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

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Abstract

The novel *trans*-[$Cl_2Ru^{(II)}(PPh_3)_2$(3,4-diaminophenyl)(phenyl)methanone] complex was obtained by reacting $RuCl_2(PPh_3)_3$ with equimolar amounts of (3,4-diaminophenyl)(phenyl)methanone as diamine co-ligand in CH_2Cl_2. One of the PPh_3 ligand was quantitatively exchanged by (3,4-diaminophenyl)(phenyl)methanone, even when excess diamine was added. The *trans*-$RuCl_2$ desired complex was characterized on the basis of elemental analysis, elemental analysis, FAB-MS, IR, UV-vis, ^1H, ^{13}C and $^{31}P\{^1H\}$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)$RuCl_2$(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 CH_2Cl_2, *n*-hexane, and Et_2O were distilled from CaH_2, $LiAlH_4$, and from sodium/benzophenone, respectively. Diamines were purchased from Fluka and purified by distillation before use. (3,4-diaminophenyl)(phenyl) methanone and $RuCl_3{\bullet}3H_2O$ were available from Merck and Chempur, respectively, and were used without further purification. $RuCl_2(PPh_3)_3$ was prepared according to literature methods [27].

2.2 Preparation of *tran*-[$Cl_2Ru^{(II)}(PPh_3)_2$(3,4-diaminophenyl)(phenyl)methanone]

The precursor compound of general formula *trans*-$Cl_2Ru(PPh_3)_2$N-N was obtained by a substitution reaction starting from $Cl_2Ru(PPh_3)_3$ 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 $Cl_2Ru(PPh_3)_3$ 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. *tran*-[$Cl_2Ru^{(II)}(PPh_3)_2$(3,4-diaminophenyl)(phenyl)methanone]

$Cl_2Ru(PPh_3)_2$ (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 ($CDCl_3$): δ (ppm) 3.48 (br, 4H, NH_2), 7.17 - 7.80 (m, 20H, C_6H_5). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ (ppm) 45.2. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ (ppm) 128.3 – 138.3 (m, C_6H_5), FAB – MS; *(m/z)*: 908.1 (M^+).

2.3. Instrumentation

Elemental analyses were carried out on an Elementar Vario EL analyzer. High-resolution ^1H, $^{13}C\{^1H\}$, DEPT 135, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker DRX 250 spectrometer at 298 K. Frequencies are as follows: ^1H NMR 250.12 MHz, $^{13}C\{^1H\}$ NMR 62.9 MHz, and $^{31}P\{^1H\}$ NMR 101.25 MHz. Chemical shifts in the ^1H and $^{13}C\{^1H\}$ NMR spectra were measured relative to partially deuterated solvent peaks which are reported relative to TMS. ^{31}P chemical shifts were measured relative to 85% H_3PO_4. EI-MS, Finnigan TSQ70 (200 ^oC) 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 [$Cl_2Ru(PPh_3)_3$] and (3,4-diaminophenyl)(phenyl) methanone at room temperature using degassed dichloromethane as solvent as een in Scheme 1.

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

The complex has been characterized by elemental analysis, infrared spectroscopy, UV-visible, ^1H , $^{13}C\{^1H\}$, $^{31}P\{^1H\}$ 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, caluclated from formula $C_{49}H_{42}Cl_2N_2OP_2Ru$: 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 $[C_{49}H_{42}Cl_2N_2OP_2Ru]^+$ at 15% of the base peak intensity. The main first three fragments that appeared in the spectrum correspond to m/z = 873.1 [$[C_{49}H_{42}ClN_2OP_2Ru]^+$, 10%, [$M^+$]-Cl, and 836.2 $[C_{49}H_{42}N_2OP_2Ru]^+$, 12%, [$M^+$]-2Cl as in Fig 1.

