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REACTIONS OF GROUP VII METAL HALOGENOPENTACARBONYLS WITH *E*- AND *Z*-PYRIDINE-2-CARBALDEHYDE 2′-PYRIDYLHYDRAZONE. THE FORMATION OF LINKAGE ISOMERS

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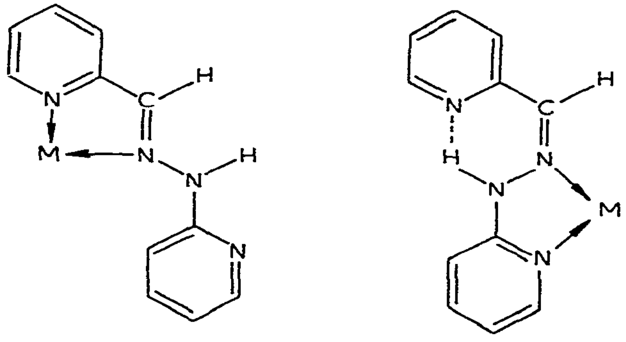
SUMMARY

Compounds of the type $M(CO)_3X$(*Z*-Paphy) have been prepared, where M = Mn and Re, X = Cl, Br and I, *Z*-Paphy = *Z*-pyridine-2-carbaldehyde 2′-pyridylhydrazone. *Z*-Paphy acts only as a bidentate ligand due to strong intramolecular hydrogen bonding. *E*-Paphy has been stabilised in the compounds $Mn(CO)_3X$(*E*-Paphy), and although this isomer can act as a terdentate ligand, it is believed to be only bidentate in these compounds. The $Mn(CO)_3X$(*Z*-Paphy) and $Mn(CO)_3X$(*E*-Paphy) pairs are linkage isomers.

INTRODUCTION

The geometrical isomers of pyridine-2-carbaldehyde 2′-pyridylhydrazone, (Paphy), have *E*, (I), and *Z*, (II), configurations[1], as shown in Fig. 1. *E*-Paphy has been much used[2] as a terdentate ligand. *Z*-Paphy has only recently been isolated, and a few complexes have been prepared[1] which illustrate the bidentate nature of this isomer.



E-Paphy (I)

Z-Paphy (II)

Fig. 1. Configurations of Paphy.

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We have previously shown[3] that starting with the *E*-isomer a variety of substituted Group VI metal carbonyls, $M(CO)_4$(Paphy) and $Mo(CO)_3Y$(Paphy), (M=Cr, Mo and W; Y=monodentate ligand), can be prepared in which *E*-Paphy has isomerized to the *Z*-form. The same compounds can also be prepared directly from *Z*-Paphy. By moderating the reaction conditions whilst using *E*-Paphy a few compounds, *e.g.* $Mo(CO)_4$(*E*-Paphy) and $Mo(CO)_3(PPh_3)$(*E*-Paphy), can be prepared in which ligand isomerisation has not occurred. However, in such compounds *E*-Paphy is bidentate leaving one potential nitrogen donor atom uncoordinated. Other workers[4,5] have also prepared the $Mo(CO)_4$(Paphy) isomers. Different pairs of nitrogen atoms of the *E*- and *Z*-isomers, as shown in (I) and (II), are coordinated in these compounds, so the pairs $Mo(CO)_4$(*E*-Paphy), $Mo(CO)_4$(*Z*-Paphy), and $Mo(CO)_3(PPh_3)$(*E*-Paphy), $Mo(CO)_3(PPh_3)$(*Z*-Paphy) are rare examples of linkage isomers involving chelating ligands.

We now report some reactions of Group VII metal halogenopentacarbonyls with the two geometrical isomers of Paphy. The linkage isomers $Mn(CO)_3X$(*E*-Paphy) and $Mn(CO)_3X$(*Z*-Paphy) where X=Cl, Br and I, have been isolated.

EXPERIMENTAL

IR spectra were recorded on Unicam SP 100 and Perkin–Elmer 237 spectrophotometers. Conductance measurements in nitromethane were made at 25° using a Wayne–Kerr Autobalance universal bridge and a dip-type cell with platinum electrodes. Magnetic susceptibility measurements were made at room temperature by the Gouy method.

