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## REACTIONS OF DIPYRIDYLKETONE WITH GROUP 8 METAL CARBONYLS IN DIFFERENT MEDIA

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### Abstract

Reaction of di-(2-pyridyl)ketone (dpk) with  $[M_3(CO)_{12}]$ ,  $M = Ru$  or  $Os$  in dioxan under reduced pressure gave the tricarbonyl derivative  $[Ru(CO)_3(dpk)]$  (**1**) and  $[Os(CO)_3(dpk)]$  (**2**). When these reactions were carried out in benzene/ethanol 1:1 (v:v) under reflux and reduced pressure gave the binuclear ruthenium complex  $[Ru_2(CO)_4(\mu-CO)(\eta^3-dpkO, Oeth)_2]$  (**3**), where  $\eta^3-dpkO, Oeth$  is N,O,N-ethoxybis(2-pyridyl)-methanolato and the mononuclear  $[Os(CO)_3(\eta^3-dpkO, Oeth)]$  (**4**). All complexes were characterized by elemental analysis, infrared, mass and  $^1H$  NMR spectroscopy. The spectroscopic measurements indicated that in dioxane as solvent the dpk act as bidentate ligand while in benzene/ethanol solution the dpk act as tridentate ligand. The magnetic measurements revealed that the complexes (**3**) and (**4**) are paramagnetic with change in the formal oxidation state of the ruthenium and osmium atoms from zero to +1 via oxidative addition of the OH group to ruthenium or osmium with a proton displacement to give a low-spin  $d^7$  electronic configuration. The UV-Vis studies of the complexes showed blue shift compared to the ligand confirming complex formation.

### Introduction

Di-(2-pyridyl)ketone is a molecule that can exhibit different modes of coordination. As bidentate ligand it can bound through a N,O-coordination giving a five-membered chelate ring or a N,N-coordination forming a six-membered ring [1-4]. In the bidentate mode, delocalization of electrons through the pyridine rings and the keto group result in a wide range of charge species from a neutral precursor and a low energy metal to ligand charge transfer (MLCT) all of which are important in electronic transfer processes and catalysis [5]. It has been found that copper(I)- $PPh_3$ -dpk complexes are efficient photocatalysts for norbornadiene-quadracyclane conversion [6], which is important as a solar energy storage process [7,8]. On the other hand, the metal promoted hydration of dpk has been of interest for some time since the ligand has the ability to undergo a reaction after initial coordination to a transition metal ion [9-13]. Frequently the coordinated dpk undergoes nucleophilic addition of water or an alcohol at the carbonylic carbon atom to form the diol or the corresponding hemiacetal,  $(NC_5H_4)_2C(OR)(OH)$ , which deprotonated and acts as a mononegative, tridentate N,O,N-donor ligand (Fig.1). The three donor atoms may be coordinated to one metal atom [14-16] or to two metal atoms [17-20]. The N,O,N-

tridentate binding mode results in the loss of electronic withdrawing properties of the ligand and enhances the electron density around the metal center [5]. Recently, the reaction of molybdenum(0) hexacarbonyl,  $[\text{Mo}(\text{CO})_6]$ , with dpk in refluxing toluene lead to the formation of a high-valent molybdenum(VI)-dioxo compound of hydrated di-2-pyridyl ketone,  $[\text{Mo}(\text{O})_2(\mu\text{-O})(\eta^3\text{-dpkO,OH})_2]$  [21].

Ruthenium and osmium chemistry of heterocyclic ligands containing nitrogen has developed due to their valence isomerism, different chemical, photophysical, photochemical, catalytic and redox activities [22]. In a previous study, reaction of  $\text{Ru}_3(\text{CO})_{12}$ , with 2-(2'-pyridyl)benzimidazole (HPBI) resulted in the formation of  $\text{Ru}(\text{CO})_3(\text{HPBI})$  complex. In presence of pyridine or bipyridine, the two derivatives  $[\text{Ru}(\text{CO})_3(\text{HPBI})]\cdot\text{py}$  and  $[\text{Ru}(\text{CO})_3(\text{HPBI})]\cdot\text{dpy}$  were isolated. The corresponding reactions of  $\text{Os}_3(\text{CO})_{12}$  yielded only one single product;  $[\text{Os}(\text{CO})_2(\text{HPBI})_2]$  [23].  $\text{Ru}_3(\text{CO})_{12}$  reacted with 2,3-bis(2'-pyridyl)quinoxaline (dpq) in benzene in presence of either 2,2'-dipyridine (dpy) or pyridine (py) to give the mononuclear complex  $[\text{Ru}(\text{CO})_3(\text{dpq})]$  or  $[\text{Ru}(\text{CO})_2(\text{dpq})(\text{py})]$  [24]. In this article, we report the synthesis and characterization of some ruthenium and osmium complexes of dpk.