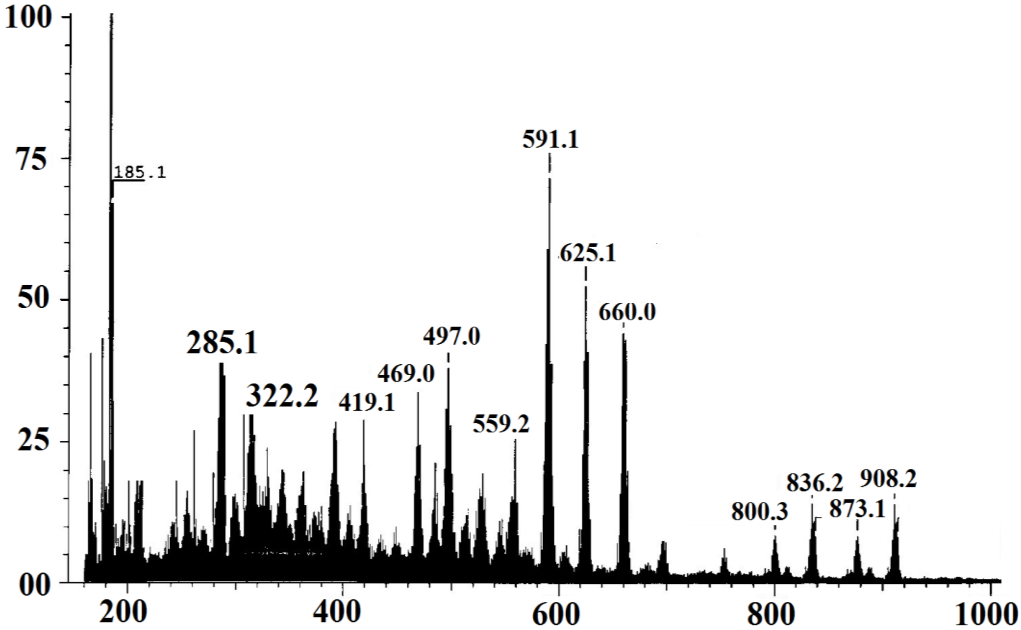

Fig. 1. FAB-MS spectrum of the complex.

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 disered 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 –NH_2, 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.

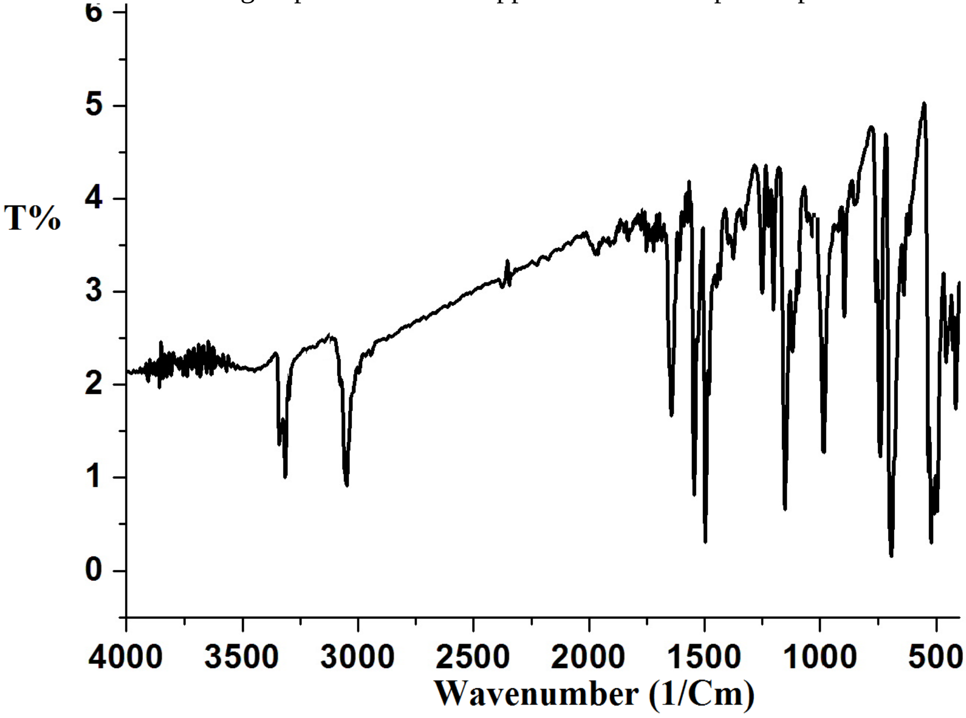

Fig. 2. IR-KBr disk spectrum of the complex.

3.4 Electronic absorption spectral studies

The electronic absorption spectrum of desired complexes was acquired in CH_2Cl_2 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 has been tentatively assigned to 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 $M_{d\pi}$-$L_{\pi*}$ metal to ligand charge transfer transitions (MLCT) [1-4, 31-33], see the electronic absorption of the desired complexe as in Fig 3.

