Ruthenium(II) diphosphine(phosphine)/imine/amine/CO complexes as efficient catalysts in transfer hydrogenation of ketones

Sai Ge [a], Jin Zhang [a], Jianguo Zhao [a, *], Imran Ulhaq [b], Guibin Ma [b, **], Robert McDonald [b]

[a] Institute of Carbon Materials Science, Shanxi Datong University, Datong, Shanxi Province, 037009, PR China
[b] Department of Chemistry, University of Alberta, Edmonton, Alberta, T6G 2G2, Canada

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ABSTRACT

Treatment of $[RuCl_2(CO)_2]_n$ with different phosphine ligands, four Ru(II) complexes of cis-, cis-, trans-$RuCl_2(CO)_2L_2$ ($L = PH(C_6H_{11})_2$ (**1**), PPh_3 (**2**), $PPh_2(C_6F_5)$ (**3**) and PMe_3 (**4**)), in which **1** and **3** are novel complexes, have been generated in methylene chloride and isolated as pure compound in solid. In CH_2Cl_2 mixed 1:1 molar ratio of $RuCl_2(PPh_3)_3$ and 1,1′-bis(diphenylphosphine)ferrocene (DPPF), and further reacted with quantitative 2-aminopyridine (ampy), 2-picolylamine (picam) and pyridine ligands, the complexes of $RuCl_2(DPPF)(ampy)$ (**5**), $RuCl_2(DPPF)(picam)$ (**6**) and $RuCl_2(DPPF)(Py)_2$ (**7**) were generated in situ and isolated in solid. All complexes are fully characterized by multinuclear NMR (^1H, ^{13}C, ^{31}P and ^{19}F), element analysis and FTIR spectroscopies. Meanwhile, the single crystal structures of **1** and **8** complexes were determined by X-ray crystallography. The observed IR and crystal data of **1** ~ **4** clearly indicate that different phosphine donor ligands occupying trans axis position of $Ru(II)Cl_2(CO)_2$ skeleton can affect the coordination carbonyl C-O bond distance (1.143(3) Å (**1**), 1.135(3) Å (**4**) and 1.131(5) Å (**2**)), and this interaction can be quantitatively detected by its FTIR vibration frequencies. The homogeneous hydrogenation transfer catalytic reactivity of so-synthesized complexes has been tested in a basic 2-propanol solution and they indeed perform the catalytic activities in different behavior, e.g. complexes **1** and **6** are the most active catalysts and represent maximum conversion yield (**1**: 90.4% and **6**: 90.0%) and turnover frequency (TOF) (**1** 18.84 h^{-1} and **6** 37.5 h^{-1}) at our tested experimental condition of these two types of structural complexes, which are discussed in the details.

1. Introduction

Transfer hydrogenation of ketones by ruthenium(II) catalysts is currently one of the most appealing synthesis routes to generate alcohols [1]. Ruthenium(II) complexes containing both nitrogen and phosphino ligands are well-known since the pioneering works for the synthesis of $[RuCl_2(PPh_3)_3]$ [2], and of a large number of derivatives with different combinations of P and N donor ligands [3]. Noyori and co-workers have developed highly active catalyst precursors of the type trans-$RuCl_2$(diphosphine)(1,2-diamine) with both chiral P-P and $H_2N–NH_2$ ligands for highly stereoselective hydrogenation of ketones [4]. It is evident from their mechanism that the Ru-H/−NH₂ motif is a crucial component for the efficient activity of these catalysts [4d,4e]. It is well-established that these

types of ruthenium complexes can also catalyze the transfer hydrogenation of ketones by means of 2-propanol as the hydrogen source.

Dihalodicarbonylruthenium(II) compounds were first reported by Manchot and Konig in 1924 [5]. Cotton and Farthing [6], and later Cleare and Griffith [7], have reported that refluxing $RuCl_3 \cdot xH_2O$ with formic acid produced $[RuCl_2(CO)_2]_n$ almost quantitatively. So halocarbonylruthenium(II) $[RuX_2(CO)_2]_n$ has been considered to be a very useful precursor for the synthesis of a variety of complexes [8]. Wilkinson [2b,9] first reported compounds of type $[RuCl_2(CO)_2L_2]$ ($L = PPh_3$ or $AsPh_3$). Later, Walter and Peter [10] reported $[RuX_2(CO)_2L_2]$ (L is mono- and bidentate ligands containing N, P S Se and Te donor atoms). Thereafter, a variety of Ru(II) complexes containing CO and various ligands, have been synthesized [11] due to their structural novelty and catalytic applicability [12]. To be an effective catalyst for these saturated coordinative complexes, it must first dissociate a ligand in order to bind one of the substrates and gain entry into a catalytic cycle. Krassowski and Nelson

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discovered that complexes of *trans*-(R$_3$P)$_3$RuCl$_2$(CO) isomerize to the thermodynamically preferred *cis* isomer by a dissociation of phosphine [12a]. Similarly, complex of *ttt*-(R$_3$P)$_2$RuCl$_2$(CO)$_2$ thermally isomerize through a dissociation of CO [13]. The CO dissociation is considered to be the control key for the initialization of the catalytic cycles. The catalytic hydrogenation activity of (R$_3$P)$_2$RuCl$_2$(CO)$_2$ might improve by using the cocatalyst of trimethylamine oxide, which can help remove CO as CO$_2$ [14]. This reaction is generally limited to the complexes with ν(CO) greater than 2000 cm^{-1} and CO force constants greater than 16.0 mdyn/cm^{-1} [14c].

We had previously synthesized a series of Ru(II) complexes and studied their hydrogenation transfer reactivity by selecting 1,1′-bis(diphenylphosphino)ferrocene (DPPF) as a 'constant' bidentate P-P ligand while varying the bidentate N-N ligand using different diamine and diimine ligands [15]. At the time we found that diimine has comparable catalytic ability as diamine. We wanted more evidence to understand the catalytic mechanism of systems such as mixed amine and imine ligands, different types of phosphine ligand replacement, as well as replacing the N donor ligands with CO. In our current work, we synthesized a few complexes using 2−aminopyridine (ampy) and 2−picolylamine (picam) bidentate mixed amine and imine coordination atomic ligands. Four different phosphine substituted ligands of P(CH$_3$)$_3$, PH(C$_6$H$_{11}$)$_2$, PPh$_3$ and P(C$_6$H$_5$)$_2$(C$_6$F$_5$) were selected because with these types of functional groups substituted to the phosphorus atom, they can tune the phosphorus coordination ability to ruthenium metal ion center to form complexes with different stability. Herein four different phosphine substituted ligands L and four [RuCl$_2$(CO)$_2$(L)$_2$] complexes of (L: PH(C$_6$H$_{11}$)$_2$ (**1**), PPh$_3$ (**2**) [9], P(C$_6$H$_5$)$_2$(C$_6$F$_5$) (**3**) and P(CH$_3$)$_3$ (**4**) [16]) with a series of different substituted phosphine ligands are synthesized and further tested for their catalytic reactivity of hydrogen-transfer to acetophenone in identical conditions, which generated more evidence to help us fully understand the mechanism and catalytic reactivity.