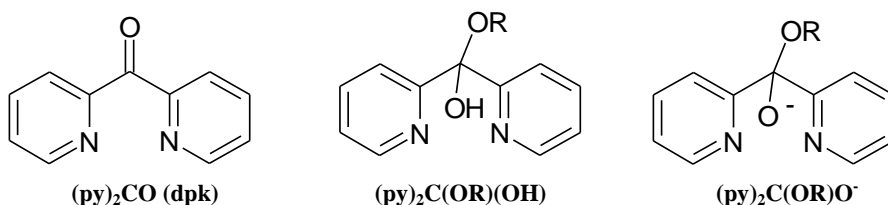


Fig. 1 The structural formula of the ligand discussed in the text. The two formulae  $(\text{py})_2\text{C}(\text{OR})(\text{OH})$  and  $(\text{py})_2\text{C}(\text{OR})\text{O}^-$  can exist only after coordination..

## Experimental

### Reagents

$\text{Ru}_3(\text{CO})_{12}$ ,  $\text{Os}_3(\text{CO})_{12}$  and di-2-pyridylketone were supplied from Aldrich. All the solvents were reagent grade and purified prior to use.

### Instruments

IR measurements were recorded as KBr pellets on a Unicam-Mattson 1000 FT-IR spectrometer. Electronic absorption spectra were measured on a Unicam UV2-300 UV-vis spectrophotometer.  $^1\text{H-NMR}$  measurements were performed on a Varian-Mercury 300 MHz spectrometer. Samples were dissolved in  $(\text{CD}_3)_2\text{SO}$  with

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TMS as internal reference. Magnetic susceptibility (Gouy method) measurements of the paramagnetic complexes were carried out on a Sherwood Scientific magnetic susceptibility balance. The complexes were also characterized by elemental analysis (Perkin-Elmer 2400 CHN elemental analyzer) and mass spectroscopy (Finnigan MAT SSQ 7000). Table (1) gives the elemental analysis and mass spectrometry data for the complexes.

**Table 1 Elemental analysis and mass spectrometry data of the complexes**

Complex	Elemental analysis						Mass spectroscopy	
	Found			Calculated			Mwt	<i>m/z</i>
	%C	%H	%N	%C	%H	%N		
[Ru(CO) <sub>3</sub> dpk]	44.96	2.21	7.52	45.54	2.18	7.59	369	369 [P <sup>+</sup> ]
[Os(CO) <sub>3</sub> dpk]	35.58	2.12	6.09	36.60	1.76	6.10	459	431 [P-CO] <sup>+</sup>
Ru <sub>2</sub> (CO) <sub>4</sub> (μ-CO)(dpkO, Oeth)	45.89	3.36	6.74	46.49	3.28	7.00	800.18	744 [P-2CO] <sup>+</sup>
Os(CO) <sub>3</sub> (dpkO, Oeth)	36.45	2.65	5.84	38.08	2.60	5.56	492.08	493 [P <sup>+</sup> ]

**Synthesis of the complexes:**

**[Ru(CO)<sub>3</sub>(dpk) complex:**

A mixture of Ru<sub>3</sub>(CO)<sub>12</sub> (0.10 g, 0.16 mmol) and dpk (0.10 g, 0.44 mmol) were mixed in 30 ml dioxane. The mixture was degassed with one freeze-thaw cycle and refluxed for 8h where a brown precipitate was formed. The solvent was removed by decantation and the solid residue was washed several times by hot petroleum ether (60-80) and recrystallized from hot benzene to give dark yellowish-orange amorphous solid (yield 55%).

