

Synthesis and Spectroscopic Studies of Molybdenum (0) and Ruthenium(II) Complexes of 2,2'-Dipyridylamine⁺

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Summary: The reaction between neutral electron donor ligand 2,2'-dipyridylamine (dpa) with Mo(CO)₆ or [RuCl₂(CO)₂]_n in (1:1) molar ratio in refluxing THF affords Mo(CO)₄ dpa and RuCl₂(CO)₂ dpa complexes in high yields. On the basis of spectroscopic studies it is suggested that the ligand (dpa) in these complexes acts as bidentate and coordinates to the metals through pyridine-N atoms rather than with the amino group. The complex Mo(CO)₄ dpa reacts with iodine to give seven coordinated Mo(CO)₃ dpaI₂ complexes. All the complexes were characterised by their ¹H-NMR, IR and elemental analyses.

Introduction

Transition metal carbonyls are known to coordinate with neutral electron donor ligands to form stable complexes [1,2]. The complexes so formed are electron rich and of low ionization energy. Thus the ligand (dpa) reacts with molybdenum hexacarbonyl and dichlorodicarbonylruthenium(II) in refluxing THF giving bright yellow Mo(CO)₄ dpa and pale yellow RuCl₂(CO)₂ dpa solid complexes respectively. The ligand (dpa) acts as bidentate in these complexes. The bidentate nature of (dpa) has recently been reported in Cu(I) complex by X-ray as a dimer [dpaCu₂Cu(dpa)] showing that it is coordinated to metal through the pyridine-N atom [3]. The dpa complexes of Zn(II), Ni(II) and UO₂Cl₂(VI) have also been reported from our laboratories [4]. The complex Mo(CO)₄ dpa on treatment with iodine at room temperature gave an orange brown seven coordinated solid diiodotricarbonyl 2,2'-dipyridylamine molybdenum(II) complex.

The salt [RuCl₂(CO)₂]_n has been proved to be a useful precursor for the synthesis of dichlorodicarbonylruthenium(II) complexes [5-8]. The pale yellow complex RuCl₂(CO)₂ dpa was prepared on treatment of [RuCl₂(CO)₂]_n with dpa in THF.

All the complexes were characterised by their infrared, proton magnetic resonance spectra and elemental analyses. On the basis of the data it has been proved that the ligand (dpa) acts as bidentate

and the mode of its coordination to the metal is through pyridine-N atoms.

Results and Discussion

The ligand 2,2'-dipyridylamine (dpa) on treatment with Mo(CO)₆ or [RuCl₂(CO)₂]_n in (1:1) molar ratio in THF, yields very stable bright yellow Mo(CO)₄ dpa and a pale yellow RuCl₂(CO)₂ dpa solid respectively. These complexes can be handled in air for a short time period without decomposition.

The IR spectrum of the complex Mo(CO)₄ dpa showed bands of a typical octahedral cis-tetracarbonyls with four characteristic metal-terminal ν_{M-CO} stretching frequencies Fig(A) which were analogous to the complex tetracarbonyl-2,5-dithiahexanemolybdenum [9]. The decrease in the ν_{M-CO} stretching frequencies may be attributed to the flow of electron density from the ligand to the metal. The complex also showed an increase both in ν_{N-H} stretching frequencies (-96 cm⁻¹) and in δ_{N-H} (35 cm⁻¹) with respect to the free ligand.

This increase suggests that the mode of coordination of the ligand (dpa) to the metal is through the pyridine-N atoms rather than with the amino group as shown in Fig(A). A similar trend has been observed in the complex RuCl₂(CO)₂ dpa. The presence of only two strong ν_{M-CO} bands in

⁺ Dedicated to Dr. M. Tufall on his 60th birthday.

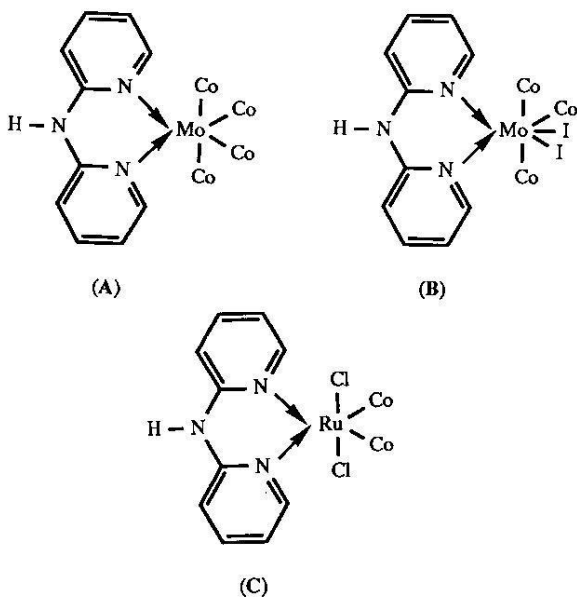
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Table 1: Infrared spectra (cm^{-1}).^a

No. Complex	V _{N-H} (asym) and (sym)	$\delta_{\text{N-H}}$	V _{M-CO}	Other bands
1 2,2'-dipyridylamine (dpa)	3245,3160	1590	-	3080,1560,1525,1490 1455,1430,1335,1305 1140,1044,985,905, 850,760,725
2 $[\text{RuCl}_2(\text{CO})_2]_n$ [11]	-	-	2145, 2075,2020	-
3 $\text{Mo}(\text{CO})_4\text{dpa}$	3350	1615	2000,1900 1856,1780	1580,1775,1450, 1345,1224,1155,760,735
4 $\text{Mo}(\text{CO})_3\text{dpaI}_2$	3340	1640	2055,1996 1930	1615,1570,1460,1220 1150,1000,750
5 $\text{RuCl}_2(\text{CO})_2\text{dpa}$	3280,3190,	1624	2040, 1974	1578,1465,1225, 1150,1015,765

