

Synthesis and Structural Characterization of Ru(II) and Tetracarbonyl Molybdenum(0) Complexes Containing 2,2'-Biquinoline*

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Abstract. The bidentate N-donor ligand 2,2'-biquinoline $C_{18}H_{12}N_2$ [I] reacts with the salt $[Ru(CO)_2Cl_2]_n$ [II] in (1:1) mole in THF. This gives a stable yellow crystallized solid dichlorodicarbonyl 2,2'-biquinoline ruthenium (II) $[Ru(CO)_2Cl_2C_{18}H_{12}N_2]$ complex [III]. Similarly treatment of molybdenum hexacarbonyl with 2,2'-biquinoline in (1:1) mole ratio in toluene gives a very dark violet crystals of tetracarbonyl 2,2'-biquinoline molybdenum (0) $[Mo(CO)_4C_{18}H_{12}N_2]$ complex [IV]. Spectroscopic data indicates that metal atoms in these complexes are coordinated through both the N-atoms of 2,2'-biquinoline thus maintain an octahedral geometry of these complexes. The complex (IV) on treatment with triphenylphosphine in (1:1) mole ratio gives mono substituted tricarbonyl triphenylphosphine 2,2'- biquinoline molybdenum(0) complex (V). Similarly the complex (IV) on treatment with (1:2) mole ratio with triphenylphosphine or with large excess of triphenylphosphine gives disubstituted dicarbonyl bis-triphenylphosphine molybdenum(0) complex (VI).

All the complexes were characterized by IR & 1H NMR spectroscopy, and by elemental analysis.

Introduction

The synthesis and study of transition metal complexes have been subjects of great interest especially with respect to the role of these compounds in catalytic reactions^[1-5]. The usefulness of metals containing ligands with N-donor atom have shown a significant biological activities against certain microbes, viruses and

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tumours than the free ligands^[6-7]. It has been reported previously from these laboratories that Ru(II) form stable complexes with O, S and N donor ligands^[8-10]. We now report here the preparation of complexes of 2,2'-biquinoline which acts as bidentate ligand in which both its N atoms coordinate with Ru or Mo metal.

Results and Discussion

Treatment of the salt $[\text{Ru}(\text{CO})_2\text{Cl}_2]_n$ with 2,2'-biquinoline in THF in (1:1) mole ratio gave a yellow crystallized solid dichlorodicarbonyl 2,2'-biquinoline ruthenium (II) complex [III]. Similarly on treatment of 2,2'-biquinoline and Mo $(\text{CO})_6$ in (1:1) mole ratio in refluxing toluene gave a dark violet crystallized solid, 2,2'-biquinoline tetracarbonyl molybdenum (0) complex [IV].

Both complexes [III] and [IV] are stable in air, moderately soluble in common polar organic solvents such as acetone or ethanol and are sparingly soluble in benzene and pet. ether. The complex [IV] on treatment with (1:1) mole ratio triphenylphosphine gave only mono-substituted tricarbonyl triphenylphosphine 2,2'-biquinoline molybdenum (0) complex [V] and with two mole or with large excess of tri-phenylphosphine gave disubstituted dicarbonyl bis-triphenylphosphine molybdenum (0) complex (VI). It has been mentioned briefly about the complex (III) without any details and data^[11]. All these complexes have been characterized by IR spectroscopy (Table 1). ¹HNMR spectroscopy (Table 2) and by elemental analyses (Experimental).

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

| # | Complex | $\nu(\text{M-CO})$ | Other bands |
|------|-------------------------------------------------------------------------------|--------------------------------------|-------------------------------------------------------------------------|
| I. | 2,2'- Biquinoline ($\text{C}_{18}\text{H}_{12}\text{N}_2$) | | 3050, 1980, 1830 1597, 1552, 1496 1419, 1329, 1134, 1057, 945, 831, 742 |
| II. | $[\text{Ru}(\text{CO})_2\text{Cl}_2]_n$ | 2145 m 2075 s 2020 s | |
| III. | $[\text{C}_{18}\text{H}_{12}\text{N}_2\text{-Ru}(\text{CO})_2\text{Cl}_2]$ | 2054 s 1983 s | 3074, 1590, 1509 1370, 1144, 1105, 968, 822, 782 |
| IV. | $[\text{C}_{18}\text{H}_{12}\text{N}_2\text{-Mo}(\text{CO})_4]$ | 2002 s 1892 s 1876 s 1815 s | 3067, 1596, 1505 1428, 1371, 1143 955, 824, 746 |
| V. | $[\text{C}_{18}\text{H}_{12}\text{N}_2\text{-Mo}(\text{CO})_3\text{P}\phi_3]$ | 2006 s 1904 s 1810 s | 1547, 1506 1144, 1088, 820 746, 677 |
| VI. | $\text{C}_{18}\text{H}_{12}\text{N}_3\text{-Mo}(\text{CO})_2\text{.2P}\phi_3$ | 1900 s 1797 s | 3066, 2965, 2853 1596, 1506, 1438, 1084, 819, 747, 697 |

(a) Spectra measured as K Br pellets.

