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REACTIONS OF HALOGENOPENTACARBONYLS OF GROUP VI METALS WITH LIGANDS

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Work from these Laboratories[1,2,3] had shown that halopentacarbonylmetal compounds of the type $[MX(CO)_5]^-$ (with M being chromium, molybdenum and tungsten) react in mild conditions with a variety of ligands. When the ligand is isonitrile[2] or amine[3], substitution compounds of the type $M(CO)_{6-n}L_n$ are normally obtained, whereas allyl halides[1], Allyl–X, give rise to allyl derivatives of a new type, namely $[M_2X_3(CO)_4(Allyl)_2]^-$.

Halogenopentacarbonyl anions of group VI metals, originally described by two different research groups[4,5,6] are unique among halogenocarbonyls of transition metals[7] in that the central metal atom is in a formal oxidation state of zero. Substitution of the halo group by an uncharged ligand becomes therefore possible without alteration of the formal charge on the central metal atom. The substitution in these compounds can therefore occur by one of the two equally possible paths:

$$[MX(CO)_5]^- + n\,L \rightarrow M(CO)_{6-n}L_n + (n-1)\,CO + X^- \qquad (1)$$

$$[MX(CO)_5]^- + n\,L \rightarrow [MX(CO)_{5-n}L_n]^- + n\,CO \qquad (2)$$

The occurrence of one or the other of the two reactions will depend essentially on the type of ligand employed, as discussed later.

We have now extended the reactions of halogenopentacarbonylmetal anions to some bidentate amines (LL) (1,10-phenanthroline and 2,2′-bipyridine) and to two compounds containing active olefinic double bonds, namely maleic anhydride and maleimide.

EXPERIMENTAL

All the operations were carried out in an atmosphere of prepurified nitrogen.

The maleimide and maleic anhydride complexes are rapidly decomposed by N-bromosuccinimide with quantitative evolution of carbon monoxide. The CO content of the complexes was determined by making use of this reaction in 2,2′-dimethoxydiethyl ether as solvent.

The infrared spectra were measured with a Perkin–Elmer model 521 instrument equipped with grating. Each spectrum was calibrated with CO. The nuclear magnetic spectra were measured with a DP60A Varian instrument.

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I. Reaction of $[MX(CO)_5]^-$ *anions with bidentate amines. Preparation of* $M(CO)_4LL$

1,10-Phenanthroline (1.5 g; 8.3 mmoles) and $NEt_4[MoCl(CO)_5]$ (2 g; 5.0 mmoles) in 75 ml of tetrahydrofuran were reacted at room temperature. After one hour no starting anionic complex was present as indicated by the infrared spectrum. The precipitate of NEt_4Cl was eliminated by filtration and petroleum ether was added to the filtrate. Tetracarbonylphenanthrolinemolybdenum was so obtained as dark red crystals in practically quantitative yields and was recrystallised from tetrahydrofuran/petrol ether. (Found: C, 49.40; H, 2.22; N, 7.29; CO, 27.5. $C_{16}H_8MoN_2O_4$ calcd.: C, 49.50; H, 2.08; N, 7.22; CO, 28.86%.) The infrared spectrum in tetrahydrofuran has bands in the CO stretching region at 2011 (m–w), 1901 (s), 1883 (m) and 1843 (m–s) cm^{-1} in agreement with the published spectrum[8] and with the number of bands required by the C_{2v} symmetry of the molecule.

By substantially identical procedures all the other $M(CO)_4LL$ compounds (with LL being 2,2'-bipyridine and 1,10-phenanthroline and M being Cr, Mo and W) were prepared in practically quantitative yields. Good analytical data and consistent infrared spectra were obtained for all these compounds. All the compounds of the type $M(CO)_4LL$ obtained from the $[MX(CO)_5]^-$ anions had been previously reported in the literature[9,10]. They have been obtained from the corresponding hexacarbonyl by thermal reactions or in the presence of ultraviolet irradiation. The infrared spectra of two phenanthroline derivatives obtained in the present study have not been measured before and are therefore reported in Table 1.

TABLE 1

INFRARED CO STRETCHING VIBRATIONS OF TETRACARBONYLPHENANTHROLINECHROMIUM AND -TUNGSTEN[a]

Compound	$\nu_{CO}(cm^{-1})$			
$Cr(CO)_4phen$	2007 m–w	1897 s	~1885 sh	1839 m–s
$W(CO)_4phen$	2004 m–w	1889 s	~1877 sh	1839 m–s

[a] Tetrahydrofuran solutions.