2. Experimental

All experiments and manipulations were conducted under an inert atmosphere using standard Schlenk techniques. The solvents used in preparations were rigorously dried, and either distilled under Ar immediately prior to use, or stored with Teflon taps inside the dry-box. CH$_2$Cl$_2$ (CaH$_2$); benzene, diethyl ether (sodium metal/benzophenone). The ruthenium precursors of [RuCl$_2$(PPh$_3$)$_3$] [17] and [RuCl$_2$(CO)$_2$]$_n$ [6,7] were prepared exactly as described in the literature.

NMR solvents in solution were dried with 4 Å molecular sieves. NMR spectra were recorded at room temperature (~20 °C) on a Bruker AV 400 instrument (400.0 MHz for ^{1}H, 162.0 MHz for ^{31}P{^{1}H}, and 100.6 MHz for ^{13}C{^{1}H} NMR); CD$_2$Cl$_2$, CD$_3$Cl and DMSO-d_6 solutions of the complexes were used. Residual protonated species in the deuterated solvents were used as internal references; all ^{1}H and ^{13}C shifts are reported in ppm (s = singlet, d = doublet, t = triplet, m = multiplet), relative to external TMS, while ^{31}P{^{1}H} NMR shifts are reported relative to external 85% aqueous H$_3$PO$_4$; J values are given in Hz. IR spectra data were recorded using a Nic-Plan FTIR Microscope. Elemental analyses were performed on a The Carlo Erba EA 1108 elemental analyzer. Gas Chromatography (GC) analyses were performed using an HP Hewlett Packard 5890 GC, fitted with an HP-5 column (50 m × 0.32 mm x 0.52 μm phase thickness), the oven temperature ranged from 50 to 280 °C (10 °C/min) with an injection and detector temperature of 220 °C. IR, GC and EA were carried out in The Analytical and Instrumentation Laboratory, Chemistry Department, University of Alberta.

2.1. Synthesis of cis-, cis-, trans-[RuCl$_2$(CO)$_2$(PH(C$_6$H$_{11}$)$_2$)$_2$] (**1**)

A typical procedure involved the following. The complex [RuCl$_2$(CO)$_2$]$_n$ (23.0 mg; 0.1 mmol) were loaded in a round-bottom tube under N$_2$ and dissolved in 10 ml CH$_2$Cl$_2$; and a slight excess of the ligand dicyclohexylphosphine PH(C$_6$H$_{11}$)$_2$ (44.0 mg; 0.22 mmol) were added. The mixture was stirred under nitrogen for 2 h. The solvent was removed under reduced pressure. The remaining residue was stirred in diethyl ether (10 ml) for approximately 10 min and then filtered. The pure light yellow to white solid was dried under vacuum for 2 h. Data for complex **1**: Yield 80%. Anal. Calc. for C$_{26}$H$_{46}$O$_2$P$_2$Cl$_2$Ru: C, 50.0; H, 7.37. Found: C, 49.84; H, 7.37. ^{1}H NMR (399.79 MH, CD$_2$Cl$_2$, 22 °C): 2.52 (m, 1H, PC**H**), 1.26−2.02 (m, 12H, -C**H**$_2$- ring). ^{13}C{^{1}H} (100.58 MHz, CD$_2$Cl$_2$, 22 °C): 194.90 (t, $^2J_{P-C}$ = 10.7 Hz, CO), 33.35 (t, $^1J_{P-C}$ = 12.21 Hz), 32.43(s), 30.72(s), 27.47 (d, $^2J_{P-C}$ = 5.73 Hz), 27.37 (d, $^2J_{P-C}$ = 5.73 Hz), 26.06(s). ^{13}C{^{1}H, ^{31}P} (100.58 MHz, CD$_2$Cl$_2$, 22 °C): 194.90 (s) (CO), 33.35(s), 32.43(s), 30.72(s), 27.41(s), 27.37(s), 26.06(s); ^{31}P{^{1}H} (162.0 MHz, CD$_2$Cl$_2$, 22 °C): 37.21. IR: 2928s, 2848s (-CH$_2$ C-H stretching), 2349s (-PH P-H stretching), 2035vs, 1974vs (C≡O stretching), 1626s, 1444vs, 1342s, 1303s, 1271s, 1205s, 1184s, 1174s, 1116s, 1073s, 1043 m, 1005s, 915s, 898 m, 859s, 837s, 829s, 817s, 722s. The abbreviations are: vs, very strong; s, strong; m, medium. The white crystal suitable for X-ray structural determination was obtained from the CH$_2$Cl$_2$ solution by very slow evaporation of the solvent.

2.2. Synthesis of cis-, cis-, trans-[RuCl$_2$(CO)$_2$(PPh$_3$)$_3$] (**2**)

The synthesis procedure for **2** was similar as **1**. Data for complex **2**: Yield 81.0%. Anal. Calc. for C$_{38}$H$_{30}$O$_2$P$_2$Cl$_2$Ru: C, 60.59; H, 4.02. Found: C, 60.53; H, 4.12. ^{1}H NMR (399.79 MHz, CD$_2$Cl$_2$, 22 °C): 7.41 (m), 7.43 (m), 7.45 (m), 7.47 (m) (10H); 7.90 (m), 7.91 (m), 7.93 (m), 7.94 (m) (5H). ^{13}C{^{1}H} (100.58 MHz, CD$_2$Cl$_2$, 22 °C): 193.01 (t, $^2J_{P-C}$ = 10.5 Hz, CO), 134.72 (t, $^2J_{P-C}$ = 5.3 Hz), 132.12 (t, $^1J_{P-C}$ = 23.9 Hz), 131.10(s), 128.61 (t, $^4J_{P-C}$ = 5.2 Hz). ^{13}C{^{1}H, ^{31}P} (100.58 MHz, CD$_2$Cl$_2$, 22 °C): 193.02(s) (CO), 134.72(s), 132.12(s), 131.10(s), 128.61(s); ^{31}P{^{1}H} (162.0 MHz, CD$_2$Cl$_2$, 22 °C): 19.91. IR: 3057 m, 2973 m, 2862 m (Ph C-H stretching), 2055vs, 1991vs (C≡O stretching), 1586 m, 1572s, 1482s, 1433vs, 1316 m, 1286 m, 1268 m, 1190s, 1159s, 1088vs, 1028s, 998s, 935 m, 758 m, 746s, 689vs.

