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## Introduction

Selective activation of paraffins (alkanes) has remained an area of active research interest due to the relative inertness of the saturated hydrocarbon bonds. The inertness of paraffins is due to strong, localized C-C and C-H bonds, which makes it difficult for them to participate in chemical reactions. This is because they lack empty orbitals of low energy or filled orbitals of high energy necessary for most chemical transformations.<sup>1,2</sup> Most attempts at paraffin activation aim to convert the inert alkane to relatively more reactive or value-added products which amongst other uses serve as feedstock, additives or solvents for pharmaceutical and other chemical industries.<sup>3</sup> Oxygenates (alcohols, ketones and carboxylic acids), which result from oxidative functionalization of alkanes, are the most desired products of paraffin activation in chemistry. These are generally believed to be obtained by activation of the C-H bond via bond cleavage, followed by insertion of a single

## Coordination chemistry of Co complexes containing tridentate SNS ligands and their application as catalysts for the oxidation of *n*-octane<sup>†</sup>

Lynette Soobramoney, Muhammad D. Bala\* and Holger B. Friedrich\*

The selective oxidation of saturated hydrocarbons to terminal oxygenates under mild catalytic conditions has remained a centuries long challenge in chemical catalysis. In an attempt to address this challenge, two series of tridentate donor ligands {2,6-bis(RSCH<sub>2</sub>)pyridine and bis(RSCH<sub>2</sub>CH<sub>2</sub>)amine [R = alkyl, aryl]} and their respective cobalt complexes {Co[2,6-bis(RSCH<sub>2</sub>)pyridine]Cl<sub>2</sub> and Co[bis(RSCH<sub>2</sub>CH<sub>2</sub>)amine]Cl<sub>2</sub>} were synthesized and characterized. Crystal structures of Co[2,6-bis(RSCH<sub>2</sub>)pyridine]Cl<sub>2</sub> [R =  $-CH_3$  (**1**),  $-CH_2CH_3$  (**2**),  $-CH_2CH_2CH_2CH_3$  (**3**) and  $-C_6H_5$  (**4**)] are reported in which **1** crystallized as a homo-bimetallic dimer that incorporated two bridging chloride atoms in an octahedral geometry around each cobalt center, while **2**, **3** and **4** crystallized as mono-metallic species characterized by trigonal bipyramidal arrangement of ligands around each cobalt center. As catalysts for the homogeneous selective oxidation of *n*-octane, the catalysts yielded ketones as the dominant products with a selectivity of *ca*. 90% for the most active catalyst Co[bis(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)amine]Cl<sub>2</sub> (**6**) at a total *n*-octane conversion of 23%. Using *tert*-butyl hydroperoxide (TBHP) as an oxidant, optimization of reaction conditions is also reported.

oxygen atom from an appropriate donor to the activated species.<sup>4</sup>

Although a number of researchers have reported on the use of transition metal complexes in the catalytic activation of paraffins,<sup>4-11</sup> the employment of pincer complexes in this regard has remained challenging to scientists worldwide. Hence, there are only a handful of reported examples on the utilization of pincer ligand-based metal complexes for the catalytic activation of mainly aryl and vinyl C–H bonds.<sup>2,12–23</sup>

Since their discovery in the mid-1970s, pincer-type ligands have become increasingly important in chemistry,<sup>24</sup> and owing to their ability to tailor the reactivity, selectivity and stability of the ligands towards a specific reaction pathway or product, the application of pincer-based metal complexes has dramatically increased.18,25-27 These advantages are due to the terdentate binding mode of the ligands which implies that they are able to stabilize metal centers more effectively than related mono or bidentate variants. In addition to imparting stability, simultaneous occupation of multiple coordination sites around a metal center allows the ligands to control access to the center which in turn affects binding of reactive species, thus providing enhanced selectivity towards a desired substrate during catalysis. The ligands are also easily tuned, both electronically and sterically, to ensure catalyst versatility.25,27 It is worth noting that in spite of the increased interest in pincer complexes, those complexes stabilized by ligands typified by SNS

School of Chemistry and Physics, University of KwaZulu-Natal, Private Bag X54001, Durban 4000, South Africa. E-mail: bala@ukzn.ac.za, friedric@ukzn.ac.za; Fax: +27 31 260 3091

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donor atom combination have in general received relatively less attention.

However, since the discovery of SNS complexes of  $Cr^{28}$  as excellent ethylene trimerization catalysts, interest in SNS ligands has also increased amongst researchers. In addition to the seminal report by McGuinness, Wasserscheid and coworkers,<sup>28</sup> SNS complexes of Mo,<sup>29</sup> Pt,<sup>30</sup> Pd,<sup>31</sup> Ru,<sup>32</sup> Cu,<sup>33</sup> Ni,<sup>34</sup> and Zn<sup>35</sup> have to date been synthesized and characterized. One of the key features of the SNS pincer ligand relevant to its application in catalysis is that it may be designed to adopt a hemilabile binding mode.<sup>36</sup> This is usually achieved by exploiting the relative difference in binding abilities between the hard nitrogen donor and the soft sulfur donor atoms to metal centers.<sup>37</sup> Being hemilabile also affords the metal complex with greater flexibility and balance between stability and reactivity.<sup>38,39</sup>

To the best of our knowledge, there has been no work reported on Co-based SNS complexes or the application of SNS pincer complexes for C–H or paraffin activation. Hence this study reports on the first examples of a new range of Co-based SNS pincer complexes and their successful application as catalysts in the activation and functionalization of *n*-octane.

### **Experimental section**

#### General

All manipulations were carried out using standard Schlenk techniques under a nitrogen atmosphere. Solvents were dried according to established methods<sup>40</sup> and purged with high purity nitrogen gas prior to use. Diethyl ether (Et<sub>2</sub>O) and tetrahydrofuran (THF) were dried over sodium wire and benzophenone, absolute ethanol (EtOH) was dried over magnesium turnings/iodine, and dichloromethane (DCM) was dried over phosphorous pentoxide. All other reagents were purchased commercially and used as received. All NMR spectra were recorded using a Bruker Avance III 400 MHz spectrometer at ambient temperature. The <sup>1</sup>H NMR data are reported as chemical shifts ( $\delta$ , ppm) and referenced to the solvent peak CDCl<sub>3</sub>. The proton decoupled <sup>13</sup>C NMR data are presented as chemical shifts ( $\delta$ , ppm) and referenced to the solvent peak CDCl<sub>3</sub> with the specific carbon indicated in parentheses. The <sup>13</sup>C DEPT 135 NMR data, which distinguish between CH, CH<sub>2</sub> and  $CH_3$ , are listed as chemical shifts ( $\delta$ , ppm) and positive (pos) or negative (neg) with the corresponding carbons in parentheses. The IR spectra were recorded on a Perkin Elmer Attenuated Total Reflectance (ATR) spectrophotometer and elemental analyses were performed on a LECO CHNS elemental analyzer, while the melting points were determined using Stuart Scientific melting point apparatus.