Table 2. ¹HNMR spectra^(a).

| Complex # | Chemical shift (ppm) | Relative intensity | Multiplicity | Assignment |
|-----------|----------------------------------------------------------|--------------------|--------------|------------|
| 1, 3, 4 | 8.8 ^b 9.2 ^c 8.9 ^d | 2 | d | 4,4' |
| | 8.3 ^b 8.5 ^c 8.4 ^d | 2 | d | 3,3' |
| | 8.2 ^b 8.3 ^c 8.3 ^d | 2 | d | 5,5' |
| | 7.8 ^b 8.0 ^c 8.3 ^d | 2 | d | 8,8' |
| | 7.7 ^b 7.9 ^c 7.9 ^d | 2 | t | 7,7' |
| | 7.5 ^b 7.7 ^c 7.8 ^d | 2 | t | 6,6' |

(a) TMS as internal reference. (b) Free ligand, 2,2'-biquinoline.

(c) C₁₈H₁₂N₂-Ru(CO)₂Cl₂ (d) C₁₈H₁₂N₂-Mo(CO)₄

The IR spectra of complex [III] shows two strong bands at 2054 cm⁻¹ and 1983 cm⁻¹ that may be assigned as ν (Ru-CO) group which appears to adopt a **cis** disposition^[9,10]. The IR spectrum of complex [IV] shows four strong bands at 2002 cm⁻¹, 1992 cm⁻¹, 1990 cm⁻¹ and 1814 cm⁻¹ that may be assigned to ν (Mo-CO) group. This spectrum may be compared with 2,2'-dipyridine tetracarbonylmolybdenum^[12] thus maintains an octahedral geometry, (see Fig. 1). It is noteworthy that IR spectrum of complex [III] shows a lowering in the ν (Ru-CO) stretching frequencies and increase of 2,2'- biquinoline ring system is an indicative of coordination of 2,2'- biquinoline ligand and the metal ruthenium. A similar trend was observed in complex [IV].

The ¹HNMR spectra of the complexes [III] and [IV] shown in Table (2) show a slight down field shift of the protons of 2,2'- biquinoline which may be attributed due to the deshielding effect of electron deficient ruthenium and molybdenum metal atom.

Experimental

The salt $[\text{Ru}(\text{CO})_2\text{Cl}_2]_n$ was prepared as reported in the literature^[13,14], 2,2'-biquinoline and triphenylphosphine were purchased from Aldrich, U.K. and $\text{Mo}(\text{CO})_6$ was purchased from Fluka, U.K. The IR spectra were measured as KBr pellets on FTIR model RX1(PERKIN) spectrometer. The ^1H NMR spectra were recorded on a VARIAN EM 390-90 MHz spectrometer. Elemental analyses were carried out by the Microanalysis laboratory of King Abdulaziz University, Jeddah.

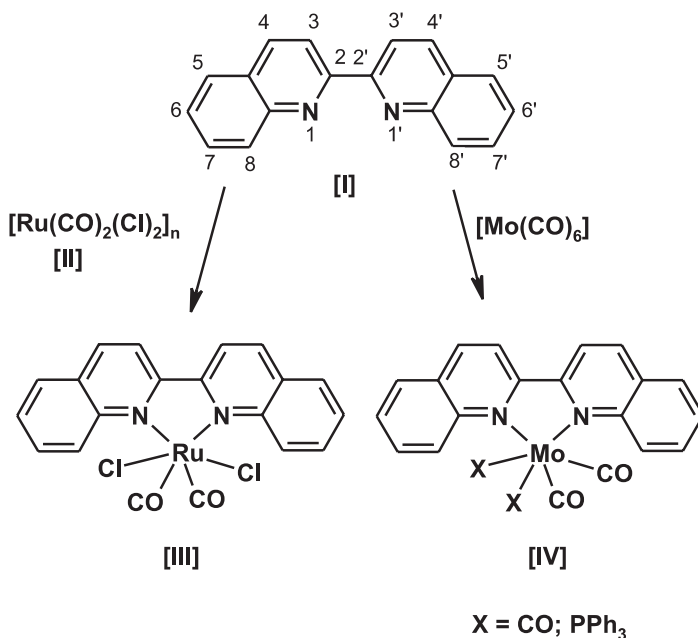


Fig. 1.