2.3. Synthesis of cis-, cis-, trans-[RuCl$_2$(CO)$_2$(PPh$_2$(C$_6$F$_5$))$_2$] (**3**)

The synthesis procedure for **3** was similar as **1**. Data for complex **3**: Yield 80.43% (75.0 mg). ^{1}H NMR (399.79 MH, CD$_2$Cl$_2$, 22 °C): 7.52−7.44 ppm (m, Ph group). ^{13}C{^{1}H} (100.58 MHz, CD$_2$Cl$_2$, 22 °C): 192.05 (t, $^2J_{P-C}$ = 10.8 Hz, CO), 134.23 (t, $^1J_{P-C}$ = 6.1 Hz), 131.90 (s), 129.61(s), 128.91 (t, $^3J_{P-C}$ = 5.4 Hz) (Ph group); 147.18 (dm, $^1J_{C-F}$ = 253.46 Hz), 143.74 (dm, $^1J_{C-F}$ = 258.2 Hz), 138.67 (dm, $^1J_{C-F}$ = 252.2 Hz), 107.60 (t, $^2J_{C-F}$ = 18.8 Hz) (-C$_6$F$_5$ group). ^{13}C{^{1}H, ^{31}P} (100.58 MHz, CD$_2$Cl$_2$, 22 °C): 192.06(s, CO), 134.24(s), 131.90(s), 129.60(s), 128.91(s) (Ph group), 147.18 (double multiple (dm), $^1J_{F-C}$ = 256 Hz), 143.73(dm, $^1J_{F-C}$ = 258 Hz), 138.66(dm, $^1J_{F-C}$ = 252 Hz), 107.61(t, $^2J_{F-C}$ = 16.7 Hz); ^{13}C{^{19}F, ^{31}P} (100.58 MHz, CD$_2$Cl$_2$, 22 °C): 192.06(s, CO), 134.20(double triplet (dt), $^1J_{H-C}$ = 162.4 Hz), 131.80(dt, $^1J_{H-C}$ = 161.4 Hz), 131.80(dt, $^1J_{H-C}$ = 161.4 Hz), 129.69(t, $^1J_{H-C}$ = 6.4 Hz), 128.11(d, $^1J_{H-C}$ = 7.4 Hz) (Ph group), 147.20(s), 143.74(s), 138.66(s), 107.61(s) (-C$_6$F$_5$ group). ^{31}P{^{1}H} (162.0 MHz, CD$_2$Cl$_2$, 22 °C): 13.82. ^{19}F (376.3 MHz, CD$_2$Cl$_2$, 22 °C): −121.79 (d, 2F), −148.02 (triple triplet (tt), 1F), −159.61 (tt, 2F). IR: 3060 m, 2957 m, 2927 m, 2860 m (Ph, C-H stretching), 2062vs, 2002vs (C≡O stretching), 1642s, 1589 m, 1575 m, 1520vs, 1475vs, 1437s, 1388s, 1294s, 1194s, 1093vs, 1027 m, 999 m, 981vs, 842 m, 742s, 691s.

2.4. Synthesis of cis-, cis-, trans-[RuCl₂(CO)₂(P(CH₃)₃)₂] (4)

The compound was synthesized with the reaction between [RuCl₂(CO)₂]ₙ and trimethylphosphine (P(CH₃)₃). The crystal structure determination showed it was the cis-, cis-trans-[RuCl₂(CO)₂(P(CH₃)₃)₂] (4), exactly identical to the structure published in literature which was prepared by passing CO gas through a mixture of RuCl₃ and P(CH₃)₃ in 2-methoxyethanol [16].

2.5. trans-RuCl₂(DPPF)(ampy) (5)

DPPF (55 mg, 0.1 mmol) was added to a rapidly stirred, 10 ml CH_2Cl_2 suspension of RuCl₂(PPh₃)₃ (96 mg, 0.1 mmol). A color change from purple-black to red was observed within a few minutes. The solution was stirred for 30 min, then a CH_2Cl_2 solution of 2-aminopyridine (9.4 mg, 0.1 mmol) was added, giving an immediate color change to yellow-green. After a further 30 min, the solvent was removed in vacuo and 5 ml of diethyl ether (Et₂O) were added. The yellow product was filtered off, washed twice with ether (2 × 5 ml), and then dried under vacuum. Yield: 73 mg (93%). Anal. Calcd for $C_{39}H_{34}Cl_2N_2P_2FeRu$: C, 57.07; H, 4.15; N, 3.41. Found: C, 56.73; H, 4.16; N, 3.42. ^{1}H NMR (DMSO-d_6): 4.32 (s, br. 8H, C₅H₄), 4.55 (s, br. 2H, -NH₂, Py), 6.44 (m, 1H, CH, Py), 7.20–7.34 (m, 20H, Ph), 7.38 (m, 1H, CH, Py), 7.87 (m, 1H, CH, Py). ^{13}C{^{1}H} NMR (DMSO-d_6): 72.1 (s, C₅H₄), 75.0 (s, C₅H₄), 79.1 (s, C₅H₄), 107.9 (s, Py), 111.7 (s, Py), 126.2 (d, $^2J_{C-P}$ = 5.0, Ph), 128.7 (d, $^1J_{C-P}$ = 6.5, Ph), 133.2 (d, $^1J_{C-P}$ = 19.0, Ph), 135.8 (d, $^1J_{C-P}$ = 98.0, Ph), 136.8 (s, Py), 147.6 (s, Py),. 159.7 (s, Py). ^{13}C{^{1}H,^{31}P} NMR (DMSO-d_6): the above ^{13}C{^{1}H } signals became singlets. ^{31}P{^{1}H} NMR (DMSO-d_6): 32.34 (br, s). IR (cm^{-1}): 3298, 3188, 3102, 3057 (ν_{N-H} and ν_{C-H}); 1875, 1602, 1533, 1478, 1433 ($\nu_{C=C}$, and C-H, N-H bending), 1154, 1095, 1032, 747, 697 (ν_{C-C}, ν_{C-N}, ν_{C-P} and bending).

2.6. trans-RuCl₂(DPPF)(picam) (6)

Complexes 6 were synthesized using the same procedure and solvents as described for the synthesis of 5. Yield: 81 mg (97%). Anal. Calcd for $C_{40}H_{36}Cl_2N_2P_2FeRu$: C, 57.42; H, 4.31; N, 3.35. Found: C, 57.73; H, 4.35; N, 3.36. ^{1}H NMR (CD₂Cl₂): 2.12 (s, 2H, CH₂), 4.12 (s, 2H, NH₂), 4.23 (s, 2H, C₅H₄), 4.30 (s, 2H, C₅H₄), 4.40 (s, 2H, C₅H₄), 4.82 (s, 2H, C₅H₄), 7.17–8.19 (m, 20H, Ph), 6.67–8.61 (m, 4H, Py). ^{13}C{^{1}H}: 50.5 (s, CH₂), 69.3 (d, CH of C₅H₄, $^3J_{P-C}$ = 5.15 Hz), 72.1 (d, CH of C₅H₄, $^3J_{P-C}$ = 5.91 Hz), 75.9 (d, CH of C₅H₄, $^2J_{P-C}$ = 7.06 Hz), 78.0 (d, CH of C₅H₄, $^2J_{P-C}$ = 7.44 Hz), 82.5 (d, C of C₅H₄, $^1J_{P-C}$ = 46.92 Hz), 120.9 (s, CH of Py), 122.4 (s, CH of Py), 127.6 (q, CH of Ph), 129.6 (t, CH of Ph), 134.7 (d, CH of Ph), 135.9 (d, CH of Ph), 139.0 (d, C of Ph), 156.4 (d, CH of Py), 163.9 (d, CH of Py). ^{13}C{^{1}H, ^{31}P}: 50.5 (s, CH₂), 69.3 (s, CH of C₅H₄), 72.1 (s, CH of C₅H₄), 75.9 (s, CH of C₅H₄), 78.0 (s, CH of C₅H₄), 82.5 (s, C of C₅H₄), 120.9 (s, CH of Py), 122.4 (s, CH of Py), 127.6 (s, CH of Ph), 129.6 (s, CH of Ph), 134.7 (s, CH of Ph), 135.9 (s, CH of Ph), 139.0 (s, C of Ph), 156.4 (s, CH of Py), 163.9 (s, CH of Py). ^{31}P{^{1}H} NMR: 52.1 (d, $^2J_{P-P}$ = 38.3), 41.5 (d, $^2J_{P-P}$ = 38.3). ESI-MS (THF): m/z 798 [M-Cl⁻]⁺. IR (cm^{-1}): 3332, 3225, 3055, 2915 (ν_{N-H} and ν_{C-H}), 1573, 1481, 1435, 1302 ($\nu_{C=C}$, and C-H, N-H bending), 1154, 1120, 1090, 1032, 812, 755, 747, 697 (ν_{C-C}, ν_{C-N}, ν_{C-P} and bending).

