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Arenetetracobaltnonacarbonyls as π-arene complexes and clusters

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Abstract

The arenetetracobaltnonacarbonyls represent an interesting class of compounds combining the properties of π-complexes and clusters. The chemistry of these compounds is summarized. The methods of synthesis, structures and properties of these compounds are discussed; in some cases there differ markedly from the properties of mononuclear complexes.

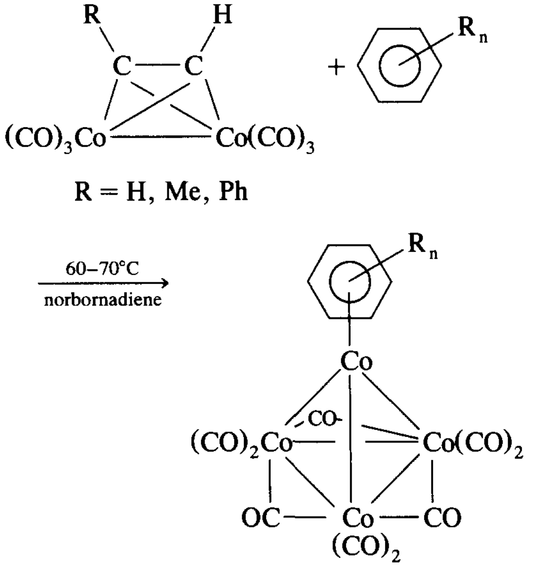
Keywords: Arene π-complexes; Cobalt clusters

1. Introduction

In contrast to the widely investigated mononuclear η^6-arene complexes of transition metals, clusters with aromatic ligands are little known. In most cases these complexes have been obtained by chance and their structures were determined only after X-ray investigations (see, for example, Refs. [1–10]). So far, only two groups of such compounds have been studied more or less systematically. The first are arenecarbonylcarbide clusters of ruthenium of the types (arene)$Ru_6C(CO)_{14}$ and $(arene)_2Ru_6C(CO)_{11}$. Reviews on the chemistry of these compounds are available (see, for example Refs. [11] and [12] and references cited therein.) The second group are arenecarbonyl clusters of cobalt of the type (arene)$Co_4(CO)_9$, which were prepared for the first time for benzene, anisole and their homologues by Pauson and co-workers more than 20 years ago [13], but no reviews on these compounds have appeared. During recent years, these complexes have been studied more in detail, mainly by the present authors, and we have now systemized the material on the chemistry of these compounds for the first time.

2. Synthesis and the structure of π-arenetetracobaltnonacarbonyls

The first work devoted to the synthesis of arenecarbonyl clusters of cobalt (η^6-arene)$Co_4(CO)_9$ (1) was published in 1973 [13] (although a preliminary communication by the same authors, without giving details of the experiment, had appeared in 1971 [14]). The complexes 1 were prepared for benzene, anisole and their homologues by heating cobalt–acetylene complexes in the arene as solvent in the presence of norbornadiene. In the case of solid arenes, isooctane has been used as the solvent [13]:



1

The yield of the products was 15–49%. In the same work a simpler method of obtaining the complexes 1 using $Co_4(CO)_{12}$ was proposed:

$$Co_4(CO)_{12} + \text{arene} \xrightarrow{60\text{–}70^\circ C} \mathbf{1}$$

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However, in this case the yield was lower. Still lower was the yield in an attempt to use $Co_2(CO)_8$ in the reaction:

$$Co_2(CO)_8 + \text{arene} \xrightarrow{60\text{–}70°C} \mathbf{1}$$

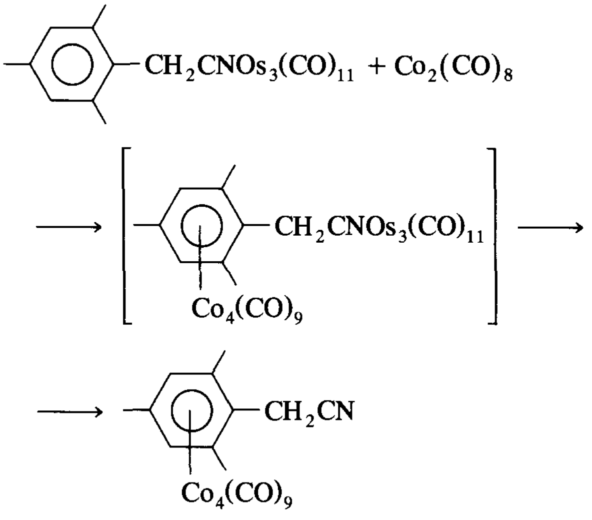
It should be noted that all the reactions with cobalt carbonyls have been carried out in an arene as solvent.

Other workers [15] have also investigated the interaction of $Co_4(CO)_{12}$ with an excess of arene on heating, the yields being 2–35%.

