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# Re(I) carbonyl complexes containing pyridyl-imine and amine ligands: Synthesis, characterization and their catalytic olefin epoxidation activities

Xiaolu Song [a, b], Min Hwee Lim [b], Dara Khairunnisa Binte Mohamed [b], See Mun Wong [b], Jin Zhao [a, b, *], T.S. Andy Hor [a, b, c, **]

[a] Institute of Materials Research and Engineering, Agency for Science, Technology and Research, 2 Fusionopolis Way, Innovis, Singapore 138634, Singapore
[b] Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543, Singapore
[c] Department of Chemistry, The University of Hong Kong, Pokfulam, Hong Kong, China

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## ABSTRACT

Re(I) carbonyl complexes containing pyridyl-imine or amine ligands have been synthesized and crystallographically characterized. Their catalytic activity for the *cis*-cyclooctene epoxidation with *tert*-butyl hydroperoxide (TBHP) as oxidant and the oxidation of these Re(I) complexes by TBHP have been investigated.

## 1. Introduction

Rhenium complexes in the highest oxidation state, methyltrioxorhenium(VII) (MTO) and a number of MTO-Lewis base adducts have been proven to be efficient catalyst for olefin epoxidation catalyst [1]. Common ligands such as Schiff base ligands have also been introduced to the Re based catalyst systems for olefin epoxidation [1–4]. For example, some MTO adducts with Schiff base ligands derived from salicylaldehyde and aniline [2a–2f], or pyridine-imine based ligands [2g,2h], are known to be active for the epoxidation of *cis*-cyclooctene when $H_2O_2$ or urea hydrogen peroxide was used as oxidant. Re(V) oxo complexes containing Schiff base ligands [3], such as tetradentatebis(salicylidene)imine [3a], acetylacetone derived Schiff base ligands [3b], have been also used as catalyst for the *cis*-cyclooctene epoxidation with *tert*-butyl hydroperoxide (TBHP) as oxidant. The oxidation of Re(V) to Re(VII) complexes was proposed to occur in the course of the catalytic reaction although no structurally defined Re(VII) complexes have been isolated [3]. Re(I) carbonyl precursors can be oxidized to Re(VII) oxo complexes through oxidative decarbonylation. It has been reported that $(\eta^5\text{-}C_5R_5)Re(CO)_3$ (R=H or Me) reacted with $H_2O_2$ or TBHP to form $(\eta^5\text{-}C_5R_5)ReO_3$ [5]. Complex *fac*-$[L_3Re(NO)(CO)_2]^+$ (L = 1,4,7-triazacyclononane) could undergo an exhaustive oxidative decarbonylation in the presence of $H_2O_2$ to afford $[L_3ReO_3]^+$ [6]. Therefore, it should be possible and desirable to use air-stable Re(I) carbonyl complexes instead of air-sensitive high-valent Re(VII) complexes as pre-catalyst for olefin epoxidation in the presence of a suitable oxidant. This strategy has been successfully used in Mo based catalyst systems for olefin epoxidation [1d,7]. Among the Re(I) complexes, only the Re(I) carbonyl complexes containing Schiff base derived from 2-amino-2′-hydroxy-1,1′-binaphthyl (NOBIN) and 3,5-dichlorosalicylaldehyde have been tested as catalyst for the epoxidation of styrene and its derivatives with TBHP as oxidant, giving the epoxide yields ranged from 7 to 25% after 10 h with 20 mol% of the catalyst loading [4]. As

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* Corresponding author. Institute of Materials Research and Engineering, Agency for Science, Technology and Research, 2 Fusionopolis Way, Innovis, Singapore 138634, Singapore

** Corresponding author. Department of Chemistry, The University of Hong Kong, Pokfulam, Hong Kong, China.

*E-mail addresses:* zhaoj@imre.a-star.edu.sg (J. Zhao), andyhor@hku.hk (T.S.A. Hor).

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part of our continuous interest in using air-stable low oxidation state metal complexes as pre-catalyst for olefin epoxidation [8], we herein report the synthesis, characterization of a series of Re(I) carbonyl complexes containing pyridyl-imine ligand and those containing pyridyl-amine ligands derived from the pyridyl-imines, and the examination of the catalytic activity of these Re(I) complexes in the *cis*-cyclooctene epoxidation, a benchmark reaction in olefin epoxidation catalysis. The oxidation of the Re(I) complexes by TBHP has also been studied.