2.7. trans-RuCl₂(DPPF)(Py)₂ (7)

Complexes 7 were synthesized using the same procedure and solvents as described for the synthesis of 5. Yield: 81 mg (92%). Anal. Calcd for $C_{44}H_{38}Cl_2N_2P_2FeRu$: C, 59.80; H, 4.30; N, 3.16. Found: C, 60.00; H, 4.49; N, 3.06. ^{1}H NMR (CD₃Cl): 4.27 (s, 4H, C₅H₄), 4.76 (s, 4H, C₅H₄), 7.20–8.81 (m, 10H, Py), 6.90–7.68 (m, 20H, Ph). ^{13}C{^{1}H}: 69.9 (t, CH of C₅H₄), 77.2 (t, CH of C₅H₄), 87.3 (t, CH of C₅H₄), 122.5 (s, CH of Py), 126.5 (t, CH of Ph), 128.3 (s, CH of Ph), 134.7 (t, CH of Ph),

135.1 (t, CH of Py), 139.0 (t, CH of Ph), 154.2 (s, CH of Py). ^{13}C{^{1}H, ^{31}P}: 69.9 (s, CH of C₅H₄), 77.3 (s, CH of C₅H₄), 87.3 (s, CH of C₅H₄), 122.5 (s, CH of Py), 126.5 (s, CH of Ph), 128.3 (s, CH of Ph), 134.7 (s, CH of Ph), 135.1 (s, CH of Py), 139.0 (s, CH of Ph), 154.2 (s, CH of Py). ^{31}P{^{1}H} NMR: 46.25 (s). IR (cm^{-1}): 3105, 3052(ν_{C-H}), 1483, 1444, 1432 ($\nu_{C=C}$, and C-H, N-H bending), 1217, 1086, 1038, 1020, 811, 745, 696 (ν_{C-C}, ν_{C-N}, ν_{C-P} and bending).

2.8. cis-RuCl₂(DPPF)(Phen) (8)

The synthesis and characterization of complex 8 has been published in our previous work [15]. However, the crystal structure was not included at that time. The square needle red crystals were grown from the CH_2Cl_2 solution by very slow evaporation of the solvent.

2.9. Crystal structure determination

Suitable crystals were mounted on glass fibers by means of mineral oil, and the data were collected using graphite-monochromated MoKα radiation (0.71073Å). Data collection was performed on a Bruker PLATFORM/SMART 1000 CCD diffractometer. The structures were solved by direct methods using the Patterson search/structure expansion (DIRDIF-99) [18], and were refined using full-matrix least-squares on F^2(SHELXL-93) [19]. All non-hydrogen atoms in structures 1 and 8 were refined with anisotropic displacement parameters. The selected crystal data and structural refinement details for 1 and 8 are listed in Table 1.

3. Results and discussion

3.1. Synthesis of complexes

Reaction of polymeric [RuCl₂(CO)₂]ₙ with two molar equiv (Ru:L = 1:2) of the ligands, four cis, cis, trans-[RuCl₂(CO)₂(L)₂] Ru(II) complexes formed in CH_2Cl_2 and isolated in white solid (L = PH(C₆H₁₁)₂ (1), PPh₃ (2), PPh₂(C₆F₅) (3) and P(CH₃)₃ (4)) (see Scheme 1). The complexes 1 to 4 are preparation while 2 and 4 were reported in literature [9,10,11c,16], but herein we updated the preparation for 2 and 4 by using precursor of [RuCl₂(CO)₂]ₙ instead of CO gas. Complexes 5–7, of formulation RuCl₂(DPPF)(N-N) [N-N = ampy (5), picam (6), and RuCl₂(DPPF)(Py)₂] (7) (see Scheme 2), were synthesized from complex of RuCl₂(PPh₃)₃ via consecutive substitution reactions. Addition of one equiv of DPPF to a CH_2Cl_2 solution of RuCl₂(PPh₃)₃ under aerobic conditions resulted in a rapid color change from blackish-purple to red, subsequent addition of one equiv of 2–aminopyridine (ampy), 2–picolylamine (picam) or pyridine resulted in further color changes, and straightforward work-up of the solutions gave good to high yields of high-purity yellow products of complexes 5, 6 and 7 respectively. In addition, the crystal structure of our previously reported known complex of cis–RuCl₂(DPPF)(Phen) (8) [15] was included due to it being unsolved before.

3.2. Spectroscopic characterization

The ^{31}P{^{1}H} NMR of complexes 1–4 were all singlets, which indicate that the two trans-phosphine ligands were identical in each structure. ^{31}P{^{1}H} NMR signal of complex cis, cis, trans-[RuCl₂(CO)₂(PH(C₆H₁₁)₂)₂] (1) was monitored in CH_2Cl_2 at different molar ratio of n = Ru/PH(C₆H₁₁)₂ (1–5). The dominant peak observed of the solution was complex [RuCl₂(CO){PH(C₆H₁₁)₂}₂] (1) at n = 2, its intensity was constant and the peak of free ligand (−23.7 ppm) increased the intensity along with addition of more of PH(C₆H₁₁)₂ up to n = 5. This led us to believe that the coordinated

Table 1
Crystal data and structure refinement details for complex **1** and **8**.