**[Os(CO)<sub>3</sub>(dpk) complex**

Os<sub>3</sub>(CO)<sub>12</sub> (0.10 g; 0.11 mmol) and dpk (0.06 g; 0.33 mmol) were mixed in 30 ml dioxane. The mixture was degassed and heated to reflux for 36h. The color of the solution was changed from bright yellow to reddish-brown. The reaction mixture was cooled and the solvent was removed under vacuum. The obtained solid was washed several times with hot benzene and petroleum ether to give light brown crystals with a yield of 65%.

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### [Ru(CO)<sub>4</sub>(μ-CO)(dpkO,Oeth)<sub>2</sub>] complex

Ru<sub>3</sub>(CO)<sub>12</sub> (0.1g, 0.16 mmol) and dpk (0.10g, 0.44 mmol) were mixed together in a sealed tube containing 30ml benzene/ethanol (1:1). The mixture was degassed with one freeze-thaw cycle and refluxed for 30h. The color of the mixture was changed from yellow to brown. The solvent was evaporated to yield brown residue. The complex was washed several times with boiling petroleum ether and then recrystallized from hot benzene to give fine brown powder (yield 60%).

### [Os(CO)<sub>3</sub>(dpkO,Oeth)] complex

A similar procedure was performed as in the case of [Ru(CO)<sub>4</sub>(μ-CO)(dpkO,Oeth)<sub>2</sub>] complex but the reaction time was three days. The solution color changed from bright yellow to light brown without formation of precipitate. The reaction mixture was cooled and the solvent was removed under vacuum. The solid residue was washed several times with petroleum ether to give light brown amorphous solid (yield 72 %) based on the metal.

## Results and Discussion

The IR spectrum of the di-2-pyridyl ketone showed characteristic bands due to  $\nu_{(C=O)}$ ,  $\nu_{(C=N)}$  and  $\nu_{(C=C)}$ , Table 2. The <sup>1</sup>H NMR spectrum of dpk showed three multiplet signals at  $\delta$  7.64, 8.06 and 8.68 ppm due to protons of the pyridyl rings.

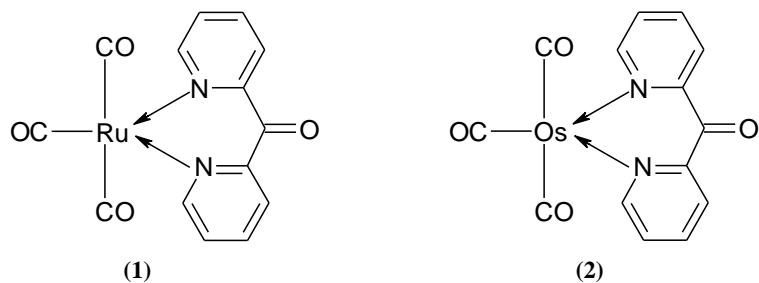
**Table 2. Important IR data for dipyridylketone and its ruthenium and osmium complexes<sup>a</sup>**

Complex	$\nu$ CO	$\nu$ C=N	$\nu$ C=C
dpk	1681(s)	1579(m)	1466 1432
[Ru(CO) <sub>3</sub> dpk]	2059m 1984vs 1907s 1676	1607(w) 1567(w)	1458
[Os(CO) <sub>3</sub> dpk]	2069(m) 1985(vs) 1907(s) 1678(m)	1607 (m) 1567 (w)	1458
[Ru <sub>2</sub> (CO) <sub>4</sub> (μ-CO)(dpkO,Oeth)]	2024(s) 1932 (vs) 1732 (m)	1604(m) 1570(w)	1450 1442
[Os(CO) <sub>3</sub> (dpkO, Oeth)]	2070(sh) 1999(vs) 1913(vs)	1606(m) 1563 (w)	1448

