

## Research Letter

# Molybdenum and Tungsten Tricarbonyl Complexes of Isatin with Triphenylphosphine

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Reaction of  $M(\text{CO})_6$ ;  $M = \text{Mo}$  or  $\text{W}$  with isatin in the presence of triphenylphosphine in THF under reduced pressure gave the tricarbonyl derivatives complexes  $[M(\text{CO})_3(\text{isatH})(\text{PPh}_3)]$ . The two complexes were characterized by elemental analysis, infrared, mass and  $^1\text{H}$  NMR spectroscopy. The spectroscopic studies show that the two complexes exist in *fac*- and *mer*-isomers in solutions through exchange the CO group and  $\text{PPh}_3$ . The Uv-Vis spectra of the complexes in different solvents were studied.

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## 1. Introduction

Isatin (2,3-dihydroindole-2, 3-dione) is a versatile lead-molecule for designing potential bioactiveagents, and its derivatives were reported to possess broad-spectrum antiviral activity [1, 2]. In the previous reports, the synthesis and characterization of group 6 and 8 complexes of isatin and 5-methylisatin in absence and presence of bipyridine were investigated [3, 4]. In this article, we report the synthesis and characterization of molybdenum and tungsten complexes of isatin in the presence of  $\text{PPh}_3$ . The aim of these reactions is the synthesis and study of mixed-ligand complexes, where the metal is surrounded by different donor atoms in the coordination sphere, that is, the oxygen from isatin and phosphorous atom from the triphenylphosphine ( $\text{PPh}_3$ ).  $\text{PPh}_3$  is different from the carbonyl group since it is a strong  $\sigma$ -donor and weak  $\pi$ -acceptor ligand. Furthermore, the organic phosphines increase the stability of the transition metal complexes in the low-oxidation state. Taking into account the electronic spectra the combination of a reducing metal and an acceptor ligand generates a metal-to-ligand charge transfer (MLCT) excited state which may appear in absorption and emission [5, 6].

## 2. Experimental

**2.1. Reagents.**  $\text{Mo}(\text{CO})_6$ ,  $\text{W}(\text{CO})_6$ , isatin, and  $\text{PPh}_3$  were supplied from (Sigma Aldrich, St. Louis, USA). All the solvents were reagent grade and purified prior to use.

**2.2. 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 TMS as internal reference. 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 analyses and mass spectrometry data for the complexes.

$[\text{Mo}(\text{CO})_3(\text{isatH})(\text{PPh}_3)]$ .  $\text{Mo}(\text{CO})_6$  (0.20 g; 0.76 mmol), isatin (0.06 g; 0.33 mmol), and  $\text{PPh}_3$  (0.09 g; 0.33 mmol) were mixed in *ca* 30 ml tetrahydrofuran. The mixture was degassed and heated to reflux for 4 hours, where the color of

TABLE 1: Elemental analysis and mass spectrometric data for the molybdenum and tungsten complexes.

Complex	Calculated			Found			Mass spectroscopy	
	%C	%H	%N	%C	%H	%N	Mwt	<i>m/z</i> ( <i>P</i> <sup>+</sup> )
[Mo(CO) <sub>3</sub> (isatH)(PPh <sub>3</sub> )]	59.09	3.42	2.37	58.57	3.42	3.05	589.39	590
[W(CO) <sub>3</sub> (isatH)(PPh <sub>3</sub> )]	51.42	2.98	2.06	52.05	3.06	2.39	677.29	678

TABLE 2: Important IR data for isatin and its complexes.

Compound	IR data (cm <sup>-1</sup> ) <sup>a</sup>		
	$\nu_{\text{(NH)}}$	$\nu_{\text{(C=C)}} + \delta_{\text{CH}}$	$\nu_{\text{(CO)}}$
IsatH	3191(s)	1615(vs), 1461(s)	1748(sh), 1727(vs)
[Mo(CO) <sub>3</sub> (isatH)(PPh <sub>3</sub> )]	3184(w)	1619(s) 1462(m) 1435(m)	2013(m), 1943(m), 1887(vs), 1725 (sh), 1703(s)
[W(CO) <sub>3</sub> (isatH)(PPh <sub>3</sub> )]	3186(m)	1619(m) 1463(m) 1435(m)	1935(m), 1879(s), 1810(w), 1727(s), 1703(s)

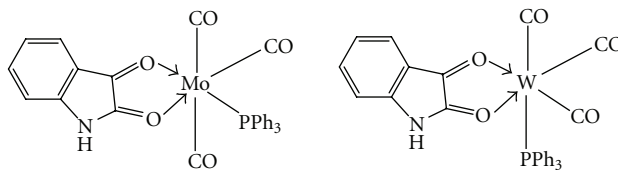
<sup>a</sup>vs, very strong; s, strong; m, medium; w, weak; sh, shoulder.

the solution changed from yellow to dark red. 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 brown crystals with a yield of 55% based on the metal.