Empirical formula	$C_{26}H_{46}Cl_2O_2P_2Ru$ (**1**)	$C_{46}H_{36}Cl_2FeN_2P_2Ru \cdot 2CH_2Cl_2$ (**8**)
Formula weight	624.54	1076.38
Crystal system	Monoclinic	Monoclinic
Crystal Dimensions	$0.55 \times 0.49 \times 0.17$ mm	$0.18 \times 0.18 \times 0.09$ mm
Space group	P21(No. 4)	I2/a (an alternate setting of C2/c (No. 15)
Unit cell parameters		
a (Å)	10.7266(15)	17.8675(14)
b (Å)	10.2196(14)	13.9858(11)
c (Å)	13.3443(19)	35.666(3)
β (°)	100.8700(19)	94.1840(13)
Volume (Å^3)	1436.6(3)	8888.8(12)
Z	2	8
Calculated density (g/cm^3)	1.444	1.609
Temperature, K	193.2(1)	193.2(1)
μ (MoKα), (mm^{-1})	0.864	1.137
θ range for data collection (°)	0.3 to 26.40	0.3 to 26.00
Index ranges		
	$-13 \leq h \leq 13$	$-22 \leq h \leq 22$
	$-12 \leq k \leq 12$	$-17 \leq k \leq 17$
	$-16 \leq l \leq 16$	$-43 \leq l \leq 43$
Independent reflections	5880	8731
Observed reflections	5697	6267
Data/restraints/parameters	5880/8/448	8731/0/515
Goodness-of-fit on F^2	1.053	0.989
Final R indices		
[$F_0^2 \geq 2\sigma(F_0^2)$]	$R_1 = 0.0189$	$R_1 = 0.0456$
wR$_2$ [$F_0^2 \geq$ -3σ(F$_0^2$)]	wR$_2 = 0.0496$	wR$_2 = 0.1017$
Large difference peak and hole	-0.263 and 0.54 e/Å^3	-0.529 and 0.605 e/Å^3
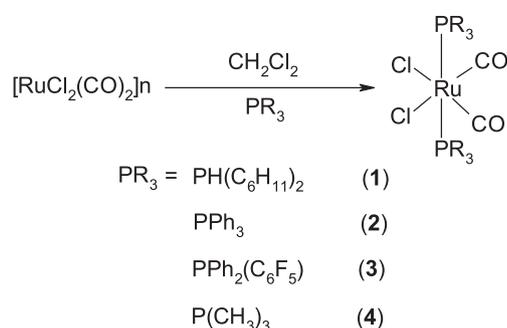
Scheme 1. The synthesized *cis*-, *cis*-, *trans*- Ru^{II}Cl$_2$(CO)$_2$(R$_3$P)$_2$ complexes.
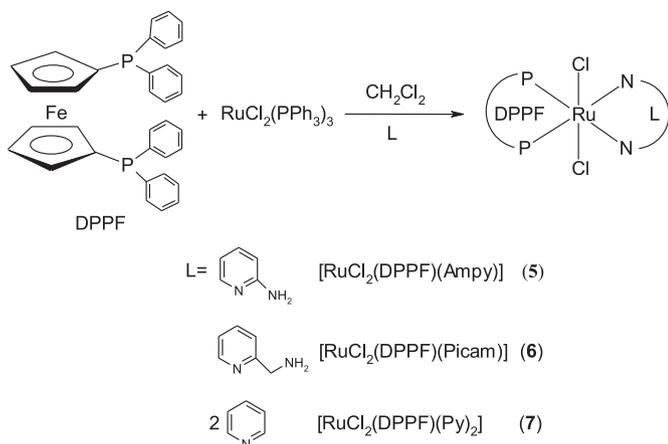
Scheme 2. The synthesized *trans*- Ru^{II}Cl$_2$(DPPF)$_2$(N)$_2$ complexes of (**5**), (**6**) and (**7**).

chloride and carbonyl groups were extremely stable inside the formed species and excess addition of phosphine ligand could not substitute to them.

The solubility of complex RuCl$_2$(DPPF)(ampy) (**5**) is incredibly low in either CDCl$_3$ or CD$_2$Cl$_2$. Its ^{31}P{^{1}H} NMR spectrum in DMSO-d_6 shows a very broad peak at 32.3 ppm indicating existence of the rapid exchange process between ligand and solvent in DMSO solution. As expected, ^{31}P{^{1}H} of complex RuCl$_2$(DPPF)(picam) (**6**) shows a typical AX double of doublets pattern at 52.1 and 41.5 ppm with $^2J_{p-p}$ value of 38.3 Hz, which is in agreement with the bonding of unsymmetrical bidentate N–NH$_2$ ligand (2-picolyamine), and it causes the two coordinated P atoms in no identical or different coordinated environment. The ^{31}P{^{1}H} of complex RuCl$_2$(DPPF)(Py)$_2$] (**7**) gives to a singlet at 46.3 ppm, which is consistent with its expected formation of symmetrical molecular geometry.

The IR spectra (as shown in Table 2) of the complexes showed two equally intense v(C≡O) bands in the range 1974−2062 cm^{-1} attributing *cis*-disposition of the two terminal carbonyl groups. The position of the v(C≡O) bands for these four *cis*-, *cis*-, *trans*- Ru(II) complexes lie in the sequence of PPh$_2$(C$_6$F$_5$) (**3**) > PPh$_3$ (**2**) > P(CH$_3$)$_3$ (**4**) > PH(C$_6$H$_{11}$)$_2$ (**1**). Compared to v(C≡O) stretching bands of the

Table 2
FTIR vibration data for the synthesized RuCl$_2$(CO)$_2$(P)$_2$ and RuCl$_2$(DPPF)(N-N) complexes. Notes: All the IR data of compounds **1** to **4** were recorded from its pure solid phase in the identical condition using a Nic-Plan FTIR Microscope Instrument.

| Species	^{31}P(ppm)	v(C≡O)	Refs
RuCl$_2$(CO)$_2$(PH(C$_6$H$_{11}$)$_2$ (**1**)	37.21	2035, 1974	
RuCl$_2$(CO)$_2$(P(CH$_3$)$_3$)$_2$ (**4**)		2040, 1980	[16]
RuCl$_2$(CO)$_2$(PPh$_3$)$_2$ (**2**)	19.91	2055, 1991	[20]
RuCl$_2$(CO)$_2$P(C$_6$H$_6$)$_2$(C$_6$F$_5$) (**3**)	13.82	2062, 2002	
[RuCl$_2$(CO)$_2$]$_n$		2145, 2073	
RuCl$_2$(CO)$_2$(Ph$_3$PX)$_2$			[11a]
X = O		2059, 1994	
= S		2054, 1991	
= Se		2052, 1989	
		v(N–H)	
RuCl$_2$(DPPF)(Ampy) (**5**)	32.34	3298, 3188	
RuCl$_2$(DPPF)(Picam) (**6**)	52.1, 41.5	3332, 3225	
RuCl$_2$(DPPF)(Py)$_2$ (**7**)	46.25		

polymeric $[RuCl_2(CO)_2]_n$ precursor, the ν bands of all complexes shifted to the lower frequency (Table 2). The interaction on the $\nu(C\equiv O)$ bands arising from the different coordinated *trans*-phosphine ligands was clearly shown in the IR spectra. The phosphine ligand donor electron ability to Ru(II) metal *d* orbit may increase in this sequence $PPh_2(C_6F_5)$ (**3**) < PPh_3 (**2**) < $P(CH_3)_3$ (**4**) < $PH(C_6H_{11})_2$ (**1**). So, the electron density increases on the central Ru metal which leads to the donation of more *d* electrons to the antibonding π^* orbits of CO and consequently slightly reduces the C-O bond order, which in turn reduces or lowers the $\nu(CO)$ frequency. The C-O bond distances were confirmed by crystal structural data (e.g. C-O bond distance 1.143(3) Å (**1**), 1.135(3) Å (**4**) [16] and 1.131(5) Å (**2**) [20]). Therefore, the $\nu(C\equiv O)$ wavelength values of *cis*-, *cis*-, *trans*-$Ru^{II}Cl_2(CO)_2(L)_2$ (**1**–**4**) (L = $PH(C_6H_{11})_2$ (**1**), PPh_3 (**2**), $PPh_2(C_6F_5)$ (**3**) and $P(CH_3)_3$) (**4**)) complexes are considered as possible probes to evaluate the ligands (or L (R_3P) coordination atoms) donor electron ability, and to determine their donation order of the different P ligands based on $\nu(C\equiv O)$ wavelength.