<sup>a</sup> s= strong, m = medium, vs= very strong, sh=shoulder, w= weak

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Thermal reactions of the cluster compounds  $M_3(CO)_{12}$ ,  $M=Ru$  and  $Os$ , with di-2-pyridyl ketone (dpk) were found to be dependent on both the reaction medium and the type of metal. Reaction of dpk with  $[M_3(CO)_{12}]$ ,  $M=Ru$  or  $Os$  in dioxane under reduced pressure gave the tricarbonyl derivative  $[Ru(CO)_3(dpk)]$  and  $[Os(CO)_3(dpk)]$ . The mass spectra of  $[Ru(CO)_3(dpk)]$  and  $[Os(CO)_3(dpk)]$  showed a molecular ion peak at  $m/z = 369$  (63%) due to the parent ion of the ruthenium complex  $[P]^+$  and at  $m/z = 431$   $[P-CO]^+$  ion for osmium complex. The IR spectra of the two complexes showed that carbonyl stretching frequency appeared at  $1681\text{ cm}^{-1}$  in the spectrum of free dpk was shifted to  $1676\text{ cm}^{-1}$  in the spectrum of  $[Ru(CO)_3(dpk)]$ , and to  $1679\text{ cm}^{-1}$  for the osmium complex (**2**) suggesting that the C=O group does not participate in the coordination. It is well known that coordination via the lone pair of electrons of the nitrogen atom of the pyridine can shift the ring vibrations to higher frequencies [25]. This is shown in the IR spectrum as the nearest absorption at  $1607\text{ cm}^{-1}$  assigned as a 2-pyridyl stretching mode raised from  $1579\text{ cm}^{-1}$  on coordination in addition to the lower band at  $1567\text{ cm}^{-1}$  in both complexes, Table 2. The IR spectra of  $[Ru(CO)_3(dpk)]$  and  $[Os(CO)_3(dpk)]$  exhibited a pattern of three CO stretching frequencies with symmetry of  $2a'' + a''$  due to three carbonyl groups attached to the ruthenium or osmium atom in a trigonal bipyramidal structure, Table 2 [25]. The ruthenium complex was diamagnetic and insoluble in DMSO or chloroform, thus we could not obtain the  $^1H$  NMR spectrum. On the other hand, the  $^1H$  NMR spectrum of the  $[Os(CO)_3(dpk)]$  gave three multiplets at  $\delta$  8.86, 8.04, 7.32 ppm with corresponding shift due to coordination. According to the spectroscopic data of the two complex, it can be concluded that the ruthenium and osmium complex have a trigonal bipyramidal arrangement with two axial and one equatorial CO groups, and the dpk ligand occupied the other two equatorial positions, Scheme 1.