## 2. Experimental

### 2.1. General considerations

All preparations and manipulations were performed without taking vigorous precaution to exclude air and moisture unless stated somewhere. All chemicals were used as received. Elemental analyses for C, H, and N were performed on a Perkin-Elmer PE 2400 CHNS elemental analyzer. $^1H$ NMR spectra were measured at room temperature with Brucker ACF300 or Bruker DRX400 MHz FT NMR spectrometer using $CDCl_3$ as solvent. ESI-MS was performed on a Finnigan LCQ quadrapole ion trap mass spectrometer. Catalytic runs were monitored by GC methods on Shimadzu GC-2010 instrument with a J&W DB-1 column. GC-MS was carried out on Agilent 7890A Series GC System with Agilent 5975C inert MSD. All pyridyl-imine [9] and pyridyl-amine [10] ligands (see Supplementary Material), and $Re(CO)_5Br$ [11] were prepared according to the literature procedures.

### 2.2. Synthesis of Re(I) complexes **1**–**6** and **1′**–**5′**

General method: Ligand $\mathbf{L^1}$-$\mathbf{L^6}$ or $\mathbf{L^{1'}}$-$\mathbf{L^{5'}}$ (0.5 mmol) and $Re(CO)_5Br$ (0.203 g, 0.5 mmol) were dissolved in methanol (10 mL) and the mixture was refluxed overnight. After removing all solvent under reduced pressure, the residue was dissolved in $CH_2Cl_2$. The product was precipitated upon addition of hexane. After filtration, the product was dried under reduced pressure.

**1:** (Yield: 0.180 g, 67%) ESI-MS (*m*/*z*): 465 ($[L^1Re(CO)_3]^+$). $^1H$ NMR: $\delta$(ppm) = 9.06(d, 1H, py), 8.79(s, 1H, CH=N), 8.06(t, 1H, py), 7.93(d, 1H, py), 7.58(t, 1H, py), 4.35(m, 2H, $NCH_2$), 2.66(m, 2H, $CH_2S$), 2.42(m, 2H, $CH_2CH_2CH_2$), 2.13(s, 3H, $CH_3$). $^{13}C$ NMR (100.62 MHz): $\delta$(ppm) = 196.8, 196.2, 186.4(CO), 167.2(CH=N), 155.4, 153.8, 139.4, 128.8, 128.4 (py), 64.4 ($NCH_2$), 31.2 ($CH_2S$), 28.4 ($CH_3$), 15.5 ($CH_2CH_2CH_2$). IR (KBr)/cm$^{-1}$: ν(CH) 3045(vw), ν(CH) 2915(w), ν(CO) 2019(vs), ν(CO) 1899(vs), ν(CO) 1886(vs), ν(C=N) 1598(w), 1475(m), 1436(w), 1299(m), 1234(m), 1159(w), 1055(w), 786(m), 531(w). Anal.Calcd for $C_{13}H_{14}BrN_2O_3SRe$: C, 28.68; H, 2.59; N, 5.15; S, 5.89. Found: C, 28.55; H, 2.71; N, 5.47; S, 5.64.

**2:** (Yield: 0.170 g, 66%) ESI-MS (*m*/*z*): 435 ($[L^2Re(CO)_3]^+$).$^1H$ NMR: $\delta$(ppm) = 9.02(d, 1H, py), 8.70(s, 1H, CH=N), 8.05(d, 1H, py), 7.90(t, 1H, py), 7.56(t, 1H, py), 4.32–4.23(m, 2H, $CH_2O$), 3.99–3.92(t, 2H, $NCH_2$), 3.39(s, 3H, $CH_3$). $^{13}C$ NMR (100.62 MHz): $\delta$(ppm) = 196.9, 196.3, 186.4(CO), 167.9(CH=N), 155.5, 153.7, 139.4, 128.7, 128.5(py), 69.6($CH_2O$), 65.6($NCH_2$), 59.2($CH_3$). IR(KBr)/cm$^{-1}$: ν(CH) 3033(vw), ν(CH) 2922(m), ν(CO) 2018(vs), ν(CO) 1920(vs), ν(CO) 1888(vs), ν(C=N) 1598(m), 1474(m), 1301(m), 1222(m), 784(m), 758(m), 643(m), 623(m), 540(m), 520(m), 483(m). Anal.Calcd for $C_{12}H_{12}BrN_2O_4Re$: C, 28.02; H, 2.35; N, 5.45. Found: C, 28.04; H, 2.66; N, 5.64.