TABLE 1

GROUP VII HALOGENOTRICARBONYL–PAPHY COMPOUNDS

Reactants	*Conditions*[a]	*Product*	*Yield* (%)	*Analysis found (calcd.) (%)*			
				C	*H*	*N*	*X*
0.20 g $Mn(CO)_5Cl$/	Benzene	$Mn(CO)_3Cl$(*Z*-Paphy)	45	44.6	2.75	14.8	10.3
0.17 g *Z*-Paphy	25° 2h	Yellow		(45.2)	(2.69)	(15.1)	(9.6)
0.20 g $Mn(CO)_5Br$/	Benzene	$Mn(CO)_3Br$(*Z*-Paphy)	46	40.4	2.47	13.7	19.0
0.14 g *Z*-Paphy	35° 2h	Yellow		(40.3)	(2.40)	(13.4)	(19.1)
0.14 g $Re(CO)_5Cl$/	DMP	$Re(CO)_3Cl$(*Z*-Paphy)	77	33.4	2.42	11.1	6.9
0.08 g *Z*-Paphy	Reflux ½h	Colourless		(33.4)	(1.98)	(11.1)	(7.1)
0.20 g $Re(CO)_5Br$/	DMP	$Re(CO)_3Br$(*Z*-Paphy)	85	30.6	2.02	10.4	15.0
0.10 g *Z*-Paphy	Reflux 1h	Colourless		(30.7)	(1.82)	(10.2)	(14.6)
0.20 g $Re(CO)_5I$/	DMP	$Re(CO)_3I$(*Z*-Paphy)	90	28.4	1.44	8.8	21.5
0.09 g *Z*-Paphy	Reflux 1h	Colourless		(28.2)	(1.68)	(9.4)	(21.4)
0.60 g $Mn(CO)_5Cl$/	DMP	$Mn(CO)_3Cl$(*E*-Paphy)	22	44.5	3.33	14.9	9.5
0.51 g *E*-Paphy	25° 2h	Yellow		(45.2)	(2.69)	(15.1)	(9.6)
0.40 g $Mn(CO)_5Br$/	DMP	$Mn(CO)_3Br$(*E*-Paphy)	54	40.4	2.74	13.1	18.9
0.28 g *E*-Paphy	25° 15h	Yellow		(40.3)	(2.40)	(13.4)	(19.1)
0.50 g $Mn(CO)_5I$/	DMP	$Mn(CO)_3I$(*E*-Paphy)	58	36.1	2.43	12.2	28.0
0.31 g *E*-Paphy	25° 20 h	Deep Yellow		(36.3)	(2.16)	(12.1)	(27.4)

[a] DMP=2,2-dimethoxypropane

Benzene and chloroform were dried before use. *E*-Paphy[6] and *Z*-Paphy[3] were prepared as before. Reactions were carried out under dry oxygen-free nitrogen.

Since the preparations are all similar and quite straightforward only a typical example is described. The conditions for the preparation of the remaining compounds are shown in Table 1, together with analytical data.

Iodotricarbonyl(Z-Paphy)manganese (I)

Iodopentacarbonylmanganese (I) (0.07 g) and *Z*-Paphy (0.05 g) were heated together in 2,2-dimethoxypropane (15 ml) under gentle reflux for 15 min. After cooling, the deep yellow crystals were filtered off, washed with further portions of 2,2-dimethoxypropane, and dried *in vacuo*. Yield 66%. (Found: C, 35.9; H, 2.30; N, 12.1. $C_{14}H_{10}IMnN_4O_3$ calcd.: C, 36.3; H, 2.16; N, 12.1%.)

RESULTS AND DISCUSSION

Because of the presence of strong intramolecular hydrogen bonding between the imino group and the ring nitrogen of the pyridinecarbaldehyde residue, *Z*-Paphy, (II), behaves as no more than a bidentate ligand towards acceptors. Such hydrogen bonding is absent in *E*-Paphy, (I), which is therefore able to act as a terdentate ligand. However in complexes with Group VI metal carbonyls this isomer also acts in a bidentate manner, one potential donor nitrogen atom remaining uncoordinated.