[W(CO)<sub>3</sub>(isatH)(PPh<sub>3</sub>)]. A similar procedure was performed as in the case of [Mo(CO)<sub>3</sub>(isatH)(PPh<sub>3</sub>)] but the reaction time was 11 hours (reddish brown powder, yield 48%).

### 3. Results and Discussion

**3.1. IR and NMR Studies.** Reactions of M(CO)<sub>6</sub>; M = Mo or W with isatin in the presence of PPh<sub>3</sub> resulted in the formation of [M(CO)<sub>3</sub>(isatH)(PPh<sub>3</sub>)] complexes. The IR spectra of the complexes exhibited characteristic bands of the isatin and PPh<sub>3</sub> ligands with the corresponding shifts, Table 2. In addition, the IR spectra of the complexes showed that the  $\nu_{\text{CO}}$  of isatin ligand exerted 20–45 cm<sup>-1</sup> shift to lower frequency suggesting that the coordination of isatin occurred in the range of ketoform in both complexes. On the other hand, the IR spectra of the two complexes exhibited three bands in the metal terminal carbonyl region [7] with shifts toward the low-frequency region, Table 2. Also, the IR spectra exhibited two medium bands at 1099, 1102 cm<sup>-1</sup> characteristic  $\nu(\text{P}-\text{C}_{\text{Ph}})$  bands indicates the presence of coordinated PPh<sub>3</sub> in the complexes, similar to the literature trend [8] and suggesting similarity of the structure of the two complexes. It is generally difficult to determine the stretching frequency  $\nu_{\text{(M-P)}}$  that contains PPh<sub>3</sub> because it has many stretching frequencies in the lower-frequency region [9]. However, the IR spectra of the two complexes showed interesting differences. The  $\nu_{\text{CO}}$  of the three terminal



SCHEME 1

carbonyls in the tungsten complex exhibit more shift to lower frequencies than that of the molybdenum complex. This can be contributed to the difference in the metal and arrangements of the ligands in the two complexes. From the positions of the three CO groups and their intensities, it can be concluded that the complex [Mo(CO)<sub>3</sub>(isatH)(PPh<sub>3</sub>)] could be presented in the meridional (*mer*)-isomer in the solid state and tungsten complex in the facial (*fac*)-isomer as shown in Scheme 1.

The <sup>1</sup>H NMR spectrum of isatH in deuterated DMSO showed signals at 6.9(d), 7.06(t), 7.5(t), 7.61(d) ppm due to protons of the benzene ring and a signal at 10.98(s) ppm due to proton of NH group [3]. The <sup>1</sup>H NMR spectrum of PPh<sub>3</sub> showed multiplets in the range of 6.93–7.24 ppm. <sup>1</sup>H NMR spectra of the molybdenum complex exhibited two broad singlet signals at 11.02 and 10.86 ppm due to NH and appearance of a new doublet signal at 9.05 ppm due to one proton in the isatin phenyl ring, in addition to the shifts of isatin and PPh<sub>3</sub> as a result of coordination. The ratios of the signals at 11.02 and 10.86 ppm were of (1:3) and 2:1 for molybdenum and tungsten complexes, respectively, suggesting that the complex present in two-tautomeric structure. The appearance of the new signal and change in the chemical shift of NH proton is essentially

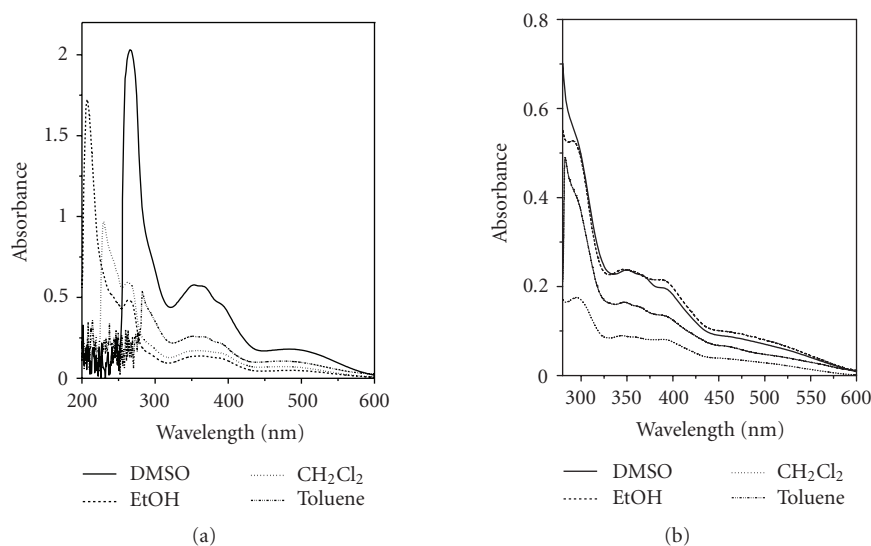
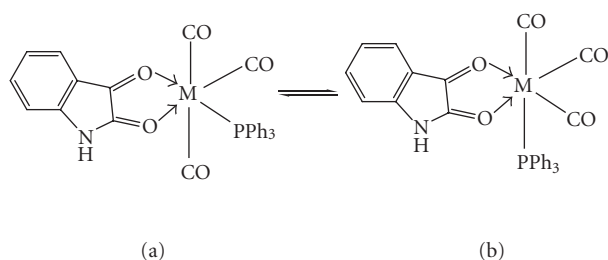


