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Preliminary communication

BASICITY OF TRANSITION METAL CARBONYL COMPLEXES

XII*. REACTIONS OF $C_5H_5M(CO)(NO)(PPh_3)$ COMPLEXES (M = Mo, W) WITH APROTIC ACIDS

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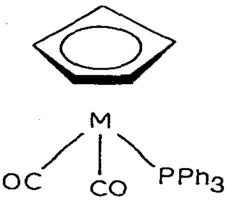
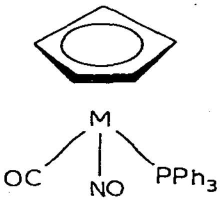
Summary

The aprotic acids $HgCl_2$ and $SnCl_4$ react with the complexes $C_5H_5Mo(CO)(NO)(PPh_3)$ (M = Mo, W) by electrophilic attack at the transition metal centre. In the case of $SnCl_4$ the initial reaction is followed by elimination of Cl^-. This reaction can be viewed as a S_N displacement of chloride by the transition metal centre.

We have earlier studied the reactions with aprotic acids and the basicity of $C_5H_5M(CO)_2L$ (I) complexes, where M = Mn [1,2] or Re [2,3] and L = PPh_3. Pursuing systematic investigation of the basicity of π-complexes of transition metals, we have studied the reactions with aprotic acids of complexes of Group VIB metals which are isoelectronic with I and corresponding to the formula $C_5H_5M(CO)(NO)(PPh_3)$ (II), where M = Mo (IIa) or W (IIb).



I M = Mn, Re.



II M = Mo, W.

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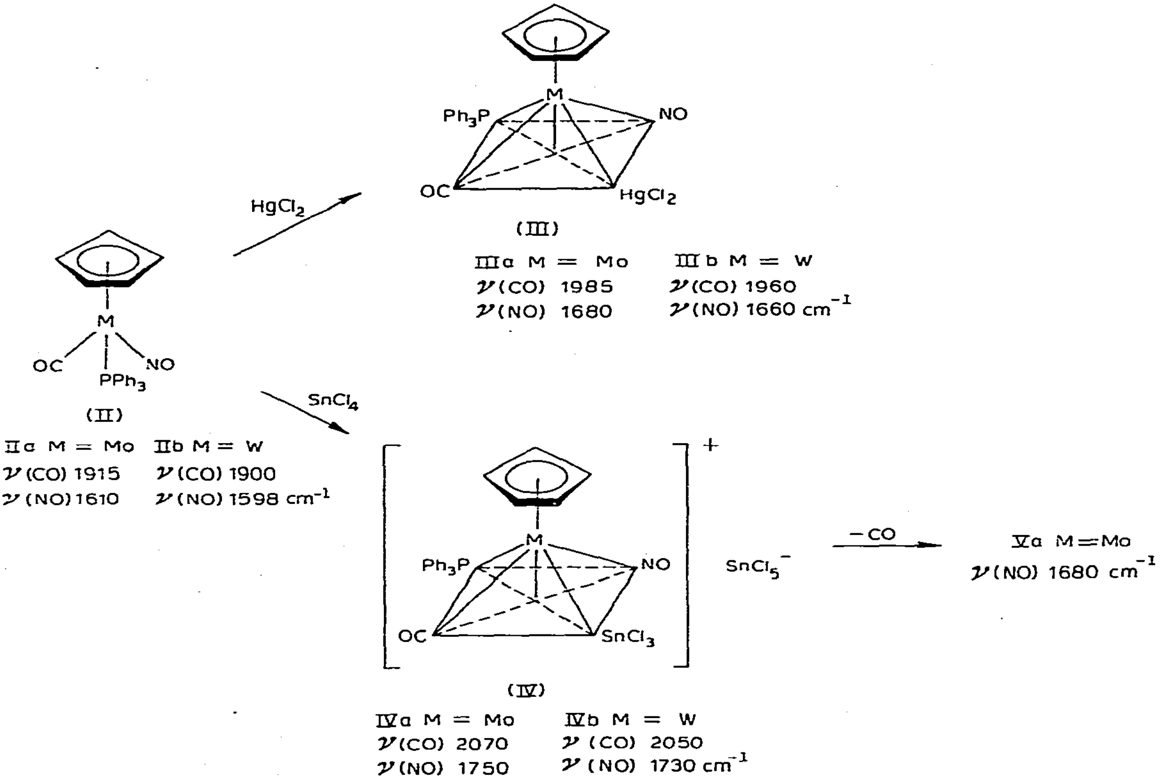
*For part XI, see ref. 1.

The addition of equimolar amounts of $HgCl_2$ to solutions of complexes IIa and IIb in CH_2Cl_2 results in the formation of covalent neutral adducts $C_5H_5M(CO)(NO)(PPh_3)(HgCl_2)$* (IIIa and IIIb) with ν(CO) and ν(NO) in their IR spectra increased by 60—70 cm^{-1} as compared to the initial II, which indicates to the coordination of $HgCl_2$ with the central atoms of Mo and W.

Compounds IIa and IIb rapidly react with an excess of $SnCl_4$ in CH_2Cl_2 with the formation of complexes IVa and IVb. An ionic structure for IV is indicated by the substantially higher values of $\Delta\nu$(CO), 155 and 150 cm^{-1}, and $\Delta\nu$(NO), 140 and 135 cm^{-1}, when passing from II to IV, as compared to values of $\Delta\nu$(CO) and $\Delta\nu$(NO) of 60—70 cm^{-1} in the formation of the covalent complexes III from II.