The reactions of $M(CO)_5X$, (M = Mn and Re; X = Cl, Br and I), with *Z*-Paphy lead to the formation of compounds of general formula $M(CO)_3X$(*Z*-Paphy). These compounds are univalent octahedral derivatives of the metals, being diamagnetic and non-conducting in nitromethane [*e.g.* $Re(CO)_3I$(*Z*-Paphy), $\Lambda_M = 2.3$ ohm^{-1}·cm^2 for a 10^{-3} *M* solution at 25°]. For these compounds, in which the two coordinated nitrogen atoms must be mutually *cis*, two stereochemical possibilities occur: (*i*) both nitrogens and the halogen are *trans* to three mutually *cis* carbonyl groups (a *fac*-stereochemistry), and (*ii*) one nitrogen *trans* to the halogen, the other *trans* to a carbonyl group, leaving the remaining two carbonyl groups mutually *trans* (a *mer*-stereochemistry). Assuming effective equivalence of the donor nitrogens both structures possess C_s local symmetry and three infrared active ν(CO) modes, ($2A' + A''$), are

TABLE 2

INFRARED SPECTRA (cm^{-1})

Compound	*ν(CO)*[a]			*ν(NH)*
$Mn(CO)_3Cl$(*Z*-Paphy)	2035	1955	1932[b]	
$Mn(CO)_3Br$(*Z*-Paphy)	2035	1952	1932[b]	
$Mn(CO)_3I$(*Z*-Paphy)	2035	1947	1930[b]	
$Re(CO)_3Cl$(*Z*-Paphy)	2028	1915	1880[c]	
$Re(CO)_3Br$(*Z*-Paphy)	2035	1937	1910[b]	
$Re(CO)_3I$(*Z*-Paphy)	2030	1925	1900[c]	
$Mn(CO)_3Cl$(*E*-Paphy)	2040	1948	1901[c]	3210 w
$Mn(CO)_3Br$(*E*-Paphy)	2040	1950	1935[b]	3200 mw
$Mn(CO)_3I$(*E*-Paphy)	2040	1937	1918[c]	3240 mw

[a] All bands strong. [b] $CHCl_3$ solution. [c] Nujol mull.

predicted in each case. However, for (*i*) the band intensities should all be similar, whereas for (*ii*) the highest energy band should be weaker than the other two bands[7]. The observed ν(CO) frequencies are shown in Table 2 and all three bands are of similar intensity, so structure (*i*) is the most acceptable for these compounds. Structure (*ii*) is unlikely to be formed since it is known that in $M(CO)_5X$ (X = halogen) species, the carbonyl group *trans* to the halogen is more strongly bonded to the metal and so less easily replaced than the other four carbonyl groups.

Some room temperature reactions between the manganese halogenopentacarbonyls and *E*-Paphy have also been examined. $Mo(CO)_4$(*E*-Paphy), in which the ligand is only bidentate, using the two nitrogens shown in (I), could only be prepared at room temperature[3] from $Mo(CO)_5Cl^-$ or $Mo(CO)_4$(Norbornadiene), higher temperatures causing isomerisation of the ligand. The reactions between manganese halogenopentacarbonyls and *E*-Paphy carried out in refluxing benzene or 2,2-dimethoxypropane give products whose IR spectra show bands which can be attributed to both coordinated *E*-Paphy and *Z*-Paphy. Thus ligand isomerisation also occurs in these reactions, but unlike the Group VI carbonyl reactions, complete isomerisation to give exclusively $Mn(CO)_3X$(*Z*-Paphy) does not take place. Attempts to separate the isomeric mixtures by column chromatography failed. Thus pure samples of $Mn(CO)_3X$(*Z*-Paphy) compounds can only be obtained by starting with the less accessible *Z*-isomer.

We believe that the room temperature reactions between manganese halogenopentacarbonyls and *E*-Paphy lead to the alternative linkage isomers, $Mn(CO)_3$-X(*E*-Paphy). These complexes are diamagnetic and non-conducting in nitromethane [*e.g.* $Mn(CO)_3Br$(*E*-Paphy), $\Lambda_M = 1.1$ ohm$^{-1}\cdot$cm^2 for a 10^{-3} *M* solution at 25°]. The IR ν(CO) frequencies (Table 2) show only minor shifts compared to the corresponding bands of $Mn(CO)_3X$(*Z*-Paphy) and are again typical of the expected C_s local symmetry, with the three carbonyls arranged facially. The potentially terdentate *E*-Paphy is thus assumed to be bidentate only, since if all three donor nitrogen atoms are coordinated the metal would be seven coordinate and the eighteen valence electron concept would be exceeded by two. Other potentially terdentate ligands are known to behave as bidentate donors in related compounds such as $Mn(CO)_3Br$-(Terpyridyl)[8], $Mn(CO)_3Br$(3,6,9-trithiaundecane)[9], $Re(CO)_3Cl$(*v*-Triars)[10] [*v*-Triars = tris-1,1,1-(dimethylarsinomethyl)ethane], and $Re(CO)_3H$(DPME)[11], [DPME = tris-1,1,1-(diphenylphosphinomethyl)ethane].

