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Cobalt aminodiphosphine complexes as catalysts in the oxidation of *n*-octane.

Dunesha Naicker,[a] Holger.B. Friedrich[b] and Bernard O. Omondi

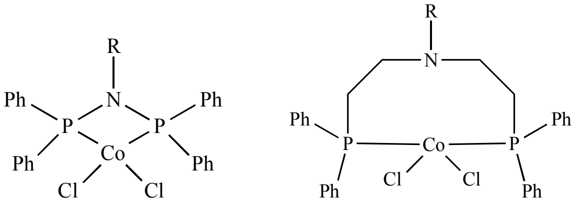
Two types of cobalt aminodisphosphine complexes have been synthesized and characterized by IR spectroscopy, elemental analyses and single crystal x-ray diffraction. These are $[Ph_2PN(R)PPh_2]CoCl_2$, **1** and $[Ph_2P(CH_2)_2N(R)(CH_2)_2PPh_2]CoCl_2$, **2** where R= C_6H_{11} **(a)**; C_5H_{11} **(b)**; C_3H_7 **(c)**. The functional groups on the nitrogen atom (R) were varied from a cyclohexyl ring, to *n*-pentyl alkyl chain, to an *iso*-propyl branched substituent. Complexes **2a** and **2c** were analyzed using single crystal x-ray diffraction. The geometry around the metal centers in **2a** and **2c** were distorted tetrahedral. All complexes showed good activity as catalysts for the oxidation of *n*-octane using *tert*-butyl hydroperoxide (TBHP) as the oxidant. The complex bearing the flexible ligand backbone with the cyclohexyl substituent on the nitrogen atom was the most active and showed high selectivity towards ketones with 2-octanone being the dominant product.

Keywords: Aminodiphosphine; cobalt; oxidation; n-octane; *tert*-butyl hydroperoxide

1. Introduction

The conversion of paraffins or saturated hydrocarbons to more valuable products has drawn the interests of many scientists over the last twenty years.[1-3] This is due to the central problem, where general, selective, efficient and catalytic functionalisation reactions of unactivated paraffin C–H bonds remains unsolved.[1-10] The need for paraffin activation has practical implications in the replacement of current petrochemical feedstocks (olefins) by economical and easily accessible alkanes, which can result in more efficient strategies for fine chemical synthesis and the proficient use of energy.[11-13] However, the conversion of alkanes to desired functionalized products suffers many shortcomings. These include the chemical inertness of the alkanes, the preferential activation of substrates containing sp^2 hybridized C–H bonds over sp^3 hybridized C–H bonds and cases were the intermediate products are more reactive than the alkane which may react more effortlessly with the metal center.[2,3,14-18] Taking into account such shortcomings, a well-suited ligand system is needed. One such system could include the aminodiphosphine ligands. These bi-dentate or multidentate ligands have been used extensively in ethylene oligomerization with chromium as the active metal.[19-25] These ligands are ideally suited for catalytic applications in that they are part of a system that displays high activity, stability and variability.[26-28] Modification of the ligand backbone, by using different donor substituents or central anionic atoms, tailors the activity of the metals, allowing the reactions of the metal ions to be selective, due to the high demand ligands place on the stereochemistry of the complex.[29,30]

In this work, a new approach has been undertaken in using cobalt aminodiphosphine complexes in the C-H activation of *n*-octane. Transition metal-mediated oxidative functionalization of hydrocarbons into useful organic compounds has become an area of immense interest and has led to great advancements in large-scale industrial and synthetic organic processes.[31-34] The development of synthetic models has been biologically inspired by a number of enzymes such as methane monooxygenase and cytochrome P450, which make use of a reactive iron-oxo species in the oxidation of a number of alkanes.[13,35-39] With the success of first row transition metals, such as iron and copper in the aforementioned enzymes, cobalt serves as promising candidate in the C–H activation of alkanes.[40,41] White and co workers have reported site selective C–H activation by a non-heme iron complex in trying to mimic enzymatic activation.[3,17,42-44] More recently Tordin and coworkers have used cobalt complexes with tripodal 4N ligands in the oxidation of alkanes, while SNS cobalt complexes have also been studied in the oxidation of *n*-octane.[40,45] Phosphine based ligands have not been widely explored due to ligand degradation or loss of ligand from the metal complex.[46] However, Wong and co-workers have used ruthenium based phosphine complexes in the oxidation of *n*-octane and reported low conversions.[47,48] These catalytic oxidation processes are carried out using a variety of oxidants, namely, PhIO, NaOCl, H_2O_2, alkyl hydroperoxides, percarboxylic acids and molecular oxygen.[33,49-52]



1 **2**

Figure 1. Representation of complexes **1** and **2**; R = cyclohexyl for **1a** or **2a**; *n*-pentyl for **1b** or **2b** and *iso*- propyl for **1c** or **2c**.

