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The Reaction of Aluminium Trichloride with M ixed-Ligand Transition M etal Carbonyls

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SEZIONE II

(Fisica, chimica, geologia, paleontologia e mineralogia)

Chimica inorganica. — *The Reaction of Aluminium Trichloride with Mixed-Ligand Transition Metal Carbonyls.* Nota di LAJOS BENCZE (*), VILMOS GALAMB (*), ANDRÁS GUTTMANN (**) e GYULA PÁLYI, presentata (***) dal Corrisp. A. MANGINI.

RIASSUNTO. — Sono stati fatti reagire con $AlCl_3$ carbonili a legante misto mono, di e trinucleari di W. e Co. È stata osservata la formazione dei prodotti ed è stato determinato con metodi spettroscopici il sito d'attacco dell'acido di Lewis.

INTRODUCTION

Reactions of hard Lewis acids with metal carbonyls were studied in detail [1–3]. The results indicate (*a*) metal basicity, (*b*) ligand abstraction or (*c*) ligand bridge (e.g. C , O-bonded carbonyl) formation and—after (*b*) or (*c*)—a complete restructurization of the complex (e.g. [4, 5]). Within this general frame mostly the reactivity of the carbonyl ligands was studied and not too much attention has been devoted to other ligands as possible site(s) of attack in mixed-ligand carbonyls. In the last years we have intestigated some systems of this type and we report a summary of our results here.

RESULTS AND DISCUSSION

We used $AlCl_3$ as hard Lewis acid in all experiments. The transition metal compounds studied by us were catalytic intermediates of metal carbonyl catalysed reaction cycles or models of such compounds.

Mononuclear compounds.

The olefin metathesis reaction is known to be catalysed (among others) by transition metal carbonyl + Lewis acid "systems" [6]. In attempts to isolate an active species from such systems we reacted $M(CO)_3L_2X_2$

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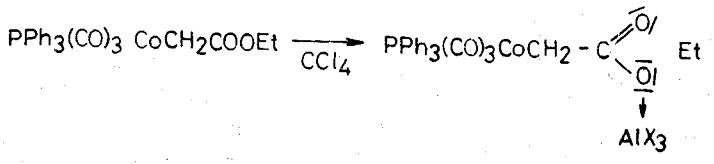
($M = Mo , W ; L = EPh_3 , E = P , As , Sb ; X = Cl , Br$) compounds with Lewis acids such as $AlCl_3$, $FeCl_3$ or $SbCl_5$. We found that in chlorobenzene the following (ligand-abstraction type) transformations take place:

$$\begin{aligned} &M(CO)_3(EPh_3)_2X_2 + 2AlCl_3 \xrightleftharpoons{PhCl} [M(CO)_3(EPh_3)_2]^{2\oplus}[AlCl_4]_2^{\ominus} \\ &[M(CO)_3(EPh_3)_2]^{2\oplus}[AlCl_4]_2^{\ominus} \xrightleftharpoons{PhCl} [M(CO)_3(EPh_3)_2]^{2+} + 2[AlCl_4]^{\ominus} \end{aligned} \qquad (1)$$

The equilibria (1) were studied in most detail for $M = W . E = P , X = Cl$, Br and $AlCl_3$ as Lewis acid. Our findings are based on (*a*) analyses of (II), (*b*) independence of the ν (C—O) spectrum on the nature of the Lewis acid, (*c*) dependence of the ν (C—O) band position on E, (*d*) the lack of ν (C—O) band(s) which would indicate the presence of W—C—O—Al-type bridges [3] and the change of electric conductivity of solutions of (I) upon stepwise addition of $AlCl_3$ [7].

Solutions of (II) are active catalysts in ring-opening polymerization of cycloolefins such as norbornen or norbornadiene that we explain by the coordinative unsaturation of the inner coordination sphere of the (II) species.

