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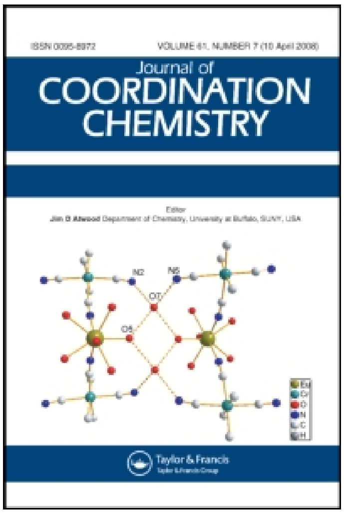

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Reactions and spectroscopic studies of Group 6 metal carbonyls with pyrazinecarboxamide and certain phosphine ligands

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Substitution reactions of phosphine ligands, triphenylphosphine (PPh_3), tri(*m*-chlorophenyl)-phosphine (*m*-$ClPPh_3$), tri(*p*-methoxyphenyl)phosphine (*p*-$MeOPPh_3$) and tri(benzyl) phosphine (PBz_3) with $[M(CO)_4(PCA)]$ (M = Cr, Mo and W, PCA = pyrazinecarboxamide) were found to be dependent on the type of metal and phosphine ligand. The complexes were characterized by elemental analysis, mass spectrometry, and IR and ^1H NMR spectroscopy. UV–vis spectra of the complexes in different solvents showed bands due to metal-to-ligand charge transfer.

Keywords: Chromium; Metal carbonyl; Phosphines; Mixed ligands; Spectra

1. Introduction

Coordination chemistry of nitrogen donor ligands is studied extensively primarily because of their relevance to biological systems [1]. Transition metal complexes of heterocyclic compounds containing nitrogen, such as pyridine, di- and polypyridine, azines and their derivatives, are also of great interest because of their facile electrochemical processes [2, 3]. Their ability to absorb visible light and act as electron reservoirs also makes them promising for applications as photosensitizers [4–8]. For example, ruthenium and osmium complexes of nitrogen donor ligands, especially

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azine derivatives, absorb or emit visible light and reversibly exchange electrons. These compounds could thus find application as components in molecular electronics and as photochemical molecular devices for solar energy conversion and information storage [9]. Metal carbonyl derivatives of nitrogen donor ligands are important in the preparation metal carbonyl complexes [10]. Organophosphorus compounds continue to play a central role in the behavior and catalytic activity of inorganic and organometallic compounds [11]. With phosphine ligands of the type PR_3, where $R = alkyl$ or aryl, the substituents can be systematically varied to change the basicity, π-accepting ability and steric effect of the ligand, causing dramatic changes in the chemical behavior and activity of these complexes as well as influencing reaction rates and product distributions [12].

Recently, we reported that the interaction of $M(CO)_6$ ($M = Cr$, Mo and W) with 2-(2′-pyridyl)benzimidazole (pbiH) in the presence of 2,2′-bipyridine (bpy) gave 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 [13]. Reactions of $M(CO)_6$ with pbiH in the presence of PPh_3 gave the tricarbonyl monosubstituted derivatives $[M(CO)_3(PPh_3)(pbiH)]$ [13]. In this article, we report the reactions of Group 6 metal carbonyls with pyrazinecarboxamide and certain phosphine ligands. Different structural features were observed depending on the type of phosphine ligand.

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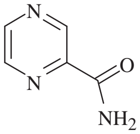
2. Experimental

2.1. *Reagents*

$[M(CO)_6]$ ($M = Cr$, Mo and W), pyrazinecarboxamide (PCA) (scheme 1), triphenylphosphine (PPh_3), tri(*m*-chlorophenyl)phosphine (*m*-$ClPPh_3$), tri(*p*-methoxyphenyl) phosphine (*p*-$MeOPPh_3$) and tri(benzyl)phosphine (PBz_3) were supplied by Aldrich. All solvents were purified by distillation before use.

2.2. *Instrumentation*

Infrared measurements (KBr pellets) were carried out on a Unicam-Mattson 1000 FT-IR spectrometer. Electronic absorption spectra were measured on a Unicam UV2-300 spectrometer. NMR measurements were performed on a Spectrospin-Bruker AC 200 MHz spectrometer. Samples were dissolved in deuterated DMSO using TMS as internal reference. Elemental analyses were performed on a Perkin-Elmer 2400 CHN instrument. Mass spectrometry measurements of the solid



PCA

Scheme 1. Pyrazinecarboxamide ligand.

complexes (70 eV, EI) were carried out on a Finnigan MAT SSQ 7000 spectrometer. Table 1 gives the elemental analysis and mass spectrometry data for the complexes.

