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New Group 6 metal carbonyl derivatives of 2-(2′-pyridyl)benzimidazole: synthesis and spectroscopic studies

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Abstract

Reaction of $Cr(CO)_6$ with 2-(2′-pyridyl)benzimidazole (pbiH) under reduced pressure resulted in the formation of the dinuclear complex $[Cr_2(CO)_6(pbiH)_2]$. Infra-red (IR) spectroscopy revealed the presence of terminal and bridge Cr–CO bonds. Interaction of $M(CO)_6$, M=Cr, Mo and W, with pbiH in the presence of 2,2′-bipyridine (bpy) gave the tetracarbonyl complexes $[M(CO)_4(pbiH)]\cdot bpy$. Spectroscopic studies of the complexes indicated the presence of hydrogen bonding between the bpy nitrogen and the NH group of pbiH. Reactions of $M(CO)_6$ with pbiH in the presence of PPh_3 gave the tricarbonyl monosubstituted derivatives $[M(CO)_3(PPh_3)(pbiH)]$. The spectroscopic studies of the complexes suggested the proposed structures.

Keywords: Metal carbonyls; Benzimidazole complexes; PPh_3 complexes; Spectra; Charge transfer; Hydrogen bonding; Proton transfer

1. Introduction

Interest in transition metal complexes of imidazoles and benzimidazoles stems from their abilities of proton, metal-to-ligand or ligand-to-metal charge transfers [1–4]. For example, iron and ruthenium complexes of the type $[M-LH]_n$ (where $M=[Ru(NH_3)_5]^{2+,3+}$ or $[Fe(CN)_5]^{3-,2-}$ and LH=benzotriazole or benzimidazole) were characterized by electrochemical and spectro electro-chemical methods. The $E_{1/2}$ versus pH curves were used to illustrate the relationship between the redox and acid–base species, and their interconversion equilibrium. The dependence of the M^{III}/M^{II} couple on the pH was taken into account in order to evaluate the usefulness of such simple complexes as models for proton-coupled electron transfer. The results were interpreted in terms of the acceptor/donor electronic character of the ligands and σ, π-metal–ligand interactions in both redox states of the metal ion [5]. On the other

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hand, the binuclear ruthenium complexes $[(NH_3)_5Ru{-}L{-}Ru(edta)]^n$ (where L=benzotriazolate or benzimidazolate; edta=ethylenediaminetetraacetate; $n = 1, 0, -1$) exhibited intramolecular electron transfer phenomena with a distinct redox and metal-to-ligand and ligand-to-metal charge transfer behaviour [6]. Previous reports showed the synthesis of $[M(CO)_4(pbiH)]$, M=Mo and W, from the reactions of $M(CO)_6$ with 2-(2′-pyridyl)benzimidazole (pbiH) [7]. Also, the complexes $[Ru(CO)_3(pbiH)]$, $[Ru(CO)_3(pbiH)]\cdot py$, $[Ru(CO)_3(pbiH)]\cdot bpy$ and $[Os(CO)_2(pbiH)_2]$ were isolated from the reactions of the cluster compounds $M_3(CO)_{12}$, M=Ru and Os, with pbiH alone or in presence of pyridine (py) or 2,2′-bipyridine (bpy) [8]. Spectroscopic studies of these Group 6 and 8 complexes revealed the presence of intramolecular metal-to-ligand charge transfer interactions. In addition, the ruthenium complexes with py or bpy exhibited intramolecular hydrogen bonding between the NH proton of the imidazole group and the hetero nitrogen of py or bipyridine [8].

In this paper, we report the synthesis and spectroscopic studies of the Group 6 metal complexes of pbiH with either bpy or triphenyl phosphine.

2. Experimental

2.1. Reagents

$M(CO)_6$, M=Cr, Mo and W; PPh_3 and bpy were supplied from Aldrich. pbiH was purchased from Across. All the solvents were of analytical reagent grade and were purified by standard methods.

2.2. Instruments

Infra-red (IR) measurements, KBr discs, were carried out on a Unicam-Mattson 1000 FT-IR spectrometer. Electronic absorption spectra were measured on a Unicam UV2-300 UV–vis spectrophotometer. Proton NMR measurements were performed on a Spectrospin-Bruker AC 200 MHz spectrometer. Samples were dissolved in $(CD_3)_2SO$ 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).

