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Platinum Group Metal Chelates Derived from 2-Mercapto-, 2-Hydroxy- and 2-Amino-pyridines and -pyrimidines

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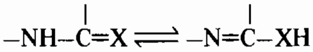
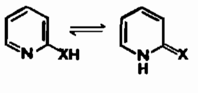
The title ligands **I** and **II** (X = S, O or NH) are amongst the simplest molecules containing the tautomeric system:

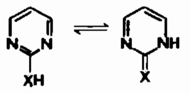


$$-NH-\overset{|}{C}=X \rightleftharpoons -N=\overset{|}{C}-XH$$

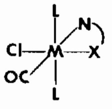
and are therefore useful model compounds for a range of important biological molecules – notably purine and pyrimidine bases – which encompass the same groupings. In view of current interest in the bonding of DNA bases to platinum group metals [1, 2], we have begun to investigate the reactions of the title ligands, **I** and **II** (X = S, O or NH), with a range of platinum group metal complexes. In this preliminary report we describe products obtained using low oxidation state or hydrido complexes of the rarer platinum metals.



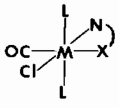
I (a ⇌ b)



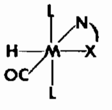
II (a ⇌ b)



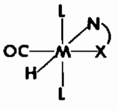
IIIa



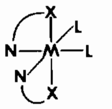
IIIb



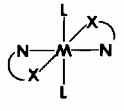
IVa



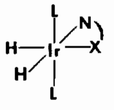
IVb



V



VI



VII

L = PPh_3

A representative selection of precursors used together with products obtained from 2-mercapto-, 2-hydroxy-, and 2-amino-pyridines is presented in Table I, reaction conditions employed are given in footnotes to the same. All the complexes isolated are air-stable crystalline solids ranging in colour from white through pale yellow to orange. Stereochemical assignments have been made where possible using ^1H, ^{13}C and ^{31}P NMR data.

A few of the complexes listed in Table I have been previously reported [3, 4]. However the present work affords the first general method for the preparation of this class of chelates.

The complexes $MCl(pyX)(CO)(PPh_3)_2$ (M = Ru or Os, X = O or S) all have *trans*-phosphine ligands [$^{31}P\{^1H\}$ NMR singlets] and thus possess stereochemistry **III** (**a** or **b**). However, the osmium complex $OsCl(pyO)(CO)(PPh_3)_2$ has also been observed

TABLE I. Precursors and Products Obtained, L = PPh_3.

Precursors	pySH Products	pyOH Products	pyNH2 Products
$RuHCl(CO)L_3$	$RuCl(pyS)(CO)L_2$[a]	$RuCl(pyO)(CO)L_2$[b]	
$RuH_2(CO)L_3$	$RuH(pyS)(CO)L_2$[b]	$RuH(pyO)(CO)L_2$[b]	$RuH(pyNH)(CO)L_2$[a]
$Ru(CO)_3L_2$	$Ru(pyS)_2(CO)L$[b]	$RuH(PyO)(CO)L_2$[b]	
RuH_2L_4	$Ru(pyS)_2L_2$[a]	$Ru(pyO)_2L_2$[b]	
$RuCl_2L_3$		$RuCl_2(pyO)L_2$[c]	
$RuCl_2L_3$	$Ru(pyS)_2L_2$[d]	$Ru(pyO)_2L_2$[e]	$Ru(pyNH)_2L_2$[d]
$RuCl_2(CO)_2L_2$		$RuCl(pyO)(CO)L_2$[e]	$RuCl(pyNH)(CO)L_2$[e]
$OsHCl(CO)L_3$	$OsCl(pyS)(CO)L_2$[b]	$OsCl(pyO)(CO)L_2$[b]	
$OsH_2(CO)L_3$	$OsH(pyS)(CO)L_2$[b]	$OsH(pyO)(CO)L_2$[f]	
OsH_4L_3	$Os(pyS)_2L_2$[a]		
IrH_3L_3	$IrH_2(pyS)L_2$[a]	$IrH_2(pyO)L_2$[f]	

[a] Refluxing benzene. [b] Refluxing toluene. [c] Warm benzene/O_2. [d] Refluxing benzene/NEt_3. [e] Refluxing toluene/NEt_3. [f] Refluxing 2-methoxyethanol.

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as a kinetically controlled *cis*-phosphine isomer [$^{31}P\{^1H\}$ NMR AB pattern (δ 5.90 and 3.40 ppm $^2J(PH)$ 12 Hz]. The hydrides $MH(pyX)(CO)(PPh_3)_2$ exist as a mixture of two isomeric forms **IV** (**a** and **b**) when X = O or S [^1H NMR, 2 high field triplets, $^{31}P\{^1H\}$NMR two singlets] but afford only a single isomer **IV** (**a** or **b**) when X = NH. The bis-chelates $M(pyX)_2(PPh_3)_2$ (X = O, S or NH) display a fine balance between *cis*- and *trans*-phosphine structures (**V** and **VI**). The complexes $Ru(pyS)_2(PPh_3)_2$ [3] and $Ru(6\text{-Me-pyO})_2(PPh_3)_2$ [4] have previously been shown by X-ray diffraction methods to adopt *cis*- and *trans*-phosphine structures respectively. However NMR data clearly establish that the ruthenium complexes $Ru(pyX)_2(PPh_3)_2$ and their osmium analogs adopt *trans* stereochemistry in solution (C_6H_6 or $CHCl_3$). Thus in each case the *ortho* to *meta*/*para* proton separation for solutions in C_6D_6 is greater than 0.5 ppm indicating a *trans* triphenylphosphine arrangement [5]. This stereochemical assignment is confirmed for the complexes $M(pyS)_2(PPh_3)_2$ by the $^{13}C\{^1H\}$ NMR spectra which contain $^{13}C-^{31}P$ virtual coupling triplet patterns for all triphenylphosphine carbon atom save those in the *para* position [6] but display no evidence of $^{13}C-^{31}P$ couplings in the resonances of the pyS carbon atoms. The latter result is particularly significant since, in our experience, structures with pyS *trans* to PPh_3 ligands do show such couplings.

The ruthenium(III) products $RuCl_2(pyX)(PPh_3)_2$, obtained from $RuCl_2(PPh_3)_3$ and pyXH in the presence of air, are analogs of the previously reported osmium complex $OsCl_2(pyO)(PPh_3)_2$ [7] and are closely related to the known ruthenium(III) and osmium(III) carboxylates $MCl_2(O_2CR)(PPh_3)_2$ [8]. Finally the iridium dihydrides $IrH_2(pyX)(PPh_3)_2$ each display NMR resonances [^1H, high field 2 doublets of triplets; $^{31}P\{^1H\}$, singlets.] indicative of stereochemistry (**VII**). This structure has recently been confirmed for $IrH_2(pyS)(PPh_3)_2$ by X-ray crystallography [9].

Analogous complexes containing chelate ligands derived from 2-mercapto-, 2-hydroxy-, and 2-aminopyrimidines are in the course of preparation and attempts to extend the preparative method to include the DNA bases – adenine, cytosine, guanine, and thymine – are in progress.

Acknowledgements

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