2.3. *Syntheses of complexes*

A general procedure was used for the synthesis of the reported complexes. A mixture of equimolar (0.5 mmol) amounts of [M(CO)$_6$], M = Cr (0.11 g), Mo (0.13 g) or W (0.18 g), and PCA (0.06 g) in *ca.* 30 cm^3 of THF was heated to reflux for 30 min. The phosphine ligand (0.5–2.0 mmol) was then introduced to the reaction mixture and heating to reflux was continued for 5 to 10 h depending on the type of metal. The reaction mixture was cooled and the solvent was removed on a vacuum line. The solid residue was washed with hot petroleum ether and then recrystallized from hot ethanol. Table 1 gives the reaction time, colour of the complex and the percent yield.

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3. Results and discussion

3.1. *IR and NMR studies*

Among the complexes containing nitrogen-donor ligands, azine and imidazole metal carbonyl derivatives were found to be more susceptible to CO substitution reaction [13]. This could be attributed to the special structural features of these ligands and the existence of two nitrogen atoms in the aromatic ring, which may lead to the formation of labile metal derivatives. [M(CO)$_6$] (M = Cr, Mo and W) reacts with PCA to give the tetracarbonyl derivative [M(CO)$_4$(PCA)] [14]. The number of substituted CO groups in [M(CO)$_4$(PCA)] was found to be dependent on the type of phosphine ligand. The reactivity of the phosphine ligands depends on their basicity (p-MeOPPh$_3$ > PPh$_3$ ≈ PBz$_3$ > m-ClPPh$_3$), π-acceptor ability (m-ClPPh$_3$ > PPh$_3$ ≈ PBz$_3$ > p-MeOPPh$_3$) and the steric effect (the order of cone angle [15]: m-ClPPh$_3$ ≈ PBz$_3$ > PPh$_3$ = p-MeOPPh$_3$). Reactions of [M(CO)$_4$(PCA)] (M = Cr and W) with PPh$_3$ gave the complex [M(CO)$_3$(PCA)(PPh$_3$)] by substitution of one CO group. The corresponding reactions with the stronger π-acceptor phosphine ligand, m-ClPPh$_3$, resulted in substitution of all the CO groups to give the complex [M(PCA)(m-ClPPh$_3$)$_4$]. On using the p-MeOPPh$_3$ ligand, the number of substituted CO groups was found to be dependent on the metal. While chromium gave the dicarbonyl derivative [Cr(CO)$_2$(PCA)(p-MeOPPh$_3$)$_2$], tungsten formed the monocarbonyl derivative [W(CO)(PCA)(p-MeOPPh$_3$)$_3$]. For tribenzylphosphine, the corresponding reactions with [M(CO)$_4$(PCA)] (M = Mo or W) gave the dicarbonyl derivative [M(CO)$_2$(PCA)(PBz$_3$)$_2$]. Therefore, it can be concluded that the steric properties of the phosphine ligands have little effect in these reactions; rather the basicity and π-acceptor ability were the dominant factors.

IR spectra of the complexes displayed bands due to the functional groups of the ligands with the appropriate shifts. Table 2 gives the important IR data for these complexes. The number of CO groups in the complexes was determined from the number of stretching CO bands in the IR spectra as well as from the mass spectra of the complexes. The two complexes [Cr(CO)$_3$(PCA)(PPh$_3$)] and [W(CO)$_3$(PCA)(PPh$_3$)] exhibited three CO bands in the terminal metal carbonyl range (table 2). The number

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Table 1. Elemental analysis, reaction time, color of complexes, percentage yield and mass spectrometry data for the reported complexes.