Another mononuclear model was chosen from the stable cobalt alkyl series, $L(CO)_3CoCH_2COOR$ ($L = PPh_3 , CO ; R = alkyl$) (IV) that we studied [8] as models for the hydroformylation of acrylates. We found that (*IV*, $L = PPh_3 , R = Et$) reacted with AlX_3 ($X = Cl , Br$) in the following manner:



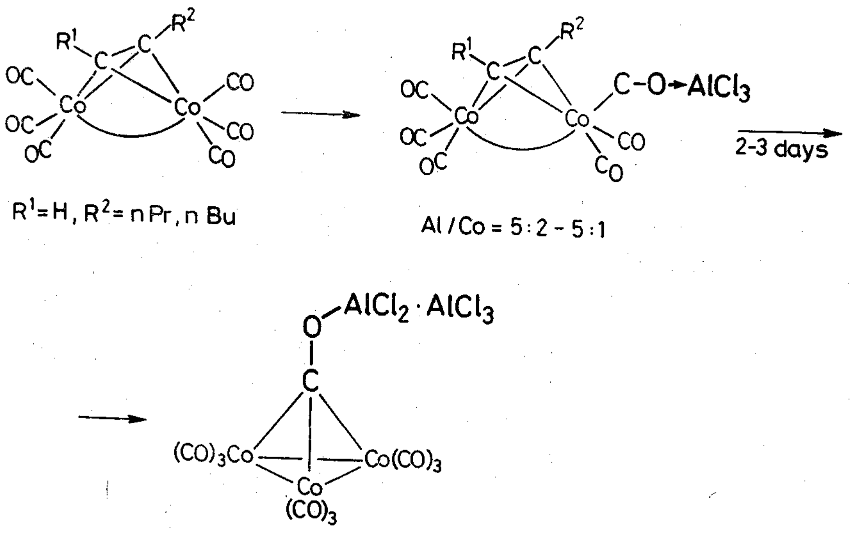
$$PPh_3(CO)_3CoCH_2COOEt \xrightarrow[CCl_4]{} PPh_3(CO)_3CoCH_2-C(=O)-\overset{\displaystyle\downarrow AlX_3}{O}-Et \qquad (2)$$

(V)

Compound (V) could not be isolated but its structure may be evidenced by the ν (C—O) spectra: (*a*) the terminal part of the spectrum remains unchanged in shape but (*b*) it is shifted by 10–12 cm^{-1} towards higher wave numbers, while (*c*) the "organic" ν (C—O) band suffers an ~40 cm^{-1} shift towards *higher* wave numbers. All these arguments show that coordination of the Lewis acid took place (ligand abstraction excluded), while comparison of (*b*) and (*c*) excludes that the Co atom was attacked, (*a*) excludes a Co—C—O—Al type bridging and (*c*) excludes coordination at the organic carbonyl group. The starting (IV) compound could be recovered by treatment of (V) with a slight excess pf pyridine.

Binuclear compounds.

The acetylene-bridged cobalt carbonyls $(\mu_2R^1C_2R^2)Co_2(CO)_6$ (VI) are regarded [9, 10] as intermediates in the catalytic synthesis of bifurandiones. (VI) compounds were treated with $AlCl_3$ in CH_2Cl_2 solution. The ν (C—O) spectrum remained practically unaltered until a 5 to 10-fold molar excess of the Lewis base was present. Then a low-wave number band appeared (~ 1640 cm^{-1}) and the rest of the terminal ν (C—O) spectrum was shifted by 80 to 100 cm^{-1} towards higher wave numbers and the shape resembled that of the monosubstituted phosphine derivatives (VI) [11]. From these solutions (VI) could be still recovered by hydrolysis or treatment with PPh_3. After standing for 48 hours an irreversible change occurred and the spectrum of $(CO)_9Co_3C—O—AlCl_2\cdot AlCl_3$ [12] could be observed. These findings can be rationalized by reactions (3).



(3)

There was no indication of the reaction of the Lewis acid either with the metal or with $R^1C_2R^2$ ($R^1 = H$), The necessity of a high excess of $AlCl_3$ can be attributed to the relatively soft character of the terminal carbonyl oxygen.

The reaction of (VI, $R^1 = H$, $R^2 = CH_2NEt_2$) with an equimolar amount of $AlCl_3$ and other Lewis bases leads to an N—Al adduct as reported recently [13].