Preparation of dichlorodicarbonyl 2,2'- biquinoline-ruthenium [III]

A typical reaction is described. In a 100 ml three necked round bottom flask fitted with magnetic stirrer, N_2 gas inlet and water condenser was added 0.20g (0.87 mmole) of $[\text{Ru}(\text{CO})_2\text{Cl}_2]_n$ and 0.22 g (0.87 mmole) of 2,2'- biquinoline (1:1) mole ratio in 20 ml THF. The mixture was refluxed for ~ 2 h. The solution was concentrated under reduced pressure which on cooling gave an orange yellow solid. This was washed twice with pet.ether (b.p. 30-40°C) and dried under vacuum yield 80% m.p. 180°C. Analysis found: C, 50.4; H, 2.5; N, 5.8; $\text{C}_{20}\text{H}_{12}\text{O}_2\text{N}_2\text{Cl}_2\text{Ru}$ Calcd; C, 49.6; H, 2.5; N, 5.7%.

Preparation of tetracarbonyl 2,2'-biquinoline molybdenum (0)

In a 100 ml three necked round bottom flash fitted with magnetic stirrer, N₂ gas inlet and water condenser was added 0.5 g (1.96 mmole) of 2,2'-biquinoline and 0.5 g (1.96 mmole) of Mo(CO)₆ in (1:1) mole ratio in 20 ml toluene. The mixture was refluxed for 2h. The solution was concentrated under reduced pressure which on cooling gave very dark violet solid. This was washed twice with pet.ether. (b.p.30-40%) and dried under vacuum. Yield 85% m.p. 200°C. Analysis Found: C, 57.1; H,2.5; N,6.1; C₂₂H₁₂N₂O₄Mo Calcd; C, 56.9; H,2.6; N, 6.0 %.

Preparation of Tricarbonyl triphenylphosphine 2,2'-biquinoline molybdenum (0)

In a 100 ml three necked round bottom flask fitted with magnetic stirrer, N₂ gas inlet and water condenser was added 210 mg (0.45 mmole) of tetra carbonyl 2,2'-biquinoline molybdeneum (0) in 20 ml of toluene. To this was added 120 mg (0.45 mmole) of triphenylphosphine. The solution was heated at reflux for ~ 1h. and concentrated under reduced pressure which on cooling gave dark violet crystalline solid. This was washed twice with pet.ether (bp. 30-40°C) and dried under vacuum. Analysis: Found: C,70.4; H,3.9; N,4.1%; C₃₉H₂₇N₂O₃ P Mo Calcd; C, 76.6; H,3.5; N, 4.0%. It was found that by taking 2 mole or even large excess of triphenylphosphine the complex [IV] gave disubstituted dicarbonyl bis-triphenylphosphine molybdenum (0) complex [VI]. Analysis: Found: C,78.5; H,4.6; N,3.2% C₅₆H₄₂N₂O₂P₂Mo Cald; C,78.1; H,4.8; N,3.2%.

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تحضير وخصائص التركيب الفراغي لمتراكبات رثينيوم (II) ورباعي الكاربونيل موليبدنيوم (٠) مع المتصلة ٢،٢- ثنائي كينولين ذات الإعطاء الثنائي النتروجيني

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المستخلص. تتفاعل المتصلة ثنائية النتروجين ٢،٢- ثنائي كينولين $C_{18}H_{12}N_2$ مع المركب $[Ru(CO)_2Cl_2]_n$ في تتراهيدروفيران بمعدل ١:١، يعطي المتراكب الصلب الثابت البلوري أصفر اللون ثنائي الكلوروثنائي الكاربونيل ٢،٢- ثنائي كينولين رثينيوم $[Ru(CO)_2Cl_2C_{18}H_{12}N_2]$.

وبالمثل فإن تفاعل سداسي الكاربونيل موليبدنيوم $[Mo(CO)_6]$ مع نفس المربوطة السابقة بنسبة معدل ١:١ في التلوين يعطي بلورات بنفسجية داكنة اللون من رباعي الكاربونيل ٢،٢- ثنائي كينولين موليبدنيوم $[Mo(CO)_4C_{18}H_{12}N_2]$.

الشواهد الطيفية تشير إلى أن الفلز في هذه المتراكبات مرتبط ارتباطاً تناسقياً من خلال كلتا ذرتي نيتروجين المربوطة ٢،٢- ثنائي كينولين، وبهذا يحافظ المتراكب على شكله الهندسي ثماني السطوح.

وعند تفاعل المتراكب $[Mo(CO)_4C_{18}H_{12}N_2]$ بالمربوطة ثلاثي فينيل فوسفين بمعدل تفاعل ١:١ يعطي أحادي استبدال من ثلاثي فينيل فوسفين ٢،٢- ثنائي كينولين موليبدنيوم ، وعند تفاعل نفس المتراكب بمعدل تفاعل ٢:١ من ثلاثي فينيل فوسفين أو زيادة وافرة هذه المربوطة يعطي ثنائي استبدال من ثنائي كاربونيل - بس - ثلاثي فينيل فوسفين موليبدنيوم .

جميع المتراكبات السابقة حضرت وأمكن التعرف عليها من خلال طيف الأشعة تحت الحمراء ، وطيف $^1H NMR$ ، وكذلك التحاليل الدقيقة للعناصر .