Complex	Reaction time (h)	Color	Yield (%)	Found (Calcd) (%) C	Found (Calcd) (%) H	Found (Calcd) (%) N	Mass spectrometry Mol. wt	Mass spectrometry m/z
$[Cr(CO)_3(PCA)(PPh_3)]$	6	Pale brown	85	59.7 (59.9)	3.7 (3.9)	7.9 (8.1)	521.44	522 $[P]^+$
$[W(CO)_3(PCA)(PPh_3)]$	9	Brown	64	47.9 (47.8)	3.3 (3.1)	6.2 (6.4)	653.34	653 $[P]^+$
$[Cr(PCA)(m\text{-}ClPPh_3)_4]$	7	Brown	79	56.1 (56.5)	3.3 (3.3)	2.8 (2.6)	1637.56	1638 $[P]^+$
$[W(PCA)(m\text{-}ClPPh_3)_4]$	10	Brown	58	52.6 (52.3)	2.9 (3.0)	2.3 (2.4)	1769.46	1754 $[P–NH_2]^+$
$[Cr(CO)_2(PCA)(p\text{-}MeOPPh_3)_2]$	7	Brown	71	63.1 (62.9)	4.9 (5.1)	4.6 (4.5)	935.74	936 $[P]^+$
$[W(CO)(PCA)(p\text{-}MeOPPh_3)_3]$	8	Reddish brown	48	59.5 (59.5)	4.8 (4.9)	3.1 (3.2)	1391.92	1392 $[P]^+$
$[Mo(CO)_2(PCA)(PBz_3)_2]$	5	Red	82	66.3 (66.6)	5.4 (5.4)	4.7 (4.8)	883.88	884 $[P]^+$
$[W(CO)_2(PCA)(PBz_3)_2]$	9	Brown	53	60.3 (60.6)	4.8 (4.9)	4.1 (4.3)	971.64	972 $[P]^+$

Table 2. IR data ($\mathrm{cm^{-1}}$) for PCA, phosphine ligands and their complexes.

	$\nu_{(\mathrm{NH})}$	$\nu_{(\mathrm{C=N})}$	$\nu_{(\mathrm{C=O})}$(PCA)	$\nu_{(\mathrm{M–C=O})}$	$\gamma_{(\mathrm{C–H})}$(phosphine)
PCA	3414(s) 3290(m)	1610(s) 1579(s)	1714(s)	–	–
PPh_3	–	–	–	–	1474(s), 1433(s) 742(s), 693(s)
m-$ClPPh_3$	–	–	–	–	1462(s), 1392(s) 782(s), 685(s)
p-$MeOPPh_3$	–	–	–	–	1283(s), 1245(s) 1177(s), 831(s) 795(s)
PBz_3	–	–	–	–	1493(s), 1449(s) 767(s), 699(s)
$[Cr(CO)_3(PCA)(PPh_3)]$	3430(s) 3306(m)	1601(s) 1584(s)	1678(s)	1980(m) 1936(m) 1879(s)	804(m), 780(m)
$[W(CO)_3(PCA)(PPh_3)]$	3428(m) 3285(w)	1601(sh) 1585(m)	1675(s)	1973(m) 1934(m) 1879(s)	722(s), 695(s)
[Cr(PCA)(*m*-$ClPPh_3)_4$]	3427(m) 3284(m)	1603(m) 1582(m)	1675(s)		686(m), 663(m)
[W(PCA)(*m*-$ClPPh_3)_4$]	3428(s) 3286(m)	1600(m) 1582(m)	1675(s)		687(s), 662(s)
[$Cr(CO)_2$(PCA)(*p*-$MeOPPh_3)_2$]	3425(s) 3288(m)	1596(s) 1569(m)	1680(s)	1934(m) 1877(m)	831(m), 802(m)
[W(CO)(PCA)(*p*-$MeOPPh_3)_3$]	3426(s) 3286(m)	1597(s) 1568(m)	1676(s)	1911(m)	831(m), 801(m)
$[Mo(CO)_2(PCA)(PBz_3)_2]$	3429(s) 3284(m)	1600(s) 1560(sh)	1675(s)	1942(s)	840(s), 809(m) 768(s)
$[W(CO)_2(PCA)(PBz_3)_2]$	3428(s) 3283(m)	1600(s) 1560(sh)	1674(s)	1953(m) 1886(m)	840(s), 809(m) 768(s)

