Synthesis, Spectral and Structural Characterization of Novel Dichloro-Ruthenium(II)/triphenylphosphine/(3,4-diaminophenyl)(phenyl)methanone Complex

Ismail Warad

Department of Chemistry, AN-Najah National University, Nablus, State of Palestine.

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* Corresponding author. E mail: i.kh.warad@gmail.com, warad@najah.edu.

Abstract
The novel trans-[Cl₂Ru(II)(PPh₃)₂(3,4-diaminophenyl)(phenyl)methanone] complex was obtained by reacting RuCl₂(PPh₃)₃ with equimolar amounts of (3,4-diaminophenyl)(phenyl)methanone as diamine co-ligand in CH₂Cl₂. One of the PPh₃ ligand was quantitatively exchanged by (3,4-diaminophenyl)(phenyl)methanone, even when excess diamine was added. The trans-RuCl₂ desired complex was characterized on the basis of elemental analysis, elemental analysis, FAB-MS, IR, UV-vis, ¹H, ¹³C and ³¹P{¹H}NMR.

Keywords: Ruthenium(II) complexes; phosphines; Diamine ligands, NMR.

1. Introduction
Ligands with phosphorus atom (phosphine) have been intensively used in coordination chemistry because of their electron-donating power [1-9]. Ligands with two phosphorus atoms (diphosphine) have received more particular attention compared by mono-phosphine, because in general they form more stable complexes than their non-chelating phosphine analogues under the harsh reaction conditions required for catalysis [10-20]. Partially we are interested in fluxional processes of ruthenium(II) and palladium(II) complexes containing monodentate (P~0) and bidentate (P^0) ether-phosphines because of their potential in synthesis and catalysts [1-20]. These ligands form a close metal-phosphorus contact and only weaker metal-oxygen bonds which may be cleaved reversibly [8-14].

Ruthenium complexes with a diphosphine and diamine ligand in the presence of a base catalyzed effectively ketones with no secondary binding functionality [12-20]. These complexes have received much attention in recent years due to their remarkable performance in the asymmetric catalytic hydrogenation of carbonyl compounds [10-18].

The most general and efficient catalyst for this reaction was pioneered by Noyori, who showed that ruthenium complexes of the type [(diphosphine)RuCl₂(diamine)], used in the presence of a base in 2-propanol, are extremely efficient and selective catalysts for the asymmetric reduction of unfunctionalized ketones [21-26]. Much less effort has been dedicated since Noyori’s work using his well-known bulky XylBinap as chiral ligand in ruthenium system [27-29], numbers of other groups have demonstrated the use of other diphosphines and diamines that give rise to high activities and selectivities when used in this catalyst system [1-6, 15-20].

2. Experimental
2.1 materials
All reactions were carried out in an inert atmosphere (argon) by using standard high vacuum and Schlenk-line techniques unless otherwise noted. Prior to use CH₂Cl₂, n-hexane, and Et₂O were distilled from CaH₂, LiAlH₄, and from sodium/benzophenone, respectively. Diamines were purchased from Fluka and purified by distillation before use. (3,4-diaminophenyl)(phenyl) methanone and RuCl₂•3H₂O were available from Merck and Chempur, respectively, and were used without further purification. RuCl₂(PPh₃)₃ was prepared according to literature methods [27].
2.2 Preparation of trans-[Cl₂Ru(II)(PPh₃)₂(3,4-diaminophenyl)(phenyl)methanone]
The precursor compound of general formula trans-Cl₂Ru(PPh₃)₂N-N was obtained by a substitution reaction starting from Cl₂Ru(PPh₃)₃ and (3,4-diaminophenyl)(phenyl)methanone in dichloromethane. The corresponding 1,2 diamine (3,4-diaminophenyl)(phenyl)methanone, 10 % excess) was dissolved in 10 mL of dichloromethane then added dropwise to a stirred solution of Cl₂Ru(PPh₃)₃ dissolved in 10 mL of dichloromethane within 5 min. The mixture was stirred for ca. 10-30 min at room temperature while the color changed from brown to yellow. After removal of any turbidity, the volume of the solution was concentrated to about 2 ml under reduced pressure. The product was precipitated by addition of 40 mL of diethyl ether a re-crystallized from dichloromethane/n-hexane.

2.2.1. trans-[Cl₂Ru(II)(PPh₃)₂(3,4-diaminophenyl)(phenyl)methanone]
Cl₂Ru(PPh₃)₂ (500 mg, 0.52 mmol) was treated with (3,4-diaminophenyl)(phenyl)methanone (0.11 ml, 0.55 mmol) to give the desired complex. Yield (87%) of a yellow powder. ¹H NMR (CDCl₃): δ (ppm) 3.48 (br, 4H, NH₂), 7.17 - 7.80 (m, 20H, C₆H₄). ³¹P{¹H} NMR (CDCl₃): δ (ppm) 45.2. ¹³C{¹H} NMR (CDCl₃): δ (ppm) 128.3 - 138.3 (m, C₆H₂), FAB – MS; (m/z): 908.1 (M⁺).