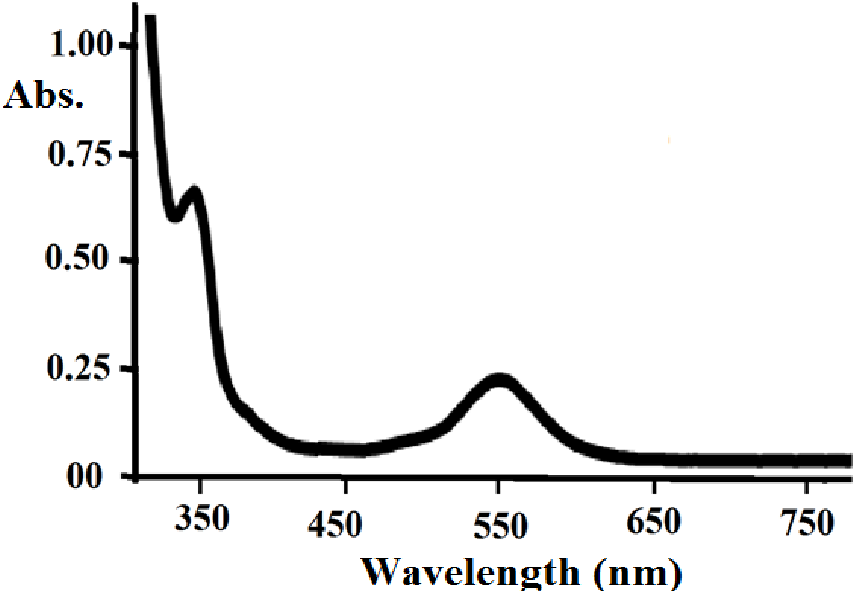

Fig.3. UV–Vis spectra of the complex direct dissolved in CH_2Cl_2 at RT.

3.4 NMR investigation

In the $^{31}P\{^1H\}$ NMR spectra of the desired complex and due to asymmetric diamine without the C_2 axis which results in a splitting of the ^{31}P resonances into AB patterns. The $^{31}P\{^1H\}$ NMR spectra of the complex dissolved in $CDCl_3$ showed dd AB pattern signal (with $\delta_A = 45.3$ and $\delta_B = 45.7$ ppm, coupling constant of P-P atoms, J_{AB} = 34.2 Hz). The ^{31}P chemical shifts and the ^{31}P-^{31}P coupling constants are consistent with unequivalent P atoms of PPh3 ligands in a *trans*-Cl_2Ru arrangement as in Scheme 1 and Fig. 4.

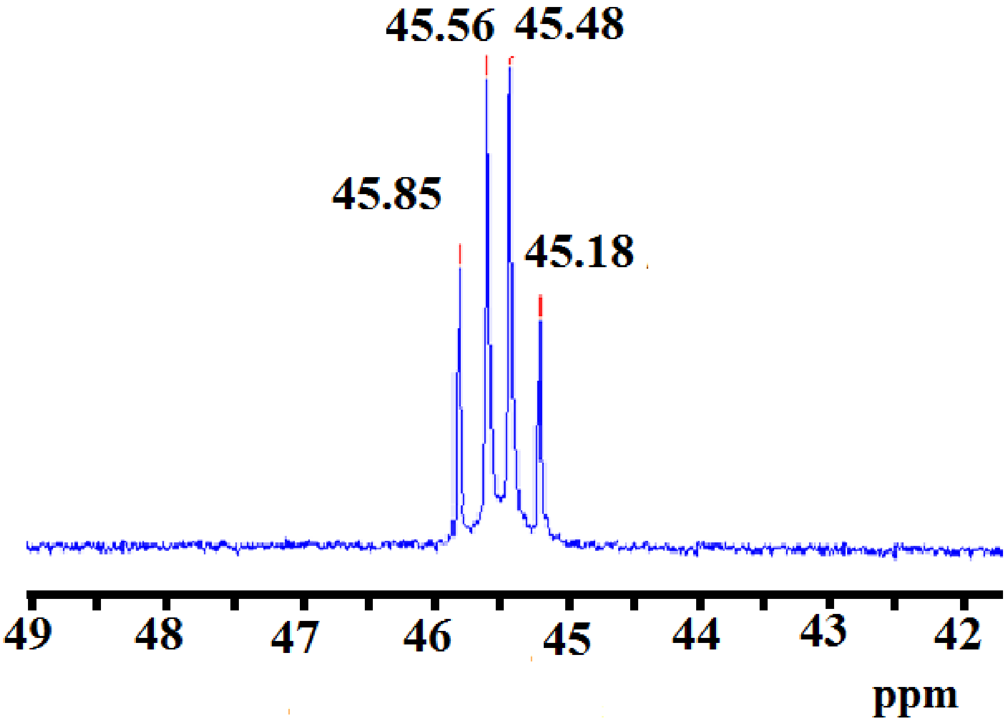

Fig. 4. $^{31}P\{^1H\}$NMR spectrum of the desired direct dissolved in in $CDCl_3$ at RT

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. Tow 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 .