**3:** (Yield: 0.200 g, 70%) ESI-MS (*m*/*z*): 497 ($[L^3Re(CO)_3]^+$). $^1H$ NMR: $\delta$(ppm) = 9.04(d, 1H, py), 8.50(s, 1H, CH=N), 8.0(t, 1H, py), 7.82(d, 1H, py), 7.52(t, 1H, py), 7.44(m, 2H, Ar), 7.06(t, 1H, Ar), 6.97(d, 1H, Ar), 5.37(m, 2H, $NCH_2$), 3.82(s, 3H, $CH_3$). $^{13}C$ NMR (100.62 MHz): $\delta$(ppm) = 197.4, 196.3, 190.3(CO), 165.3(CH=N), 155.8, 153.7, 139.1(py), 132.9, 131.4(Ar), 128.4, 128.2(py), 122.3, 121.5, 114.4, 111.3(Ar), 64.5($NCH_2$), 55.8($CH_3$). IR(KBr)/cm$^{-1}$: ν(CH) 3032(vw), ν(CH) 2962(w), ν(CH) 2921(w), ν(CO) 2015(vs), ν(CO) 1908(vs), ν(CO) 1887(vs), ν(C=N) 1599(m), 1492(m), 1251(m), 1122(m), 1029(m), 758(s). Anal.Calcd for $C_{17}H_{14}BrN_2O_4Re$: C, 35.42; H, 2.45; N, 4.86. Found: C, 35.52; H, 2.69; N, 4.67.

**4:** (Yield: 0.201 g, 73%) ESI-MS (*m*/*z*): 473 ($[L^4Re(CO)_3]^+$). $^1H$ NMR: $\delta$(ppm) = 9.04(d, 1H, py), 8.56(s, 1H, CH=N), 8.03(d, 1H, py), 7.85(t, 1H, py), 7.57(m, 1H, py), 7.46(m, 1H, thiophene), 7.13(m, 2H, thiophene), 5.54(s, 2H, $CH_2$). $^{13}C$ NMR (100.62 MHz): $\delta$(ppm) = 197.1, 196.1, 186.2(CO), 165.5(CH=N), 155.5, 153.8, 139.3(py), 135.3, 130.9(thiophene), 128.8(py), 128.7(thiophene), 128.5(py), 128.3(thiophene), 62.3 ($CH_2$). IR(KBr)/cm$^{-1}$: ν(CH) 3025(vw), ν(CH) 2923(w), ν(CO) 2015(vs), ν(CO) 1900(vs), ν(CO) 1884(vs), ν(C=N) 1597(m), 1478(m), 1446(m), 1310(m), 1230(w), 1034(w), 847(w), 768(m), 722(m). Anal.Calcd for $C_{14}H_{10}BrN_2O_3SRe$: C, 30.44; H, 1.82; N, 5.07; S, 5.80. Found: C, 30.03; H, 2.12; N, 4.78; S, 5.81.

**5:** (Yield: 0.198 g, 73%) ESI-MS (*m*/*z*): 462 ($[L^5Re(CO)_3]^+$). $^1H$ NMR: $\delta$(ppm) = 9.04(d, 1H, py), 9.0(s, 1H, CH=N), 8.04(d, 1H, py), 7.96(t, 1H, py), 7.54(t, 1H, py), 4.39–4.21(m, 2H, $CH{=}NCH_2$), 2.54(m, 2H, $CH_2N(CH_3)_2$), 2.38(s, 6H, $CH_3$), 2.26(m, 2H, $CH_2CH_2CH_2$). $^{13}C$ NMR (100.62 MHz): $\delta$(ppm) = 196.9, 196.4, 186.5(CO), 168.0(CH=N), 155.5, 153.7, 139.5, 128.8, 128.6(py), 63.5($CH{=}NCH_2$), 55.9($CH_3$), 53.6($CH_3$), 45.2($CH_2N(CH_3)_2$), 26.8($CH_2CH_2CH_2$). IR (KBr)/cm$^{-1}$: IR (KBr)/cm$^{-1}$: ν(CH) 3020(vw), ν(CH) 2951(m), ν(CO) 2020(vs), ν(CO) 1909(vs), ν(CO) 1884(vs), ν(C=N) 1598(m), 1473(m), 1383(w), 1299(m), 783(m). Anal.Calcd for $C_{14}H_{17}BrN_3O_3Re$: C, 31.06; H, 3.16; N, 7.76. Found: C, 31.29; H, 3.12; N, 7.53.

