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Metal carbonyls: new methods of synthesis and investigations *

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Abstract

Despite the century-long history, the chemistry of metal carbonyls is still developing. However, up to now there has been insufficient progress in the development of new effective synthetic methods for metal carbonyls and their derivatives. This paper reports the results of our studies in the field of development of new methods for synthesizing metal carbonyls and arenemetal tricarbonyls, as well as studies of complexes comprising dichlorides of group IV elements and metal carbonyls, and also application of the compounds considered for olefin hydrosilylation and amine silylation.

New methods of carbonyl metal synthesis

The first carbonyls, $Ni(CO)_4$ and $Fe(CO)_5$, were obtained by the carbonylation of nickel and iron powders [1]. Ni and Fe carbonyls are still produced by this simple method. Other metal carbonyls are produced by the carbonylation of metal derivatives (oxides, sulphides, chlorides, carboxylates and other salts), in the presence of strong reducing agents (powders, suspensions and organometallic compounds of group I–III metals). In the first attempt to synthesize $M(CO)_6$ (M = Cr, Mo, W), phenylmagnesium bromide was used to activate metal chlorides [2]. Then Nesmeyanov showed that virtually any Grignard reagent acted as a reducing agent, and he successfully used zinc dust to synthesize $M(CO)_6$ (M = Mo, W) [3]. However, the compounds of group I–III metals are irreplaceable in the processes of metal carbonyl preparation.

It was of interest to apply preparation of organometallic compounds by thermal decomposition of metal carboxylates to metal carbonyl synthesis. This method has been well studied for mercury compounds, but only a few examples of the decarboxylation of nickel carboxylates yielding the corresponding organonickel compounds

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* Dedicated to the centenary of the discovery of metal carbonyls.

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are known [4]. The reaction proceeds best when strong electron-accepting substituents, such as metal trifluoroacetates, are present in the carboxylate group.

While studying the reaction of perfluoroacetatte carbonylation, we found that under severe conditions (200 °C, 210–250 atm, without solvent) the complete carbonylation of nickel and iron salts took place, yielding the corresponding metal carbonyls [5]:

$$(CF_3COO)_2M + CO \longrightarrow M(CO)_n + 2CO_2 + CF_3CF_3$$

$$(M = Ni,\ n = 4;\ M = Fe,\ n = 5)$$

We succeeded in applying this method to the more complex synthesis of cobalt carbonyl. Numerous methods of preparating $Co_2(CO)_8$ are well known [6]. The synthesis from cobalt carbonate or acetate by the action of a gaseous $CO + H_2$ mixture (160–180 °C, 160 atm) in acetic anhydride or some other organic solvents was of interest to us.

We believed that during the carbonylation of acetate or other cobalt carboxylates there was no need to use reducing agents, in particular hydrogen, because the decarboxylation of cobalt salts yielding organocobalt compounds, which convert under carbonylation conditions, into $Co_2(CO)_8$ was possible under the process conditions.

We studied the carbonylation of diacetate under various conditions both in the presence and in the absence of a solvent. In the absence of a solvent, $Co_2(CO)_8$ forms up to 200 °C as well as at high pressures up to 280 atm. The maximum yield, 97%, was obtained at 200 °C and 280 atm within 8–10 h. Under such conditions, a solid consisting of $Co_2(CO)_8$ and a gaseous phase consisting of carbon dioxide and ethane are obtained. The synthesis of $Co_2(CO)_8$ proceeds well in solvents such as hexane, heptane, benzene and toluene, but in this case severe process conditions are required [5].

Decarboxylation is known the be a radical process initiated by benzoyl peroxide [4]. When benzoyl peroxide was used in amounts up to 1 wt% of the salt, we succeeded in lowering sharply both the working pressure (up to 120 atm) and the temperature (160 °C). In this case, the process should be performed in hexane, toluene and other solvents. Under such conditions, $Co_2(CO)_8$ forms in a quantitative yield within approximately 5 h. Along with $Co_2(CO)_8$, only carbon dioxide and ethane are identified.

We obtained data which allow us to make a conclusion concerning the mechanism of the process, the first stage of which is benzoyl peroxide-initiated, stepwise decarboxylation of two carboxylate groups. The complete process can be represented as follows:

$$(CH_3COO)_2Co \longrightarrow (CH_3)_2Co + 2CO_2$$

It is possible that subsequently thermal degradation of $(CH_3)_2Co$ takes place, yielding active metal which undergoes carbonylation to give cobalt carbonyl:

$$(CH_3)_2CO \longrightarrow 2CH_3^{\cdot} + [Co]\ 2[Co] + 8CO \longrightarrow Co_2(CO)_8$$

However, cobalt metal was not one of the reaction products and it is not improbable that step-by-step carbonylation of the gradually forming organocobalt compound takes place.

Many methods of chromium hexacarbonyl synthesis use various reducing agents [6]. Two methods are of particular interest: the Fischer–Hafner method, which employs a mixture of stoichiometric amounts of aluminium powder and aluminium chloride in benzene solution at high CO pressure (up to 150 atm) [8]; and a method which employs a mixture of stoichiometric amounts of magnesium and iodine activator [9]. Disadvantages include the large amount of waste, the complexity of the reaction, as well as the high pressure in the first case and the use of stoichiometric amounts of iodine for magnesium activation in the second case.

The still more complex method of magnesium activation during $Cr(CO)_6$ synthesis is proposed in [10]: reduction of magnesium chloride by potassium in the presence of potassium iodide. However, the high CO pressure (280 atm) and the long duration of the process (more than 16 h) do not allow this method to be employed for $Cr(CO)_6$ synthesis.

We also chose magnesium as the reducing agent and searching for more efficient activators. During our investigation we checked compounds of titanium, iron and nickel, as well as compounds of lanthanides and anthracene. Compounds of nickel and titanium, especially $Ni(CO)_4$, give the best effect; for example, in the case of $Ni(CO)_4$, carbonylation of $CrCl_3$ in the presence of magnesium proceeds at 30 ° C and at a CO pressure of about 30 atm. A small amount of hydrogen (up to 5 atm) and from 1 to 10% of activator were introduced in all cases.

Activation of magnesium by titanium tetrachloride (up to 5%) is of industrial importance. $Cr(CO)_6$ is formed, (with up to 90% yield0 under the following conditions: total $H_2 + CO$ pressure up to 50 atm, temperature 40 ° C, stoichiometric amount of magnesium activated by $TiCl_4$ and process duration 8–10 h [11].

$$2CrCl_3 + Mg + 12CO \xrightarrow{THF} 2Cr(CO)_6 + 3MgCl_2$$

The reaction proceeds exothermally only in THF and cyclic ethers and therefore cooling is necessary.

The synthesis of $M(CO)_6$ and $W(CO)_6$ under the same conditions gave a yield of more than 80% [12].