2.3. Syntheses of complexes

2.3.1. Synthesis of $[Cr_2(CO)_6(pbiH)_2]$

A mixture of $Cr(CO)_6$ (0.10 g, 0.45 mmol) and pbiH (0.09 g, 0.45 mmol) in a sealed tube containing approximately 30 ml THF was degassed and then heated for 18 h at which the colour of solution changed from yellow to deep red. The reaction mixture was cooled and the solvent was removed on a vacuum line. The residue was washed several times with boiling petroleum ether and then recrystallized from hot ethanol to give fine reddish brown crystals (yield 53%). Analysis of $C_{30}H_{18}O_6N_6Cr_2$ gave: 54.4% C, 2.7% H, 12.7% N; found: 54.1% C, 2.6% H, 12.8% N. $M_w = 662.25$, value of $m/z = 635$ $[P-CO]^+$.

2.3.2. Synthesis of $[Cr(CO)_4(pbiH)]\cdot bpy$

$Cr(CO)_6$ (0.11 g, 0.50 mmol), pbiH (0.10 g, 0.50 mmol) and bpy (0.08 g, 0.51 mmol) were mixed together in a sealed tube containing THF solvent. The reaction mixture was degassed and heated for 20 h. The colour of the solution changed from yellow to red and finally to dark red. The reaction mixture was cooled and the solvent was removed on a vacuum line. The residue was washed several times by boiling petroleum ether followed by cold benzene. The solid was then recrystallized from hot benzene to give fine reddish brown crystals (yield 73%). Analysis of $C_{26}H_{17}O_4N_5Cr$ gave: 60.6% C, 3.3% H, 13.6% N; found: 60.3% C, 3.5% H, 13.7% N. $M_w = 515.45$, value of $m/z = 360$ $[P-bpy]^+$.

2.3.3. Synthesis of $[Cr(CO)_3(PPh_3)(pbiH)]$

A mixture of $Cr(CO)_6$ (0.10 g, 0.45 mmol), pbiH (0.09 g, 0.45 mmol) and PPh_3 (0.11 g, 0.45 mmol) were mixed together in a sealed tube containing approximately 25 ml THF. The solution was degassed and heated to reflux for 18 h. The colour of the solution changed from yellow to red and finally to dark red. The reaction mixture was cooled and the solvent was then removed on a vacuum line. The residue was washed several times with boiling petroleum ether and then recrystallized from hot benzene/diethyl ether mixture to give reddish brown crystals (yield 76%). Analysis of $C_{33}H_{24}O_3N_3PCr$ gave: 66.8% C, 4.1% H, 7.1% N; found: 66.5% C, 4.2% H, 7.0% N. $M_w = 593.57$, value of $m/z = 594$ [P^+].

2.3.4. Synthesis of [Mo(CO)$_4$(pbiH]) · bpy

A similar procedure was performed as in the case of [Cr(CO)$_4$(pbiH)] · bpy complex. The reaction period was 10 h and the complex was reddish brown (yield 68%). Analysis of $C_{26}H_{17}O_4N_5Mo$ gave: 55.8% C, 3.1% H, 12.5% N; found: 55.6% C, 3.2% H, 12.7% N. $M_w = 559.39$, value of $m/z = 404$ $[P - bpy]^+$.

2.3.5. Synthesis of [Mo(CO)$_3$(PPh$_3$)(pbiH)]

A similar procedure was carried out as in the case of [Cr(CO)$_3$(PPh$_3$)(pbiH)] complex. The reaction period was 15 h and the complex was reddish brown (yield 73%). Analysis of $C_{33}H_{24}O_3N_3PMo$ gave: 62.2% C, 3.8% H, 6.6% N; found: 61.9% C, 3.6% H, 6.7% N. $M_w = 637.48$, value of $m/z = 638$ [P^+].

