

DOCTORAL THESIS

Synthesis, structure and catalytic property of transition metal complexes with phosphorus-nitrogen and sulfur-nitrogen ligands

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**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 Fe₃(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)₃]₂(4-PyCN₂S₂) C₁₋₇ and Fe₂(CO)₄[P(OEt)₃]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(Py)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(κ⁴-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(κ⁴-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 phosphine 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 C₂₋₁, C₂₋₅, C₂₋₆, C₂₋₇ and C₂₋₈ were ascertained by X-ray crystallography. Other than Ru complexes, three Mo complexes [Mo₂(CO)₈(L₂₋₁)] C₂₋₁₀, [Mo₂(CO)₈(L₂₋₃)] C₂₋₁₁ and C₂₋₁₂ were synthesized. The structure of C₂₋₁₂ 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 NH₂.

In chapter 3, the interaction of *N,N'*-bis[2-(diphenylphosphino)benzylidene]-1*R*,2*R*-diiminocyclohexane L₃₋₁ with RuCl₂(PPh₃)₃ in CH₂Cl₂ at ambient temperature affords RuCl₂(κ⁴-L₃₋₁) C₃₋₁, but two complexes C₃₋₁ and C₃₋₂ were obtained when L₃₋₁ reacted with RuCl₂(DMSO)₄ in refluxing benzene. In the structure of C₃₋₂, L₃₋₁ become a tridentate ligand. The interaction of RuCl₂(PPh₃)₃ with one equivalent of *N,N'*-bis[2-(diphenylphosphino)benzylidene]-1*R*,2*R*-diaminocyclohexane L₃₋₂ in dichloromethane at room temperature gave *trans*-RuCl₂[κ³-L₃₋₂](PPh₃) C₃₋₃. When refluxed in toluene under a nitrogen atmosphere, C₃₋₃ was converted to *trans*-RuCl₂[κ⁴-L₃₋₂] C₃₋₄; however, when stirred at room temperature in air, C₃₋₃ was oxidized to C₃₋₅. Depending on the reaction condition, C₃₋₅ was converted to C₃₋₆ when heated to 80°C in toluene in air, to C₃₋₇ when stirred at room temperature in acetone in air, and to C₃₋₈ when refluxed in acetone in a nitrogen atmosphere. C₃₋₈ was slowly reduced to C₃₋₄. The solid state structures of C₃₋₃, C₃₋₅ and C₃₋₇ were ascertained by X-ray crystallography. The interaction of *trans*-RuCl₂[κ⁴-L₃₋₁] C₃₋₁ and *trans*-RuCl₂[κ⁴-L₃₋₂] C₃₋₄ with AgBF₄ in acetonitrile at room temperature gave two novel ruthenium complexes, *cis*-{RuCl(CH₃CN)[κ⁴-L₃₋₁]}BF₄ C₃₋₉ and *cis*-{RuCl(CH₃CN)[κ⁴-L₃₋₂]}BF₄ C₃₋₁₁. When C₃₋₉ was refluxed in pyridine, pyridine replaced CH₃CN to form *cis*-{RuCl(Py)[κ⁴-L₃₋₁]}BF₄ C₃₋₁₀. However, when C₃₋₁₁ was refluxed in pyridine, one of the -CH-NH₂- single bond in C₃₋₁₁ was oxidized to -C=N- double bond and CH₃CN was also substituted by pyridine to produce C₃₋₁₂. 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 $RuCl_2(PPh_3)_3$ produced *trans*- $RuCl_2(\kappa^4-L_{3-3})$ C_{3-13} , *trans*- $RuCl_2(\kappa^4-L_{3-4})$ C_{3-14} , *trans*- $RuCl_2(\kappa^3-L_{3-5})$ C_{3-15} . C_{3-13} , C_{3-14} , C_{3-15} were characterized by 1H -NMR, ^{31}P -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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