Synthesis and properties of arenemetaltricarbonyls

The above-described methods of $C_6H_6Cr(CO)_3$ and $C_6H_6Mo(CO)_3$ synthesis, as well as derivatives of the last two complexes, suffer from many disadvantages, but the most important one is the low yield of arenemetal tricarbonyls [13]. In the case of direct reaction between $Mo(CO)_6$ and benzene, the maximum $C_6H_6Mo(CO)_3$ yield is about 14%. When using derivatives (pyperidine and acetonitrile derivatives) of the corresponding metal carbonyls, whose synthesis also presents some difficulties, to synthesize arenemolybdenum-tungsten tricarbonyls, higher yields were obtained [14].

The interaction between benzene and metal hexacarbonyls is a multi-stage process:

$$M(CO)_6 + C_6H_6 \rightleftharpoons C_6H_6M(CO)_5 + CO$$

$$C_6H_6M(CO)_5 \rightleftharpoons C_6H_6M(CO)_4 + CO$$

$$C_6H_6M(CO)_4 \rightleftharpoons C_6H_6M(CO)_3 + CO$$

When the mixture is heated in an autoclave, equilibrium is quickly attained and $C_6H_6M(CO)_3$ formation stops because the evolving carbon monoxide remains in the reactor. Attempts to discharge CO after cooling (this operation was repeated several times during the process) are not very effective because unstable intermediates, $C_6H_6M(CO)_5$ and $C_6H_5M(CO)_4$, decompose during heating in the absence of CO (Fischer obtained 6 and 2% yields of $C_6H_6Mo(CO)_3$ and $C_6H_6W(CO)_3$, respectively) [13]. We increased the yields sharply when the following conditions were met: CO pressure discharge in excess of 6–8 atm and a device to return the sublimating metal carbonyl.

The second problem which was necessary to solve during the development of an effective method of $C_6H_6M(CO)_3$ preparation (especially in the case of molybdenum and tungsten) involved lowering the process temperature. In particular, Rausch proposed adding α-picoline to the reaction mixture to synthesize $C_6H_6Cr(CO)_3$; the yield reached 91%, however, in the open system and the process lasted 4–5 days [15]. Combining the above reactor and catalytic additives (not more than 1% of pyridinetetrahydrofuran, picoline, or their complexes containing the corresponding molybdenum and chromium carbonyls), we succeeded in obtaining within several hours high yields of ($C_6H_6Cr(CO)_3$ and $C_6H_6Mo(CO)_3$, 93 and 71%, respectively, as well as in producing them in any amount which depended only on the reactor dimensions [16]. It should be noted that quantitative formation of the complexes takes place in the course of synthesis and the decrease in the yields is connected with losses during their isolation, especially in the case of molybdenum.

Application of pyridine and other donors for the synthesis of $C_6H_6(CO)_3$ and its derivatives does not give a positive effect, because pyridine and picoline complexes of tungsten carbonyl are stable complexes at temperatures of 200 °C and higher, i.e. at the temperature when the tarred $C_6H_6W(CO)_3$ begins to decompose.

When NH_4BF_4 was used as the initiator, we obtained a high yield of this complex and its derivatives. On heating the mixture of C_6H_6 and $W(CO)_6$ at 190–200 °C for 6 h and adding up to 1% initiator and up to 10% THF, we obtained a $C_6H_6W(CO)_3$ yield of 80%. The role of NH_4BF_4 probably lies in interacting with tungsten carbonyl, yielding a complex with ammonia, but HBF_4 initiates the reaction of displacement of ammonia molecules by benzene [16]:

$$W(CO)_6 + NH_4BF_4 \longrightarrow (NH_3)_3W(CO)_3 + HBF_4$$

$$(NH_3)_3W(CO)_3 + C_6H_6 + HBF_4 \longrightarrow C_6H_6W(CO)_3 + NH_4BF_4$$

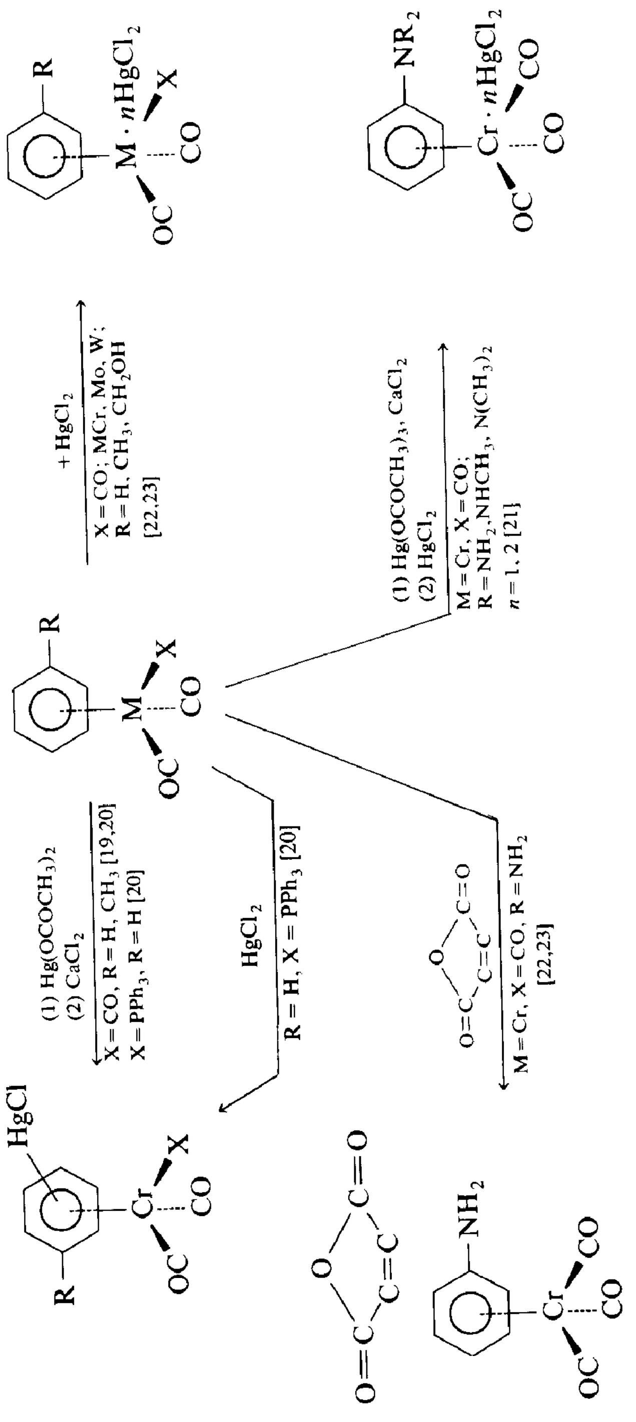
This method is universal in its nature. We used it to synthesize some π-complexes of tungsten carbonyl; in particular, we isolated under these conditions in quantitative yield $[C_5H_5W(CO)_3]_2$ which could not be isolated by known methods [17]:

$$C_{10}H_{12} + W(CO)_6 \longrightarrow [C_5H_5W(CO)_3]_2 + H_2 + CO$$

The synthesis proceeds under the above-mentioned conditions in THF solution.