We herein report the synthesis and characterization of two sets of cobalt aminodiphosphine complexes (**1** and **2**) and their application in the catalytic oxidation of *n*-octane in acetonitrile using *tert*-butyl hydroperoxide (TBHP) as the oxidant (Fig. 1). The rigidity (**1**) and flexiblity (**2**) of the ligand backbone was varied to asses whether this will influence the catalytic activity. The substituent on the nitrogen atom was also varied making use of three different types of functional groups, a ringed (cyclohexyl), straight chained (*n*-pentyl) and a branched (*iso*-propyl) substituent with the intention of observing if these groups have an effect on the catalytic activity and selectivity to the products of oxidation. To our knowledge the complexes used in this study are new. Furthermore, limited studies have been carried out in the activation of *n*-alkanes, as compared to cycloalkanes, due to their low activity and tendency to undergo over oxidation. However, valorization of medium length chain *n*-alkanes is of special importance since these are the building blocks in the chemical industry and provide a cheaper alternate feedstock.[53-56]

2. Experimental

2.1 Synthesis ad characterization of the compounds

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 benzophenoneketyl under nitrogen. Dichloromethane was distilled from P_2O_5, and ethanol from magnesium turnings. Deuterated solvents were used as received and stored in a desiccator. The NMR spectra were recorded at 400 MHz (^1H), 100 MHz (^{13}C) and 162 MHz (^{31}P) using a Bruker Ultrashield 400 MHz spectrometer. ^1H NMR and $^{13}C\{^1H\}$ NMR chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane. ^1H NMR and $^{13}C\{^1H\}$ NMR signals were referenced to the residual hydrogen signal of $CDCl_3$ (7.26 ppm) and (77.16 ppm) respectively. ^{31}P NMR chemical shifts were reported in parts per million (ppm) from triphenylphosphine (-17.6 ppm). The FT-IR spectra were recorded using a Perkin Elmer Universal Attenuated Total Reflection (ATR) Sampling Accessory attached to the FT-IR series 100. Elemental analyses were carried out on a Thermo-Scientific Flash 2000 CHNS/O analyzer. All PNP (**1** and **2**) ligands were synthesized with modification of literature procedure.[20,57]

Synthesis of $[Ph_2PN(Cy)PPh_2]CoCl_2$ (1a). The synthesis was adapted from a reported procedure in literature.[58] To a 100 ml two necked round bottom flask, 10 ml of ethanol was added and purged with nitrogen for 10 minutes. Thereafter, $[Ph_2PN(Cy)PPh_2]$ (0.62 mmol, 0.29 g) and $CoCl_2.6H_2O$ (0.63 mmol, 0.15 g) were added. The solution was slowly stirred at room temperature. The round bottom flask was equipped with a condenser and the solution was brought to reflux at 77 °C. After 15 minutes under reflux the solution changed color from blue to green. After 24 hours diethyl ether was added to allow precipitation of the complex. The solvent was decanted and the complex was washed with diethyl ether (3 x 10 ml) and dried under high vacuum. Crystals were grown from diethyl ether and dichloromethane through vapour diffusion. Yield: 59%, 0.22 g. Decomposes >192°C. IRν_{max} (ATR)/cm^{-1}: 997 (*m*), (P-N); 1067 (*m*) (cyclohexyl ring vibrations); 1433 (*m*) (aromatic ring); 2852 (*s*) (CH_2). Anal. (%) Calcd for $C_{30}H_{31}Cl_2CoNP_2$: C: 60.3%; H: 5.2%; N: 2.3%. Found: C: 60.3%; H: 5.2%; N: 2.3%.

Synthesis of $[Ph_2PN(C_5H_{11})PPh_2]CoCl_2$ (1b). Synthesized according to the procedure described for **1a** except that $[Ph_2PN(C_5H_{11})PPh_2]$ (0.62 mmol, 0.290 g) was used. Yield: 45%, 0.16 g. Decomposes >227 °C. IRν_{max} (ATR)/cm^{-1}: 998 (*s*), (P-N); 1434 (*m*) (aromatic ring); 2945 (*s*) (CH_2). Anal. (%) Calcd for $C_{29}H_{31}Cl_2CoNP_2$: C: 59.5%; H: 5.3%; N: 2.4%. Found: C: 58.6%; H: 6.0%; N: 2.2%.