Synthesis of the precursor 2,6-pyridine-dimethylene-ditosylate (PMT). The reported protocols for the preparation of the pyridine-based ligands involve expensive starting materials like 2,6-bis(chloromethyl)pyridine, therefore an alternate synthetic route was followed to reduce the costs. A more suitable starting material, 2,6-pyridine-dimethylene-ditosylate (PMT), was employed which involves the use of cheaper reagents to prepare, and the method followed was adapted from a study by Reger *et al.*<sup>41</sup> In a 500 ml round bottom flask (RBF), a solution containing 8.0 g (0.20 mol) of NaOH and 2.78 g (0.020 mol) of 2,6-pyridinedimethanol was prepared in 150 ml THF-water (1 : 1). The solution was then cooled to 0 °C to which a mixture of *p*-toluenesulfonyl chloride in 75 ml THF was added. After stirring at room temperature for four hours, the mixture was poured into 200 ml water and extracted with 75 ml dichloromethane (DCM) and this was repeated three times. The organic phase was washed with a saturated NaCl solution and distilled water, and dried with Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under vacuum yielding a crystalline white product (6.57 g, 73%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  2.4 (s, 6H), 5.1 (s, 4H), 7.3 (d, 6H), 7.7 (t, 1H), 7.8 (d, 4H).

Synthesis of 2,6-bis(CH<sub>3</sub>SCH<sub>2</sub>)pyridine (L1). To prepare this ligand a modified protocol adapted from a study by Canovese et al. was followed.<sup>31</sup> In a 50 ml two neck RBF fitted with a nitrogen tap, 1.79 g of PMT was dissolved in ~40 ml of THF and this solution was cooled in an ice bath. A mass of 0.62 g of sodium methanethiolate was added to the ice cooled solution after which the mixture was stirred for 2 hours at room temperature. At the end of the reaction the solvent was evacuated under reduced pressure and the resulting cream residue was partitioned between DCM (200 ml) and water (100 ml). After washing several times with water, the organic phase was dried with MgSO4 and the solvent was removed to yield the product as impure pale yellow oil. The product was purified by elution with DCM through a silica packed column (0.53 g, 66%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 2.0 (s, 6H), 3.8 (s, 4H), 7.2 (d, 2H), 7.6 (t, 1H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): δ 15.2 (CH<sub>3</sub>-S), 40.0 (py-CH<sub>2</sub>-S), 121.1 (CH-py), 137.3 (CH-py), 158.2 (C-py). <sup>13</sup>C DEPT 135 (400 MHz, CDCl<sub>3</sub>): δ 15.2 (CH<sub>3</sub>-S) neg, 40.0 (CH<sub>2</sub>-S) pos, 121.1 (CH-py) neg, 137.3 (CH-py) neg. IR  $\nu_{max}$ (cm<sup>-1</sup>): 3058 (w), 2966 (m), 2914 (m), 2856 (m), 1589 (s), 1572 (s), 1451 (s), 747 (s), 813 (m).

Synthesis of 2,6-bis(CH<sub>2</sub>CH<sub>3</sub>SCH<sub>2</sub>)pyridine (L2). The procedure followed for the synthesis of L2 was adapted from a study by Teixidor et al.35 with a few modifications. Sodium metal (0.23 g, 10 mmol) and ethanethiol (0.5 ml, 10 mmol) were stirred together in ethanol (10 ml) for 20 min in a 20 ml Schlenk tube. This solution was added to another ethanol solution (50 ml) of PMT (2.24 g, 5 mmol) in a 100 ml two neck RBF fitted with a nitrogen inlet, and the reaction mixture was left to reflux overnight. The solvent was removed in vacuo and the residue was extracted twice with diethyl ether (150 ml) and the remaining insoluble residue was discarded. The extract was washed with aqueous Na<sub>2</sub>CO<sub>3</sub> and twice with water (150 ml) and dried with MgSO4. The solvent was removed in vacuo to yield the impure product which was purified analogously to L1 to give a pale yellow oil (0.62 g, 54%). <sup>1</sup>H NMR (400 MHz,  $CDCl_3$ ):  $\delta$  1.2 (t, 6H), 2.5 (q, 4H), 3.8 (s, 4H), 7.2 (d, 2H), 7.6 (t, 1H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): δ 14.5 (CH<sub>3</sub>CH<sub>2</sub>-S), 25.6 (CH<sub>3</sub>CH<sub>2</sub>-S), 37.8 (py-CH<sub>2</sub>-S), 121.0 (CH-py), 137.2 (CH-py), 158.5 (C-py). <sup>13</sup>C DEPT 135 (400 MHz, CDCl<sub>3</sub>): δ 14.5 (CH<sub>3</sub>-S) neg, 25.6 (CH<sub>2</sub>-S) pos, 37.8 (py-CH<sub>2</sub>-S) pos, 121.0 (CH-py) neg, 137.2 (CH-py)

neg. IR  $\nu_{max}$  (cm<sup>-1</sup>): 3056 (w), 2971 (m), 2926 (m), 2869 (m), 1590 (s), 1573 (s), 1451 (s), 747 (s), 788 (m).

Synthesis of 2,6-bis(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>SCH<sub>2</sub>)pyridine (L3). A similar procedure to that for L2 was followed for L3 with the following masses and volumes: sodium metal (0.14 g, 6.18 mmol), butanethiol (0.7 ml, 6.18 mmol), PMT (1.38 g, 3.09 mmol). No further purification was required as the TLC showed only one spot; however the oil was dried under reduced pressure for several hours to remove any solvent, thus yielding the product as a yellow oil (0.55 g, 63%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.9 (t, 6H), 1.4 (m, 4H), 1.6 (m, 4H), 2.5 (t, 4H), 3.8 (s, 4H), 7.3 (d, 2H), 7.6 (t, 1H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  13.7 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-S), 22.0 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-S), 31.3 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-S), 31.4 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-S), 38.1 (py-CH<sub>2</sub>-S), 121.0 (CH-py), 137.2 (CH-py), 158.5 (C-py). <sup>13</sup>C DEPT 135 (400 MHz, CDCl<sub>3</sub>): δ 13.7 (CH<sub>3</sub>-S) neg, 22.0 (CH<sub>2</sub>-S) pos, 31.4 (CH<sub>2</sub>-S) pos, 38.1 (CH<sub>2</sub>-S) pos, 121.0 (CH-py) neg, 137.2 (CH-py) neg. IR  $\nu_{\rm max}$  (cm<sup>-1</sup>): 3056 (w), 2956 (m), 2926 (m), 2871 (m), 1589 (s), 1573 (s), 1451 (s), 747 (s), 812 (m).