2.3.6. Synthesis of [W(CO)$_4$(pbiH)] · bpy

A similar procedure was performed as in the case of [Cr(CO)$_4$(pbiH)] · bpy complex. The reaction period was 24 h and the complex was brown (yield 54%). Analysis of $C_{26}H_{17}O_4N_5W$ gave: 48.2% C, 2.7% H, 10.8% N; found: 47.9% C, 2.6% H, 10.8% N. $M_w = 647.30$, value of $m/z = 464$ $[P - (bpy + CO)]^+$.

2.3.7. Synthesis of [W(CO)$_3$(PPh$_3$)(pbiH)]

A similar procedure was carried out as in the case of [Cr(CO)$_3$(PPh$_3$)(pbiH)] complex. The reaction period was 24 h and the complex was orange red (yield 62%). Analysis of $C_{33}H_{24}O_3N_3PW$ gave: 54.6% C, 3.4% H, 5.8% N; found: 54.8% C, 3.5% H, 5.9% N. $M_w = 725.39$, value of $m/z = 698$ $[P - CO]^+$.

3. Results and discussion

3.1. IR and NMR studies

In contrast to the behaviour of molybdenum and tungsten [7], reaction of Cr(CO)$_6$ with 2-(2′-pyridyl)benzimidazole under reduced pressure in THF yielded a dinuclear complex with a molecular formula [Cr$_2$(CO)$_6$(pbiH)$_2$]. It gave a molecular ion peak at $m/z = 635$ in the mass spectrum which was corresponding to the $[P - CO]^+$ ion peak. The IR spectrum of the complex displayed two asymmetric and symmetric CO stretching frequencies in the terminal metal carbonyl region (Table 1). Also, the spectrum showed a strong band at 1790 cm^{-1} with a shoulder at 1759 cm^{-1}. This band could be assigned for bridging carbonyl groups [9]. In addition, the IR spectrum of the complex exhibited characteristic bands due to the C=N, C=C and NH groups of the ligand moiety with the corresponding shifts (Table 1). These shifts indicated coordination through the py-type nitrogen of the imidazole ring of pbiH. Furthermore, the in-plane ring deformation bands of py part were shifted to higher frequencies suggesting the bonding through the pyridyl nitrogen [10].

The ^1H NMR spectrum of pbiH in DMSO displayed two multiplets and two doublets due to the protons in the benzimidazole and pyridyl rings (Table 2). It also showed a broad singlet at 12.70 ppm corresponded to the NH proton. On the other hand, the proton NMR spectrum of the chromium complex displayed a similar pattern similar to that of ligand (Table 2). The NH groups of imidazole rings displayed a slightly broad singlet and exerted down field shift (Table 2). According to the spectroscopic data, the complex might consist of two chromium atoms bridged by two CO groups. Each chromium is also bonded to two terminal carbonyl groups in the trans positions and a pbiH ligand through the nitrogen of the pyridyl ring and the py-type nitrogen of the imidazole moiety in the cis positions (Scheme 1).

When the reactions of M(CO)$_6$, M=Cr, Mo and W, with pbiH were carried out in the presence of bpy, the [M(CO)$_4$(pbiH)] · bpy complexes were isolated. The IR spectra of the three complexes exhibited characteristic bands due to the C=N,