Synthesis of $[Ph_2PN(C_3H_7)PPh_2]CoCl_2$ (1c). Synthesized according to the procedure described for **1a** except that $[Ph_2PN(C_3H_7)PPh_2]$ (0.62 mmol, 0.27 g) was used. Yield: 61%, 0.21 g. Decomposes >165 °C. IRν_{max} (ATR)/cm^{-1}: 998 (*s*), (P-N); 1434 (*m*) (aromatic ring); 2933 (*s*) (CH_2). Anal. (%) Calcd for $C_{27}H_{27}Cl_2CoNP_2$: C: 58.2%; H: 4.9%; N: 2.5%. Found: C: 58.0%; H: 5.2%; N: 2.4%.

Synthesis of $[Ph_2PC_2H_4N(Cy)C_2H_4PPh_2]CoCl_2$ (2a). Synthesized according to the procedure described for **1a** except that $[Ph_2PC_2H_4N(Cy)C_2H_4PPh_2]$ (0.62 mmol, 0,32 g) was used. Yield: 81 %, 0.33 g. Melting point: 251-252 °C. IRν_{max} (ATR)/cm^{-1}: 1030 (*m*) (cyclohexyl ring vibrations); 1434 (*m*) (aromatic ring); 2931 (*s*) (CH_2). Anal. (%) Calcd. for $C_{34}H_{39}Cl_2CoNP_2$: C: 62.5%; H: 6.02%; N: 2.14%. Found: C: 61.8%; H: 6.08%; N: 2.08%.

Synthesis of $[Ph_2PC_2H_4N(C_5H_{11})C_2H_4PPh_2]CoCl_2$ (2b). Synthesized according to the procedure described for **1a** except that $[Ph_2PC_2H_4N(C_5H_{11})C_2H_4PPh_2]$ (0.62 mmol, 0,32 g) was used. Yield: 82 %, 0.26 g. Melting point: 190-192 °C. IRν_{max} (ATR)/cm^{-1}: 1434 (*m*) (aromatic ring); 2952 (*s*) (CH_2). Anal. (%) Calcd. for $C_{34}H_{39}Cl_2CoNP_2$: C: 61.8%; H: 6.13%; N: 2.18%. Found: C: 62.1%; H: 6.18%; N: 2.18%.

Table 1. Crystal data and structure refinement for complexes **2a** and **2c**.

	2a	**2c**
Empirical formula	$C_{34}H_{39}Cl_2CoNP_2$	$C_{31}H_{35}Cl_2CoNP_2$
Formula weight	653.43	613.37
Temperature K	173(2)	173(2)
Wavelength Å	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	9.7475(16)	9.1436(3)
b (Å)	11.1289(18)	16.8343(5
c (Å)	30.195(5)	19.0478(6)
α (°)	90	90
β (°)	104.044(9)	95.1650(10
γ (°)	90	90
Volume (Å^3)	3177.6(9)	2920.05(16)
Z	4	4
Density$_{calc}$ Mg/m^3	1.366	1.395
Absorption coefficient mm^{-1}	0.833	0.902
F(000)	1364	1276
Crystal size (mm^3)	0.19 x 0.11 x 0.11	0.19 x 0.11 x 0.11
Theta range (°)	1.96 to 25.00	2.15 to 25.00
Index ranges	$-11 \leq h \leq 11; -13 \leq k \leq 13; -30 \leq l \leq 35$	-10<=h<=10; -20<=k<=20; -22<=l<=22
Independent reflections	5547 [R(int) = 0.1299]	5132 [R(int) = 0.0314
Completeness to theta	25.00°; 99.1%	100.0
Max. and min. trans	0.9139 and 0.8577	0.9073 and 0.8473
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	5547 / 0 / 361	5132 / 0 / 336
Goodness-of-fit on F^2	1.170	1.025
Final R indices [$I>2\sigma(I)$]	R1 = 0.1014, wR2 = 0.2331	R1 = 0.0229, wR2 = 0.0496
R indices (all data)	R1 = 0.1375, wR2 = 0.2449	R1 = 0.0301, wR2 = 0.0534
Largest diff. peak and hole (e.Å^{-3})	1.035 and -0.804	0.364 and -0.268