Reactions of arenemetaltricarbonyls with mercury salts

In comparison with $(C_5H_5)_2Fe$ and $C_5H_5Mn(CO)_3$, the $C_6H_6M(CO)_3$ complexes have been insufficiently studied. Only a few reactions of the electrophilic substitution of the ring in $C_6H_6Cr(CO)_3$ have been successful. This can be explained by the



+ HgCl2
X = CO; MCr, Mo, W;
R = H, CH3, CH2OH
[22,23]
(1) Hg(OCOCH3)3, CaCl2
(2) HgCl2
M = Cr, X = CO;
R = NH2, NHCH3, N(CH3)2
n = 1, 2 [21]
(1) Hg(OCOCH3)2
(2) CaCl2
X = CO, R = H, CH3 [19,20]
X = PPh3, R = H [20]
HgCl2
R = H, X = PPh3 [20]
M = Cr, X = CO, R = NH2
[22,23]
M · nHgCl2
Cr · nHgCl2
HgCl
NR2
NH2

Scheme 1

decreased nucleophilicity of the benzene ring [18]. We studied the relative reactivity of arenemetal tricarbonyls in their reactions with mercury salts (Scheme 1) [19–23].

As can be seen from the scheme, mercuration of $C_6H_6Cr(CO)_3$ takes place during refluxing with mercury acetate in dry ethanol, but under the influence of such a weak mercurating agent as $HgCl_2$ the adduct $C_6H_6Cr(CO)_3 \cdot nHgCl_2$ is formed, whose structure was confirmed by X-ray analysis [21]. The displacement of CO by PPh_3 in benzenechromium tricarbonyl causes an increase in the nucleophilicity of the ring, which is mercurated by the action of both reagents [22]. $CH_3C_6H_5Cr(CO)_3$ mercuration proceeds only during reaction with mercury acetate in THF. Other $C_6H_6Cr(CO)_3$ derivatives, and even complexes with increased nucleophilicity of the ring, e.g. anilinechromium tricarbonyls, are not mercurated under such conditions.

As can be seen from Scheme 1, benzenemolybdenum and benzenetungsten tricarbonyls are not mercurated by the action of mercury salts, but form $C_6H_6M(CO)_3 \cdot nHgCl_2$ adducts [23,24].

Summing up the results, obtained one can assume that the mercuration of arenechromium tricarbonyls proceeds by way of preliminary coordination of the mercurating agent with the chromium atom, yielding an adduct. When the adduct is stable, as in the case of $C_6H_6Cr(CO) \cdot nHgCl_2$ and complexes of anilinechromium tricarbonyls and mercury salts, mercuration of the ring does not occur.

The possibility of ring mercuration also depends on the ring nucleophilicity. The increased nucleophilicity of the ring in $C_6H_6Cr(CO)_2PPh_3$ is responsible for the complex mercuration by even such a strong acceptor and weak mercurating agent as $HgCl_2$. The weak nucleophilicity of the rings in $C_6H_6M(CO)_3$ ($M = Mo, W$) eliminates the possibility of ring mercuration of these complexes.

The synthesis and properties of dichloride complexes of group IV elements and group VI metal carbonyls

Despite the fact that Fischer [25] discovered carbene complexes of metal carbonyls as early as the 1960s, complexes of the carbene analogues the compounds of silicon, germanium, tin and lead, were unknown up to the beginning of the 1970s. At the same time, the electron structure of bivalent derivatives of group IV elements in the singlet state is typical of monodentate ligands: there is a non-bonding electron pair, ns^2, at the element ($M \leftarrow :EX_2$ donor–acceptor interaction is possible) as well as np free orbitals ($M: \rightarrow EX_2$ dative interaction is also possible).

We began to study the photochemical reaction of one of the most easily available stannylenes, $SnCl_2$, with chromium, molybdenum and tungsten hexacarbonyls, and found that CO is displaced by tin chloride [26]. By that time, Marks [27] published his paper describing the synthesis of chromium carbonyl complexes with dialkylstannylenes and germylene:

$$Na_2Cr_2(CO)_{10} + 2ER_2Cl_2 \xrightarrow{THF} 2Cr(CO)_5ER_2 \cdot THF$$

$$(E = Ge, Sn;\ R = CH_3,\ C_4H_9^t)$$

Complexes of dimethylstannylene and di-t-butylstannylene and dimethylgermylene are not entirely analogues of carbene complexes because the Ge–Sn bond is stabilized by coordination of the THF molecule, i.e. similarity of ylide bonds is realized and the carbenoid complexes are classified according to Petz, as the second

Table 1

Properties of metal carbonyl complexes with derivatives of divalent tin and lead as ligands

Compound	Colour	M.p. (°C)	IR[a] $\nu(CO)$ (cm^{-1})				Ref.
			A_1^2	B_1	E	A_1^1	
Ligand SnR_2							
$(OC)_5CrSnCl_2 \cdot THF$[b] **(1)**	yellow	96	2072m,	1933s,	1956vs		29–31, 41
$(OC)_5CrSnCl_2$ ↑ $O(COCH_3)_2$ **(2)**	yellow	125	2065m,	1986s,	1945vs		34
$(OC)_5MoSnCl_2 \cdot THF$[b] **(3)**	yellow	74	2083m,	1994s,	1963vs		29–31, 41
$(OC)_5WSnCl_2 \cdot THF$[b] **(4)**	yellow	106	2081m,	1990s,	1956vs		29–31, 41
$(OC)_5CrSnCl_2$ **(5)**	yellow	150 dec.	2086m,	1997s,	1954vs		29–31
$(OC)_5MoSnCl_2$ **(6)**	grey	120 dec.	2090m,	1995s,	1954vs		29–31
$(OC)_5WSnCl_2$ **(7)**	yellow	180 dec.	2093m,	1995s,	1950vs		29–31
$(OC)_5CrSn(OH)_2$ **(8)**	yellow	250 dec.	2067m, $\nu(OH)$ 3600m,	1987s,	1945vs 3525m		31, 41
$(OC)_5MoSn(OH)_2$ **(9)**	yellow	215 dec.	2078m, $\nu(OH)$ 3595m,	1985s,	1950vs 3525m,		31, 41
$(OC)_5WSn(OH)_2$ **(10)**	yellow	280 dec.	2070m,	1980s,	1950vs		31, 41
$(OC)_5CrSnO$ **(11)**	yellow	250 dec.	2067m,	1987s,	1945vs		31, 41
$(OC)_5MoSnO$ **(12)**	yellow	215 dec.	2078m,	1985s,	1950vs		31, 41
$(OC)_5WSnO$ **(13)**	yellow	280 dec.	2070m,	1980s,	1955vs		31, 41
$(OC)_5CrSnS$ **(14)**	pale brown	167 dec.	2064m,	1989s,	1946vs		31, 41
$(OC)_5WSnS$ **(15)**	dark orange	87	2065m,	1980s,	1958vs		31, 41
$(OC)_5CrSn(N{=}C{=}S)_2$ **(16)**	yellow	125 dec.	2100w, $\nu(N{=}C{=}S)$ 2065vs	1987s,	1945vs,	1880s	31, 41
$(OC)_5WSn(N{=}C{=}S)_2$ **(17)**	dark yellow	88	2100m, $\nu(N{=}C{=}S)$ 2070vs	1983s,	1945vs,	1880s	31, 41
$(OC)_5CrSn(OCOCH_3)_2$ | $O(COCH_3)_2$ **(18)**	yellow	137	2063m, $\nu(CO)$ in $OCOCH_3$; $\nu(CO)$ in $(CH_3CO)_2O$	1985s,	1935vs 1760m, 1660m	 1735m	31, 41
$(OC)_5MoSn(OCOCH_3)_2$ | $O(COCH_3)_2$ **(19)**	pale brown	112	2076m, $\nu(CO)$ in $OCOCH_3$: $\nu(CO)$ in $O(COCH_3)_2$	1988s,	1955vs 1760m, 1663m	 1735m	31, 41
$(OC)_5WSn(OCOCH_3)_2$ | $O(COCH_3)_2$ **(20)**	pale	178	2075m, $\nu(CO)$ in $OCOCH_3$: $\nu(CO)$ in $(CH_3CO)_2O$	1986s,	1946 1760m, 1662m	 1735m	31, 41
$(OC)_5Cr{=}Sn[Mn(CO)_5]_2$ **(21)**	dark red	170 dec.	$Cr(CO)_5$: 2078m, $Mn(CO)_5$: 2090w,	 1990s, 2050m,	 1950vs 2025vs,	 1925m	39