Synthesis of 2,6-bis(C6H5SCH2)pyridine (L4). This method was adapted from a study by Teixidor et al.<sup>37</sup> Sodium metal (0.14 g, 6 mmol) was stirred with thiophenol (0.61 ml, 6 mmol) in ethanol (10 ml) in a 20 ml Schlenk tube for 10 min. The solution was then added dropwise to an ice cooled solution of PMT (1.52 g, 3 mmol) in THF (20 ml) and the resulting solution was stirred for a further three hours at 0 °C. The solvent was then removed in vacuo and the resulting residue was extracted with 70 ml diethyl ether and washed with 1 M NaOH solution (25 ml  $\times$  2) after which the organic layer was dried with MgSO4. The solvent was removed in vacuo to yield the product as pale yellow oil and no further purification was required (0.90 g, 82%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  4.2 (s, 4H), 7.1 (d, 4H), 7.2 (t, 4H), 7.3 (d, 4H), 7.5 (t, 1H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): δ 40.3 (py-CH<sub>2</sub>-S), 121.3 (CH-py), 126.2 (CH-ph), 128.9 (CH-ph), 129.6 (CH-ph), 135.7 (C-ph), 137.2 (CH-py), 157.3 (C-py). <sup>13</sup>C DEPT 135 NMR (400 MHz. CDCl<sub>3</sub>): δ 40.3 (py-CH<sub>2</sub>-S) pos, 121.3 (CH-py) neg, 126.2 (CHph) neg, 128.9 (CH-ph) neg, 129.6 (CH-ph) neg, 137.2 (CH-py) neg. IR  $\nu_{\text{max}}$  (cm<sup>-1</sup>): 3064 (w), 2962 (m), 2923 (m), 1590 (s), 1571 (s), 1450 (s), 1436 (s), 737 (s), 809 (m).

Synthesis of 2,6-bis(C<sub>6</sub>H<sub>11</sub>SCH<sub>2</sub>)pyridine (L5). This method was adapted from a study by Temple et al.42 In a 20 ml Schlenk tube, NaOH (0.32 g, 8.2 mmol) and cyclohexylmercaptan (1.0 ml, 8.2 mmol) were stirred together in ethanol (10 ml) for 30 min. This mixture was added dropwise to a THF solution (20 ml) of PMT (1.79 g, 4 mmol) in a 100 ml two neck RBF fitted with a nitrogen inlet. After stirring at room temperature overnight, the solvent was removed in vacuo and the residue was partitioned between DCM and deionized water (50 ml each). The organic layer was collected, while the aqueous layer was washed with DCM (20 ml  $\times$  3), and then the organics were combined and dried with MgSO4. After the solvent was removed in vacuo the product was obtained as yellow oil and no further purification was required (1.21 g, 91%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 1.3 (m, 10H), 1.6 (m, 2H), 1.7 (m, 4H), 1.9 (m, 4H), 2.6 (m, 2H), 3.8 (s, 4H), 7.2 (d, 2H), 7.6 (t, 1H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): δ 25.9 (CH<sub>2</sub>-cy), 26.1 (CH<sub>2</sub>-cy), 33.5 (CH<sub>2</sub>-cy), 36.6 (py-CH<sub>2</sub>-S), 43.4 (CH-cy), 121.0 (CH-py), 137.3 (CH-py), 158.8 (C-py). <sup>13</sup>C DEPT 135 NMR (400 MHz. CDCl<sub>3</sub>): δ 25.9 (CH<sub>2</sub>-cy) pos, 26.1 (CH<sub>2</sub>-cy) pos, 33.5 (CH<sub>2</sub>-cy) pos, 36.6 (py-CH<sub>2</sub>-S) pos, 43.4 (CH-cy) neg, 121.0 (CH-py) neg, 137.3 (CH-py) neg. IR  $\nu_{max}$  (cm<sup>-1</sup>): 3064 (w), 2962 (m), 2923 (m), 1590 (s), 1571 (s), 1480 (s), 1449 (s), 737 (s), 809 (m).

Synthesis of bis(CH<sub>2</sub>CH<sub>3</sub>SCH<sub>2</sub>CH<sub>2</sub>)amine (L6). The method for the preparation of L6 was adapted from a study by Konrad et al.<sup>34</sup> In a 250 ml Schlenk flask, 8.79 g (50 mmol) of bis(2chloroethyl)amine hydrochloride was dissolved in 100 ml ethanol. The solution was added to a 500 ml Schlenk flask which contained a mixture of NaOH (5.99 g, 150 mmol) and ethanethiol (11.0 ml, 150 mmol) in ethanol (150 ml) at 0 °C. The resulting mixture was stirred for two hours, filtered via a cannula and the filtrate was dried in vacuo. Diethyl ether was added to the residue and once again the mixture was filtered and the filtrate was dried in vacuo to yield the product as a pale yellow oil (6.66 g, 69%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  1.3 (t, 6H), 1.8 (s, 1H, N-H), 2.6 (q, 4H), 2.7 (t, 4H), 2.8 (q, 4H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): δ 14.9 (CH<sub>3</sub>CH<sub>2</sub>-S), 25.9 (CH<sub>3</sub>CH<sub>2</sub>-S), 31.9 (CH<sub>2</sub>CH<sub>2</sub>-N), 48.3 (CH<sub>2</sub>CH<sub>2</sub>-N). <sup>13</sup>C DEPT 135 NMR (400 MHz. CDCl<sub>3</sub>): δ 14.9 (CH<sub>3</sub>-S) neg, 25.9 (CH<sub>2</sub>-S) pos, 31.9 (CH<sub>2</sub>-N) pos, 48.3 (CH<sub>2</sub>-N) pos. IR  $\nu_{max}$  (cm<sup>-1</sup>): 3288 (w), 2962 (s), 2921 (s), 2864 (s), 2823 (s), 1451 (s), 739 (m).

