Solvent and temperature dependent oxidative dehydrogenation reaction of ruthenium ions

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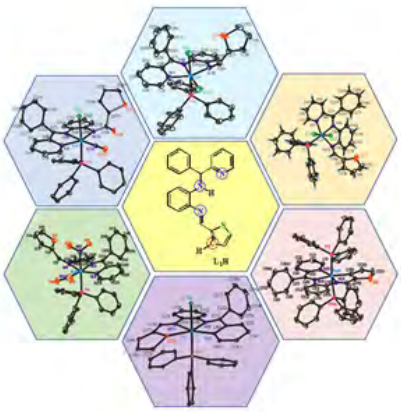
The versatile redox activities of (R1)CH=N-C6H4-NH-C(H)(Ph)(R2) (L1H), an o-phenylenediamine derivative where R1 = thiophene and R2 = pyridine functions, that exhibits flexidenticity and ambidenticity towards ruthenium(II) ion and undergoes oxidative dehydrogenation (OD) of the amine function, thiophene metalation via C-H activation, imine → imidic acid conversion and affords dinitro and [RuNO]7 complexes are reported. Reaction of L1H with [RuII(PPh3)3Cl2] (RuP) in boiling toluene in air promotes OD reaction affording cis-[RuII(L2NNN 0)(PPh3)Cl2] (cis-1), where L1H has been modified to (R1)CH=N-C6H4-N=C(Ph)(R2), a neutral [NNN] donor o-phenylenediimine derivative (L2NNN 0). The same reaction at room temparature furnishes the trans analogue, trans-[RuII(L2NNN 0)(PPh3)Cl2] (trans-1). Conversion of trans-1 → cis-1 has been achieved in boiling xylene. Reaction of cis-1 with I2 and PPh3 in toluene produces [RuII(L2NNNS 0)(PPh3)Cl]I3 (3+I3-), where L1H has been modified to (R1)CH=N-C6H4-N=C(Ph)(R2), a neutral tetradentate [NNNS] donor ligand (L2NNNS 0), where the coordination of thiophene to ruthenium(II) ion has been achieved. Reaction of L1H and RuP in boiling ethanol promotes a C-H activation reaction generating a thiophene metallated complex, trans-[RuII(L2NNNC-)(PPh3)2]+ (trans-2+), where, L1H has been modified to a tetradentate [NNNC] donor ligand (L2NNNC-). The same reaction in presence of excess NaNO2 promotes OD and chloride substitution reactions affording a cis-dinitro complex, cis-[RuII(L2NNN 0)(PPh3)(NO2)2] (cis-4), while the same reaction in presence of HClO4 promotes OD and the oxidation of the imine to imidic acid reactions producing a [RuNO]7 complex of the type [RuII(LOHNNN 0)(PPh3)(NO)Cl]+ (5+), where L1H has been modified to (R1)(OH)C=N-C6H4-N=C(Ph)(R2), o-phenylene-imine-imidic acid derivative (LOHNNN 0). The molecular structures of all the complexes were confirmed by single crystal X-ray crystallography and the electronic structure of 5+ ion was investigated by EPR spectroscopy and DFT calculations.



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