continued

Table 1 (continued)

$(OC)_5Cr{=}Sn[Re(CO)_5]_2$ **(22)**	dark yellow	98–100	$Cr(CO)_5$: 2078w, $Re(CO)_5$: 2110w,	 1990s, 2050m,	 1950vs 2018vs,	 1900s	39
$(OC)_5W{=}Sn[Mn(CO)_5]_2$ **(23)**	dark red	62–65	$W(CO)_5$: 2078w, $Mn(CO)_5$: 2100w,	 1980s, 2052m,	 1956vs 2015vs,	 1930s	39
$(OC)_5W{=}Sn[Re(CO)_5]_2$ **(24)**	dark red	78–80	$W(CO)_5$: 2078m, $Re(CO)_5$: 2112w,	 1990s, 2050m,	 1950vs 2018vs,	 1900s	39
$(C)_5Cr{=}Sn{=}Cr(CO)_5$ **(25)**	yellow	185 dec.	2065w,	1990m,	1940vs		36
$(OC)_5W{=}Sn{=}W(CO)_5$ **(26)**	yellow	260 dec.	2975w,	1978m,	1945vs		36
$[(OC)_5Mn]_2Sn$ **(27)**	yellow	172 dec.	2085m,	2052m,	2015vs,	1925s	38, 41
$[(OC)_5Re]_2Sn$ **(28)**	yellow	245 dec.	2108m,	2078m.	2025vs,	1900s	38, 41
Ligand PbR₂							
$(OC)_5CrPbCl_2$ $\nearrow$ $C_2H_5OCOCH_3$ **(29)**	dark yellow	95	2070w,	1980s,	1936vs,	1872s	33, 34
$(OC)_5WPbCl_2$ $\nearrow$ $C_2H_5OCOCH_3$ **(30)**	brown	101	2080w,	1982s,	1948s,	1900s	33, 34
$(OC)_5CrPb(OCOCH_3)_2$ $\uparrow$ $O(COCH_3)_2$ **(31)**	dark yellow	103	2070w,	1985s,	1940vs,	1860s	33, 34
$(OC)_5WPb(OCOCH_3)_2$ $\uparrow$ $O(COCH_3)_2$ **(32)**	brown	105	2076w,	1995s,	1935vs,	1900s	33, 34

[a] IR measured in THF solution. [b] IR measured in hexane solution.

type of carbenoid complexes [28]. Moreover, these compounds could not become the basis for development of the chemistry of carbanoid complexes because the atoms of group IV elements bear no functional groups.

Therefore, the complexes of metal carbonyls and dihalides, in particular the complexes of metal carbonyls and dichlorides of group IV elements, are of great interest. Berens [29] and Morozova and co-workers [26,30,31] synthesized the first representatives of complexes with $SnCl_2$ by a photochemical reaction in THF:

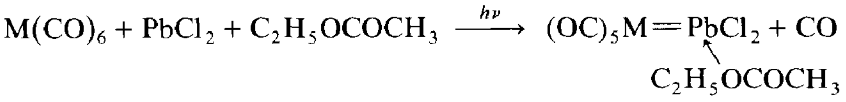
$$M(CO)_6 + SnCl_2 + THF \longrightarrow M(CO)_5SnCl_2 \cdot THF + CO$$

The M–Sn bond in the $M(CO)_5SnCl_2 \cdot THF$ complexes is also stabilized by coordination of the THF molecule with the tin atom. It should be noted that none of the papers describes the very sharp melting points of these complexes, which we determined (see Table 1). Similar complexes with $GeCl_2$ are described in ref. 32.

These papers gave rise to the chemistry of carbenoid complexes of metal carbonyls. All successes in this field, except our studies, are described in ref. 28.

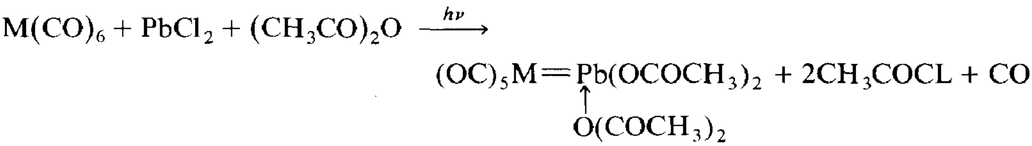
The preparation method of $M(CO)_5SnCl_2THF$ in high yields is developed on the basis of the CO thermal displacement reaction in an autoclave.