**6:** (Yield: 0.21 g, 81%) ESI-MS (*m*/*z*): 528 ($[L^6ReBr(CO)_3{+}H]^+$). $^1H$ NMR: $\delta$(ppm) = 9.02 (d, 1H, py), 8.77 (s, 1H, CH=N), 8.04(t, 1H, py), 7.94(d, 1H, py), 7.55(t, 1H, py), 4.29–4.15(m, 2H, $CH{=}NCH_2$), 3.10–2.87 (m, 2H, $CH_2N(CH_3)_2$), 2.37 (s, 6H, $CH_3$). $^{13}C$ NMR (100.62 MHz): $\delta$(ppm) = 196.8, 196.4, 186.5(CO), 167.9(CH=N), 155.5, 153.6, 139.4, 128.7(py), 62.6($CH{=}NCH_2$), 58.2($CH_2N(CH_3)_2$), 45.6($CH_3$). IR (KBr)/cm$^{-1}$: ν(CH) 3018(vw), ν(CH) 2960(w), 2858(w), 2828(w), 2785(w), ν(CO) 2024(vs), ν(CO) 1922(vs), ν(CO) 1894(vs), 1727(w), ν(C=N) 1596(w), 1458(m), 1299(m), 1264(m), 1071(m), 936(w), 785(s), 641(m), 532(m). Anal. Calcd for $C_{13}H_{15}BrN_3O_3Re$: C, 29.61; H, 2.87; N, 7.97. Found: C, 29.28; H, 2.98; N, 7.77.

**1′:** (Yield: 0.186 g, 68%) ESI-MS (*m*/*z*): 467 ($[L^{1'}Re(CO)_3]^+$). $^1H$ NMR: $\delta$(ppm) = 8.85(d, 1H, py), 7.90(t, 1H, py), 7.46(d, 1H, py), 7.37(t, 1H, py), 4.76(m, 1H, $pyCH_2$), 4.17(m, 1H, $pyCH_2$), 3.88(s, 1H, NH), 3.44(m, 2H, $NCH_2$), 2.86(m, 2H, $CH_2S$), 2.15(s, 3H, $CH_3$), 2.13(m, 2H, $CH_2CH_2CH_2$). $^{13}C$ NMR (100.62 MHz): $\delta$ 196.8, 195.9, 192.0(CO), 158.8, 153.8, 139.5, 125.8, 122.3(py), 60.9($pyCH_2$), 57.4($NCH_2$), 31.9($CH_2S$), 28.0($CH_3$), 16.1($CH_2CH_2CH_2$). IR (KBr)/cm$^{-1}$: ν(NH) 3178(w), ν(CH) 3020(vw), ν(CH) 2916(w), ν(CO) 2019(vs), ν(CO) 1911(vs), ν(CO) 1882(vs), 1612(w), 1482(w), 1449(m), 770(m). Anal.Calcd for $C_{13}H_{16}BrN_2O_3SRe$: C, 28.57; H, 2. 95; N, 5.13; S, 5.87. Found: C, 28.79; H, 2.92; N, 5.04; S, 5.62.

**2′:** (Yield: 0.233 g, 90%) ESI-MS(*m*/*z*): 437($[L^{2'}Re(CO)_3]^+$). $^1H$ NMR: $\delta$(ppm) = 8.84(d, 1H, py), 7.89(t, 1H, py), 7.45(d, 1H, py), 7.36(t, 1H, py), 4.80(m, 1H, $pyCH_2$), 4.19(s, 1H, NH), 4.15(m, 1H, $pyCH_2$), 3.74(m, 2H, $CH_2O$), 3.56(m, 2H, $NCH_2$), 3.43(s, 3H, $CH_3$). $^{13}C$ NMR (100.62 MHz): $\delta$(ppm) = 196.8, 196.0, 192.1(CO), 159.2, 153.7, 139.4, 125.6, 122.4(py), 69.7($pyCH_2$), 60.5($NCH_2$), 59.3($CH_2O$), 57.7($CH_3$), IR(KBr)/cm$^{-1}$: ν(NH) 3174(s), ν(CH) 3020(vw), ν(CH) 2933(m), ν(CH) 2862(m), ν(CO) 2022(vs), ν(CO) 1935(vs), ν(CO) 1884(vs), 1612(m), 1486(s), 1451(s), 1225(m), 1125(s), 1047(s), 946(s), 770(s), 636(m), 533(m). Anal.Calcd for $C_{12}H_{14}BrN_2O_4Re$: C, 27.91; H, 2.73; N, 5.43. Found: C, 27.81; H, 2.81; N, 5.05.

**3′:** (Yield: 0.210 g, 73%) ESI-MS(*m*/*z*): 499($[L^{3'}Re(CO)_3]^+$).$^1H$ NMR: $\delta$(ppm) = 8.90(d, 1H, py), 7.83(t, 1H, py), 7.41(d, 1H, py), 7.27(m, 1H, py), 7.25(m, 2H, Ar), 6.98(m, 2H, Ar), 4.93(s, 1H, NH),