the deep oxidation pathway and they yielded ketones and acids as the major products, while following the inner-sphere mechanism, and involvement of M-alkyl radicals during the reaction. Interestingly, this mechanism seems to also promote the activation of internal carbons and ketone formation. Rh-based catalysts showed better selectivity for alcohols than the Ir complexes, suggesting a slightly greater contribution of the outer-sphere mechanism (A) (however, mechanism B is still dominant in this case as well) and forms more alcohols, while facilitating terminal carbon activation with high commercial values as starting materials for $\alpha$-olefin formation. This study showed that mechanism A is sensitive to the structure of the complexes and the employed metals [high alcohol selectivity using sterically hindered ligands (hexyl and isopropyl)]. In contrast, the catalysts following mechanism B are not structure-sensitive, and can be recycled with the same performance, in spite of some structural changes to the catalyst during different cycles of the reaction.

**Experimental**

**Material and methods**

All experiments were performed using standard Schlenk techniques under inert conditions in moisture-free glassware with anhydrous solvents. All solvents were analytical grade. To render the reaction glassware moisture-free, it was heated with a heat gun followed by cycles of vacuum and nitrogen pressure. Diethyl ether and hexane were distilled from sodium benzophenone ketyl under nitrogen. Dichloromethane was distilled from P$_2$O$_5$, and ethanol from magnesium turnings. Deuterated solvents were used as received and stored in a desiccator. The NMR spectra were recorded at 162 MHz ($^{1}$H) using a Bruker Ultrashield 400MHz spectrometer. $^{31}$P NMR chemical shifts are reported in ppm from triphenylphosphine (17.6 ppm). All PNP ligands were synthesized using a procedure reported by our group.\textsuperscript{74}

**Oxidation of $n$-octane**

All products of the $n$-octane oxidation were analyzed using a PerkinElmer Auto System gas chromatograph connected to a
flame ionization detector (FID) set at 260 °C. A PONA column (50 m × 0.20 mm × 0.5 μm) was utilized with the injector temperature set at 240 °C. Catalytic testing was carried out in a two-necked pear-shaped flask charged with 10 mg of the respective catalyst, pentanoic acid (as an internal standard), n-octane, the respective oxidant, and 10 mL of the solvent. The flask was equipped with a reflux condenser, and the contents were stirred, heated to the required temperature, and maintained at this temperature for 48 h in an oil bath. After that time period, an aliquot was removed using a Pasteur pipette and filtered through cotton wool and a silica gel plug, after which PPh₃ was added (for reduction of the remaining TBHP and alkylperoxides which are formed as primary products in alkane oxidation). An aliquot (0.5 μL) was injected into the gas chromatograph (GC) and quantified. A preliminary experiment showed that the standard, pentanoic acid, is not affected by the reaction medium.

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Figure 10. 31P NMR spectra of the fresh and recovered catalysts 1c and 2c.
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