FIGURE 1: The UV-vis spectra of the (a)  $[\text{Mo}(\text{CO})_3(\text{isatH})(\text{PPh}_3)]$ , (b)  $[\text{W}(\text{CO})_3(\text{isatH})(\text{PPh}_3)]$  complexes in different solvents.



SCHEME 2

related to the presence of the  $\text{PPh}_3$  and its effect on the chemical shifts of the isatin protons. This shift may be due to mutual anisotropic deshielding between the phenyl group of  $\text{PPh}_3$  and one proton of the benzene ring of isatin which can affect the signal of  $\text{NH}$ . This effect is due to magnetic field through space and not through chemical bond by inductive effect [10]. This indicates the possibility of exchange between  $\text{CO}$  and  $\text{PPh}_3$  groups in the solution in the axial position [11, 12].

X-ray studies of  $\text{cis-RuCl}_2(\text{trpy})(\text{PPh}_3)$ ; where  $\text{trpy}$  = terpyridine, showed that the  $\text{PPh}_3$  has two phenyl rings parallel to the  $\text{trpy}$  while the third phenyl ring nearly perpendicular to the external pyridine of  $\text{trpy}$  and this lead to low-field shift of the parallel pyridine proton by 1.09 ppm. This was not observed for  $\text{trans-RuCl}_2(\text{trpy})(\text{PPh}_3)$  [13]. From the spectroscopic data, we can conclude that the complexes can exist in *mer*- and *fac*-isomers in solution as shown in Scheme 2.

**3.2. UV-vis Studies.** The absorption spectra of isatin and its complexes were measured in ethanol. Isatin displayed three bands at 249, 296, and 420 nm due to  $\pi$ - $\pi^*$  and  $n$ - $\pi^*$  transitions, Table 3. The solvent effect on the position of the longer wavelength absorption band of isatin

TABLE 3: Absorption data of isatin and its complexes in different solvents.

Compound	Solvent	$\lambda$ (nm)
Isatin	DMSO	334, 418
	Ethanol	249, 296, 420
	Toluene	295, 405
	$\text{CH}_2\text{Cl}_2$	249, 296, 415
$[\text{Mo}(\text{CO})_3(\text{isatH})(\text{PPh}_3)]$	DMSO	284, 363, 389 <sup>a</sup> , 481
	Ethanol	265, 353, 363, 393, 491
	Toluene	282, 349, 361, 387, 473
	$\text{CH}_2\text{Cl}_2$	263, 291, 365, 473
$[\text{W}(\text{CO})_3(\text{isatH})(\text{PPh}_3)]$	DMSO	248, 349, 365, 358, 448
	Ethanol	243, 261, 290 <sup>a</sup> , 389, 481
	Toluene	289, 345, 357, 387, 452
	$\text{CH}_2\text{Cl}_2$	263, 297, 343, 379, 446

<sup>a</sup>shoulder

indicates that the  $n\pi^*$  transition has some charge transfer (CT) character; the nitrogen atom being the electron donor and the  $\beta$ -carbonyl group the acceptor. Absorption spectra of the complexes obtained from the reaction of  $\text{M}(\text{CO})_6$ ;  $\text{M} = \text{Cr}$  or  $\text{Mo}$  with isatin only as a ligand showed a shift or disappearance of the CT band due to complexation through carbonyl group in isatin [3]. The electronic spectra of the complexes showed new bands in the range 360–387 nm due to complexation and a weak band in the range of 445–490 nm. The longer wavelength band could be attributed to metal-to-ligand charge transfer transitions. The charge transfer bands for the  $[\text{Mo}(\text{CO})_3(\text{isatH})(\text{PPh}_3)]$  were appeared at longer wavelength than the  $[\text{W}(\text{CO})_3(\text{isatH})(\text{PPh}_3)]$  Figure 1. This trend was observed for the complexes  $[\text{Mo}(\text{CO})_3(\text{pbiH})(\text{PPh}_3)]$  and  $[\text{W}(\text{CO})_3(\text{pbiH})(\text{PPh}_3)]$ ;  $\text{pbiH} = 2$ -(2'-pyridyl)benzimidazole [14].

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