II. Reactions between the $[MX(CO)_5]^-$ *anions and olefinic substances*

The reactions of the $[MX(CO)_5]^-$ anions with maleimide and maleic anhydride apparently take place according to the following stoichiometry:

$$[MX(CO)_5]^- + 3\ \text{Olefin} \rightarrow 3\ CO + [MX(CO)_2(\text{Olefin})_3]^- \qquad (3)$$

In the case of the reaction with maleic anhydride, however, the evolution of CO is less than that expected for stoichiometry. The reasons for this are explained later.

(*a*) *Preparation of* $[MX(CO)_2(Maleimide)_3]^-$. Maleimide (3.5 g; 36 mmoles) and $NEt_4[MoCl(CO)_5]$ (3.0 g; 7.5 mmoles) were reacted for 2 h in tetrahydrofuran at reflux temperature. The deep red precipitate obtained was then filtered, washed with tetrahydrofuran and dried (3.7 g; 81% yield). The product so obtained [compound (I) in Table 2] is insoluble in all nonpolar organic solvents, is slightly soluble in acetone and dimethyl sulphoxide, and is readily decomposed by water. It is stable in air, but somewhat sensitive to light.

All the other maleimide derivatives of Table 2 were obtained similarly and have similar properties. The soluble lithium derivative reported in Table 3 was prepared by the same procedure from $Li[MoCl(CO)_5] \cdot \sim 2$ diglyme. No precipitate was formed during the reaction and the final reaction mixture was worked up in order to obtain from it an orange solid, containing some lithium chloride and solvent of crystallization. The infrared spectra excluded the presence of any other metal carbonyl compound except the expected anionic dicarbonyl.

(*b*) *Preparation of* $[MX(CO)_2(\textit{Maleic anhydride})_3]^-$. By a procedure substantially identical to that reported above for the maleimide case, but by increasing the reaction time to 4–6 h, the dicarbonyl complexes of maleic anhydride reported in Table 2 were obtained. These are all red amorphous solids reasonably stable in air in the solid state, somewhat sensitive to light, insoluble in nonpolar solvents, but soluble in water. Because of their insolubility, the compounds could not be recrystallised and were therefore always contaminated by variable amounts of tetraethylammonium halide arising from the competitive reaction:

$$[MX(CO)_5]^- + CO \rightarrow M(CO)_6 + X^- \qquad (4)$$

Reaction (4) which did not interfere significantly in the previous case of maleimide, becomes now important due to the comparatively smaller reaction rates of $[MX(CO)_5]^-$ anions with maleic anhydride.

In a control experiment carried out with $[NEt_4][MoCl(CO)_5]$ in the absence of maleic anhydride at reflux temperature of tetrahydrofuran, a strong infrared band of $Mo(CO)_6$ at 1982 cm^{-1} was observed after 2-h reaction, whilst the infrared bands of the starting material had almost completely disappeared.

From their orange aqueous solutions, the $[MX(CO)_2(\text{Maleic anhydride})_3]^-$ anions could be precipitated as $[Ni(phen)_3]^{2+}$ salts in practically quantitative yields based on the amount of metal present in the dicarbonyl anions. By operating rapidly, no complexed maleic acid was observed in the infrared spectrum of the precipitate.

Satisfactory analytical data (Table 2) were obtained for all the maleimide derivatives and for the nickel–phenanthroline salts of the maleic anhydride derivatives. Compounds (V), (VI) and (VII), for which significant elemental analyses could not be obtained because of the unavoidable presence of NEt_4X, are nevertheless believed to be correctly formulated. The nickel–phenanthroline salts obtained from them analyse correctly; the experimentally determined CO/metal ratio is 2 or very close to it and finally the infrared data in the terminal CO stretching region are consistent with the proposed formulation and essentially similar to those of the maleimide derivatives.

The maleic anhydride derivatives (V) and (VII) in Table 2 decomposes at 150–200° in high vacuum: CO, triethylamine, CO_2, ethyl chloride and succinic anhydride were identified among the decomposition products by NMR and IR spectroscopy.

Bromine oxidation of compound (V) gave 2,3-dibromosuccinic anhydride identified by infrared and NMR spectra. Heating compound (I) in tetrahydrofuran with 1,4-dimethylbutadiene for 6 h left the compound substantially unchanged.