Compounds (VI) can be carbonylated stoichiometrically to the $(\mu_2—C_4O_2R^1R^2)(\mu_2CO)Co_2(CO)_6$ (VII) compounds [9/*a*] which step is accepted as one of the catalysis steps in the catalytic bifurandion synthesis. The (VII) compounds are particularly interesting as regards the reaction with Lewis acids since they contain *six* sets of oxygen atoms with a different chemical environment.

We treated CH_2Cl_2 solutions of (VI) compounds with 0.5 equivalent portions of CH_2Cl_2 solution of $AlCl_3$. The following changes in the ν(C—O) spectrum (Fig. 1) could be observed.

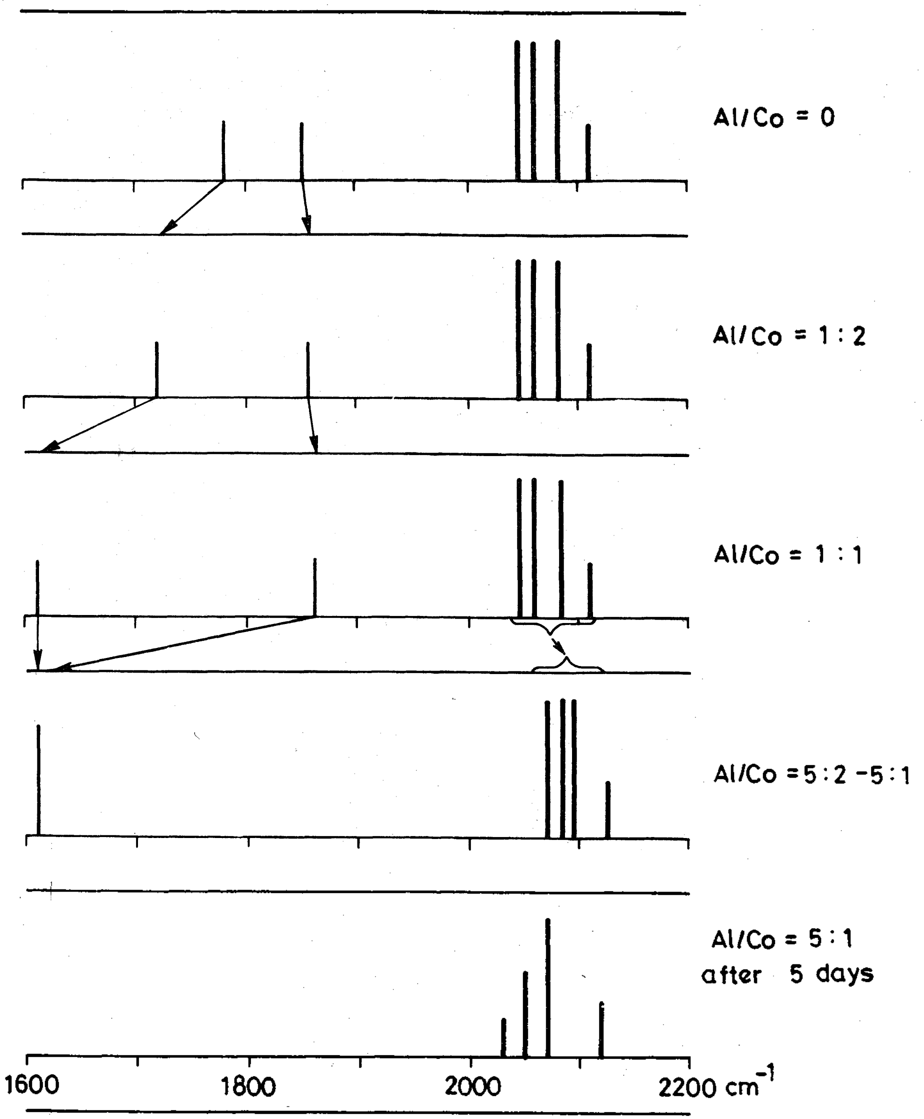
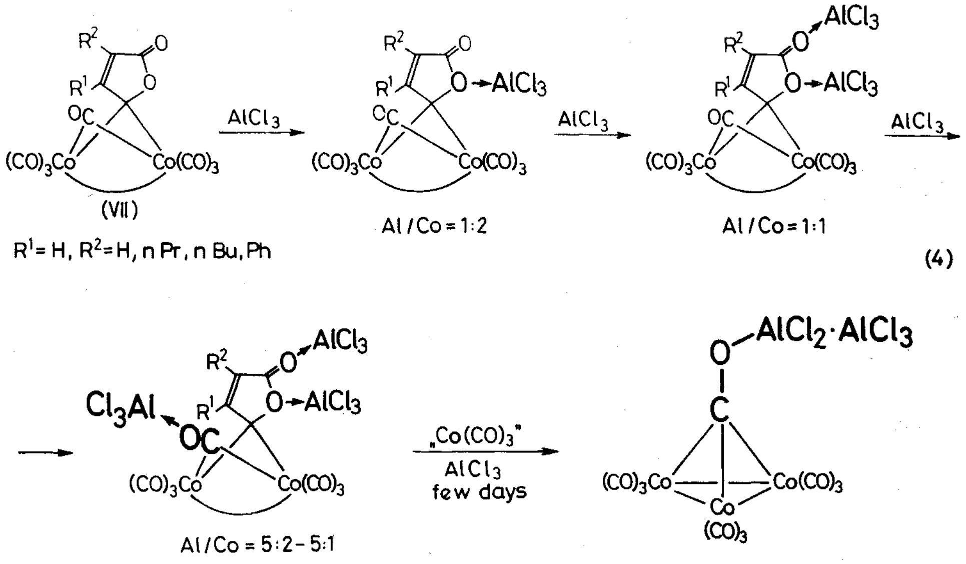