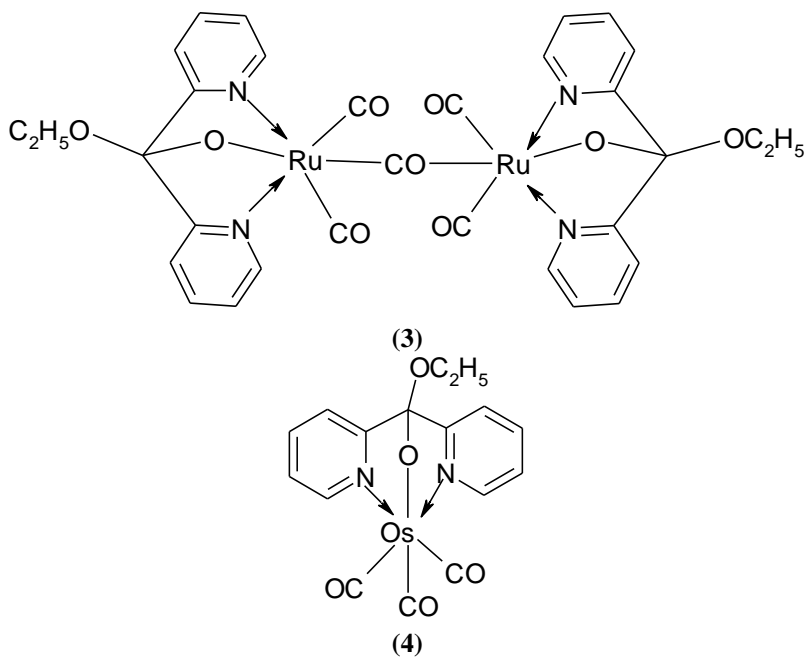


**Scheme 1.** proposed structures of  $[Ru(CO)_3(dpk)]$  and  $[Os(CO)_3(dpk)]$  complexes

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Reaction of dpk with  $[\text{Ru}_3(\text{CO})_{12}]$  in benzene/ethanol mixture 1:1 (v/v) gave a binuclear complex  $\text{Ru}_2(\text{CO})_4(\mu\text{-CO})(\eta^3\text{-dpkO,Oeth})_2$ , where  $\eta^3\text{-dpkO,Oeth}$  is N,O,N-ethoxybis(2-pyridyl)-methanolato. The IR spectrum of the complex showed different pattern from that of  $\text{Ru}(\text{CO})_3(\text{dpk})$ . It exhibited disappearance of the carbonyl stretching band of dpk and appearance of a new medium band at  $1732\text{ cm}^{-1}$  that attributed to the bridged carbonyl [26]. Furthermore, the IR spectra showed two strong CO stretching frequencies bands at  $2024$  and  $1932\text{ cm}^{-1}$  due to carbonyl groups attached to the ruthenium atom, Figure 2a, Table 2. The disappearance of CO group of dpk suggested that the coordinated dpk undergoes nucleophilic addition of ethanol at the carbonylic carbon atom to form the corresponding hemiacetal  $(\text{py})_2\text{C}(\text{Oeth})(\text{OH})$ , which, upon deprotonation, acts as a mononegative, tridentate N,O,N-donor ligand. It was found that on storage of  $[\text{Ru}(\text{dpk})(\text{CO})_2\text{Cl}_2]$  of its methanolic solution in the dark resulted in the addition of methanol to coordinated dpk and crystallised a product  $[\text{Ru}(\text{dpk-O,OCH}_3)(\text{CO})_2\text{Cl}]$ . The deprotonated ketal formed from this addition, methoxydi(2-pyridyl)methoxide, coordinates facially such that the ketal oxygen is *trans*- to the chloride and the pyridyl nitrogens are *trans*- to the carbonyls [27]. A zerovalent ruthenium complex would expect to have a five coordinate arrangement. In fact, the isolated six coordinate complex was found to be paramagnetic and it gave no  $^1\text{H}$  NMR spectrum. Magnetic susceptibility measurement of the complex at 295K showed a value of  $2.2 \times 10^{-6}$  e.m.u.  $\text{g}^{-1}$  with an effective magnetic moment  $\mu_{\text{eff}}$  of 1.40 BM for each ruthenium atom. The  $\mu_{\text{eff}}$  value is slightly smaller than the spin-only moment of an unpaired electron (1.73 BM). Thus, it can be suggested that a change in the formal oxidation state of the ruthenium atom from zero to +1 was achieved via oxidative addition of the OH group to ruthenium with a proton displacement to give a low-spin  $d^7$  electronic configuration  $\text{Ru}_2(\text{CO})_4(\mu\text{-CO})(\eta^3\text{-dpkO,Oeth})$  complex, Scheme 2 [23,28]. The small  $\mu_{\text{eff}}$  was obtained for the  $\text{Ru}(\text{CO})_4(\text{satpH})$ ;  $\text{satpH}$  = deprotonated salicylideneimine-2-thiophenol [23]. From the spectroscopic data it can be concluded that the ruthenium complex consisted of two metals in + 1 formal oxidation state coordinated to one bridged carbonyl. Each metal coordinated to a tridentate dpk-O,Oeth ligand and two terminal carbonyl groups, Scheme 2

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Scheme 2. proposed structures of  $[\text{Ru}_2(\text{CO})_4(\mu\text{-CO})(\eta^3\text{-dpkO, Oeth})_2]$  and  $[\text{Os}(\text{CO})_3(\eta^3\text{-dpkO, Oeth})]$  complexes