DISCUSSION

Only a very limited number of mono-olefin complexes of Group VI transition metals in the zero oxidation state have been reported[11]. In view of that, it appeared

TABLE 2

PROPERTIES, ANALYSES AND SPECTROSCOPIC DATA OF $[MX(CO)_2(Olefin)_3]^-$ ANIONS AND DERIVATIVES[a]

	Analysis[b]					ν_{CO}
	C	*H*	*Metal*	*CO*	*N*	*(cm^{-1})*
[NEt$_4$][MoCl(CO)$_2$- (Maleimide)$_3$] (I)	42.00 (43.40)	5.66 (4.80)	15.99 (15.76)	9.19 (9.20)		1951 1884
[NEt$_4$][MoBr(CO)$_2$- (Maleimide)$_3$] (II)	39.36 (40.44)	4.41 (4.47)	15.32 (14.68)	8.14 (8.57)		1955 1890
[NEt$_4$][WCl(CO)$_2$- (Maleimide)$_3$] (III)	38.05 (37.92)	4.54 (4.19)	27.10 (26.38)	7.97 (8.04)	7.78 (8.04)	1952 1881
[NEt$_4$][WBr(CO)$_2$- (Maleimide)$_3$] (IV)	35.63 (35.65)	3.83 (3.94)	25.17 (24.80)	6.40 (7.56)		1952 1880
[NEt$_4$][MoBr(CO)$_2$- (Maleic anhydride)$_3$] (V)[c,d]						1949 1875
[NEt$_4$][WCl(CO)$_2$- (Maleic anhydride)$_3$] (VI)[c,e]						1943 1863
[NEt$_4$][WBr(CO)$_2$- (Maleic anhydride)$_3$] (VII)[c,f]						1949 1867
[Ni(phen)$_3$][MoBr(CO)$_2$- (Maleic anhydride)$_3$]$_2$ (VIII)	47.47 (46.55)	2.93 (2.20)			4.23 (5.09)	1968 1893
[Ni(phen)$_3$][WCl(CO)$_2$- (Maleic anhydride)$_3$]$_2$ (IX)	43.96 (44.22)	2.13 (2.09)		6.35 (6.44)		1966 1879

[a] Tetraethylammonium salts are all red or deep red. The nickel–phenanthroline salts are orange-yellow. Infrared spectra measured on nujol mulls. The intensities of the two infrared bands are m and s, the latter being that at lower wavenumbers. All the compounds reported decompose at temperatures comprised between 195 and 250° in capillaries sealed under nitrogen. [b] Calculated values in parentheses. [c] Product contaminated by NEt$_4$X. [d] Ratio CO/Molybdenum found 1.99. [e] Ratio CO/Tungsten found 1.95. [f] Ratio CO/Tungsten found 1.75.

very interesting to establish the way of attachment of maleic anhydride and maleimide to the central metal atom in the anionic compounds described in this paper. In this connection, to measure the proton resonance spectra was crucially important and the soluble lithium salts of the $[MX(CO)_2(Olefin)_3]^-$ anions were therefore prepared from $LiMX(CO)_5 \cdot \sim 2$ diglyme, as described in the experimental section. The isolation of these compounds in an analytically pure state was not even attempted because of their tendency to crystallize with retention of solvent molecules by the cation. Their NMR and infrared data are, on the other hand, perfectly consistent with the proposed formula (see Table 3). In particular it will be noticed that the C–O stretching vibrations of the lithium salts agree well for number, relative intensities and wavenumbers with the vibrations of the corresponding tetraethylammonium salts, when allowance is made for the different cation and the different medium.

The coordination of maleimide and maleic anhydride through the double bond is clearly indicated by the large chemical shift (about 3 ppm to high fields) of the olefinic protons, compared with the uncomplexed ligands (see Table 3). A similar shift to high field is quite common in olefin metal complexes[12] and has also been found in the tetracarbonyliron derivatives of maleic anhydride and other substituted olefinic substances[13].