Attempts to synthesize another $PbCl_2$ carbenoid-type complex in THF failed due to the insolubility of $PbCl_2$ in it. However, during the photolysis of $M(CO)_6$ and $PbCl_2$ ine thyl acetate the corresponding complexes with chromium and tungsten carbonyls were isolated [33]:



$$M(CO)_6 + PbCl_2 + C_2H_5OCOCH_3 \xrightarrow{h\nu} (OC)_5M{=}\underset{\substack{\nwarrow\\ C_2H_5OCOCH_3}}{Pb}Cl_2 + CO$$

When the reaction proceeds in acetic anhydride, the $M(CO)_5PbCl_2$ complexes which were formed in the first stage react with acetic anhydride yielding complexes of lead diacetate [33]:



$$M(CO)_6 + PbCl_2 + (CH_3CO)_2O \xrightarrow{h\nu}$$
$$(OC)_5M{=}\underset{\substack{\uparrow\\ O(COCH_3)_2}}{Pb}(OCOCH_3)_2 + 2CH_3COCL + CO$$

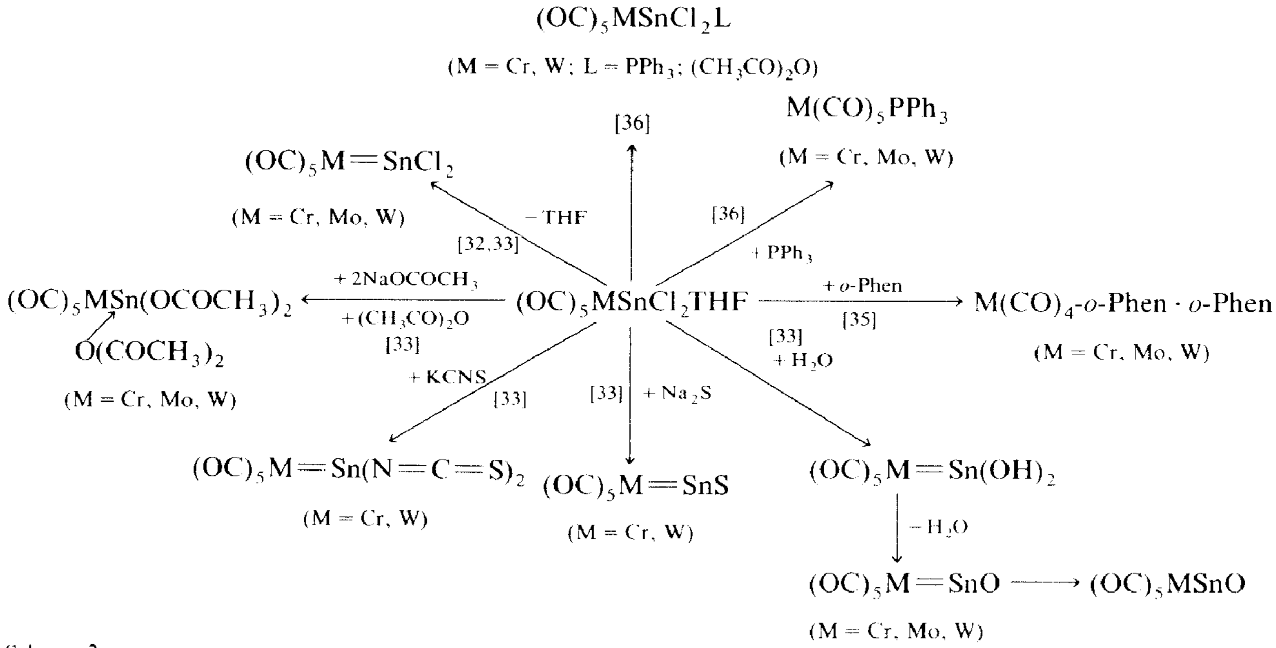
Under the same conditions, $SnCl_2$ forms with metal carbonyls the complexes $\underset{\substack{\uparrow\\ O(COCH_3)_2}}{M(CO)_5SnCl_2}$, in which acetolysis of the Sn–Cl bond is absent and a molecule of acetic anhydride, instead of THF, is coordinated to tin. the syntheses of $SnCl_2$ and $PbCl_2$ complexes made possible their systematic study for the purpose of obtaining new unusual complexes. We were successful in the case of stannylene derivatives.

Chemical properties of $(OC)_5MeCl_2L$

When investigating the chemical propterties $(CO)_5M{=}ECl_2 \cdot L$, we found that ECl_2 coordination causes a change of the activity series relative to nucleophile action.

So, as related to water and alcohols, the reactivity of carbenoids increases in the order $PbCl_2 < SnCl_2 < GeCl_2$, but when these molecules are coordinated with metal, the reactivity of the E–Cl bond decreases sharply in the same order. For example, at room temperature the $M(CO)_5SnCl_2L$ complexes undergo hydrolysis and alcoholysis of the E–Cl bond the action of water and alcohols, yielding the corresponding derivatives, but complexes having $PbCl_2$ ($PbCl_2$ is completely stable in uncoordinated state towards the action of water and alcohols) convert to complexes of lead dihydroxide on exposure to atmosphere moisture and then the M–Pb bond breaks down, causing disproportionation of the $M(CO)_5$ fragment to the metal hexacarbonyl [34,33]. At the same time, dichlorogermylene, which is reactive in the free state, is stable towards the action of water and alcohols [32].

We studied the following types of reaction of $SnCl_2$ complexes: reactions of ligand substitution at the carbenoid atom [34,33], reactions of chlorine atom displacement by various nucleophilic groups [31,34] and reactions of carbenoid


$(OC)_5MSnCl_2L$
(M = Cr, W; L = PPh$_3$; $(CH_3CO)_2O$)
[36]
$M(CO)_5PPh_3$
(M = Cr, Mo, W)
$(OC)_5M{=}SnCl_2$
(M = Cr, Mo, W)
− THF
[32,33]
[36]
+ PPh$_3$
+ 2NaOCOCH$_3$
+ $(CH_3CO)_2O$
[33]
$(OC)_5MSn(OCOCH_3)_2$
$O(COCH_3)_2$
(M = Cr, Mo, W)
$(OC)_5MSnCl_2THF$
+ o-Phen
[35]
$M(CO)_4$-o-Phen · o-Phen
(M = Cr, Mo, W)
[33]
+ H$_2$O
+ KCNS
[33]
[33]
+ Na$_2$S
$(OC)_5M{=}Sn(N{=}C{=}S)_2$
(M = Cr, W)
$(OC)_5M{=}SnS$
(M = Cr, W)
$(OC)_5M{=}Sn(OH)_2$
− H$_2$O
$(OC)_5M{=}SnO$
$(OC)_5MSnO$
(M = Cr, Mo, W)

Scheme 2

ligand substitution [36,40] (the transformations of stannylene complexes are shown in Scheme 2). As a result of our studies, some new stannylene complexes of types I and II are obtained (Scheme 2).

The compounds obtained by the action of reagents such as water, potassium rhodanide and sodum sulphide on $M(CO)_5 \cdot SnCl_2$ are of particular interest, because in this case stable complexes of type I, i.e. typical carbenoid complexes, are formed. Thus, complexes of tin dihydroxide are formed during the action of water which, in the course of evacuation or heating, lose water and convert to complexes of tin monoxide which is the CO analogue. Freshly obtained complexes dissolve well in diethyl ether, alcohol and THF, but after a few days their solubility decreases sharply while their IR spectra, appearance and decomposition temperature remain virtually unchanged (see Table 1). The molecular weights of fresh samples agree with the monomer form and some time later with the dimer form. Samples that are insoluble in diethyl ether correspond to the tetramer form. During the action of silicon triphenylsilanolate on $M(CO)_5SnCl_2 \cdot THF$, complexes with tin dihydroxide, $M(CO)_5Sn(OH)_2$ (Cr, W), were isolated but they have a considerably lower decomposition temperature, about 150 °C (cf. data listed in Table 1) [35].