Table 1
Important IR data for 2-(2′-pyridyl)benzimidazole and its complexes

Compound	IR data (cm^{-1})[a]					
	$\nu_{(NH)}$	$\nu_{(NH\cdots N)}$	$\nu_{(C=N)}$	$\nu_{(C=C)}$	$\nu_{(CO)}$	$\delta_{(py)}$
PbiH	3061(s)		1600(m) 1568(w)	1445 (s)	–	620(mw), 590(w), 547(mw)
[$Cr_2(CO)_6(pbiH)_2$]	3079(s)		1612(s) 1566(m)	1520(m) 1450(s)	1890(s) 1867(m) 1790(s) 1759(sh)	648(m), 540(m), 509(m)
[$Cr(CO)_4(pbiH)$]·bpy		3015(m)	1605(s) 1566(m)	1520(m) 1443(m)	2006(s) 1920(s) 1875(vs) 1813(vs)	640(m), 548(m)
[$Cr(CO)_3(PPh_3)(pbiH)$]	3055(m)		1612(s)	1520(m) 1450(s)	1890(s) 1865(s) 1805(s)	648(m), 540(s)
[$Mo(CO)_4(pbiH)$]·bpy		3022(m)	1597(m)	1465(m) 1443(m)	2014(m) 1911(sh) 1867(s) 1813(s)	640(mw), 579(m)
[$Mo(CO)_3(PPh_3)(pbiH)$]	3078(m)		1609(w) 1597(m)	1465(m) 1442(m)	2014(m) 1890(s) 1867(s) 1813(s)	640(w), 540(s)
[$W(CO)_4(pbiH)$]·bpy		3019(m)	1605	1465	2006(m) 1902(sh) 1962(s) 1811(s)	625(m), 569(m)
[$W(CO)_3(PPh_3)(pbiH)$]	3071(m)		1605(m)	1466(m) 1443(m)	2006(m) 1902(sh) 1859(s) 1805(s)	632(mw), 540(m)

[a] s, strong; m, medium; w, weak; sh, shoulder

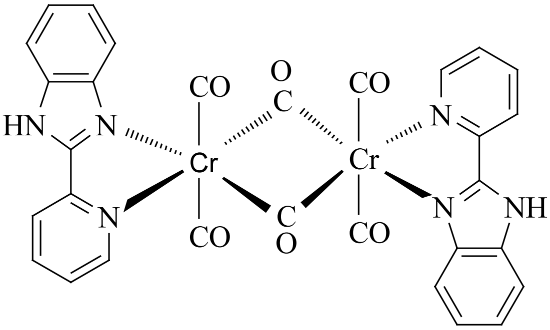
C=C groups of the ligands moieties with the corresponding shifts (Table 1). In addition, the in-plane ring deformation bands of the py moiety of bipyridine were shifted to higher frequencies due to coordination of the pyridyl nitrogen. The IR spectra of the complexes also showed similar IR patterns to that of [$M(CO)_4(pbiH)$], M=Mo and W, in the terminal metal carbonyl region [7] with shifts toward the low frequency range (Table 1). On the other hand, the NH frequency exhibited shift to lower frequency range to give a medium weak band at around 3015–3022 cm^{-1}. This shift could be assigned to the streching frequency of N–H···N bond [11]. Therefore, the bonding of bpy to the complex moiety [$M(CO)_4(pbiH)$] was probably through hydrogen bonding between the nitrogen of the base and the N–H group of the imidazole part (Scheme 2). Solvent effect, for example, in the charge-transfer transition of some ruthenium-amine complexes was interpreted by the hydrogen bonding type interaction involving electron–pair donation from a solvent molecule to the N–H bond [12].

The ^1H NMR spectra of [$M(CO)_4(pbiH)$]·bpy complexes exhibited signals due to both the pbiH and bpy moieties (Table 2). On the other hand, the spectra of the three complexes displayed some discrepancies with respect to the signal due to the NH proton. While the chromium complex did not show any signals due to the NH group, the

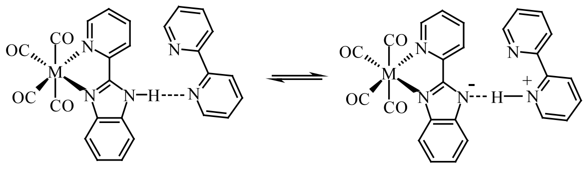
Table 2
Important ^{1}H NMR data for 2-(2′-pyridyl)benzimidazole and its complexes