^a + KBr pellet

$\text{RuCl}_2(\text{CO})_2\text{dpa}$ complex Fig(C) indicates that the two CO groups are cis [10]. The IR spectrum of $\text{Mo}(\text{CO})_3\text{dpaI}_2$ complex Fig(B) shows an expected high $\nu_{\text{M-CO}}$ stretching frequencies compared with the tetracarbonyl $\text{Mo}(\text{CO})_4\text{dpa}$ complex (Table 1). Recently, White and co-workers have reported the bidentate nature of 2,2'-dipyridylamine with Cu(I) by X-ray structure [3]. They have shown that the ligand coordinates to the metal through the pyridine-N atoms and not through the amino group.



The proton magnetic resonance spectrum of $\text{Mo}(\text{CO})_4\text{dpa}$ complex showed an expected spectrum of the ligand except that there was a low field shift of all the metal bonded ligand protons.

This low field shift may be attributed to the nuclear deshielding effect by the $\text{Mo}(\text{CO})_4$ moiety. This deshielding effect was even more noticeable on the protons of the ligand in the complex $\text{Mo}(\text{CO})_3\text{dpaI}_2$ because of the presence of iodide groups in the complex. A similar trend was also observed in the $\text{RuCl}_2(\text{CO})_2\text{dpa}$ complex. The $^1\text{H-NMR}$ data of the complexes are given in the experimental section.

The elemental analyses of the complexes were consistent with the proposed formulations (Table 2).

Table 2: Analytical data (%)^a

No. Compound	C	H	N	Colour
1 $\text{Mo}(\text{CO})_4\text{dpa}$	44.28 (44.32)	2.50 (2.37)	11.33 (11.08)	Bright yellow
2 $\text{Mo}(\text{CO})_3\text{dpaI}_2$	25.82 (25.78)	1.52 (1.48)	6.87 (6.94)	Orang brown
3 $\text{RuCl}_2(\text{CO})_2\text{dpa}$	36.66 (36.21)	2.65 (2.25)	10.6 (10.52)	Pale yellow

^a = Calculated values are given in parentheses.

Experimental

Materials

Molybdenum hexacarbonyl, 2,2'-dipyridylamine were purchased from Fluka Inc. THF was dried over LiAlH_4 and distilled under nitrogen atmosphere. The salt $[\text{RuCl}_2(\text{CO})_2]_n$ was prepared as described in the literature [11,12].

Physical measurements

All the IR spectra were measured as KBr pellets using Pyc-Unicam spectrophotometer Model SP-1320. Proton magnetic resonance spectra were recorded on a Varian EM-390 90 MHz NMR spectrometer using TMS as an internal reference. Elemental analyses were carried out by the Microanalysis Laboratory of King Abdulaziz University, Jeddah (Table 2).

*Preparation of complexes**Preparation of 2, 2'-dipyridylamine tetracarbonyl molybdenum (0)*

In a 50 cm³ round bottom flask fitted with nitrogen gas inlet and water condenser, was added 0.5 g (1.9 mmole) of Mo(CO)₆ and 0.33 g (1.9 mmole) of the ligand (dpa) in 20 cm³ THF. The solution was refluxed under nitrogen for 5 h. The colour of the solution changed from grey to yellow. The solvent was reduced in volume and then passed through an alumina column made in pet.ether. The yellow band was eluted with THF. The solvent was removed under reduced pressure to a minimum volume. To this was added pet.ether (b.p. 30-40°C) which gave a bright yellow solid. This was recrystallised from THF, m.p. 145°C dec. Yield 80%. The ¹H-NMR spectrum in deuteroacetone showed resonance in (ppm δ) at 9.7 (broad NH), 8.7 (d), 7.9 (m), 7.35 (d) and 7.1 (m). The ¹H-NMR spectrum of pure ligand in CDCl₃ showed resonance at 9.0 (broad NH), 8.3(d) 7.5(m) and 6.8(m).

Preparation of di-iodotricarbonyl-2,2'-dipyridylamine molybdenum (0)

To the solution of Mo(CO)₄ dpa 0.2 g (2.53 mmole) in 25 cm³ benzene was added slowly and dropwise a solution of iodine 0.13 g (0.53 mmole) in 10 cm³ benzene. At the end of the addition the solvent was reduced to a minimum volume. Addition of pet.ether b.p. 30-40°C separated an orange-brown solid. This was recrystallized from chloroform/pet.ether and dried under vacuum.

The ¹H-NMR spectrum in deuteroacetone showed signals at δ 9.8 (broad, NH), 8.5(d), 8.2(m), 7.9(d) and 7.4(m).

Preparation of dichlorodicarbonyl-2,2'-dipyridylamine ruthenium (II)

Treatment of 100 mg (0.44 mmole) [RuCl₂(CO)₂] and 80 mg (0.44 mmole) dpa in 15 cm³ THF was refluxed for 1h. The colour of the solution turned to pale yellow. A small amount of the product was deposited on the wall of the reaction flask during the reflux. This was separated and washed with pet.ether and dried. Solvent was removed under reduced pressure giving a pale yellow solid which was washed with pet.ether b.p. 30-40°C) and dried under vacuum. The IR spectra of both products were identical.

The ¹H-NMR spectrum in dimethyl formamide showed bands at 9.1(s), 8.6(d), 8.1(m) and 7.2 (m).

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