Complexes of the second type, $(OC)_5MSn(OCOCH_3)_2O(COCH_3)_2$, are formed after reaction with sodium hydroxide.

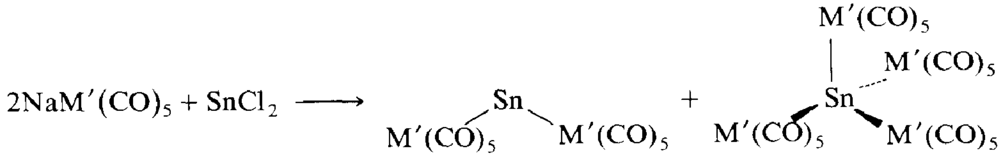
Metal carbonylstannylenes

We expected to obtain mono(metalpentacarbonyl)tin during the dehalogenation of $M(CO)_5SnCl_2 \cdot THF$ by sodium or magnesium suspensions, but instead yellow crystalline substances were isolated. The IR and mass spectra showed that these compounds have two metal pentacarbonyl fragments per tin atom [36]:

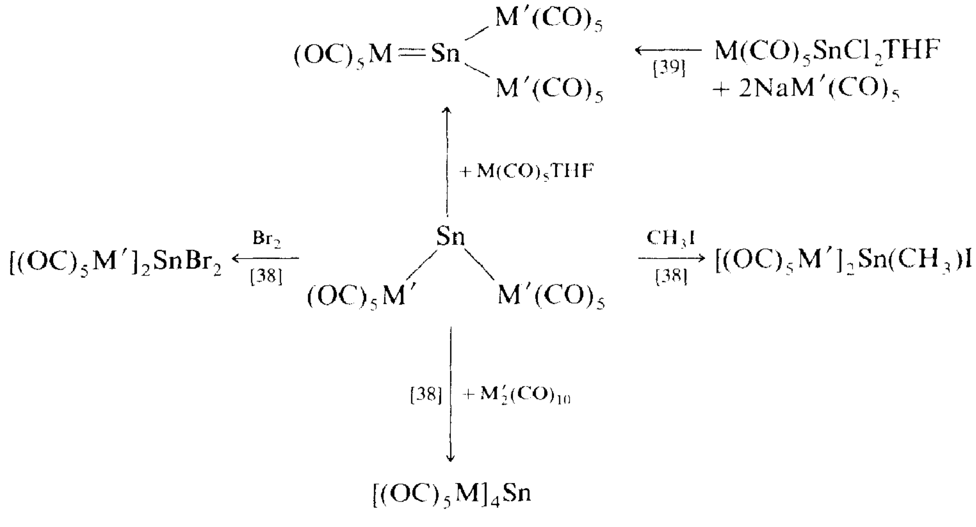
$$(OC)_5M{=}SnCl_2THF + Na/Mg \longrightarrow [M(CO)_5Sn] \longrightarrow (OC)_5M{=}Sn{=}M(CO)_5$$

Supposedly, $[(CO)_5MSn]$ is initially formed and subsequently disproportionates into $[(OC)_5M]_2Sn$. To fill the vacant sites at the chromium or tungsten atoms, it is necessary that the tin atom take part in the formation of two coordination Sn=M bonds, i.e. it must be a bidentate ligand. In this case, the metal atoms should arrange along one M=Sn=M axis, i.e. a quasi-allene structure is realized. In ref. 37, the compound $[CH_3C_5H_4(OC)_2Mn]_2Ge$ has been described. X-Ray analysis confirmed a similar linear quasi-allene structure with the metal atoms on one Mn=Ge=Mn axis for this compound.

Complexes of bivalent tin with a σ-bond, $[(OC)_5Mn]_2Sn$, were synthesized for comparison. The synthesis was performed by the reaction of dichlorostannylene with pentacarbonylmanganete or rhenate [38]:



It is clear from the reaction scheme that along with bis(metal pentacarbonyl)stannylene the previously unknown tetrakis(metal pentacarbonyl)tin is formed. The



(M = Cr, W; M′ = Mn, Re)

Scheme 3

former compound was isolated. A detailed study of $[(OC)_5M']_2Sn$ (M = Mn, Re) showed that these complexes are completely different from tin compounds containing tungsten and chromium carbonyls. In contrast to $[(OC)_5M]_2Sn$, these complexes have an angular structure with the tin atom in the triplet state. the chemical properties of these two types of complex differ greatly from each other. Thus, derivatives with a bidentate tin atom do not enter into the reactions described for stannylenes. At the same time, $[(OC)_5M']_2Sn$ complexes (M = Mn, Re) react with CH_3I with insertion into $M_2(CO)_{10}$ at an M–M bond (it is likely that $[(OC)_5M']_4Sn$ complexes are formed by this reaction during the synthesis of stannylenes, $[M'(CO)_5]_4Sn$ (M = Mn, Re) and add a bromine molecule and replace the THF molecule in $M(CO)_5THF$ yielding $M(CO)_5Sn[M'(CO)_5]_2$ complexes, where both types of bond are realized: a coordinative M=Sn bod and a M′–Sn σ-bond (see Scheme 3) [39]. It can be stated that the coordiantion tin bonds in $M(CO)_5{=}Sn{=}M(CO)_5$ keep the complex saturated and therefore it is not reative in reaction characteristics for stannylenes.

IR-Spectrometric studies

^{119}Sn Mössbauer spectroscopy has found a widespread application in th structural analysis of stannylene complexes and in the interpretation of the electronic arrangement around the tin atom [28].

IR spectroscopy gives much data concerning metal carbonyl complexes, because the number and strength of CO stretching vibrations reflect unambiguously both the structure and the electron state of the metal carbonyl fragment [41]. X-ray analysis was perfomred for some carbenoid complexes of metal carbonyls, and an octahedral structure with a carbenoid ligand on one of the vertices was confirmed for group VI metal carbonyls [28].

In this case, the IR data for the metal pentacarbonyl fragment show four vibration modes. $\nu(CO)$ $A_1^2 + B_1 + E$ with the frequency order $A_1^2 > B_1 > E \geqslant A_1^1$

and intensity ratio $E > A_1^1 > B_1 > A_2^1$ are observed in the IR and Raman spectra in accordance with $M(CO)_5$ C_{4v} symmetry [42]. As can be seen from Table 1, the complex spectra recorded in hexane, cyclohexane and THF show that all the vibration modes are sharply resolved and that the intensity ratio corresponds to theoretical calculations. The appearance of frequency B_1 in the IR spectrum is related to the fact that the stannylene bulk lowers the whole symmetry in the complexes and the local symmetry of $M(CO)_5$ fragments is not satisfied [43]. However, the IR spectra of the complexes studied confirm unambiguously the octahedral structure with a carbenoid ligand on one of the vertixes of the tetrahedron.