TABLE 3

INFRARED AND NUCLEAR MAGNETIC RESONANCE SPECTRA OF $[MX(CO)_2(Olefin)_3]^-$ ANIONS AND CORRESPONDING UNCOMPLEXED COMPOUNDS

Species	*Proton Resonance Spectrum*[a]					ν_{CO}
	Chemical shift[c] τ	*Multiplicity*	J_{AB} *(cps)*	*Integrated intensity*	*Assignment*	*(cm*$^{-1}$*)*[b]
$[MoCl(CO)_2$-(Maleimide)$_3]^{-d}$	5.90	AB spectrum	5	2	Olefinic H	1958 m
	1.10	Singlet		1	Imidic H	1886 s
Maleimide	3.20	Singlet		2	Olefinic H	
	0.33	Broad singlet		1	Imidic H	
$[MoCl(CO)_2$(Maleic anhydride)$_3]^{-d}$	5.78	AB spectrum	5			1976 m 1906 s
Maleic anhydride	2.65[e]	Singlet				

[a] Deuteroacetone solutions. [b] Tetrahydrofuran solutions. [c] From tetramethylsilane ($\tau = 10$ ppm) as internal standard; center of multiplets. [d] As lithium salt. [e] Taken from ref. 13.

Further evidence for coordination to the metal through the olefinic double bond rather than through the lone pair on nitrogen or oxygen comes from the infrared spectra of the anions as tetraethylammonium salts in the region between 1850 and 1400 cm^{-1} (nujol and halocarbon mulls). Two strong and equally intense C–O stretching vibrations of the –C(O)–O–C(O)– grouping in the maleic anhydride derivatives, (V)–(IX), are found at about 1795 and 1735 cm^{-1}; the uncomplexed anhydride absorbs[14] at 1869(s) and 1783(vs) cm^{-1} (nujol mulls). These vibrations are therefore not drastically changed on complex formation. The C=C stretching vibration, however, which in the uncomplexed anhydride is at 1596(m) cm^{-1} has shifted to below 1500 cm^{-1} (halocarbon mulls). The absorptions of the $[NEt_4]^+$ cation between 1400 and 1500 cm^{-1} do not permit the exact identification of the carbon–carbon stretching in the complex. This shift of 100 cm^{-1} or higher is to be expected as a consequence of the coordination of the metal to the double bond of the olefinic substance[15].

The situation is the same for the maleimide derivatives, (I)–(IV). They show three sharp bands between 1715 and 1640 cm^{-1} attributed to C–O stretching vibrations of the complexed maleimide groups. The infrared spectrum of the uncomplexed molecule has been studied in detail[16] and the C=C stretching vibration identified at 1580 cm^{-1}. In the maleimide complexes no bands are observed between 1550 and 1490 cm^{-1}. The infrared spectra of two complexes in the region 2000–1500 cm^{-1} are in Fig. 1. Assuming an octahedral coordination around the metal, three geometrical isomers of the species $[MX(CO)_2(Olefin)_3]^-$ are possible, isomers A and B being favoured on mechanistic grounds.

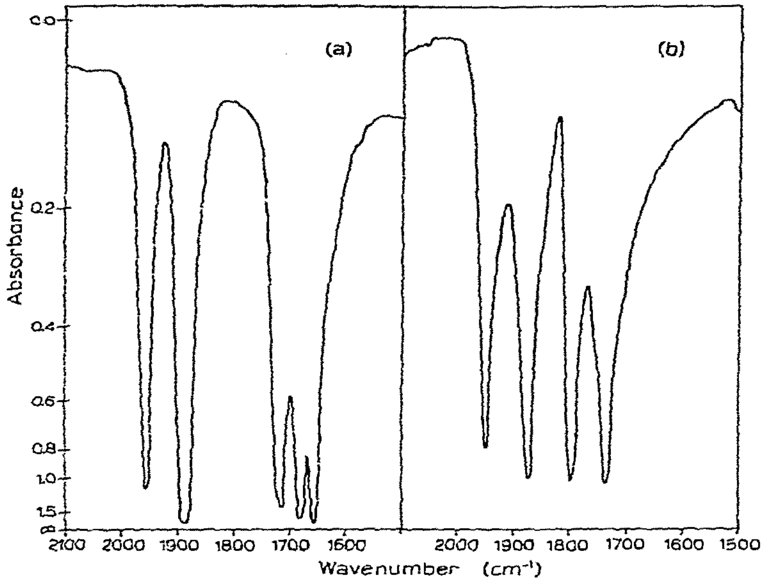
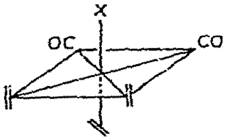
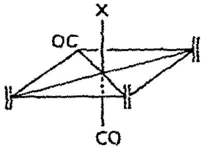


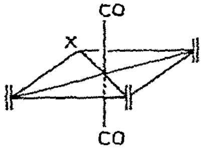
Fig. 1. Infrared spectra of $[MoBr(CO)_2(Olefin)_3]^-$ *anions as tetraethylammonium salts (nujol mulls) in the 2100–1500* cm^{-1} *region.* (a) $[MoBr(CO)_2(Maleimide)]^-$ and (b) $[MoBr(CO)_2(Maleic\ anhydride)_3]^-$.