This phenomenon has been observed in a similar complex *cis*-, *cis*, *trans*-$RuCl_2(CO)_2(Ph_3PX)_2$ [11a], where X = O, S, Se respectively (as listed in Table 2). The vibration band positions of the $\nu(CO)$ lie in the following sequence of $Ph_3PO > Ph_3PS > Ph_3PSe$. S and Se are softer than O, so the strong soft-soft interaction between Ru(II) and S or Se increases the central metal electron density and donates more electrons to the antibonding π^* orbital of the CO, and consequently weakens the CO bond order [11a].

The $\nu(N-H)$ vibration bands of complexes **5** and **6** in solid phase were observed at 3298, 3188 cm^{-1} or 3332, 3225 cm^{-1} respectively (as shown in Table 2), indicating presence of $-NH_2$. However, complex **6** exhibited the $[M - Cl]^+$ mass peak similar to $RuCl_2(DPPF)(bipy)$ and $RuCl_2(DPPF)(phen)$ [15], whereas **5** and **7** showed no molecule mass peaks, and the dissociated pyridine and 2-aminopyridine ligands mass peaks were observed respectively, indicating the dissociation of the weakly bonding ligands in the gas phase.

3.3. Crystal structures of cis−[RuCl$_2$(CO)$_2${PH(C$_6$H$_{11}$)$_2$}$_2$] (1) and cis−[RuCl$_2$(DPPF)(Phen)] (8)

The crystal structures of **2** and **4** are available in literature [16,20]. Two crystals of complexes **2** and **4** also grew successfully and the structural determination proved they are the identical structures to *cis*-, *cis*-, *trans*-$RuCl_2(CO)_2(PPh_3)_2$ [20] and *cis*-, *cis*-, *trans*-$RuCl_2(CO)_2(P(CH_3)_3)_2$ [16] in the literature. The crystals of **1** were obtained from the CH_2Cl_2 solution and crystal structure has been determined and shown in Fig. 1. The selected bond lengths and bond angles are given in Table 3. In the molecular structure, the ruthenium atom has a slightly distorted octahedral coordination with two phosphine ligands occupying the two *trans*-octahedral sites, two *cis* CO and two *cis* chlorides. The angle of P1-Ru-P2 is 177.54° and they are very close to linear, and four atoms of H1, P1, P2 and H2 are located almost inside one plane. The torsion angle is 176.0°, which is a slight deviation of 4° to 180°. The average Ru-Cl bond lengths are very close in these three structures (**1**, 2.429 Å; **2**, 2.439 Å; **4**, 2.436 Å), while the average Ru-P bond length in **2** (2.425 Å) is slightly longer than in **1** (2.403 Å) and **4** (2.380 Å). Meanwhile, the average distances of Ru-C are 1.877 Å (**1**), 1.856 Å (**4**), and 1.860 Å (**2**). The average C-O bond lengths of coordination CO ligands are 1.143(3), 1.135(3) [16] and 1.131(5) Å [20] in **1**, **4** and **2** respectively, which display the CO bond order (or bond energy) in the sequence of **2** > **4** > **1**. These data are well in agreement with the observed IR data of the corresponding compounds (Table 2), the longest C-O bond distance of **1** having the lowest vibration frequency, whereas the shortest C-O distance of **2** having the highest frequency. It clearly indicates the different phosphine ligands
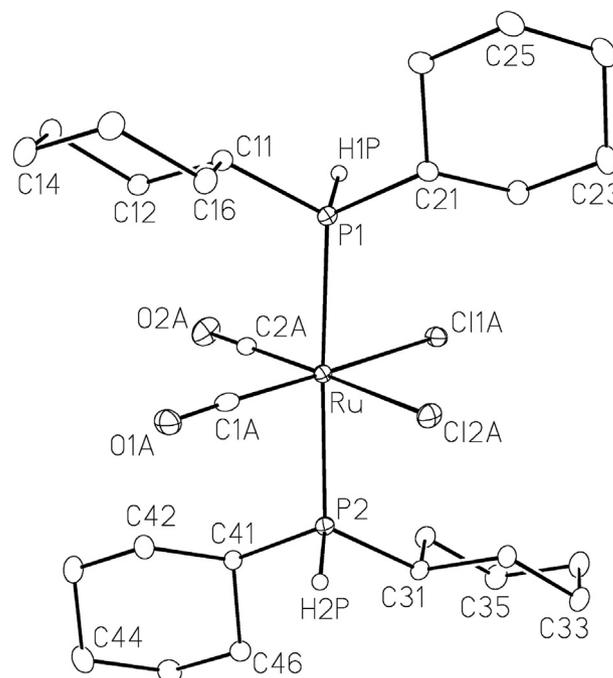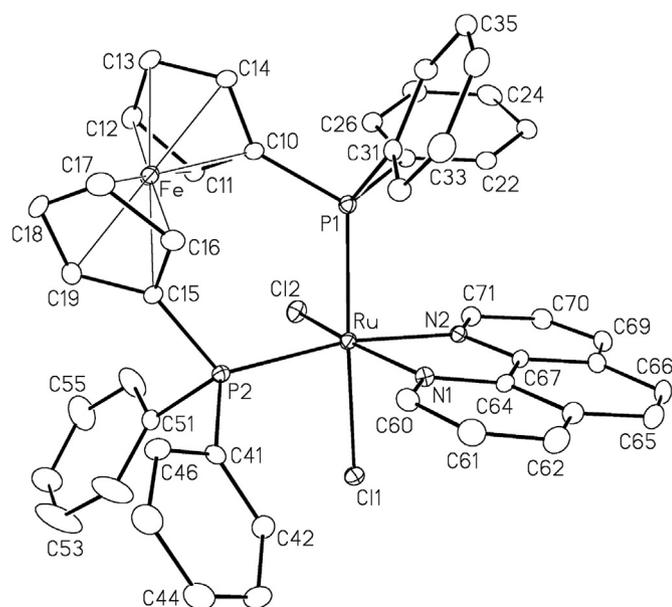

Fig. 1. Perspective view of the *cis*-, *cis*-, *trans*-$RuCl_2(CO)_2\{(PH(C_6H_{11})_2)_2$ (**1**) molecule showing the atom labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. The phosphorus-bound hydrogen atoms are shown with arbitrarily small thermal parameters; cyclohexyl group hydrogens are not shown.

Table 3
Selected Bond Lengths (Å) and Angles (°) for *cis*−$RuCl_2(CO)(PH\{C_6H_{11}\}_2)_2)$ (**1**).