Synthesis of $[Ph_2PC_2H_4N(C_3H_7)C_2H_4PPh_2]CoCl_2$ (2c). Synthesized according to the procedure described for **1a** except that $[Ph_2PC_2H_4N(C_3H_7)C_2H_4PPh_2]$ (0.62 mmol, 0,31 g) was used. Yield: 40 %, 0.15 g. Melting point: 250-253 °C. IRν_{max} (ATR)/cm^{-1}: 1435 (*m*) (aromatic ring); 2869 (*s*) (CH_2); 2964 (*s*) (CH). Anal. (%) Calcd. for $C_{31}H_{35}Cl_2CoNP_2$: C: 60.7%; H: 5.75%; N: 2.28%. Found: C: 60.4%; H: 5.83%; N: 2.19%.

2.2 Crystal structure analysis

Crystals of compounds **2a** and **2c** were grown by the vapour diffusion of diethyl ether into a solution of the complexes in dichloromethane at room temperature to give blue crystals for **2a** and **2c**. The crystals of the complexes were each selected and glued onto the tip of glass fibers separately. The crystals were then mounted in a stream of cold nitrogen at 100(1) K and centered in the X-ray beam by using a video camera. Crystal evaluation and data collection were performed on a Bruker Smart *APEX*II diffractometer with Mo Kα radiation (λ = 0.71073 Å) and a diffractometer to crystal distance of 4.00 cm. The initial cell matrix was obtained from three series of scans at different starting angles. Each series consisted of 12 frames collected at intervals of 0.5° in a 6° range with the exposure time of about 10 seconds per frame. The reflections were successfully indexed by an automated indexing routine built in the *APEX*II program suite.[59] Data collection method involved ω scans of width 0.5°. Data reduction was carried using the program *SAINT*+.[59] The structure was solved by direct methods using *SHELXS* [60] and refined by *SHELXL*[59]. All structures were checked for solvent-accessible cavities using *PLATON*[61] and the graphics were performed with ORTEP3 .

Non-H atoms were first refined isotropically and then by anisotropic refinement with full-matrix least-squares calculations based on F^2 using *SHELXS*.[61] All H atoms were positioned geometrically and allowed to ride on their respective parent atoms. All H atoms were refined isotropically. Crystal data and structure refinement information for all the complexes are summarized in Table 1. (These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The data of the crystal structure are available quoting CCDC 1028260 and 1028261).

2.2 Oxidation of *n*-octane.

All catalytic reactions were performed under inert conditions in moisture free glassware with anhydrous solvents. MeCN was degassed for 10-15 minutes before use. All reagents were weighed and handled in air. All products were analyzed using a PerkinElmer Auto System gas chromatograph fitted with a Flame Ionisation Detector (FID) set at 260 °C. A Pona column (50 m x 0.20 mm x 0.5µm) was utilized with the injector temperature set at 240 °C. Catalytic testing was carried out in acetonitrile at 80 °C, using *tert*-butyl hydroperoxide (TBHP) as the respective oxidant. The catalyst to substrate ratio was kept constant at 1:100. A two-necked pear shaped flask was charged with 10 mg of the respective catalyst, pentanoic acid (as an internal standard), *n*-octane, TBHP and 10 ml of the solvent. The flask was equipped with a reflux condenser. The mixture was stirred, heated to the respective temperature and maintained for 48 hours in an oil bath. After the time period, an aliquot was removed using a Pasteur pipette and filtered through cotton wool and a silica gel plug, after which PPh_3 was added (for reduction of the remaining TBHP and alkylperoxides which are formed as primary products in alkane oxidation).[33] An aliquot (0.5 µl) was injected into the GC and quantified.

3. Results and discussion

3.1 Synthesis and characterization of the compounds

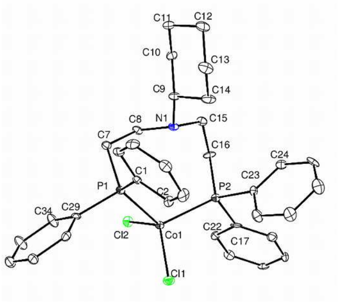
Complexes **1** and **2** were synthesized by adaptation of a procedure by Romerosa et al.[58] The respective ligands were added to a solution of $CoCl_2.6H_2O$ in ethanol and after refluxing for 24 hours, diethyl ether was added to allow precipitation of the respective complex. The precipitates of complexes **1** were green, whilst those of **2** were blue. The complexes where fully characterized by elemental analyses, infrared spectroscopy and single crystal x-ray diffraction. The complexes are paramagnetic, hence elucidation by NMR was unsuccessful.[58] The elemental analyses of the complexes matched the calculated values and this is indicative of complexation, as are the sharp melting points and crystal structures of **2a** and **2c**. A shift in the $\boldsymbol{\nu}_{\mathbf{P\text{-}N}}$ band in the IR spectra of complexes **1** and their respective ligands also are noted and shown in Table 2.