Synthesis of bis(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>SCH<sub>2</sub>CH<sub>2</sub>)amine (L7). L7 was prepared analogously to L8 with the following masses and volumes: bis(2-chloroethyl)amine hydrochloride (8.81 g, 50 mmol), NaOH (6.13 g, 150 mmol) and butanethiol (16.0 ml, 150 mmol). The product was obtained as yellow oil (10.71 g, 86%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.9 (t, 6H), 1.3 (m, 4H), 1.5 (m, 4H), 1.8 (s, 1H, N–H), 2.5 (t, 4H), 2.6 (t, 4H), 2.8 (t, 4H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): δ 13.7 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>–S), 22.0 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>–S), 31.7 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>–S), 31.8 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-S), 32.4 (CH<sub>2</sub>CH<sub>2</sub>–N), 48.4 (CH<sub>2</sub>CH<sub>2</sub>–N). <sup>13</sup>C DEPT 135 NMR (400 MHz, CDCl<sub>3</sub>): δ 13.7 (CH<sub>3</sub>–S) neg, 22.0 (CH<sub>2</sub>–S) pos, 31.7 (CH<sub>2</sub>–S) pos, 31.8 (CH<sub>2</sub>–S) pos, 32.4 (CH<sub>2</sub>–N) pos, 48.4 (CH<sub>2</sub>–N) pos. IR  $\nu_{max}$  (cm<sup>-1</sup>): 3294 (w), 2955 (vs), 2925 (vs), 2872 (vs), 1458 (s), 741 (m).

Synthesis of Co[2,6-bis(CH<sub>3</sub>SCH<sub>2</sub>)pyridine]Cl<sub>2</sub> (1). A mixture of L1 (0.4917 g, 2.5 mmol) in ethanol (5 ml) was added dropwise to a solution of CoCl<sub>2</sub>·6H<sub>2</sub>O (0.5717 g, 2.4 mmol) in ethanol (10 ml) in an almost 1 : 1 mole ratio with the ligand in slight excess. After an overnight reflux, the resulting indigo solution was concentrated by reducing the volume of the solvent to ~5 ml. At this point the product precipitated out was separated *via* cannula filtration and washed with a small amount of ethanol. Drying *in vacuo* for several hours afforded the product as a blue microcrystalline solid (0.28 g, 36%). Crystals suitable for X-ray diffraction were grown from a concentrated acetonitrile solution layered with Et<sub>2</sub>O. Elemental analysis for C<sub>9</sub>H<sub>13</sub>Cl<sub>2</sub>CoNS<sub>2</sub>: calcd C, 32.8; H, 4.0; N, 4.3; found C, 32.4; H, 4.4; N, 4.0. Melting point: 176–177 (dimer), 196–197 °C.

**Synthesis of Co[2,6-bis(CH<sub>2</sub>CH<sub>3</sub>SCH<sub>2</sub>)pyridine]Cl<sub>2</sub> (2).** Complex **2** was prepared analogously to **1** using 0.1235 g (0.52 mmol) CoCl<sub>2</sub>·6H<sub>2</sub>O and 0.1193 g (0.53 mmol) L2. A brilliant blue crystalline solid was obtained (0.086 g, 47%). Crystals suitable for X-ray diffraction were deposited from a concentrated ethanol solution. Elemental analysis for  $C_{11}H_{17}Cl_2CoNS_2$ : calcd C, 37.0; H, 4.8; N, 3.9; found C, 37.3; H, 5.2; N, 3.9. Melting point: 164–165 °C.

Synthesis of Co[2,6-bis(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>SCH<sub>2</sub>)pyridine]Cl<sub>2</sub> (3). Complex 3 was prepared analogously to 1 using 0.0843 g (0.35 mmol) CoCl<sub>2</sub>·6H<sub>2</sub>O and 0.1021 g (0.36 mmol) L3. An indigo blue crystalline solid was obtained (0.069 g, 48%). Crystals suitable for X-ray diffraction were grown from a concentrated ethanol solution. Elemental analysis for  $C_{13}H_{21}Cl_2CoNS_2$ : calcd C, 44.5; H, 6.8; N, 3.1; found C, 45.0; H, 6.6; N, 3.4. Melting point: 107–108 °C.

Synthesis of Co[2,6-bis(C<sub>6</sub>H<sub>5</sub>SCH<sub>2</sub>)pyridine]Cl<sub>2</sub> (4). Complex 4 was prepared analogously to 1 using 0.1190 g (0.50 mmol) CoCl<sub>2</sub>·6H<sub>2</sub>O and 0.1635 g (0.51 mmol) L4. An aqua blue powder was obtained (0.17 g, 77%). Crystals suitable for X-ray diffraction were grown by vapor diffusion of Et<sub>2</sub>O into a concentrated DCM solution. Elemental analysis for C<sub>19</sub>H<sub>17</sub>Cl<sub>2</sub>CoNS<sub>2</sub>: calcd C, 50.3; H, 3.8; N, 3.1; found C, 50.1; H, 4.3; N, 3.0. Melting point: 211–213 °C.

Synthesis of Co[2,6-bis(C<sub>6</sub>H<sub>11</sub>SCH<sub>2</sub>)pyridine]Cl<sub>2</sub> (5). Complex 5 was prepared analogously to 1 using 0.1188 g (0.50 mmol) CoCl<sub>2</sub>·6H<sub>2</sub>O and 0.1717 g (0.51 mmol) L5. A fine purple powder was obtained (0.10 g, 43%). Elemental analysis for C<sub>19</sub>H<sub>29</sub>Cl<sub>2</sub>CoNS<sub>2</sub>: calcd C, 49.0; H, 6.3; N, 3.0; found C, 48.6; H, 6.8; N, 2.8. Melting point: 142–143 °C.

Synthesis of Co[bis(CH<sub>2</sub>CH<sub>3</sub>SCH<sub>2</sub>CH<sub>2</sub>)amine]Cl<sub>2</sub> (6). A mixture of L6 (0.2448 g, 1.26 mmol) in ethanol (5 ml) was added dropwise to a solution of CoCl<sub>2</sub>·6H<sub>2</sub>O (0.2615 g, 1.09 mmol) in ethanol (10 ml) in an almost 1 : 1 mole ratio, with the ligand in slight excess, and a color change from dark blue to indigo-purple was observed. The reaction mixture was allowed to stir for two hours at room temperature after which the solution was concentrated to ~5 ml and the product precipitated out as a lavender colored solid which was separated *via* cannula filtration (0.23 g, 66%). Elemental analysis for C<sub>8</sub>H<sub>19</sub>Cl<sub>2</sub>CoNS<sub>2</sub>: calcd C, 29.7; H, 5.9; N, 4.3; found C, 29.6; H, 6.3; N, 4.2. Melting point: 171–172 °C.