Ru-Cl(1A)	2.4368(7)	Cl(1A)-Ru-Cl(2A)	94.71(3)
Ru-Cl(2A)	2.4201(7)	Cl(1A)-Ru-P(1)	85.49(2)
Ru-P(1)	2.4043(6)	Cl(1A)-Ru-P(2)	93.07(3)
Ru-P(2)	2.4020(6)	Cl(1A)-Ru-C(1A)	178.78(9)
Ru-C(1A)	1.862(3)	Cl(2A)-Ru-P(1)	91.16(3)
Ru-C(2A)	1.892(3)	Cl(2A)-Ru-P(2)	86.97(3)
P(1)-C(11)	1.847(2)	P(1)-Ru-P(2)	177.54(3)
P(1)-C(21)	1.841(3)		
P(1)-H(1P)	1.36(2)		
P(2)-C(31)	1.842(2)		
P(2)-C(41)	1.852(3)		
P(2)-H(2P)	1.26(2)		
O(1A)-C(1A)	1.141(4)		
O(2A)-C(2A)	1.144(4)		

occupying the *trans* axis position of Ru(II) do change the coordination carbonyl C-O bond distances and IR vibration frequency.

Similarly to the previously determined structure of *cis*-$RuCl_2(DPPF)(bipy)$ [15], the crystal structure of **8** (Fig. 2) revealed *cis*-dichloride ligands, with one chlorine being trans to a P-atom and another trans to a N-atom; the Ru-Cl bond length for the chlorine trans to phosphorus (2.4567 Å) is about 0.0384 Å longer than the one trans to nitrogen, in line with the expected trans-effect (see Table 4) [21]. In comparison to a previously generated similar structure [15], the *trans*-effect in **8** is slightly weaker because the Ru-Cl bond length difference (0.0384 Å) is less than the previous structure (0.055 Å). Generally speaking, differences in the Ru-Cl bond of the *cis*-dichloro complexes are in the 0.05−0.09 Å range [22−25]. Such $RuCl_2(P-P)(N-N)$ structures have been discussed extensively [22−25], and at least in one set of complexes, the *trans*- and *cis*-species have been shown to be the kinetic and thermodynamic products, respectively [23].

Fig. 2. Perspective view of the [RuCl$_2${k^2−Fe(C$_5$H$_4$PPh$_2$)$_2$}(k^2−1,10-phenanthroline)] (**8**) molecule showing the atom labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are not shown.
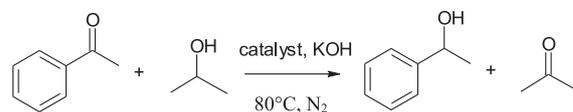
Table 4
Selected Bond Lengths (Å) and Angles (°) for *trans*-RuCl$_2$(DPPF)(Phen) (**8**).

Ru-N(1)	2.098(3)	Cl(1)-Ru-Cl(2)	86.91(4)
Ru-N(2)	2.117(3)	Cl(1)-Ru-P(1)	170.20(4)
Ru-Cl(1)	2.4567(10)	Cl(1)-Ru-P(2)	86.92(3)
Ru-Cl(2)	2.4183(10)	Cl(1)-Ru-N(1)	87.15(8)
Ru-P(1)	2.3130(10)	Cl(1)-Ru-N(2)	83.35(8)
Ru-P(2)	2.3608(10)	Cl(2)-Ru-P(1)	85.16(4)
Fe-C(10)	2.008(4)	Cl(2)-Ru-P(2)	94.00(3)
Fe-C(11)	2.031(4)	Cl(2)-Ru-N(1)	165.60(8)
Fe-C(12)	2.056(4)	Cl(2)-Ru-N(2)	87.68(8)
Fe-C(13)	2.056(4)	P(1)-Ru-P(2)	99.36(3)
Fe-C(14)	2.039(4)	P(1)-Ru-N(1)	99.22(8)
Fe-C(15)	2.020(4)	P(1)-Ru-N(2)	90.57(8)
Fe-C(16)	2.019(4)	P(2)-Ru-N(1)	98.76(8)
Fe-C(17)	2.057(4)	P(2)-Ru-N(2)	170.47(9)
Fe-C(18)	2.057(4)	N(1)-Ru(1)-N(2)	78.61(11)
Fe-C(19)	2.040(4)		

The two planar, cyclopentadienyl rings of ferrocene within structure **8** are eclipsed and are essentially co-planar, the average torsion angle (H-C—C-H) between the C-H of one ring and the most adjacent one of the other ring being 36.54°; the corresponding P-C-C-P torsion angle is 35.46°, which has more twist than the previous similar crystal structure [15]. In the solution ^{1}H NMR spectrum of complex **8**, there is more splitting of the ferrocene-^{1}H signals, consistent with the greater twist evident in the solid state [15].

3.4. Catalytic hydrogenation transfer of acetophenone

A series of Ru(II) complexes of the types (R$_3$P)$_2$RuCl$_2$(CO)$_2$ (R$_3$P = Bzl$_3$P, Ph$_3$P, Ph$_2$MeP, PhMe$_2$P and Me$_3$P) has been used as homogeneous catalysts for hydrogenation of 1-hexene (C=C bond) at 100 °C under a hydrogen pressure of 100 psi in 50% ethanol/benzene [12a]. Herein, the activity of catalytic transfer hydrogenation of ketones (C=O bond) for the synthesized precatalysts has been tested in a basic isopropanol at 80 °C under inert nitrogen atmosphere (Scheme 3). All of the tested complexes performed the homogeneous catalytic hydrogenation transfer reactivity well at the given condition (Table 5). Very interesting results were

Scheme 3. Catalytic hydrogenation transfer reaction.

Table 5
Catalyzed hydrogenation transfer reduction of acetophenone.

Precursor catalysts	Reaction time (h)	Conversion (%)	TOF (h^{-1})[a]
RuCl$_2$(PH(C$_6$H$_{11}$)$_2$)$_2$(CO)$_2$ (**1**)	24	90.4[b]	18.84
RuCl$_2$(PPh$_3$)$_2$(CO)$_2$ (**2**)	24	76.3[b]	15.90
RuCl$_2$(PPh$_2$(C$_6$F$_5$)$_2$(CO)$_2$ (**3**)	24	60.8[b]	12.66
RuCl$_2$(DPPF)(Ampy)$_2$ (**5**)	24	17.0[c]	7.08
RuCl$_2$(DPPF)(Picam) (**6**)	24	90.0[c]	37.50
RuCl$_2$(DPPF)(Py)$_2$ (**7**)	24	42.2[c]	17.58
RuCl$_2$(DPPF)(Phen) (**8**)	24	91.0[c] [15]	37.92[d]
			164.00[d]
			280.00[d]
RuCl$_2$(DPPF)(en)	24	91.0[c] [15]	37.92[e]
			170.00[e]
			312.00[e]

[a] Average calculated data in the whole reaction time 24 h, Experimental condition: in 2-propanol, under N$_2$, 80 °C, KOH.
[b] Cat:Base:S = 1:20:500.
[c] Cat:Base:S = 1:20:1000.
[d] Turnover frequency 37.92 (24 h average), 164.00 (5 h, conversion 82%) and 320.00 (2.5 h, conversion 70%) [15].
[e] Turnover frequency 37.92 (24 h average), 170.00 (5 h, conversion 85%) and 320.00 (2.5 h, conversion 78%) [15].

obtained that the conversion corresponds reversely to the CO vibration frequencies. Seemingly the strong bonded CO is disadvantageous to the catalytic activity (e.g. Ru-C (CO) bond distance = 1.877(3) Å with conversion of 90.4% (**1**) and Ru-C (CO) bond distance = 1.860(5) Å with conversion of 76.3% (**2**) respectively) (Table 5). The carbonyl complexes presented a poor catalytic hydrogenation activity as was observed in previous literature [26]. This demonstrates that CO coordinated to Ru(II) is not beneficial to its hydrogenation catalytic reactivity. As discussed in the introduction, the catalytic hydrogenation activity of (R$_3$P)$_2$RuCl$_2$(CO)$_2$ was improved by using the cocatalyst of trimethylamine oxide, which can help remove CO as CO$_2$ [14]. To the best of our knowledge, it is the first time that activities of complexes **1**–**3** as a hydrogen-transfer catalyst have been tested. These tested results provide experimental evidence to demonstrate the CO affection as hydrogen transfer catalyst.