Table 2. Comaprison of the $\boldsymbol{\nu}_{\text{P-N}}$ band shifts of complexes **1** and their respective ligands.

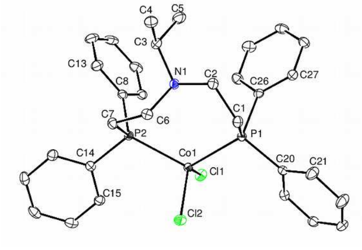
Substituent	$\nu_{\text{P-N (Ligand)}}$/ cm^{-1}	$\nu_{\text{P-N (Complex 1)}}$/ cm^{-1}
a	982	997
b	977	998
c	986	998

3.2 Description of crystal structures

Blue crystals of complexes **2a** and **2c** were obtained by vapour diffusion of diethyl ether into a dichloromethane solutions of complexes **2a** and **2c**. *ORTEP* diagrams of **2a** and **2c** are given in Fig. 2, while bond distances and bond angles are provided in Table 3. Both compounds crystallize with one molecule of the respective complexes in the asymmetric units. In both complexes the cobalt metal is bound to one ligand through the phosphorous atoms of the ligand and two chlorine atoms, resulting in a distorted tetrahedral geometry around the metal center. The P—Co—P bond angles are 116.42(9) and 116.32(2)° in **2a** and **2c** respectively, while the two Cl—Co—P angles lie between 100.53(7) and 108.35(1)°. The Cl—Co—Cl bond angles are 120.4(1) and 118.50(2)° in **2a** and **2c** respectively. The P—Co bond lengths for both complexes are comparable to related complexes found in literature.[62]



2a



2c

Figure 2. The molecular structures of complexes **2a** and **2c** showing part of the atom-numbering scheme. Displacement ellipsoids are drawn at 50% probability level and H atoms have been omitted for clarity.

Table 3. Selected bond lengths (Å) and angles (°) for complexes **2a** and **2c**.

2a		**2c**	
Bond lengths			
Co(1)—P(1)	2.348(3)	Co(1)—P(1)	2.3618(5)
Co(1)—P(2)	2.368(3)	Co(1)—P(2)	2.3684(5)
Co(1)—Cl(1)	2.225(3)	Co(1)—Cl(1)	2.2363(5)
Co(1)—Cl(2)	2.245(3)	Co(1)—Cl(2)	2.2169(5)
Bond angles			
P(1)—Co(1)—P(2)	116.42(9)	P(1)—Co(1)—P(2)	116.32(2)
Cl(1)—Co(1)—Cl(1)	120.39(10)	Cl(1)—Co(1)—Cl(1)	118.50(2)
Cl(1)—Co(1)—P(1)	106.15(7)	Cl(2)—Co(1)—P(2)	103.357(18)
Cl(2)—Co(1)—P(2)	102.53(9)	Cl(1)—Co(1)—P(1)	108.346(18)
Cl(2)—Co(1)—P(1)	100.53(7)	Cl(2)—Co(1)—P(1)	102.530(18)
Cl(1)—Co(1)—P(2)	110.99(10)	Cl(1)—Co(1)—P(2)	108.116(18)

3.3 Oxidation of *n*-octane

The catalytic activity of complexes **1** and **2** were explored in the oxidation of *n*-octane. All catalytic runs were carried out at 80 °C in acetonitrile with TBHP (*t*-BuOOH) as the oxidant under argon atmosphere. Preliminary work showed low conversions with no significant change in product selectivity at lower temperatures. TBHP as an oxidant has been used in a number of oxidation reactions and has the advantage over other oxidants in that it has higher solubility in organic solvents, which contain dissolved hydrophobic hydrocarbons.[63] Optimization of the substrate to oxidant ratio was carried out, by investigating *n*-octane to TBHP ratios of 1:2.5; 1:5; 1:7.5 and 1:10, where the ratio of 1:5 gave the highest conversion with good selectivity. Control experiments were carried out in the absence of the catalyst and oxidant respectively. In the former, a 2% conversion was observed with the highest selectivity to 2-octanone (Fig. 3). However, the latter reaction showed a 0% conversion. Testing was also carried out with cobalt chloride ($CoCl_2.6H_2O$) under the same catalytic conditions. A 2% conversion was observed, with selectivity to the over oxidized products, namely the ketones and octanoic acid. This is the same conversion as for the blank reaction with TBHP only, but with a greater selectivity to the over oxidized products.