#### X-ray structure determination

Single crystals were selected and glued onto the tip of a glass fiber, mounted in a stream of cold nitrogen at 173 K and centered in the X-ray beam using a video camera. Intensity data were collected on a Bruker APEX II CCD area detector diffractometer with graphite monochromated Mo K<sub> $\alpha$ </sub> radiation (50 kV, 30 mA) using the APEX 2 data collection software. The collection method involved  $\omega$ -scans of width 0.5° and 512 × 512 bit data frames. Data reduction was carried out using the program SAINT+ while face indexed and multi-scan absorption corrections were made using SADABS. The structures were solved by direct methods using SHELXS.43 Non-hydrogen atoms were first refined isotropically followed by anisotropic refinement by full matrix least-squares calculations based on  $F^2$  using SHELXS. Hydrogen atoms were first located in the difference map then positioned geometrically and allowed to ride on their respective parent atoms. Diagrams were generated using SHELXTL, PLATON<sup>44</sup> and ORTEP-3.<sup>45</sup> In preliminary refinements for complex 3 the butyl groups in the structure were found to be disordered and were as a consequence refined over two positions with isotropic thermal parameters. Carbon atoms in the butyl groups were refined isotropically with a common U<sub>iso</sub> parameter. Crystallographic data and additional information regarding the crystal structure determination are available as ESI.† Furthermore, CCDC 984366-984369 respectively for compounds 1-4 obtainable from the Cambridge Crystallographic Data Centre contain supplementary crystallographic data for this contribution.

#### Oxidation of n-octane

The paraffin oxidation studies were carried out using *n*-octane as the substrate with pentanoic acid as the internal standard. The catalytic reactions were performed under a nitrogen atmosphere in a 50 ml two-neck pear shaped flask equipped with a condenser. The reaction mixture consisted of 5 ml degassed acetonitrile (solvent), TBHP as the oxidant, n-octane and the respective catalyst (3 mg). The reaction mixture was stirred in an oil bath at the optimum temperature (80 °C) and after the time period (24 and 48 hours for the amine and pyridine-based catalysts respectively), an aliquot of the sample was removed with a Pasteur pipette and filtered through a cotton wool plug, after which 0.5 µL of the aliquot was injected into a GC for analysis and quantification. Masses and volumes of components of the reaction mixture were dependent on the specific catalyst; however catalyst loading was kept constant at 1 mol%, i.e. a catalyst to substrate mole ratio of 1:100. Furthermore, the *n*-octane to oxidant ratio was varied from 1:3, 1:6, 1:9, 1:12, 1:20, 1:30 to 1:40 from which the optimum ratio of 1:20 was established. At higher oxidant concentrations, substrate reactivity decreased drastically indicating that the catalyst was possibly deactivated by the excess oxidant in the reaction vessel. All reactions (including blanks) were carried out in duplicates. The average conversion was expressed as a percentage of total moles of products/initial moles of substrate, while selectivity was expressed as a percentage of moles of each product/sum total moles of all products.

### Results and discussion

#### Syntheses and characterization of new cobalt complexes

In this study, the synthesis and application of seven new Co complexes containing SNS ligands are reported in which two sets of ligands were synthesized based on variation in the architecture of the backbone N-donor atom; these are (i) a con-



Scheme 1 Synthetic route to SNS-Co(II) complexes 1-7.

strained six-membered pyridine ring and (ii) a linear straight chained amine. Synthesis of all ligands was adapted from the literature, however novel methodologies were developed for preparation of the SNS-Co( $\pi$ ) complexes as summarized in Scheme 1. Successful formation of products was monitored and confirmed by a variety of techniques, discussed later. However, it is noted that due to the paramagnetic high spin nature of the cobalt( $\pi$ ) complexes, their unresolved NMR data are not reported in this study.

Refluxing the metal salt  $(CoCl_2 \cdot 6H_2O)$  with isolated SNS ligands {2,6-bis(RSCH<sub>2</sub>)pyridine [R = methyl, L1; ethyl, L2; butyl, L3; phenyl, L4 and cyclohexyl, L5] and bis(RSCH<sub>2</sub>CH<sub>2</sub>)amine [R = ethyl, L6 and butyl, L7]} afforded the corresponding pyridyl-centered SNS complexes Co[2,6-bis(RSCH<sub>2</sub>)pyridine]Cl<sub>2</sub> (R = methyl, 1; ethyl, 2; butyl, 3; phenyl, 4 and cyclohexyl, 5) and amine-based SNS complexes Co[bis-(RSCH<sub>2</sub>CH<sub>2</sub>)amine]Cl<sub>2</sub> (R = ethyl, 6 and butyl, 7). The initial indicators of complex formation were the absence of resolvable NMR data combined with sharp melting points and distinct color changes during the reaction. For the pyridyl complexes (1–5), accurate elemental analyses were combined with data from X-ray diffraction (with the exception of 5) for confirmation of the molecular composition, structure and geometry.

The amine-based complexes (6-7) were very air sensitive, comparatively less stable than the corresponding pyridyl complexes (2-3) and decomposed on exposure to the atmosphere. Hence, all attempts at growing crystals suitable for X-ray crystallography failed. However, data from other techniques including IR spectroscopy, elemental analysis and melting point determination, conclusively confirmed isolation of the intended complexes in high purity. Table 1 presents a summary of the most important bands in the IR spectra which correspond to the N-H stretching vibration  $(3500-3300 \text{ cm}^{-1})$ , the C-H alkyl stretch and bend as well as C-H rocking vibrations. However, IR spectroscopy was unsuitable for detecting the C-S stretch for all three ligands due to overlap by strong and broad C-H rocking vibrations, but it is worth noting that the signals did intensify upon ligand coordination to the Co center. Relevant shifts in vibration frequencies, such

Table 1 Selected IR data for ligands and the corresponding complexes  ${\bf 6}$  and  ${\bf 7}$ 

| Ligand/<br>complex | IR $\nu_{\rm max}/{\rm cm}^{-1}$ |                          |                      |                  |  |  |
|--------------------|----------------------------------|--------------------------|----------------------|------------------|--|--|
|                    | N–H<br>stretch <sup>a</sup>      | C-H (alkyl) <sup>b</sup> | C–H bend $(alkyl)^b$ | C-S <sup>a</sup> |  |  |
| L6                 | 3228                             | 2864                     | 1458                 | N/A              |  |  |
| 6                  | 3228                             | 2870                     | 1465                 | 694              |  |  |
| L7                 | 3294                             | 2872                     | 1458                 | N/A              |  |  |
| 7                  | 3219                             | 2867                     | 1464                 | 744              |  |  |

<sup>a</sup> Weak (for the coordinated S donor). <sup>b</sup> Medium.

as weakening of the N–H stretching frequency of 7 from 3294 to 3219 cm<sup>-1</sup>, are interpreted as indicators of successful complexation of the SNS ligands to the metal center.