We tried to evaluate approximately the electron effects of the carbenoid ligands as well as their position in the series of known ligands. We also tried to evaluate the σ-donor and π-acceptor effects of the carbenoid ligands. The force constants k_1, k_2 and k_i were calculated by the Cotton–Kraihanzel methods; then the values of the Graham σ'- and π-parameters were calculated by the Graham's method [44]. According to the values of the σ-donor effect, the carbenoid ligands can be arranged as follows [36,43]: $C(OC_2H_5)CH_3$ $(-0.45) > PPh_3$ $(-0.27) > GeCl_2L$ * $(-0.24) > SnCl_2THF$ $(-0.11) > SnCl_2O(COCH_3)_2$ $(-0.04) > C_6H_{11}NH_2(O){=}SnO(0) > CO(+0.03) > Sn(OCOCH_3)_2O(COCH_3)_2$ $(+0.05) \approx SnS$ $(+0.06) > Sn(N{=}C{=}S)_2$ $(+0.92) > PbCl_2C_2H_5OCOCH_3$ $(+0.99) > Pb(OCOCH_3)_2O(COCH_3)_2$ $(+1.33)$.

According to the values of the π-acceptor effect, we obtained a somewhat different series: CO $(+0.69) > C(OC_2H_5)CH_3$ $(+0.55) > GeCl_2L$ * $(+0.44) > SnCl_2THF$ $(+0.38) > SnCl_2O(COCH_3)_2$ $(+0.31) \approx SnO$ $(+0.30) > SnS$ $(+0.28) > Sn(OCOCH_3)_2O(COCH_3)_2$ $(+0.22) > C_6H_{11}NH_2(0) > Sn(N{=}C{=}S)_2$ $(-0.62) > PbCl_2C_2H_5OCOCH_3$ $(-0.80) > Pb(OCOCH_3)_2O(COCH_3)_2$ (-1.06).

Thus, stannylenes are close to PPh_3, i.e. they are σ-donors and π-acceptors of medium power, but at the same time they are weaker than carbenes and germylenes. But it should be noted that dichloroplumbilene is practically unreactive in the free state.

Catalysis of olefin hydrosilylation and amine silylation by metal carbonyls

Platinum hydrochloric acid is the most common catalyst of hydrosilylation reactions [45]. At the same time, it is known that cobalt carbonyl, $Co_2(CO)_8$, is also effective for catalysing this reaction. In a review [46], papers published earlier concerning the catalysis of olefin hydrosilylation by $Co_2(CO)_8$ have been discussed in detail.

Taking as examples olefins, silanes and catalysts: metal carbonyls of the cobalt triad and their clusters [47,48], we studied this reaction in detail. It was found that metal carbonyls catalyse hydrosilylation of olefins with normal and increased electron density only [48]. In this case, the reaction proceeds at room temperature within 20–30 min, with quantitative yield of an adduct of normal structure ($Co_2(CO)_8$ concentration 0.05 M; $Rh_4(CO)_{12}$ concentration 0.0001 M):

$$RCH{=}CH_2 + HSiR_nX_{3-n} \longrightarrow RCH_2CH_2SiR_nX_{3-n}$$

($R = Me_3Si$, $C_3H_7C_{10}H_{21}$, Me_2NCH_2, $[(C_2H_5O)_3Si]_2NCH_2$, C_6H_5 $n = 0$, $X = Cl_2OC_2H_5$; $n = 1$, $X = Cl$, OC_2H_5)

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* L = benzothiazole.

By way of comparison, in the case of H_2PtCl_6 adducts with an iso-structure are formed along with adducts with a normal structure [45]. As one would expect, trichlorosilane is the most active and triethoxysilane the least active among these catalysts. However, in all cases the reaction proceeds under the aforementioned conditions with a quantitative yield of the β-adduct.

In general, only carbonyl compounds of the cobalt triad are active in this reaction [48–50]. It is shown for the first time that the rhodium cluster $Rh_4(CO)_{12}$ is the most active and that it is superior, in this respect, even to H_2PtCl_6 and other platinum compounds. The compound $RhCl(PPh_3)_3$ is considerably less effective compared to both rhodium compounds and, to a lesser degree, cobalt carbonyl.

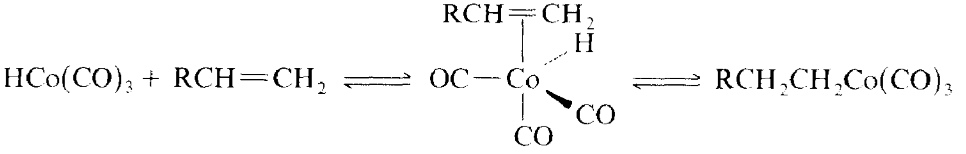
Taking as an example $C_4H_9CH{=}CH_2$ and $Me_3SiCH{=}CH_2$, we analysed the comparative activity of the compounds mentioned and obtained the following series: $Rh_4(CO)_{12}$ $(10^3) > H_2PtCl_6$ $(5 \times 10^2) > [Co(CO)_4]_2Sn$ $(1.8) > Co_2(CO)_8$ (1) $> PhCl(PPh_3)_3$ $(0.3) > CO_4(CO)_{12}$ $(0.2) \approx Ir_4(CO)_{12} > [Co(CO)_4]_2SnCl_2$ $(0.11) >$ $[Co(CO)_4]_4Sn > Rh_6(CO)_{16}$ (0).

The high activity of $Rh_4(CO)_{12}$ is not related to the cluster structure of the complex because a more complex rhodium cluster, $Rh_6(CO)_{16}$, is practically inactive under these conditions (20–30 °C). The compounds of tetravalent tin and cobalt carbonyl are also ineffective. All these data fit into a common scheme when it is considered that the intermediate $HM(CO)_4$ is the catalyst of the process. The compounds ($Co_4(CO)_{12}$, $Co(CO)_{4-n}SnR_{4-n}$, $Rh_6(CO)_{16}$ and others) under these conditions (2C–30 °C) react slowly with $HSiX_3$ are ineffective.