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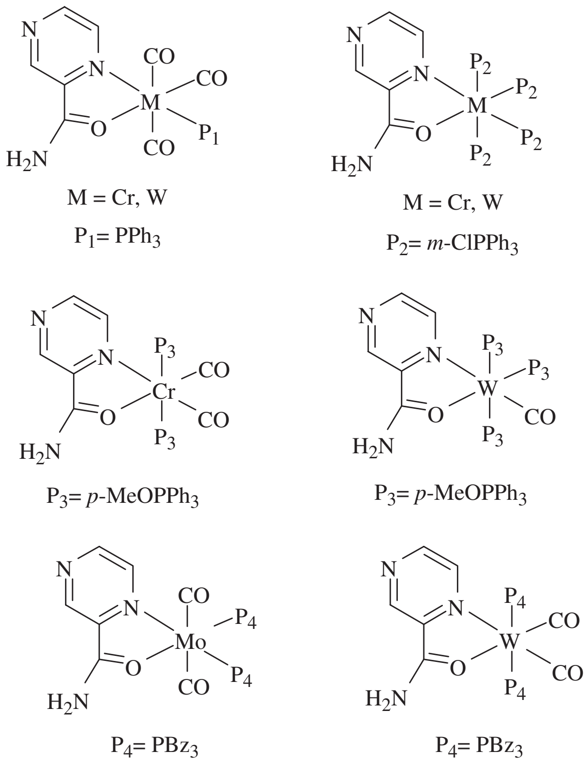
and pattern of these bands suggested that the complexes have a *mer*-geometry (scheme 2). Reactions of $[M(CO)_6]$ (M = Cr, Mo or W) with 2-(2′-pyridyl)benzimidazole (pbiH) in the presence of PPh_3 resulted in the formation of the tricarbonyl mono-substituted derivatives $[M(CO)_3(pbiH)(PPh_3)]$. IR spectra of the complexes showed, besides the pbiH and PPh_3 ligands bands, a set of bands in the terminal metal carbonyl range due to the CO groups. The CO bands of the PCA complexes appeared at higher frequency relative to those of pbiH, probably because of the more basic characteristics of the latter ligand [13].

The IR spectrum of [$Cr(CO)_2$(PCA)(*p*-$MeOPPh_3)_2$] exhibited two stretching frequencies in the terminal metal carbonyl range due to two CO groups (table 2). These CO bands suggest a *cis* configuration [16]. The tungsten derivative [W(CO)(PCA)(*p*-$MeOPPh_3)_3$] displayed only a single band in its IR spectrum due to one carbonyl group. Scheme 2 gives the proposed structures of the chromium and tungsten complexes. The two complexes $[M(CO)_2(PCA)(PBz_3)_2]$ (M = Mo or W) showed different patterns due to the CO ligands. While the molybdenum complex exhibited only one CO band in the IR spectrum corresponding to a *trans* configuration, the tungsten derivative gives two bands due to a *cis* structure [16] (scheme 2). Interaction of the *m*-$ClPPh_3$ ligand with $[M(CO)_4(PCA)]$ (M = Cr or W) resulted in



Scheme 2. Mixed ligand complexes of Cr, Mo, W with PCA and phosphine ligands.

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substitution of all CO groups to give the tetrasubstituted phosphine derivatives [M(PCA)(*m*-ClPPh$_3$)$_4$] (scheme 2).

^{1}H NMR spectra of all complexes displayed signals due to the pyrazinecarboxamide and phosphine ligands with the corresponding shifts due to complex formation. Table 3 shows the important ^{1}H NMR data for the complexes.

3.2. *UV–vis studies*

Electronic absorption spectra of the PCA ligand and its complexes were measured in three different solvents; EtOH, DMF and hexane (table 4). Two electronic spectral bands were observed for PCA in the range 265–266 and 318–325 nm due to π–π* and n–π* transitions, respectively. The position of the first band at 265–266 was slightly influenced by the solvent polarity confirming the π–π* nature of the transition leading to these bands. The other band at 318–325 nm, ascribed to transition between the π-orbital largely localized on the C=N and C=O bonds, influenced by the charge transfer within the entire molecule. For Cr, Mo and W complexes, the band at 265–266 nm showed a significant shift to longer wavelength due to chelation (table 4). The band at 318–325 nm also showed a slight shift with a considerable change in the molar absorptivity on going from ligand to complex, indicating coordination of ligand to metals through the carbonyl group and the adjacent hetero nitrogen atom [17]. In addition,

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Table 3. NMR data for PCA, phosphine ligands and the complexes.

