Synthesis, Structure and Catalytic Property
of Transition Metal Complexes with
Phosphorus-Nitrogen and Sulfur-Nitrogen Ligands

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Abstract

The present thesis is organized in four chapters.

In chapter 1, two 1,2,3,5-dithiadiazole free radicals with different pendant pyridyl groups (4-PyCN₂S₂) L₁,₁ and (3-PyCN₂S₂) L₁,₂ were prepared. Their reactions with Fe₂(CO)₁₂ are described. Two iron complexes Fe₂(CO)₆(4-PyCN₂S₂) C₁,₁ and Fe₂(CO)₆(3-PyCN₂S₂) C₁,₂ were synthesized. The CO in C₁,₁ and C₁,₂ could be substituted by PPh₃, P(OEt)₃ to form Fe₂(CO)₅(PPh₃)(4-PyCN₂S₂) C₁,₃, Fe₂(CO)₅(PPh₃)(3-PyCN₂S₂) C₁,₄, Fe₂(CO)₄(PPh₃)₂(4-PyCN₂S₂) C₁,₅, Fe₂(CO)₄(PPh₃)₂(3-PyCN₂S₂) C₁,₆, Fe₂(CO)₄[P(OEt)₂]₂(4-PyCN₂S₂) C₁,₇ and Fe₂(CO)₄[P(OEt)₂]₂(3-PyCN₂S₂) C₁,₈. The structures of C₁,₁, C₁,₃ and C₁,₅ were determined by X-ray diffraction.

In chapter 2, Ru(Ppy)₄Cl₂ C₂,₁ was prepared by refluxing Ru(DMSO)₄Cl₂ in pyridine. The interaction of N,N'-bis[o-(diphenylphosphino)benzylidene]ethylene diimine L₂,₁ with one equivalent of RuCl₂(PPh₃)₃ in dichloromethane at room temperature gave trans-RuCl₂(κ⁺L₂,₁) C₂,₂ in high yield. Differently the interaction of N,N'-bis[o-(diphenylphosphino)benzylidene]ethylenediamine L₂,₂ with one equivalent of RuCl₂(PPh₃)₃ in dichloromethane at room temperature gave trans-RuCl₂(PPh₃) (κ³-L₂,₂) C₂,₅. When refluxed in toluene in air, C₂,₅ was converted quantitatively to trans-RuCl₂(κ⁺L₂,₂) C₂,₃. When treated with one equivalent of hydrogen peroxide in chloroform C₂,₅ was oxidized to C₂,₆, in which the pendant phosphine was oxidized to a phospine oxide. C₂,₆ could be further oxidized with another equivalent of hydrogen peroxide to C₂,₇, in which the amino group trans to PPh₃ was oxidized to an imino group. When treated with an excess amount of hydrogen peroxide in ethanol, C₂,₃ was oxidized to C₂,₈, in which the diamino moiety [-N(H)CH₂CH₂N(H)-] of L₂,₂ was oxidized to a conjugated diimino moiety (-N=CHCH=N-) . The solid state structures
of C_{2,1}, C_{2,5}, C_{2,6}, C_{2,7} and C_{2,8} were ascertained by X-ray crystallography. Other than Ru complexes, three Mo complexes [Mo_2(CO)_6(L_{2,1})] C_{2,10}, [Mo_2(CO)_6(L_{2,3})] C_{2,11} and C_{2,12} were synthesized. The structure of C_{2,12} was determined by X-ray diffraction study which shows that the ligand acts as a bidentate ligand with one of the –C=N– group being broken to become NH_2.

In chapter 3, the interaction of N,N′-bis[2-(diphenylphosphino)benzylidene]-1R,2R-diiminocyclohexane L_{3,1} with RuCl_2(PPh_3)_3 in CH_2Cl_2 at ambient temperature affords RuCl_2(κ^4-L_{3,1}) C_{3,1}, but two complexes C_{3,1} and C_{3,2} were obtained when L_{3,1} reacted with RuCl_2(DMSO)_4 in refluxing benzene. In the structure of C_{3,2}, L_{3,1} become a tridentate ligand. The interaction of RuCl_2(PPh_3)_3 with one equivalent of N,N′-bis[2-(diphenylphosphino)benzylidene]-1R,2R-diiminocyclohexane L_{3,2} in dichloromethane at room temperature gave trans-RuCl_2(κ^3-L_{3,2})(PPh_3) C_{3,3}. When refluxed in toluene under a nitrogen atmosphere, C_{3,3} was converted to trans-RuCl_2(κ^4-L_{3,2}) C_{3,4}; however, when stirred at room temperature in air, C_{3,3} was oxidized to C_{3,5}. Depending on the reaction condition, C_{3,5} was converted to C_{3,6} when heated to 80°C in toluene in air, to C_{3,7} when stirred at room temperature in acetone in air, and to C_{3,8} when refluxed in acetonitrile in a nitrogen atmosphere. C_{3,8} was slowly reduced to C_{3,4}. The solid state structures of C_{3,3}, C_{3,5} and C_{3,7} were ascertained by X-ray crystallography. The interaction of trans-RuCl_2(κ^4-L_{3,1}) C_{3,1} and trans-RuCl_2(κ^4-L_{3,2}) C_{3,4} with AgBF_4 in acetonitrile at room temperature gave two novel ruthenium complexes, cis-{RuCl(CH_3CN)[κ^4-L_{3,1}]}BF_4 C_{3,9} and cis-{RuCl(CH_3CN)[κ^4-L_{3,2}]}BF_4 C_{3,11}. When C_{3,9} was refluxed in pyridine, pyridine replaced CH_3CN to form cis-{RuCl(Py)[κ^4-L_{3,1}]}BF_4 C_{3,10}. However, when C_{3,11} was refluxed in pyridine, one of the –CH-NH_2– single bond in C_{3,11} was oxidized to –C=N– double bond and CH_3CN was also substituted by pyridine to produce C_{3,12}. The
structures of C_{3-10} and C_{3-12} were ascertained by X-ray crystallography. The reaction of L_{3-3}, L_{3-4}, L_{3-5} with RuCl₂(PPh₃)₃ produced trans-RuCl₂(κ⁴-L_{3-3}) C_{3-13}, trans-RuCl₂(κ⁴-L_{3-4}) C_{3-14}, trans-RuCl₂(κ³-L_{3-5}). C_{3-15}, C_{3-13}, C_{3-14}, C_{3-15} were characterized by 'H-NMR, '³¹P-NMR, IR, MS and elemental analysis.

Catalytic studies of Ru complexes are summarized in chapter 4. The data show that C_{2-5} and C_{3-3} are effective catalysts for the oxidation of alkanes, alkenes and alcohols with air, tert-butylhydroperoxide and high pressure oxygen. The asymmetric epoxidation of olefins using chiral ruthenium complexes as catalyst have been examined. Enantioselectivity up to 24% ee was obtained for the epoxidation of styrene by complex C_{3-11}.
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