The more sterically hindered, more rigid, catalysts **1** show more limited activity in comparison to the more flexible catalysts **2**, which have a significantly larger bite angle. The bite angle is known to have an impact on the activity and selectivity of catalytic reactions.[64] It has been reported that the effect of bite angle on C-X bond activation originates from an electronic factor, where the donor-acceptor orbital interactions (metal d orbitals to the substrate $\sigma^*_{c\text{-}x}$) stabilize the transition state.[65] As the metal-ligand d-hybrid orbital is driven to smaller bite angles, the transition state becomes more stabilized.[65] Interestingly, a decrease in the activity for both catalysts **1** and **2** is observed, as one moves from the cyclohexyl (**a**) to the *iso*-propyl (**c**) substituent (Fig. 4). Noteworthy, for these ligands used in ethylene tetramerisation, a similar trend is observed in terms of their activity with chromium as the active metal.[20] This can be attributed to the basicity of the substituent on the nitrogen atom.[20]

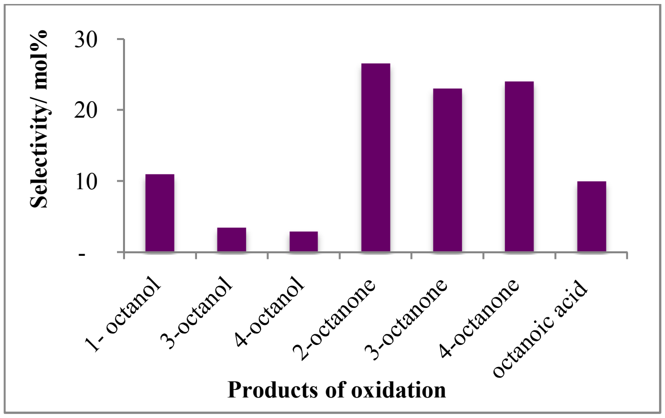


Figure 3. Selectivity of the blank reaction (no catalyst) to products of oxidation at a ratio of 1:5 of substrate to oxidant at 80 °C in acetonitrile.

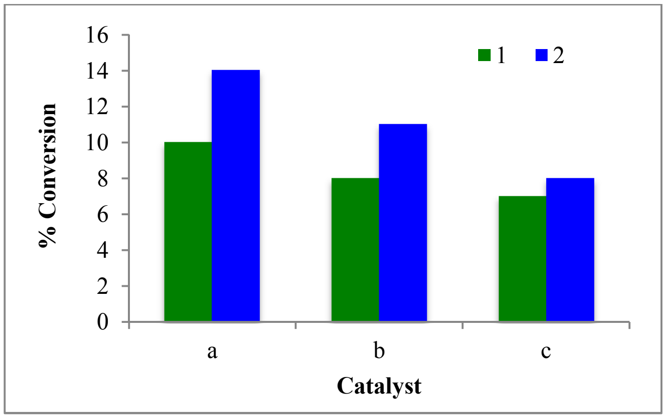


Figure 4. Conversion of *n*-octane by catalysts **1** and **2** at a ratio of 1:5 of substrate to oxidant at 80 °C in acetonitrile.