#### Crystal structures of 1-4

With the exception of the methyl substituted complex 1, which was isolated as a chloro-bridged bimetallic species containing octahedrally bonded cobalt centers (Fig. 1), the longer chain (S-bonded R substituents) analogues all crystallized with a trigonal bipyramidal geometry around each cobalt(II) center (Fig. 2, 4 and 5) with selected bond lengths and bond angles listed in Table 2. Consequently, 2, 3 and 4 all crystallized in the monoclinic crystal system, while 1 crystallized in the lower symmetry triclinic  $P\bar{1}$  space group. The molecular structure of 1, as presented in Fig. 1, shows tridentate SNS ligands each chelated in a meridional fashion to cobalt centers via two sulfur atoms and a nitrogen atom from the pyridine ring. Relatively weak metal-metal interactions were observed between the two octahedral centers of 1 separated through space by a Co…Co distance of 3.684 Å, which in perspective is weaker than similar interactions in reported square-planar SNS metal complexes bearing t-butyl groups on the S-donor atoms, having dimeric centers (respectively, 3.223 and 3.255 Å for Ir…Ir and Rh…Rh).<sup>36</sup>

Complex 2 crystallizes in the monoclinic Cc space group with four twins (two independent molecules, Fig. 2) in the asymmetric unit cell. The Co(II) ion in each molecule exists as a five coordinate center stabilized by the neutral SNS ligand and two terminal chloride ions. Due to the increased size of the S-atom substituent (R group), the geometries of the latter members of this series of complexes differ significantly in solid state structural conformations from 1. This is due to the non-constrained free rotation around C-C single bonds that result in increased steric bulk and less compact geometries. For instance, the bulkier and electronically richer ethyl R group in 2 may be partly responsible for its propensity to exist as a five coordinate monomer, while 1 easily dimerizes in an octahedral fashion. A comparison of selected bond lengths and angles shows that the N(1)-Co(1) bond of 2 is shorter than that of 1 [2.048(7) Å vs. 2.1131(17) Å], while the S(1)-Co(1) and S(2)-Co(1) bond lengths are longer, indicative of a stronger C-N bond and comparatively weaker C-S bonds in 2. This observation may be ascribed to increased back-donation and



Fig. 1 Molecular structure and atomic numbering scheme of 1 with thermal ellipsoids at the 50% probability level.



Fig. 2 Molecular structure and atomic numbering scheme of 2 showing two crystallographically independent molecules in the asymmetric unit cell. Thermal ellipsoids are drawn at the 50% probability level.

 Table 2
 Selected bond lengths (Å) and bond angles (°) for 1–4

|  | 1  | 2  | 3  | 4  |
|--|--|--|--|--|
| $ \begin{array}{c} \hline & N(1)-Co(1) \\ S(1)-Co(1) \\ S(2)-Co(1) \\ S(2)-Co(1)-S(1) \\ N(1)-Co(1)-S(1) \\ N(1)-Co(1)-S(2) \\ \end{array} $ | $\begin{array}{c} 2.1131(17)\\ 2.4980(5)\\ 2.4889(6)\\ 162.85(2)\\ 81.84(5)\\ 81.33(5)\end{array}$ | $\begin{array}{c} 2.048(7) \\ 2.521(2) \\ 2.518(3) \\ 161.90(8) \\ 82.3(2) \\ 81.5(2) \end{array}$ | $\begin{array}{c} 2.133(3)\\ 2.4496(15)\\ 2.4604(14)\\ 152.55(7)\\ 82.07(11)\\ 80.80(10)\end{array}$ | $\begin{array}{c} 2.057(5)\\ 2.5460(17)\\ 2.5208(17)\\ 161.84(6)\\ 81.94(15)\\ 81.13(14)\end{array}$ |
|  |  |  |  |  |

overlap of d-orbitals of the  ${\rm Co}(\pi)$  center and the pi-antibonding orbitals of the pyridyl N-donor as a result of the ethyl group in 2.

A distorted trigonal bipyramidal geometry is observed for 2 due to a slightly narrower 'bite angle' defined as the S(2)-Co (1)–S(1) angle. The geometry around the metal center is defined by three equatorial positions occupied by the two

chlorides and the N-donor atom, while the two axial positions are occupied by the relatively *trans* S-donor atoms. A related Zn (SNS) complex reported by Teixidor and co-workers<sup>35</sup> revealed a conformation similar to 2, but, due to the presence of bulkier bromide ions, exhibited an acute S(1)-Zn-S(2) bite angle of 157.0°, compared to 161.90° for 2.

Observation of the crystal packing between molecules of **2** revealed an ordered arrangement of crystal units containing the two molecules in alternating planes (Fig. 3), which resulted in a higher melting point of 164–165° compared to 107–108° for **3**. Primarily, the more ordered crystal in the solid state required a greater input of energy to disrupt intermolecular cohesion in the complex.<sup>46</sup>

Geometrically, complex 3 (Fig. 4) is very similar to 2 with distorted trigonal bipyramidal geometry in which the pyridyl moiety and the two chloride groups occupy equatorial positions, while the two S-donor atoms occupy axial positions. The



**Fig. 3** Wireframe representation of the crystal packing of **2** with hydrogen atoms omitted for clarity.



**Fig. 4** Molecular structure and atomic numbering scheme of **3** showing one conformation of the disordered butyl group with thermal ellipsoids at the 50% probability level.

N(1)-Co(1), S(1)-Co(1) and S(2)-Co(1) bond lengths for 3 are very similar to 1 (Table 2), but a notably more acute bite angle of 152.55(7)° is observed in comparison with either 1 or 2. The pyridyl ring is twisted such that C(2) and C(6) reside on the S-N-S-Co plane, whereas C(3), C(4) and C(5) atoms deviate from the [N(1), C(2), C(3), C(4), C(5)] plane by 0.383, 0.485 and 0.313 Å respectively, leading to a dihedral angle of 11.81°.