Compound	^{1}H NMR data (ppm)[a]
pbiH	7.12(m), 7.61(m), 8.15(d), 8.48(d), 12.70(s)
$[Cr_2(CO)_6(pbiH)_2]$	7.20(m), 7.59(m), 7.96(d), 8.32(m), 8.69(m), 13.01(s)
$[Cr(CO)_4(pbiH)]\cdot bpy$	7.48(m), 8.03(m), 8.52(m), 9.06(m)
$[Cr(CO)_3(PPh_3)(pbiH)]$	7.21(m), 7.59(m), 7.98(m), 8.32(m), 8.72(m), 13.02(s)
$[Mo(CO)_4(pbiH)]\cdot bpy$	7.21(m), 7.48(m), 7.64(m), 7.94(m), 8.17(m), 8.64(dd), 8.71(d), 8.97(d), 13.00(s), 14.19(s)
$[Mo(CO)_3(PPh_3)(pbiH)]$	7.34(m), 7.57(m), 8.26(m), 8.44(dd), 9.03(d), 13.04(bs), 14.34(bs)
$[W(CO)_4(pbiH)]\cdot bpy$	7.33(m), 7.62(m), 7.91,8.2(m), 8.62(d), 8.77(d), 9.08(d), 9.15(d), 14.49(s)
$[W(CO)_3(PPh_3)(pbiH)]$	7.65(m), 7.79(m), 8.23(m), 8.39(m), 8.67(dd), 9.08(d), 14.34(s)

[a] s, singlet; d, douplet; dd, douplet of doublets; m, multiplet; b, broad.



Scheme 1.



(A) (B)

M = Cr, Mo and W

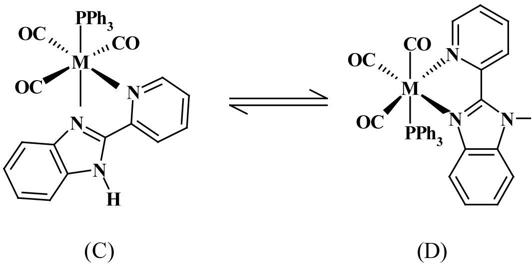
Scheme 2.

tungsten derivative showed a signal at 14.49 ppm. The molybdenum complex, on the other hand, exhibited two broad signals at 13.00 and 14.19 ppm. These results can be explained as the complex persisted in equilibrium between the two isomers (A) and (B) (Scheme 2). In case of the chromium complex, the exchange between A and B was very fast and the signals were collapsed to the base line [13,14]. For the tungsten derivative, isomer B was expected to be the predominant species at that condition. The molybdenum complex showed two signals due to both two isomers (Scheme 2).

Heating a mixture of equimolar of $M(CO)_6$, M = Cr, Mo or W, and pbiH in presence of triphenyl phosphine in THF under reduced pressure resulted in the formation of the tricarbonyl monosubstituted derivatives $[M(CO)_3(pbiH)(PPh_3)]$. The IR spectra of the complexes were almost similar, which could indicate that they have identical structures. The IR spectra of the complexes showed, besides the pbiH ligand bands, two bands at 1165 and 1119 cm^{-1} characteristic for triphenyl phosphine [9]. Also, the spectra showed a set of bands in the terminal metal carbonyl range due to the CO groups (Table 1). The ^{1}H NMR spectra of $[M(CO)_3(pbiH)(PPh_3)]$ complexes showed multiplets in the range 7.2–9.2 ppm corresponding to the protons of PPh_3 and pbiH moieties (Table 2). In addition, the spectra of the chromium and tungsten complexes displayed a singlet at 13.02 and 14.34, respectively, due to the proton of the NH group. On the other hand, the ^{1}H NMR spectrum of $[Mo(CO)_3(pbiH)(PPh_3)]$ complex showed two broad singlets for the NH proton at 13.04 and 14.34 ppm. The appearance of two NH signals in the ^{1}H NMR spectrum of molybdenum derivative indicated the possibility of the presence of two equilibrated isomeric forms (C and D, Scheme 3) depending on the position of PPh_3 ligand.

3.2. UV–vis studies

The absorption spectra of pbiH and its complexes were measured in ethanol. PbiH displayed three bands at 297, 310 and 322 nm due to π–π* and *n*–π* transitions (Table 3). The electronic



M = Cr, Mo and W

Scheme 3.

spectra of the chromium complex showed a new shoulder at 377 nm and a weak band at 450 nm. The band at 450 nm could be attributed to metal-to-ligand charge transfer transitions (pbiHπ* ← Mdπ). Other mono- and bimetallic tetracarbonyl centers bound to 2,3-bis(2'-pyridyl)pyrazine and its derivatives were found to be highly absorbing in the visible region of the spectrum, and this was attributed to the lower energy of MLCT versus LF bands [15–17]. The charge transfer bands for the complexes $[Mo(CO)_4(pbiH)]\cdot bpy$ and $[W(CO)_4(pbiH)]\cdot bpy$ were appeared at longer wavelengths than the complexes without bpy due to the hydrogen-bond formation between bipyridine and the NH group [7] (Fig. 1). Furthermore, it