Both sets of catalysts (**1** and **2**) are highly selective to the ketones, with 2-octanone being the dominant product (Fig. 5 and 6). This indicates that the catalyst causes oxidation of the internal carbons more readily than the terminal carbon. Such cases, with 2-octanone being the dominant product, have been observed in the biological hydroxylation of alkanes catalyzed by methane monooxygenase.[13] The C(2) position is three times as active as the C(1), and is most reactive in linear alkane chains as reflected by the regioselectivity in reactions for *n*-heptane, as well as *n*-octane.[5,51,63,66,67] Thus, early work by Saussine and co-workers showed that cobalt(III)alkylperoxy complexes also were highly selective to the 2-octanone in the oxidation of *n*-octane.[68] It has been shown with sandwich type tungstophosphate anions, $[M_4(H_2O)_2(PW_9O_{34})_2]^{10-}$, where M= Co^{+2}, Mn^{+2} and Fe^{+2}, that highest selectivity to the ketone product is observed when cobalt salts were used, in comparison to using the manganese and iron salts, in the oxidation of cyclohexane.[69] Ketone formation is also observed with ruthenium phosphine compounds, in which cases only 2- and 4-octanone are observed with a 4% conversion.[47,48] In addition, in the oxidation of lower chain alkanes, such as heptane and propane, using ruthenium complexes as catalysts, higher yields to the ketonic products and very low yields to the alcohols were observed.[70,71] Chen and White have reported yields to 2- and 3- octanone with no selectivity to primary products using a bulky iron electrophillic catalyst.[3] Over-oxidation is highly prevalent at the C(1) position of the *n*-octane chain for both catalysts **1** and **2**, with higher selectivity to octanoic acid and very low selectivity to 1-octanol and no selectivity to octanal. Assuming a sequential oxidation, this implies that octanal is highly reactive over these catalysts.

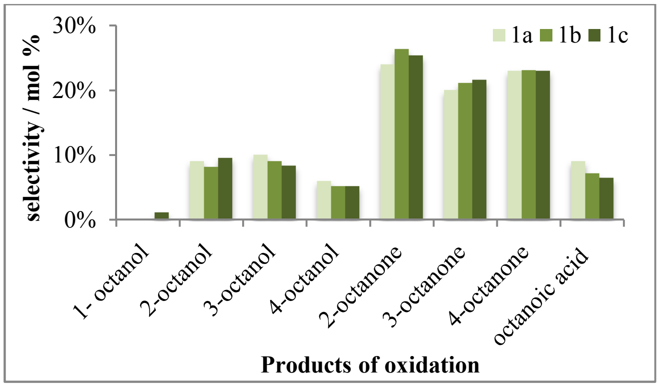


Figure 5. Selectivity of catalyst **1** to the products of oxidation at a ratio of 1:5 of substrate to oxidant at 80 °C in acetonitrile.

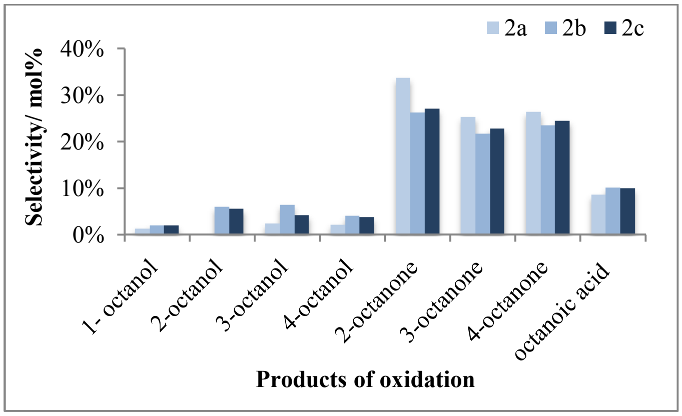


Figure 6. Selectivity of catalyst **2** the products of oxidation at a ratio of 1:5 of substrate to oxidant at 80 °C in acetonitrile.

Following the method of Shul'pin and coworkers, addition of triphenylphosphine to a filtered (through a plug of silica to remove the catalyst) aliquot of the reaction mixture 10 mins prior to GC analysis was performed, since a relative increase in the alcohol peak and a decrease in the ketone peak can result.[33] This was the true concentration of the alcohols and ketones, since the alkyl hydroperoxides that are present are completely reduced to the corresponding alcohols. For catalysts **1**, a change in the selectivity to the alcohol and ketone before and after addition of the PPh_3 was observed, however, for catalysts **2** no observable change was noted.

The regioselectivity parameters (Table 4) further indicate that the C(2) position is the most activated carbon of the *n*-octane chain, with the C(1) being the least activated. The catalysts with the pentyl and *iso*-propyl (**b** and **c**) substituents are most selective to the alcohols, with catalysts **2** being more selective to the alcohols than **1**.