The structure of IVa (M = Mo) is proven by the data from a preliminary X-ray structural analysis. Cation IVa has the structure of a square pyramid with a C_5H_5 ligand at apex and CO and NO ligands in the *trans*-positions at the pyramid base (the angle CO—Mo—NO being about 107°).



Complex IVb (M = W) is stable, whereas complex IVa in CH_2Cl_2 in the presence of an excess $SnCl_4$ readily undergoes oxidative elimination of CO with the formation of a covalent complex Va (ν(NO) 1680 cm^{-1}); its structure is being studied now by X-ray structural analysis.

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*All the compounds obtained were characterized by elemental analysis.

Under the conditions studied (CH_2Cl_2, 20°C) the complex $C_5H_5Mo(CO)_2(NO)$ containing no donor ligand PPh_3 does not react with $HgCl_2$ and $SnCl_4$. Therefore, basicity of the metal central atoms is increased with substitution of one CO group by the donor phosphine ligand. The Mo and W centres in II, like the Mn and Re centres in I are the regions with the highest basicity and the sites of attack by aprotic acids.

At present there are available numerous data on the basicity of π-complexes of transition metals. Analysis of the literature allows us to draw the conclusion that in half-sandwich complexes with one η^5-cyclopentadienyl or η^6-benzene ligand of the general formula $(\eta^n\text{-}C_nH_n)ML_m$ (wherein m is 2 or 3 and L is the two-electron ligand CO and/or tertiary phosphine), attack by an electrophilic reagent E is likely to be always initially directed towards the central metal atom, leading to the formation of a M—E bond (E = H^+, R^+, RCO^+, halogens, aprotic acids, etc.). The data listed in Table 1 show that this conclusion is of an adequately general character, since it is valid for the majority of transition metals of Groups VI—VIII and electrophilic reagents of different natures.

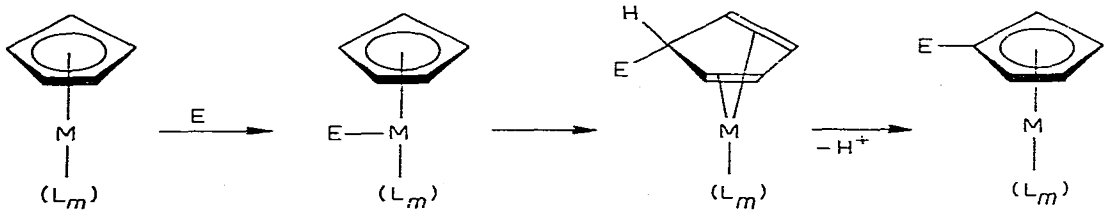
TABLE 1

REACTIONS OF π-COMPLEXES OF GROUP VI—VIII METALS WITH VARIOUS ELECTROPHILIC REAGENTS WITH ATTACK AT THE METAL ATOM

Group VI		Group VII		Group VIII			
Cr, Mo, W		Mn, Tc, Re		Fe, Ru, Os		Co, Rh, Ir	
Complex	Ref.	Complex	Ref.	Complex	Ref.	Complex	Ref.
$C_6H_6Cr(CO)_3$	4	$C_5H_5Mn(CO)_2L^a$	1,2	$C_6H_6FeL_2$ ^{c}	14	$C_5H_5Co(CO)_2$	7
$C_6H_6Mo(PR_3)_3$	5	—	—	$C_6H_6RuL_2$ ^{b}	6	$C_5H_5CoL_2$ ^{b}	8
$C_5H_5Mo(CO)(NO)(L)^a$	this work					$C_5H_5RhL_2$ ^{b}	9
$C_5H_5W(CO)(NO)(L)^a$	this work	$C_5H_5Re(CO)_2L^a$	2,3	—	—	$C_5H_5Ir(CO)(L)^a$	10, 11

^{a} L = PPh_3; ^{b} L = PMe_3; ^{c} L = $P(OMe)_3$

It should be noted that in the second stage of the reaction after the formation of the M—E bond, there may in certain cases take place a reversible or irreversible migration of the electrophile E onto the cyclic ligand with the formation of the final products of the reaction [12,13]:



Formation of complexes IV, as well as the earlier described $[C_5H_5Mn(CO)_2(PPh_3)(SnCl_3)]^+SnCl_5^-$ [1] and similar rhenium derivatives [3] may be regarded as S_N at the tin atom resulting in substitution of Cl^- by neutral nucleophiles $C_5H_5M(CO)(PPh_3)(L)$, where L = CO for M = Mn and Re, and L = NO for M =

Mo and W. By analogy to the usual O-, S- and N-nucleophiles, these nucleophiles may be referred to as M-nucleophiles. A specific feature of reactions of M-nucleophiles with $SnCl_4$ is that at an excess of $SnCl_4$ the escaping anion Cl^- may give the anion $SnCl_5^-$ with a second $SnCl_4$ molecule. Depending on how strongly nucleophilic the M-nucleophile is (i.e. how high is the metal basicity), substitution of Cl^- is possible not only in $SnCl_4$, but in alkyltin chlorides as well. Thus, the very strong nucleophile $C_5H_5Rh(PMe_3)_2$ substitutes Cl in Me_3SnCl and Me_3GeCl [9].

The structure and properties of the products of the interaction of II with $SnCl_4$ and $SnBr_4$ will be described in more detail in a later paper.

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