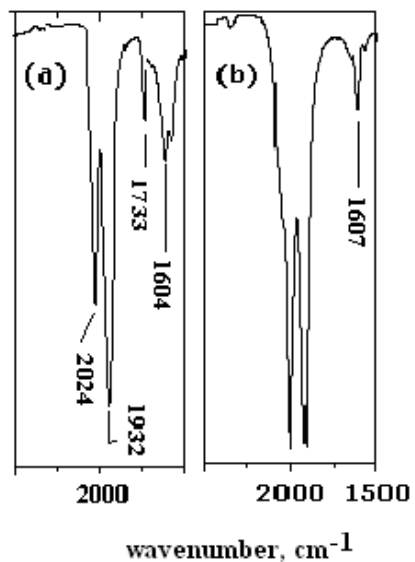


Figure 2. FTIR spectra of (a)  $[\text{Ru}_2(\text{CO})_4(\mu\text{-CO})(\text{dpkO, Oeth})]$  and (b)  $[\text{Os}(\text{CO})_3(\text{dpkO, Oeth})]$



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Reaction of  $[\text{Os}_3(\text{CO})_{12}]$  with dpk in benzene/ethanol mixture 1:1 (v/v) under reduced pressure resulted in the formation of mononuclear tricarbonyl derivative with molecular formula  $\text{C}_{15}\text{H}_{13}\text{N}_2\text{O}_5\text{Os}$ . The mass spectrum of the complex showed a molecular ion peak at  $m/z = 436$  (35%)  $[\text{P}-2\text{CO}]^+$  due to the parent ion of the osmium complex losing two carbonyl groups. IR spectrum of the complex exhibited two very strong stretching frequency bands at 1913 and 1999  $\text{cm}^{-1}$  and a shoulder at 2070  $\text{cm}^{-1}$  due to three terminal carbonyls attached to osmium atom. Furthermore, the IR spectrum showed disappearance of CO stretching frequency of dpk suggesting that the dpk behave as tridentate ligand as in the case of ruthenium complex, Figure 2b. From the previous data, the complex could have an octahedral structure with dpk as tridentate ligand. Magnetic susceptibility measurement of the complex at 295K showed a value of  $2.5 \times 10^{-6}$  e.m.u.  $\text{g}^{-1}$  with an effective magnetic moment  $\mu_{\text{eff}}$  of 1.71 BM for the osmium complex, which is closer to the spin-only moment of an unpaired electron (1.73 BM). Reaction of  $[\text{Re}(\text{CO})_5\text{Cl}]$  and  $\text{PPh}_3$  in dry toluene gave *cis*- $[\text{Re}(\text{CO})_2(\text{PPh}_3)(\text{dpk})\text{Cl}]$  which upon standing in DMSO at room temperature, yellow crystals of *cis*- $[\text{Re}(\text{CO})_2(\text{PPh}_3)(\text{dpkO},\text{OH})].0.5\text{DMSO}$  was obtained [29]. According to the spectroscopic data, coordination about Os is pseudo-octahedral, with two N atoms from the pyridyl rings, three C atoms from the carbonyl groups, one O atom from the methanolate group occupying the coordinating sites. The distortion from octahedral geometry in the complex is due to the tridentate binding of hydroxydi-2-pyridylethanolato-N,O,N to form a six-membered metallocyclic ring forming  $[\text{Os}(\text{CO})_3(\eta^3\text{-dpkO},\text{Oeth})]$ , Scheme 2, and due to Jahn-Teller effect of the low-spin  $d^7$ ,  $t_{2g}^6 e_g^1$ , arrangement.

### UV-vis Studies

The electronic absorption spectrum of dpk in benzene consists of a strong band at 288 nm ( $\pi - \pi^*$ ) and a weak broad band at 360 nm due to ( $n-\pi^*$ ) transitions from the carbonyl group and nitrogen of pyridine ring to  $\pi^*$  orbitals, Figure 3. In all complexes the band at 288 nm showed a blue shift to 268 nm in ruthenium complexes and to 272 nm in the case of osmium complex. The UV-vis spectrum of  $[\text{Ru}(\text{CO})_3(\text{dpk})]$  and  $[\text{Os}(\text{CO})_3(\text{dpk})]$  displayed additional shoulder at 297 nm complexes beside a weak band around 400 nm assigned to the metal-to-ligand charge transfer. The ( $n-\pi^*$ ) transitions displayed a shift from 360 nm to 336 nm due to complex formation.