Table 4. Selectivity parameters in the oxidation of *n*-octane by catalysts **1** and **2.**

Catalyst	Alcohol[a]	Ketone[b]	Total[c]
	C(1):C(2):C(3):C(4)	C(2):C(3):C(4)	C(1):C(2):C(3):C(4)
1a	0:1.5:1.7:1	1.2:1:1.2	1:5.5:5:4.8
1b	0:1.6:1.8:1	1.2:1:1.1	1:7.4:6.5:6.1
1c	0:2:1.6:1	1.1:1:1.0	1:7.6:6.5:6.1
2a	1:0:3.3:3.3	1.4:1:1	1:5.2:4.1:4.2
2b	1:4.2:4.2:2.9	1.1:1:1	1:4:3.5:3.4
2c	1:4.2:2.9:2.9	1.2:1:1	1:4.1:3.4:3.5

[a] Parameters C(1):C(2):C(3):C(4) are the relative reactivities of hydrogen atoms at carbon 1, 2, 3 and 4 of the *n*-octane chain.

[b] The calculated reactivities from the % selectivity are normalized, i.e. calculated taking into account the number of hydrogen atoms at each carbon.

[c] Includes the % selectivity of octanoic acid, alcohols and ketones and the values are normalized.

When using TBHP as an oxidant, the ketone product forms from the oxidation of the alcohol (over oxidation).[35] Since the selectivity to the ketones is much greater, it is likely that the oxidation reaction proceeds via the formation of hydroxyl radicals where the metal complex activates the oxidant, *t*-BuOOH, forming a reactive species, the hydroxyl radical, which attacks *n*-octane.[5,31,72-75] We assume that the reaction takes place in the coordination sphere of the metal complex which would explain the influence of the ligand system on the reaction. *t*-BuO• is proposed to form by the reduction of *t*-BuOOH by the Co(II)L which generates a hydroxo-Co(III) species.[73,74] This specie reacts further with *t*-BuOOH regenerating Co(II)L[73,74], with *t*-BuO• and O_2. The *t*-BuO• attacks the *n*-octane forming octyl radicals, R•, which react with oxygen to form octyl peroxy radicals, ROO•.[73,74] These react with the *n*-octane to form the octyl-hydroperoxide ROOH, which undergoes homolytic decomposition to form the organooxyl radical, RO•. By H-abstraction from *n*-octane, the RO• radical forms octanols (ROH), which can react further with oxygen to form the octanones.[73,74]

Isolation and characterization of the used catalysts was unsuccesful despite many attempts.

Conclusions

In this paper, new cobalt aminodisphosphine complexes have been synthesized and fully characterized and were used as catalysts in the oxidation of *n*-octane. Higher conversion is seen with the more flexible complexes **2** as compared to the more sterically hindered complexes **1** and this may be attributed to their bite angle. The substituent on the nitrogen atom has an effect of the activity, where the catalysts with the cyclohexyl ring substituents are much more active than those with branched or straight chain substituents. The ketones were the dominant product, with the C(2) position being the most activated in the octane chain contributing to the high selectivity of 2-octanone (34%). 1-octanol was prominent with catalysts **2**, however, over oxidation was also more evident with these catalysts contributing to the high selectivity of the ketones.

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Notes and references

[a] School of Chemistry and Physics, University of KwaZulu-Natal,Durban, South Africa. E-mail: duneshanaicker@gmail.com
[b] School of Chemistry and Physics, University of KwaZulu-Natal,Durban, South Africa. E-mail: friedric@ukzn.ac.za
[c] School of Chemistry and Physics, University of KwaZulu-Natal,Durban, South Africa. E-mail: owaga@ukzn.ac.za

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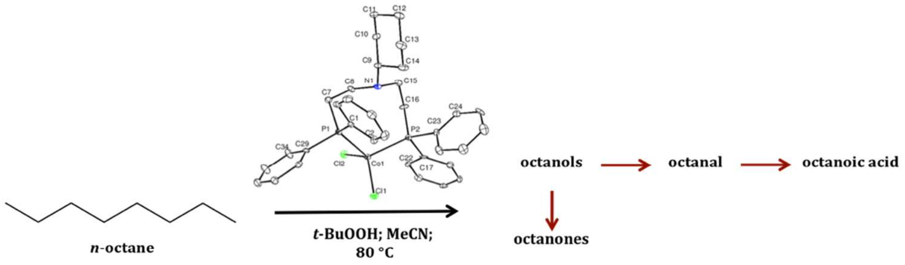

New cobalt "PNP" aminodiphosphine complexes have been prepared and characterised. They show good catalytic activity in the oxidation of *n*-octane to C8 oxygenates using *tert*-butyl hydroperoxide as an oxidant.