The assumption that the *E*-configuration of the ligand has been retained is supported by IR evidence. The three $Mn(CO)_3X$(*E*-Paphy) compounds all show a weak ν(N–H) around 3200 cm^{-1} (Table 2), whereas the $Mn(CO)_3X$(*Z*-Paphy) compounds show no obvious ν(N–H). This situation may be compared[3] to that of $Mo(CO)_4$(*E*-Paphy) with ν(N–H) at 3420 cm^{-1} and $Mo(CO)_4$(*Z*-Paphy) with a barely discernible broad ν(N–H) between 3050 and 3100 cm^{-1}. Further differences are apparent in the IR spectra of linkage isomer pairs, particularly in the 1650–1400 cm^{-1} range [pyridine ring vibrations and ν(C=N)] and in the 1000 cm^{-1} region (pyridine ring breathing modes). Also the ligand frequencies of the $Mn(CO)_3X$(*Z*-Paphy) series match those of $Mo(CO)_4$(*Z*-Paphy) extremely well, and equally the $Mn(CO)_3X$(*E*-Paphy) compounds have almost identical IR spectra [apart from ν(CO)] to $Mo(CO)_4$(*E*-Paphy). To illustrate such features Fig. 2 shows the IR spectra (1650–1500 cm^{-1}) of $Mn(CO)_3Br$(*Z*-Paphy), $Mn(CO)_3Br$(*E*-Paphy), Mo-

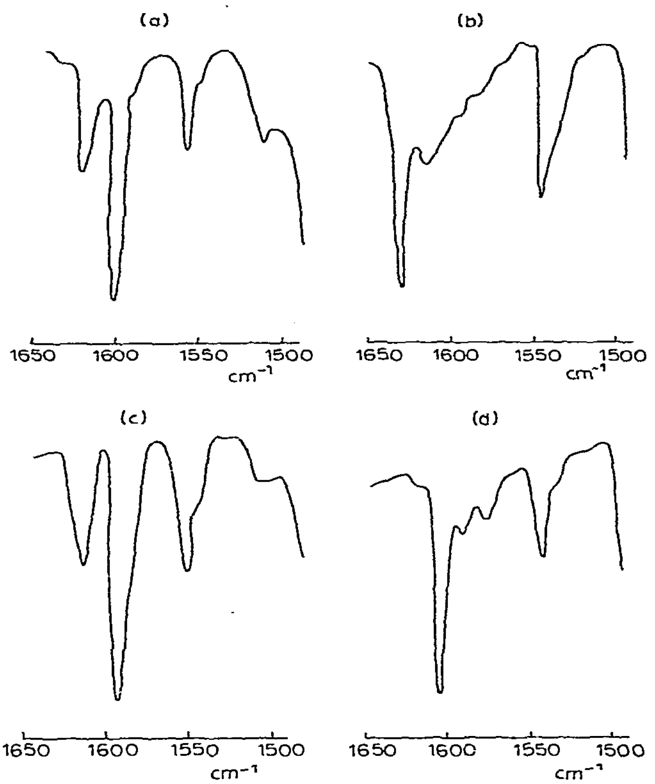

Fig. 2. Nujol mull IR spectra; (a) Mn(CO)$_3$Br(Z-Paphy); (b) Mn(CO)$_3$Br(*E*-Paphy); (c) Mo(CO)$_4$(Z-Paphy); (d) Mo(CO)$_4$(*E*-Paphy).

(CO)$_4$(*Z*-Paphy) and Mo(CO)$_4$(*E*-Paphy).

Further evidence concerning the ligand configurations in Mo(CO)$_4$(*Z*-Paphy) and Mo(CO)$_4$(*E*-Paphy) was obtained from a study of their ^{1}H NMR spectra[3,4]. Unfortunately such spectra could not be obtained for the present compounds because their solubilities in suitable solvents were very low, and the solutions obtained appeared to decompose slowly.

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