Table 3
Electronic absorption spectral data for 2-(2′-pyridyl)benzimidazole and its complexes

Compound	λ (nm)[a]
pbiH	297 (20200), 310 (22500), 322 (19000)[b]
$[Cr_2(CO)_6(pbiH)_2]$	241(19017), 296 (20763)[b], 312 (21300), 324 (17660)[b], 377 (9420)[b], 450 (1035)
$[Cr(CO)_4(pbiH)]\cdot bpy$	244(23910), 297(22839), 325 (13830), 370 (6960), 497 (2068)[c]
$[Cr(CO)_3(PPh_3)(pbiH)]$	265 (10729), 272 (10950), 310 (19550), 323 (19540), 353 (13345)[b], 378 (8260)[b], 450 (640)[c]
$[Mo(CO)_4(pbiH)]\cdot bpy$	257 (18490), 296 (20800), 325 (7820)[b], 385(2820)[b], 468 (2694)[c]
$[Mo(CO)_3(PPh_3)(pbiH)]$	259 (30145), 264 (31240), 271 (317 (24340), 335 (14610)[b], 358 (4870)[b], 453 (3530)
$[W(CO)_4(pbiH)]\cdot bpy$	254 (21960), 299 (21480), 325 (15130)[b], 484 (3660)
$[W(CO)_3(PPh_3)(pbiH)]$	259 (28310), 311 (19450), 324 (19540), 350 (10820)[b], 440 (3660)[c]

[a] Molar extinction coefficients, ε, are given in parentheses.
[b] Shoulder.
[c] Weak and broad.

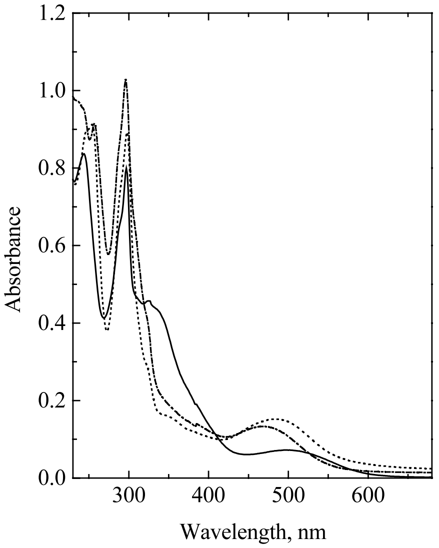


Fig. 1. The UV–vis spectra of the complexes $[M(CO)_4(pbiH)]\cdot bpy$. ((——) chromium complex, (–·–·–) molybdenum complex, (······) tungsten complex).

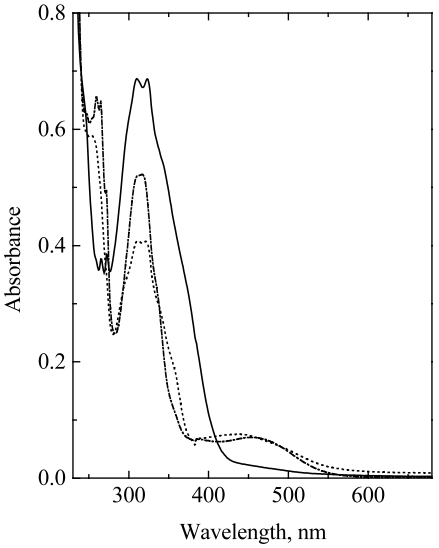


Fig. 2. The UV–vis spectra of the complexes $[M(CO)_3(PPh_3)(pbiH)]$. ((——) chromium complex, (–·–·–) molybdenum complex, (······) tungsten complex).

can be seen that the CT bands for these complexes appeared at longer wavelengths than the complexes $[M(CO)_3(pbiH)(PPh_3)]$ (Fig. 2), due to the differences in the electronic structure of the two ligands.

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