A



B



C

The occurrence of two CO stretching vibrations for the terminal carbon monoxide groups suggests that the *trans* isomer C is probably not present, at least in significant amounts.

The proton magnetic resonance data of Table 3, showing a spectrum of the AB type for the protons of the complexed molecule, are consistent with the two olefinic protons becoming structurally and magnetically non equivalent on complexation. This becomes evident by examining the three structures A, B and C and considering that the non-equivalence of the olefinic protons is determined not only by the relative position of the ligands within the coordination sphere of the metal, but also by the different orientations with respect to the environment as a consequence of restricted rotation about the metal–olefin axis[17].

A final point concerns the alternative substitution of halogen or CO groups in the $[MX(CO)_5]^-$ anions depending on the nature of the attacking ligand. The reactions reported in this paper represent two clearcut limiting cases. Halogen elimination and formation of uncharged complexes is obtained with amines (eqn. 1), whereas maleic anhydride and maleimide give anionic substitution compounds (eqn. 2). An interpretation of the results will be presented here.

Although the data available are still insufficient to establish definite rules for substitution in compounds of the type $[MX(CO)_5]^-$, an interesting aspect of the substitution reactions on $[MX(CO)_5]^-$ seems to become evident from the previous and the present results. Poor π-acceptors (amines) tend to give halogen elimination usually accompanied by CO substitution (eqn. 1), whereas good π-acceptors (olefins and, to some extent, isonitriles) give CO substitution (eqn. 2).

In the following discussion nothing is implied concerning the actual kinetic order of the reactions. Substitution products of the type $[MX(CO)_{5-n}L_n]^-$ (eqn. 2) clearly arise from intermediate $[MX(CO)_4L]^-$ anions by CO substitution in the starting $[MX(CO)_5]^-$ anions. The mechanism leading to uncharged substitution products of the type $M(CO)_{6-n}L_n$ (eqn. 1) is less obvious. Of course, halogen displacement can be the first step of the reaction and this explains the formation of monosubstitution compounds $M(CO)_5L$. However, this is believed to be a rather unusual reaction pathway occurring with amines in aqueous solution and with isonitriles only in the case of the iodo derivatives and it will not be discussed further. Bi- and trisubstitution products $M(CO)_{6-n}L_n$ are also believed to be formed more commonly via intermediates of the type $[MX(CO)_4L]^-$. This view is justified by: (*a*) the actual isolation[2] of such an intermediate in the case of the reaction with isonitriles and (b) the fact that $M(CO)_{6-n}L_n$ compounds are obtained in mild conditions (40–50°) whereas the preparation of the same products from the hexacarbonyls requires much more drastic conditions. Once the intermediate $[MX(CO)_4L]^-$ is formed, the choice between further CO substitution or X displacement is believed to depend substantially on the π-acceptor strength of the group L bonded to the metal in the intermediate $[MX(CO)_4L]^-$. A good π-acceptor (olefin) will tend to remove negative charge from the metal and therefore to weaken the remaining metal–carbon bonds, thus inducing further CO substitution to occur. Poor π-acceptors (amines) will, on the contrary, induce a higher degree of π back-bonding from the metal to the remaining carbon monoxide groups. The net result is an increase of the metal–carbon bond order and more favourable conditions for halogen substitution will result.

It is interesting to note in this connection that stable compounds of the type $[MX(CO)_{5-n}L_n]^-$ could also be obtained in the case of isonitriles. The latter have been suggested[18] as being π-acceptors of similar strength to carbon monoxide.

SUMMARY

The room temperature reactions of pentacarbonylhalogenometal anions $[MX(CO)_5]^-$ (M = Cr, Mo and W) with bidentate amines (LL), (2,2'-bipyridine and 1,10-phenanthroline) give the tetracarbonyl derivatives $M(CO)_4LL$. Analogous reactions with maleimide and maleic anhydride, on the contrary, lead to ionic products containing the $[MX(CO)_2(Olefin)_3]^-$ anions (M = Mo and W). Infrared and NMR data are presented to support the proposed structures for the anions. The general problem of the reactivity of the $[MX(CO)_5]^-$ anions toward different ligands is discussed in terms of the π-acceptor properties of the ligand.

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