Compound	^{1}H NMR data (ppm)[a]
PCA	9.18 (d, CH), 8.84 (d, CH), 8.70 (dd, CH), 8.23 (bs, NH), 7.84 (bs, NH)
PPh$_3$	7.35 (m, Ph), 7.24 (m, Ph)
m-ClPPh$_3$	7.48 (m, Ph), 7.22 (m, Ph)
p-MeOPPh$_3$	7.14 (m, Ph), 6.94 (m, Ph), 2.50 (bs, Me)
PBz$_3$	7.20 (m, Ph), 2.50 (bs, CH$_2$)
[Cr(CO)$_3$(PCA)(PPh$_3$)]	9.18 (d, CH), 8.84 (d, CH), 8.71 (dd, CH), 8.23 (bs, NH), 7.83 (bs, NH), 7.52 (m, Ph), 7.44 (m, Ph)
[W(CO)$_3$(PCA)(PPh$_3$)]	9.18 (d, CH), 8.85 (d, CH), 8.71 (dd, CH), 8.23 (bs, NH), 7.84 (bs, NH), 7.60 (m, Ph), 7.52 (m, Ph)
[Cr(PCA)(*m*-ClPPh$_3$)$_4$]	9.18 (d, CH), 8.85 (d, CH), 8.71 (dd, CH), 8.23 (bs, NH), 7.83 (s, NH), 7.62 (m, Ph), 7.50 (m, Ph)
[W(PCA)(*m*-ClPPh$_3$)$_4$]	9.18 (d, CH), 8.85 (d, CH), 8.71 (dd, CH), 8.23 (bs, NH), 7.83 (s, NH), 7.65 (m, Ph), 7.62 (m, Ph)
[Cr(CO)$_2$(PCA)(*p*-MeOPPh$_3$)$_2$]	9.18 (d, CH), 8.85 (d, CH), 8.71 (dd, CH), 8.24 (bs, NH), 7.80 (bs, NH), 7.48 (m, Ph), 6.74 (m, Ph), 2.50 (bs, Me)
[W(CO)(PCA)(*p*-MeOPPh$_3$)$_3$]	9.18 (d, CH), 8.85 (d, CH), 8.71 (dd, CH), 8.23 (bs, NH), 8.05 (s, NH), 7.48 (m, Ph), 7.07 (m, Ph), 2.47 (bs, Me)
[Mo(CO)$_2$(PCA)(PBz$_3$)$_2$]	9.18 (d, CH), 8.85 (d, CH), 8.71 (dd, CH), 8.24 (s, NH), 7.84 (s, NH), 7.23 (m, Ph), 2.50 (bs, CH$_2$)
[W(CO)$_2$(PCA)(PBz$_3$)$_2$]	9.18 (d, CH), 8.85 (d, CH), 8.71 (dd, CH), 7.84 (s, NH), 7.47 (s, NH), 7.23 (m, Ph), 2.50 (bs, CH$_2$)

Table 4. UV–vis data (λ, nm) for PCA and the phosphine complexes of chromium, molybdenum and tungsten.

Compound	EtOH	DMF	Hexane
PCA	265, 321	266, 325	266, 318
$[Cr(CO)_3(PCA)(PPh_3)]$	270, 320, 428	280, 324, 440	266, 374sh, 400
$[W(CO)_3(PCA)(PPh_3)]$	279, 320, 432	279, 324, 430	265, 325sh, 419
$[Cr(PCA)(m\text{-}ClPPh_3)_4]$	260, 320, 438	280, 324, 437	274, 370, 410
$[W(PCA)(m\text{-}ClPPh_3)_4]$	276, 321, 425	285, 324, 428	274, 330sh, 425
$[Cr(CO)_2(PCA)(p\text{-}MeOPPh_3)_2]$	262, 327sh, 430	282, 330sh, 441	269, 274sh, 398
$[W(CO)(PCA)(p\text{-}MeOPPh_3)_3]$	282, 318, 410	281, 322, 415sh	289, 325, 404
$[Mo(CO)_2(PCA)(PBz_3)_2]$	274, 319, 436	281, 321, 420	265, 330sh, 428
$[W(CO)_2(PCA)(PBz_3)_2]$	281, 321, 418	284, 324, 417sh	267, 322sh, 386sh

sh, shoulder.

all complexes exhibited absorption bands in the visible range at 386–438 nm, which could be due to metal-to-ligand charge transfer (MLCT) transitions [18, 19].

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