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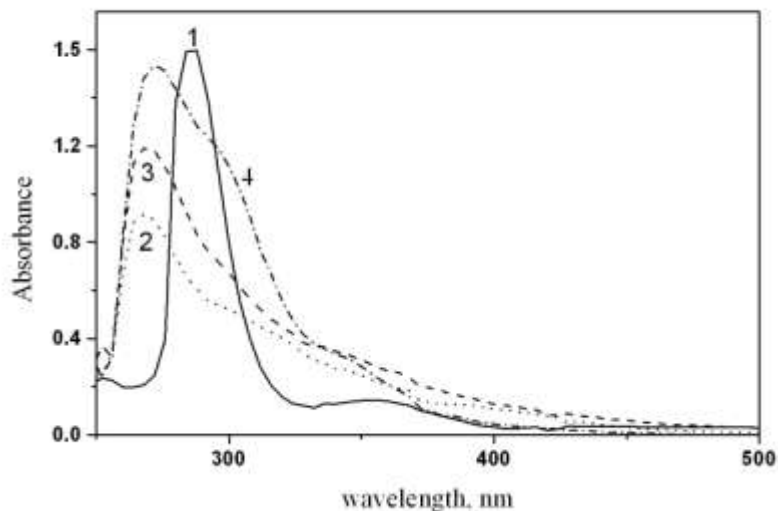


Figure 3. Absorption spectra of 1) dpk 2)  $[\text{Ru}(\text{CO})_3\text{dpk}]$  3)  $[\text{Os}(\text{CO})_3\text{dpk}]$  and 4)  $\text{Os}(\text{CO})_3(\text{dpkO}, \text{Oeth})$  in benzene.

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## الملخص العربي

### دراسة تفاعلات ثنائي 2-بيريديل الكيتون مع كربونيلات المجموعة الثامنة في أوساط مختلفة

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تم دراسة تفاعل ثنائي 2-بيريديل الكيتون (dpk) مع المترابكات العنقودية  $[Ru_3(CO)_{12}]$  و  $[Os_3(CO)_{12}]$  في كل من مذيب الديوكسان و في محلول من البنزين و الإيثانول بنسبة 1:1 (v:v) تحت ضغط منخفض. عند إجراء التفاعل في مذيب الديوكسان تم الحصول على مترابكات ثلاثية الكربونيل لها التركيب الجزيئي  $[Ru(CO)_3(dpk)](1)$  و (2)  $[Os(CO)_3(dpk)]$ . و عند إجراء التفاعل في محلول من البنزين و الإيثانول فقد أعطي مترابك ثنائي الذرة في حالة الروثينيوم وله التركيب الجزيئي  $[Ru_2(CO)_4(\mu-CO)(\eta^3-$  (3)  $dpkO, Oeth)2]$  حيث  $N, O, N = \eta^3-dpkO, Oeth$  (2-بيريديل)-ميثانوليتو و المترابك أحادي الذرة (4)  $[Os(CO)_3(\eta^3-dpkO, Oeth)]$  في حالة الأوزميوم. تم دراسة تركيب كل المترابكات باستخدام التحليل للعناصر، أطياف الأشعة تحت الحمراء، أطياف الكتلة و أطياف الرنين المغناطيسي الذري  $^1H NMR$ .

وقد أوضحت تلك الدراسات أنه في حالة إجراء التفاعل بين ثنائي 2-بيريديل الكيتون و كل من مترابك الروثينيوم و الأوزميوم فإن الليجاند dpk يعمل كليجاند ثنائي العطاء بينما عند استخدام مذيب الإيثانول فإنه يحدث أولاً تفاعل و تكون المترابكات (1) و (2) يتبعها تفاعل إضافة من المذيب الإيثانول علي مجموعة الكيتون للليجاند ليتكون  $dpkOH, Oeth$  والذي يعمل كليجاند ثلاثي العطاء. وقد أكدت نتائج قياس المغناطيسية للمترابكات (3) و (4) أنها مترابكات بارامغناطيسية ووجود الفلز في حالة التأكسد + 1. وتم قياس أطياف الأشعة فوق البنفسجية و المرئية للمترابكات وأوضحت حدوث إزاحة في الأطوال الموجية لها مقارنة لليجاند نتيجة للتناقص.