2.3. Instrumentation
Elemental analyses were carried out on an Elementar Vario EL analyzer. High-resolution ¹H, ¹³C{¹H}, DEPT 135, and ³¹P{¹H} NMR spectra were recorded on a Bruker DRX 250 spectrometer at 298 K. Frequencies are as follows: ¹H NMR 250.12 MHz, ¹³C{¹H} NMR 62.9 MHz, and ³¹P{¹H} NMR 101.25 MHz. Chemical shifts in the ¹H and ¹³C{¹H} NMR spectra were measured relative to partially deuterated solvent peaks which are reported relative to TMS. ³¹P chemical shifts were measured relative to 85% H₃PO₄. EI-MS, Finnigan TSQ70 (200 °C) and FAB-MS, Finnigan 711A (8 kV), modified by AMD and reported as mass/charge (m/z).

3. Results and Discussion
3.1 Synthesis of the complexes
The neutral trans-dichloro(bis(triphenylphosphine)(3,4-diaminophenyl)(phenyl)methanone) ruthenium(II) complexes was prepared in a good yield starting from [Cl₂Ru(PPh₃)₃] and (3,4-diaminophenyl)(phenyl)methanone at room temperature using degassed dichloromethane as solvent as een in Scheme 1.

Scheme 1. Synthesis of the desired ruthenium(II) complex.

The complex has been characterized by elemental analysis, infrared spectroscopy, UV-visible, ¹H, ¹³C{¹H}, ³¹P{¹H} NMR and FAB-MS spectroscopy.

3.2 Elemental analysis and FAB-Mass spectra
The elemental analysis of the complex is consistent with the proposed molecular formula. The found elemental Analysis: C, 64.32; H, 4.08; Cl, 7.45; N, 3.12, calculated from formula C₉₇H₇₆Cl₂N₂OP₂Ru: C, 64.76; H, 4.66; Cl, 7.80; N, 3.08; O, 1.76; P, 6.82; Ru, 11.12.

The FAB-MS spectrum of the desired complex shows a molecular ion peak [M⁺] m/z = 908.1, which corresponds to the molecular formula of its parent ion [C₉₇H₇₆Cl₂N₂OP₂Ru]⁺ at 15% of the base peak intensity. The main first three fragments that appeared in the spectrum correspond to m/z = 873.1 [[C₉₇H₇₂ClN₂OP₂Ru]⁺, 10%, [M⁺]-Cl, and 836.2 [C₉₇H₇₀N₂OP₂Ru]⁺, 12%, [M⁺]-2Cl as in Fig 1.
3.3 IR spectral investigations
The IR spectra of the desired complexes were examined in comparison relative to the spectra of free ligands. In particular, the desired complex revealed four main sets of characteristic absorptions in the ranges of 3350 to 3030, 1650 and 270-260 cm⁻¹, which can be assigned to –NH₂, Ph–H, C=O and Ru–Cl stretching vibrations, respectively. All the other function group vibrations are appeared at their expected positions as in Fig. 2.

3.4 Electronic absorption spectral studies
The electronic absorption spectrum of desired complexes was acquired in CH₂Cl₂ at room temperature. The complexes formed colorless solutions (10⁻⁴ M). The complexes displayed intense transitions in the UV–Vis region. Bands in the high-energy side at 200–280 nm that is referred to the ligand centered charge transitions.
On the basis of its intensity and position, the lowest energy transitions at ~ 352 nm have been tentatively assigned to intra-ligand π-π*/n-π* transitions [1-4, 31-33]. Lowest energy transitions in the visible region at 550 nm have been tentatively assigned to MΔπ-Lσ metal to ligand charge transfer transitions (MLCT) [1-4, 31-33], see the electronic absorption of the desired complexe as in Fig 3.

![UV-Vis spectra](image)

**Fig.3.** UV–Vis spectra of the complex directly dissolved in CH2Cl2 at RT.

### 3.4 NMR investigation

In the 31P{1H} NMR spectra of the desired complex and due to asymmetric diamine without the C2 axis which results in a splitting of the 31P resonances into AB patterns. The 31P{1H} NMR spectra of the complex dissolved in CDCl3 showed dd AB pattern signal (with δA = 45.3 and δB = 45.7 ppm, coupling constant of P-P atoms, JAB = 34.2 Hz). The 31P chemical shifts and the 31P-31P coupling constants are consistent with unequal P atoms of PPh3 ligands in a trans-Cl2Ru arrangement as in Scheme 1 and Fig. 4.

![NMR spectrum](image)

**Fig. 4.** 31P{1H} NMR spectrum of the desired directly dissolved in in CDCl3 at RT
The $^1$H-NMR and $^{13}$C($^1$H)NMR spectra of the desired complexes have been recorded in CDCl$_3$ solution to confirm the binding of the diamine and phosphine ligand to Ru(II) center and their assignments are given in section 2. Two main characteristic set of signals are observed attributed to the desired complex. The integration of the $^1$H resonances confirms the desired complexes formation, as in Fig. 5.

**Fig. 5.** $^1$H and DEPT 135 $^{13}$C($^1$H) NMR spectra corroborates the structure of the desired complex in CDCl$_3$ at RT

**Conclusions**

Novel trans-[Cl$_2$Ru$^{III}$](PPh$_3$)$_2$(3,4-diaminophenyl)(phenyl)methanone] complex was made available through direct simple procedure using equivalent of RuCl$_5$(PPh$_3$)$_3$ and (3,4-diaminophenyl)(phenyl)methanone co-ligand in good yield. The trans-RuCl$_2$ octahedral desired complex structure was characterized on the basis of elemental analysis, FAB-MS, IR, UV-vis, $^1$H, $^{13}$C and $^{31}$P($^1$H)NMR.
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References

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