By analogy with the hydroformylation process, Chalk and Harrod [46] proposed a mechanism of catalysis of olefin hydrosilylation involving dissociative activation of alkenes:

$$Co_2(CO)_8 + HSiR_nX_{3-n} \rightleftharpoons HCo(CO)_4 + X_{3-n}R_nSiCo(CO)_4$$

$$HCo(CO)_4 \rightleftharpoons HCo(CO)_3 + CO$$

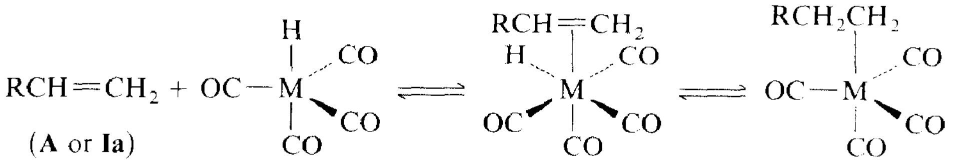


$$HCo(CO)_3 + RCH{=}CH_2 \rightleftharpoons OC{-}Co(H)(CO)_2(RCH{=}CH_2) \rightleftharpoons RCH_2CH_2Co(CO)_3$$

$$RCH_2CH_2Co(CO)_3 + HSiR_nX_{3-n} \longrightarrow RCH_2CH_2SiR_nX_{3-n} + HCo(CO)_3$$

But there are some objections to this mechanism: the reaction has no induction period, which is necessary for $HM(CO)_4$ dissociation; the existence of an intermediate in the open system in the absence of CO is hardly probable; and, as noted, the reaction proceeds successfully only for olefin with electron-donating substituents.

Therefore, we assume the associative activation of alkenes:



$$RCH{=}CH_2 + \underset{(\mathbf{A}\ \text{or}\ \mathbf{Ia})}{OC{-}M(H)(CO)_3} \rightleftharpoons (RCH{=}CH_2)M(H)(CO)_4 \rightleftharpoons OC{-}M(CH_2CH_2R)(CO)_3$$

The formation and stability of intermediate **A** depend on two factors. First, as the donor ability of the olefin becomes stronger, intermediate **A** becomes more stable; second, the stability of intermediate A related to its electron configuration. During the formation of complex A, there is a rearrangement of the *d*-orbitals of the Co atom in the $HCo(CO)_4$ bipyramid characterized by low-spin configuration of Co^{I} $3d^8$ electron (i.e. all eight electrons occupy energetically favourable orbitals) to an octahedral bipyramid where six electrons occupy the energetically favourably low t_{2g} orbitals $(dx_y, dx_z, dz_y)^6$ and two electrons occupy one of the two loosening orbitals $e_g(d_{z^2}, d_{x^2-y^2})^2$.

Because of this, complex A is unstable and tends to stabilize at the expense of electron removal with hydrides. This is accomplished by the transition of complex A into a complex having the normal coordination number 5, $RCH_2CH_2Co(CO)_4$, for Co^{I}. This mechanism explains the selectivity of carbonyl catalysts: hydride attacks the more electrophilic carbon atom; in the case of compounds with increased and normal nucleophilicity of the double bond, it is the carbon in the α-position, but in the case of compounds with decreased nucleophilicity it is the carbon in the β-position. This leads to the formation of adducts with a normal or an iso-structure, respectively.

In accordance with this scheme, we tried to activate cobalt carbonyl by additives of potential ligands, *n*- and π-donors. During the hydrosilylation experiments of trimethylvinylsilane by triethoxysilane a large number of siilar compounds has been studies and the following activity series has been obtained [51–53]: $(C_2H_5)_2O$ (13.57) > I^- (9.72) > CH_3COCH_3 (5.49) > Br^- (3.53) > $SbPh_3$ (2.41) > $C_6H_5C{\equiv}CC_6H_5$ (1.80) > THF (1.31) > CO(1) > Cl (0.67) > $AsPh_3$ (0.37) > C_5H_5N (0.32) > $SnCl_2$ (0.24) > PPh_3 (0.2) > $CS(NH_2)_2$ (0).

In accordance with the suggested mechanism of olefin associative activation, the activators should be potential ligands which decrease the electron density on the metal in intermediate A, thus stabilizing it. Indeed, as can be seen from the activity series, weak σ-donors (diethyl ether, THF, acetone) act as activators while strong σ-donors (thiourea and others) are its inhibitors. The relatively strong π-acceptors (iodine anion, triphenylstibine) are also process activators.

Except for THF, all the activators are most effective at 1/1 $Co_2(CO)_8$ ratio; the subsequent growth of the additive concentration causes a slight increase in the reaction rate but in the case of a two fold excess of activator the reverse process of reaction inhibition is observed. Also as the amount of THF increases, the reaction rate increases: with a ten-fold excess of THF, the rate increases by a factor of 30. The mechanism of action of most activators is identical because when two activators are combined, the reaction rate is determined by the more active additive; if their total concentration is twice as large as the catalyst concentration, inhibition begins. Synergism is observed only in the case of THF. The catalytic activity is especially high with a combination of iodine anion and THF. The $Co_2(CO)_8$ + THF + KI system is considerably superior because of its activity to cobalt carbonyl and approaches that of rhodium carbonyl.

When studying allylamine hydrosilylation in the presence of cobalt and rhodium carbonyls, we found that silylation of the amino group by triethoxysilane took place [54]:

$$CH_2{=}CHCH_2NH_2 + 3HSi(OC_2H_5)_3 \xrightarrow{-H_2} (C_2H_5O)_3SiCH_2CH_2CH_2N[Si(OC_2H_5)_3]$$

We studied this new catalytic reaction of metal carbonyls during silylation of ammonium as well as primary and secondary amines [56]. As a rule, the catalysts for this reaction are metal chlorides [57]. Cobalt carbonyl and especially the rhodium cluster are superior in activity to these catalysts, but their efficiency depends on the amine structure. It was found that the silylation efficiency depends on the amine basicity and as the basicity increases, the efficiency decreases. Aromatic amines and especially anilinechromium tricarbonyl are silylated best of all:

$$R_xR_yNH_n + nHSi(OC_2H_5)_3 \longrightarrow R_xR_yNH_m[Si(OC_2H_5)_3]_{n-1}$$

($x = 0$, $y = 0$, $m = 1$, $n = 3$; $x = 1$, $y = 0$, $n = 2$, $m = 0$; R $= C_6H_5Cr(CO)_3$, C_6H_5, CH_3, C_4H_9)

We studied the mechanism of this reaction. It is known that $Co_2(CO)_8$ in $HSi(OC_2H_5)_3$ solution converts to $(C_2H_5O)_3SiCo(CO)_4$. We isolated this complex quantitatively and showed that it is the final product of the aniline silylation reaction formed during the interaction with aniline [56]:

$$(C_2H_5O)_3SiCo(CO)_4 + C_6H_5NH_2 \longrightarrow C_6H_5NHSi(OC_2H_5)_3 + HCo(CO)_4$$

It is very probable that this compound is the reaction catalyst and that cleavage of its Si–Co bond by amines leads to silylamines.

$Co_2(CO)_8$ regeneration is a well-known reaction

$$2HCo(CO)_4 \longrightarrow Co_2(CO)_8 + H_2$$

In conclusion, we can only hope that the results of our study reported here will support the common opinion concerning the exclusive contribution of metal carbonyls to the development of transition metal chemistry, as well as to modern industrial homogeneous catalysis.

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