Unlike in complexes **1** and **2**, the substituent 'arms' C(1) and C(7) are positioned on the same side of the S–N–S–Co plane, deviating by just 0.155 and 0.287 Å respectively. The steric bulk and disorder brought about by the free rotation of the butyl groups accounted for the relatively low melting point

(107–108 °C) for 3 compared to the other complexes reported herein.  $^{\rm 46}$ 

Complex 4, represented in Fig. 5, crystallizes in the P21/c space group with the phenyl substituents positioned on the opposite sides of the S–N–S–Co plane, which correlates with a related Cr complex reported by Temple *et al.*<sup>42</sup> In comparison with 3, the methylene linkers C(7) and C(13) are situated on either side of S–N–S–Co plane deviating from the plane by +0.950 and -0.825 Å respectively.

#### Application of complexes 1-7 in the oxidation of *n*-octane

As noted earlier, the main goal of this study was to prepare catalysts for the selective activation of paraffins represented by *n*-octane. To test the effectiveness of complexes 1–7, *tert*-butyl hydroperoxide (TBHP) was used as a source of oxygen for *n*-octane. The choice of oxidant was based on the knowledge that it is a more effective and milder source of reactive oxygen than the more common hydrogen peroxide  $(H_2O_2)$ .<sup>47,48</sup> Exploratory work with the current set of catalysts has also showed that TBHP is the more active and stable source of oxygen, hence all data presented here are based on its use as the oxidant.

A series of exploratory experiments were conducted in order to establish optimum reaction conditions for optimal substrate conversion and product selectivity. The optimum octane to oxidant ratio was found to be 1:20 while 24 and 48 hours were the most favorable reaction times for the amine- and pyridinebased complexes respectively. Results showed that beyond these time frames no significant change in substrate conversion was obtained. Furthermore, too low conversions were observed at shorter reaction times. Blank reactions with only the oxidant TBHP in the absence of any catalyst gave a total n-octane conversion of 1% and as expected, no conversion was observed for blank runs that contained the catalyst in the absence of any oxidant. A blank run with the metal precursor (CoCl<sub>2</sub>·6H<sub>2</sub>O) as the catalyst was also performed and the results revealed 5 and 7% n-octane conversions after 24 and 48 hours respectively. Furthermore, only 2-,3- and 4-octanone were formed and no 1-octanol or other products of primary carbon activation were detected, indicating poor selectivity to primary products for the blank runs.

The oxidation of *n*-octane with catalysts 1-7 under the optimum conditions produced a mixture of isomeric octanones and octanols that were oxygenated at carbon positions 1, 2, 3 and 4 (Scheme 2), as well as other terminal products, mainly octanal and octanoic acid. Furthermore, no cracking of the substrate was observed and only C8 products were obtained. Table 3 presents data on total octane conversion and the regioselectivity parameter (C1 : C2 : C3 : C4). The regioselectivity parameter at carbon positions 1, 2, 3 and 4 along the *n*-octane backbone leading to various oxygenates (Scheme 2).

Results of the catalytic study suggest that amongst the pyridine-based catalysts, 1 was the most active, with the highest (12%) total conversion of the substrate *n*-octane. Such an outcome was not unexpected considering that 1 has the least







Scheme 2 Product distribution in the oxidation of *n*-octane.

#### Table 3 Total conversion and regioselectivity parameter C1: C2: C3: C4 in the oxidation of n-octane using TBHP as the oxidant

| Catalyst | Total conversion/% | Octanone<br>selectivity/% | Octanol<br>C1 : C2 : C3 : C4 | Octanone<br>C2 : C3 : C4 | $Total^a \\ C1: C2: C3: C4$ |  |
|----------|--------------------|---------------------------|------------------------------|--------------------------|-----------------------------|--|
| 1        | 12                 | 83                        | 1:3.5:3.1:0                  | 1.3:1:1                  | 1:5.8:4.6:3.7               |  |
| 2        | 11                 | 79                        | 1:1.7:0:1.9                  | 1.5:1.1:1                | 1:3.9:2.5:2.8               |  |
| 3        | 9                  | 83                        | 2:3.6:1:3.6                  | 1.4:1:1                  | 1:5.6:3.9:4.2               |  |
| 4        | 9                  | 82                        | 1:1.5:0:2.5                  | 1.4:1:1                  | 1:3.8:2.6:3.2               |  |
| 5        | 7                  | 77                        | 1:2.5:0:5                    | 1.4:1:1                  | 1:4.7:3.2:4.1               |  |
| 6        | 23                 | 83                        | 1:1.9:2.1:1.4                | 1.4:1.1:1                | 1:4.1:3.3:3.0               |  |
| 7        | 17                 | 90                        | 1:1:0:3.3                    | 1.4:1.1:1                | 1:8.3:6.4:6.4               |  |
|          |                    |                           |                              |                          |                             |  |

<sup>*a*</sup> The total regioselectivity parameter takes into account all products (octanones, octanols, octanal and octanoic acid). Reactions were carried out at 80 °C with a catalyst loading of 1 mol%, an octane to oxidant ratio of 1:20, pentanoic acid as the internal standard and reaction times of 24 and 48 hours for the amine- and pyridine-based catalysts respectively.

sterically hindered active site due to the relatively small methylene groups bonded to the ligand S-donor atoms. This, in theory, should render greater access to the metal center for the substrate and lead to the enhanced catalytic activity observed for **1**. In general terms, there is an inverse relationship between the reactivity of the metal complexes and the size of the R group on the S-donor atoms, which implies that the catalytic activity is dominated by steric factors.

However, in the instances where the side groups are straight chain alkyl substituents, electronic and steric contributions to reactivity are difficult to separate because the longer chain members show enhanced electronic contributions to the che-

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lating S-donors, but they are also more sterically hindered. The question that arose in these instances is whether sterics or electronics dominate the activity of the catalysts. Complexes 4 and 5 contain phenyl and cyclohexyl side groups respectively and the difference in reactivity between these two catalysts led to the belief that steric access to the metal center is the prime determinant of catalytic activity. The planar phenyl side group in 4 is less sterically demanding than the electronically richer but sterically bulkier cyclohexyl in 5. The result is consistent and showed better total conversion and selectivity for 4.

In addition to R-group steric variation as a determinant of catalytic activity in complexes 1–5, the amine N-donor containing complexes (6 and 7) displayed significantly higher catalytic activities with conversions of 23 and 17% respectively which is likely due to the additional flexibility of the amine backbone. This observation has implications for the design of catalysts stabilized by carbon chain chelated donor atoms.