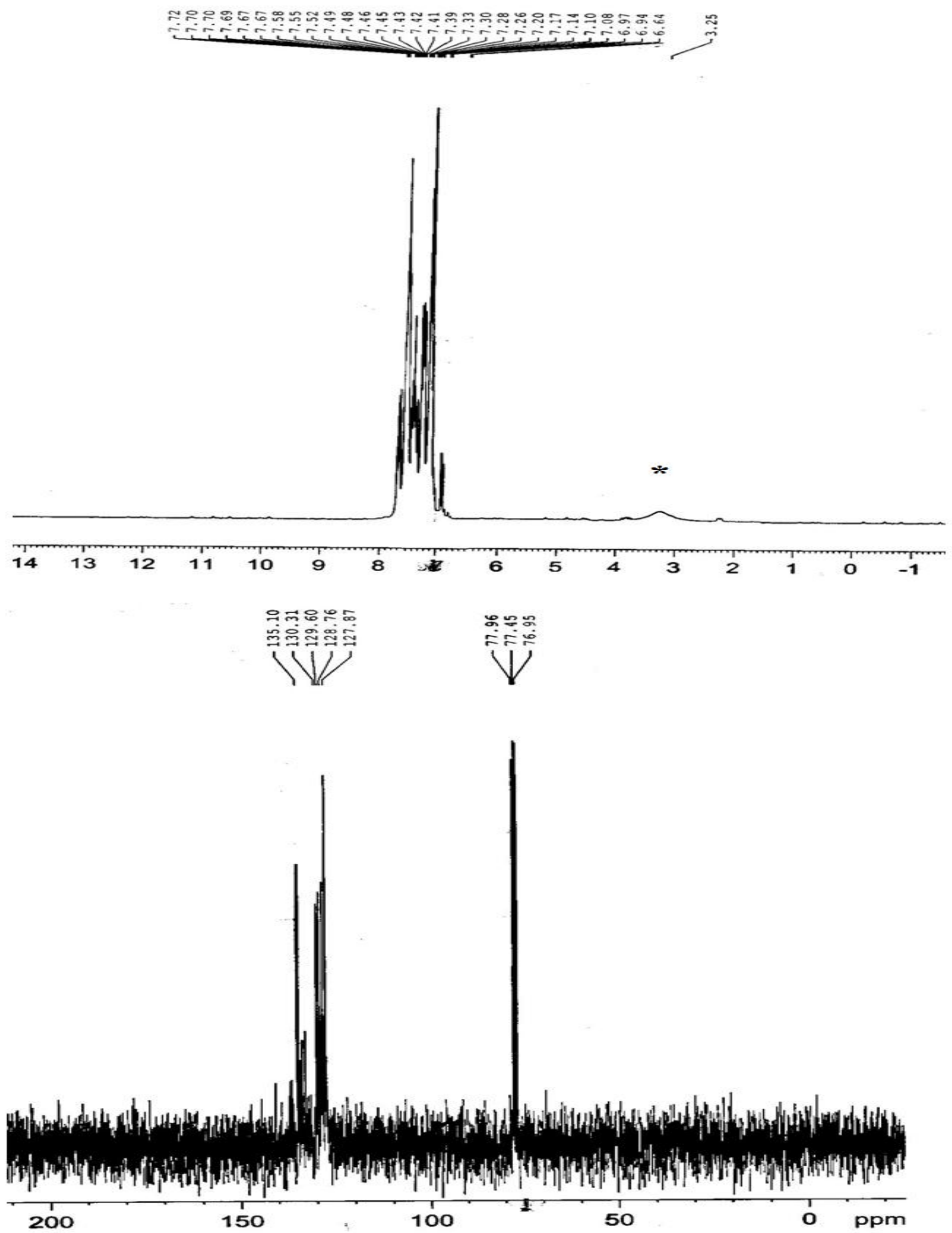

Fig. 5. ^{1}H and DEPT 135 $^{13}C\{^{1}H\}$ NMR spectra corroborates the structure of the desired complex in $CDCl_3$ at RT

Conclusions

Novel *trans*-[$Cl_2Ru^{(II)}(PPh_3)_2$(3,4-diaminophenyl)(phenyl)methanone] complex was made available through direct simple procuder using equivalent of $RuCl_2(PPh_3)_3$ 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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