Fig. 1. - Reaction of (VII, $R^1 = H$, $R^2 = nBu$) with $AlCl_3$ in CH_2Cl_2, followed by the IR ν(C—O) spectra.

At Al/Co ratio 1 : 2 the terminal and bridge region practically remained unaltered, while the "organic" band was shifted to lower wave numbers by ~60 cm^{-1}. At Al/Co = 1 : 1 again only the organic ν(C—O) band was transposed towards lower wave numbers by a further 110 cm^{-1} to 1610 cm^{-1} which is characteristic of C—O—Al type structures [3].

Further amounts of $AlCl_3$ ($Al/Co = 5:2$–$5:1$) cause also the bridging CO band to disappear at its original position while the intensity of the band at 1610 cm^{-1} is doubled and at the same time the terminal part of the spectrum is shifted by 20 to 25 cm^{-1} towards higher wave numbers.

These findings could be rationalized by supposing that first the ring—O of the furanone ligand then the " organic " carbonyl group and subsequently the bridging CO group is the site of the electrophilic attack as depicted in reactions (4). This sequence corresponds to the expected sequence of hardness of these O atoms.



(4)

The treatment of the reaction mixture (within a few hours) with PPh_3 leads to the recovery of the starting (VII) compoud while the reaction mixture in a few days (3–5) suffers irreversible change leading to $(CO)_9Co_3C$—O—$AlCl_2 \cdot AlCl_3$ [12].

Trinuclar complex.

The poisoning effect of EX_3 ($E = P$, As ; $X = Cl$, Br, I) compounds on the catalytic reactions of $Co_2(CO)_8$ was studied by investigating the reaction products of EX_3 compounds with metal carbonyls. Among these compounds the tetrahedral $(CO)_9Co_3E$ (VIII) clusters could be identified [14]. The (VIII, $E = As$) compound was also tested as ligand for soft and hard bases [15].

The treatment of (VIII, $E = As$) with $AlCl_3$ in CH_2Cl_2 leads to a greenish-black oily product the spectrum of which was unaltered in shape but shifted by 10 to 30 cm^{-1} towards higher wave numbers. This behaviour could be rationalized by reaction (5):

$$(CO)_9Co_3As + AlCl_3 \longrightarrow (CO)_9Co_3As \rightarrow AlCl_3 \cdots \quad (5)$$

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