In the same conditions, the hydrogenation transfer of acetophenone in a basic 2-propanol for complexes **5**–**7** were tested (Scheme 3, Table 5). The data indicate that complex **6** is an efficient hydrogen-transfer catalyst, whereas **5** and **7** seem not so efficiency. The catalytic ability of **6** is compatible with the previously synthesized *trans*-RuCl$_2$(DPPF)(N-N) compounds [15] (where N-N = ethylenediamine (En), diamine or diimine). To our surprise, the monodentate imine ligand Py in **7** demonstrated less activity compared to the bidentate diimine bipy or phen [15], and even worse in **5** with 2-aminopyridine ligand (Table 5). The general catalytic cycle of hydrogenation transfer from 2-propanol to ketone catalyzed by RuCl$_2$P$_2$ activated center was given in Scheme 4. Regarding these two types of catalysts (type I: RuCl$_2$P$_2$(CO)$_2$ and type II: RuCl$_2$P$_2$N$_2$), the proposed general mechanisms (Scheme 4) were either through direct bonding of the substrate (path I) or through 'metal-ligand bifunctional catalysis' (path II), for reduction of ketones implied no direct bonding of the substrate at the Ru atomic center, but via formation of an 'RuH-NH' intermediate unit to link to the ketone (path II, Scheme 4) to provide efficient way to
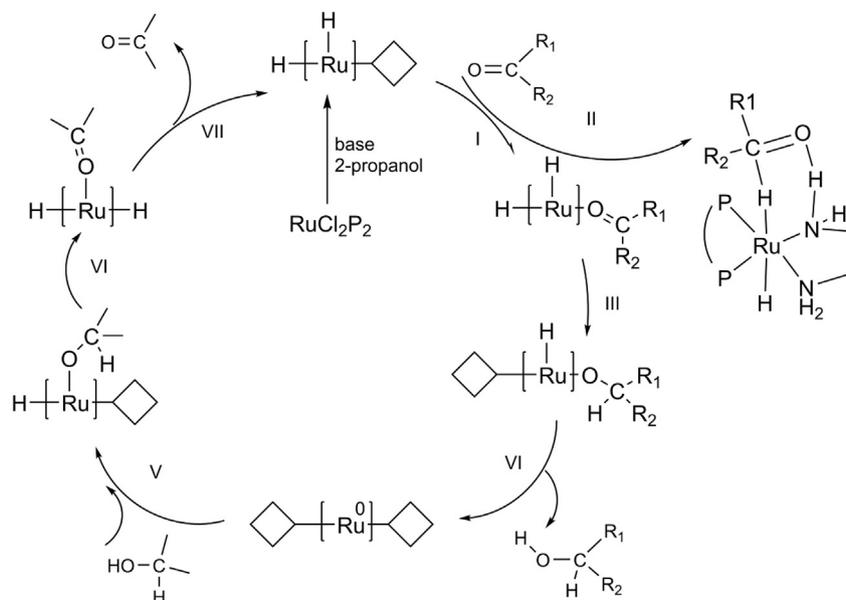
Scheme 4. Catalytic cycle of hydrogenation transfer from 2-propanol to ketones catalyzed by RuCl$_2$(P$_2$)/base. Square symbol represents other possible coordinated ligands.

transfer hydrogen to substrate [27]. Two types of precatalysts as mention above (type I and type II) were investigated (Table 5). We believe that precatalysts of type I react through path I and type II through path II as described in the mechanism cycle (Scheme 4) because it is not possible for type I to form the 'RuH-NH' intermediate. In comparing the catalytic reactivity data tested under the same conditions (Table 5), we can conclude that type I precatalysts are less efficient than type II, as the metal-ligand bifunctional catalysis of RuH-NH intermediate is much more favorable for this kind of hydrogen transfer reactivity [27]. Based on catalytic data of complexes **5 ∼ 8** (Table 5), **6** and **8** are the most efficient with compatible catalytic reactivity, which is much faster than complexes **5** and **7**. Perhaps due to the monodentate ligand Py bonding to Ru(II) being less stable than the bidentate ligands, and more easily dissociated in solution, consequently losing the chance of formation with the activation 'RuH-NH' unit. The four-member ring of Ru-bonding ampy in **5** is incredibly unstable in solution and indeed showed very weak catalytic activity. These activities are consistent with the observed mass spectroscopic results (as shown in experimental section). In addition, similar results are reported in literature [3i], such as bidentate P-P coordinated catalyst of *cis*-RuCl$_2$(Ph$_2$P(CH$_2$)$_4$PPh$_2$)(Picam) (TOF(h^{-1}) = 300000) is much more active than the monodentate P catalyst of *cis*-RuCl$_2$(PPh$_3$)$_2$(Picam) (TOF(h^{-1}) = 5200). In comparison, the turnover frequency (TOF) in literature [3i] is much higher than ours. We believe this is due to different experimental conditions and calculations done using different conversion yields (the literature condition is ketone/Ru/base = 2000/1/40 and calculated TOF at 50% conversion, whereas our condition is ketone/Ru/base = 1000/1/20 and calculated over 24 h reaction time with final obtained conversion Table 5). The interested result for hydrogenation transfer catalytic reactivity obtained is that these selected synthesized compounds all formation five-member-ring coordination to ruthenium(II) through two nitrogen atoms are all efficient hydrogenation transfer catalysts no matter with diamine, diimine [15] or bidentate ligand with mixed amine and imine (compound **6**) (Table 5). In comparison there is little difference between the activities of the amine and imine systems. The coordinated imine is not favorable to the proposed bifunctional catalytic mechanism (RuH-NH intermediate Scheme 4), implying an amine proton is slightly more beneficial to the

catalytic reactivity.

4. Conclusions

A series of carbonyl substituted complexes with *cis*-, *cis*-, *trans*−configuration of RuCl$_2$(CO)$_2$(R$_3$P)$_2$ (**1**−**4**) (type I precatalyst) and the complexes **5**−**8** (type II precatalyst) containing mixed imine and amine ligands have been synthesized and characterized. Hydrogenation transfer catalytic tests demonstrated that the CO substituted precatalysts are not as efficient as the nitrogen donor ligands because two types of precatalysts transfer hydrogen from 2-propanol to ketone through two different catalytic pathways. Through our results, we have demonstrated that the strong bonding ability of phosphine and nitrogen ligands to Ru(II), and their guaranteed formation of the stabilized 'H-Ru-N-H' unit in situ are critically important as efficient hydrogenation transfer catalysts.

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