The degree of flexibility of the carbon chain linker between the chelated donor atoms is important for the set of SNS ligands reported herein. A flexible two carbon spacer between a simple amine N-donor and the S-donor atoms yielded more effective catalysts than a rigid pyridine N-donor linked to the S-donors *via* a methylene spacer. Direct comparison of the two structurally related amine backbone complexes **6** (SNSetamine) and 7 (SNS-butamine) further confirmed the importance of the side chain steric influence as a key determinant of catalytic activity. Hence, in summary, complex **6** functionalized with a relatively smaller ethyl R group showed the best potential for *n*-octane oxidation amongst the whole range of seven catalysts studied.

Consistent with reported observations, the total regioselectivity for each catalyst (Table 3) showed that internal hydrogens at the carbon position C2 (Scheme 2) were the most reactive, while terminal hydrogens at position C1 were the least reactive.<sup>1,47</sup> Hence, the total selectivity up to 90% recorded for octanone isomers via activation of internal carbon positions (mainly C2 but also including C3 and C4) as the dominant products of the oxidation reaction is an improvement over the selectivity of ca. 80% previously reported by Pombeiro et al.47 Specifically on octanols, it was observed that the highest selectivity to 1- and 2-octanols was displayed by 3, to 3-octanol by 1 and to 4-octanol by 5, implying that the more rigid pyridine N-donor based complexes are more selective against over-oxidation of octanols to octanones than complexes 6 and 7. However, it is evident that overall, 7 displayed the highest selectivity at positions C2, C3 and C4 which accounted for the higher overall octanone production at these positions. The trends of these parameters are comparable to those reported in the literature<sup>47,49</sup> for catalytic systems that utilized TBHP as the oxidant. Furthermore, these results imply that a radical initiated mechanism is followed as proposed by Pombeiro and co-workers.47

Thus far it is safe to summarize that in these catalytic systems, over-oxidation of internal carbons has led to the production of ketones as the main dominant products. In an effort to further understand the rate of this oxidation of alcohols to ketones, an experiment was set up under similar conditions as used for the octane oxidation. Complex **6** was used as a representative catalyst, into which a fresh solution of 2-octanol was oxidized with TBHP over a 5 h period. The result revealed a time dependent production of over 86% 2-octanone within the 5 h period. This observation suggests that the overoxidation of octanols (including 1-octanol to octanal) proceeded quite early and relatively quickly in the current systems such that any alcohol that was formed almost immediately got further oxidized. To put the results of this catalytic study into context, closely related reports are summarized below:

• Kirillova *et al.* have described the use of a tetracopper( $\pi$ ) complex for the oxidation of alkanes under mild conditions using TBHP as the oxidant.<sup>49</sup> The results obtained for the oxidation of *n*-octane in particular showed that the reaction did not involve free hydroxyl radicals due to the high regioselectivity profile (1:65:32:30) after 30 min reaction time. Following an increase in the reaction time to 180 min, the parameter dropped to 1:10:6:6. In addition, over-oxidation of alcohols to the corresponding ketones was observed.

• Lau and co-workers have reported on the oxidation of alkanes with an  $[Os^{VI}(N)Cl_4]^-/Lewis$  acid system using various peroxides including TBHP.<sup>50</sup> Yields of up to 93% based on [TBHP] consumption were obtained with *cyclohexane* as the substrate. A yield of up to 69% alcohol production was achieved and further oxidation of the alcohol to cyclohexanone was also observed. Studies using open-chain alkanes (*n*-hexane and *n*-heptane) as substrates were also carried out but no oxidation of the primary C-H bond was achieved although total yields of up to 83% were obtained.

• Shul'pin *et al.* have demonstrated the oxidation of a variety of substrates using a manganese(v) complex salt.<sup>48</sup> In particular, the results obtained for the oxidation of *n*-octane with TBHP showed the production of a mixture of isomeric alcohols and ketones, with negligible activation of the primary C–H bond.

• Pombeiro, Shul'pin and co-workers have reported a tetracopper(II) triethanolaminate complex for the oxidation of alkanes using  $H_2O_2$  and acid co-catalysts.<sup>51</sup> For *n*-octane, regioselectivity parameters of 1:4.3:3.7:3.4 and 1:5.1:5.2:4.3 were reported.

• Pombeiro *et al.* have also described the oxidation of alkanes using a homogeneous and immobilized Mn(salen) complex.<sup>47</sup> The results obtained for the oxidation of *n*-octane with TBHP are as follows: no activation of the primary C–H bond was observed, isomeric alcohols and ketones were formed which were oxygenated at positions 2, 3 and 4 of the hydrocarbon chain and yields of *ca.* 1% were reported with TONs of up to 110. Furthermore, low regioselectivity profiles [C(2): C(3):C(4)] of 1:1:1.3 and 1.7:1:1.1 for the homogeneous and immobilized catalysts, respectively, were obtained.

• Finally, a report from Pombeiro, Shul'pin and co-workers described the oxidation of alkanes using a  $H_2O_2$ -NaVO<sub>3</sub>- $H_2SO_4$  catalyst system.<sup>52</sup> Regioselectivity parameters of 1:10.1:10.7:8.4 and 1:7:6:5 were obtained for this system in MeCN and  $H_2O$  respectively.

## Conclusion

The preparation of a series of cobalt complexes containing pincer-type SNS ligands with two different backbones, a constrained six-membered pyridine ring and a linear straight chain amine, was achieved. The crystal structures of complexes 1–4 confirmed that the SNS ligands were terdentate and coordinated to the metal centre *via* the N- and S-donor atoms.

All the Co complexes (1-7) were tested for the oxidative functionalization of *n*-octane with TBHP as the oxidant. Only linear C8 oxygenated products were obtained. Complex 1 was the most active catalyst in the pyridine-based series with a total conversion of 12%, while 6 was the most active amongst the two amine-based catalysts with a recorded total conversion of 23%. Overall, the amine-based complexes proved to be the most efficient catalysts in this study, as significantly higher conversions were exhibited compared to the pyridine-based catalysts. But, the more rigid pyridine-based complexes showed better alcohol selectivity.

According to the selectivity profile of each catalyst, octanones were more abundant, with 2-octanone being the dominant product formed, which is in line with the regioselectivity parameter that revealed C2 as the prominent position of attack in the hydrocarbon chain for all the catalysts studied.

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