The application of the ligand as a solvent makes these methods suitable only for liquid and cheap arenes; the use of isooctane as a solvent did not give a good yield. Considerable difficulties also arose from using as a starting compounds the acetylene complexes of cobalt or $Co_4(CO)_{12}$, which had to be previously obtained from $Co_2(CO)_8$. Therefore, with the aim of preparing arene cobalt clusters of the type **1** with various arene ligands, including expensive and solid ones, an attempt was made to carry out the synthesis by the direct refluxing of arenes and $Co_2(CO)_8$ in saturated hydrocarbons. Hexane proved to be the optimum solvent, which not only allowed us to decrease sharply the amount of arene used, but also in some cases gave an increase in the yields of up to 60% [16,17]. In the course of this reaction, the starting $Co_2(CO)_8$ is converted rapidly enough into $Co_4(CO)_{12}$. It should be noted that in refluxing pentane the reaction occurs very slowly, while the refluxing in heptane leads to considerable decomposition and lower yields. In a few cases the yields increased by refluxing the reactants in a mixture of heptane and hexane (see Table 1). By working under these new reaction conditions, a large number of arenetetracobaltnonacarbonyl clusters of the type **1** have been prepared, including those with functional groups in a side chain [16–18] (see Table 1):

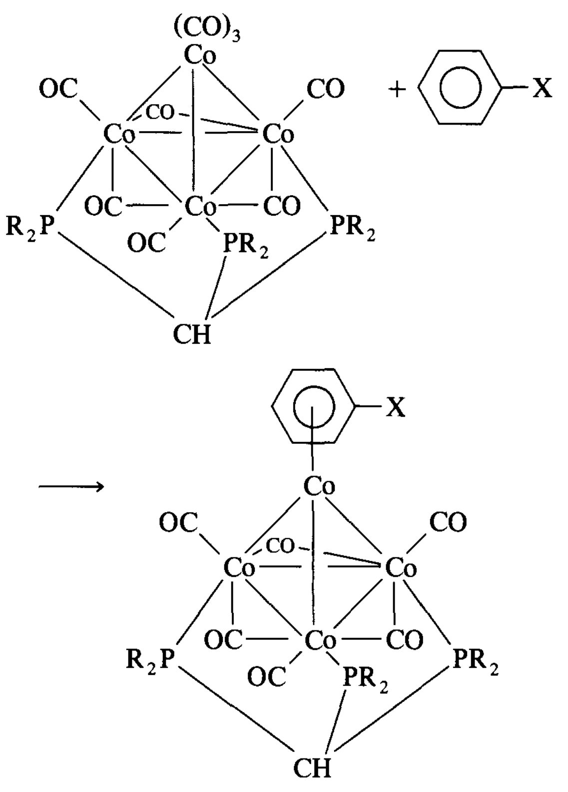
$$\text{arene} + 2Co_2(CO)_8 \xrightarrow[-7CO]{\text{hexane, }\Delta} (\text{arene})Co_4(CO)_9$$

In the same way, a number of heterometallic derivatives have been prepared based on arenes containing organometallic fragments, namely **1v**–**c′** and **1h′**–**n′** [17–21], and also complexes with phenyl-containing cyclosiloxanes, **1t** and **u** [22]. It should be mentioned that the presence of electron-withdrawing groups in the aromatic ring hinders the reaction. Thus, in the case of benzophenone or ethyl benzoate, only traces of the products were formed [16,17]. In the presence of CN or COOH substituents in the ligand the reaction was more complicated, the compounds **1q** and **r** with a CN group in a side-chain being obtained only with preliminary protection of the nitrile group. In this case the protection was removed in the course of the reaction [21,23], for example,



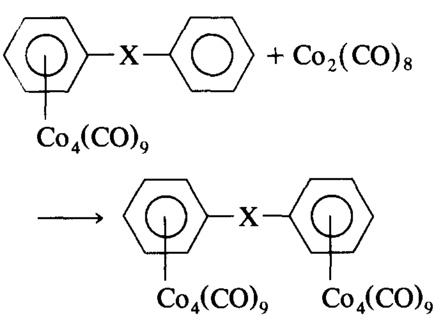
1r

The synthesis of two derivatives related to complexes **1** by the substitution of three CO groups in the Co_4 cluster, containing the tripod ligand [24–26] should also be noted:



X = H, R = H [24]
X = Me, R = Ph [25,26]

It is interesting that the application in the reaction with $Co_2(CO)_8$ of polyaromatic compounds (biphenyl, dimesitylpropane and diphenyl- and triphenyl/methane, and also Ph_2SiMe_2 and Ph_2O), even after long refluxing with a large excess of cobalt carbonyl, led only to the monocluster products **1c**–**e**, **g**, **o** and **s** [27–29]. It was found that, as a rule, to obtain the bicluster derivatives **1d′**–**g′** and **o′**, it is necessary to introduce the isolated monocluster complexes again in the reaction with $Co_2(CO)_8$, for example,



$X = CH_2, CHPh, SiMe_2$

In the case of diphenyl ether, however, even this did not lead to success [29].

The structure of complexes **1** proposed by the first authors [19] has been confirmed by X-ray analysis of the complex with benzene and also of the mixed crystal of complexes with *o*- and *m*-xylene [30]. The structure of these compounds represents a somewhat distorted cobalt tetrahedron, where one of the corners is bonded with arene and others are connected in pairs with bridging CO and carry two terminal CO groups (equatorial and axial):

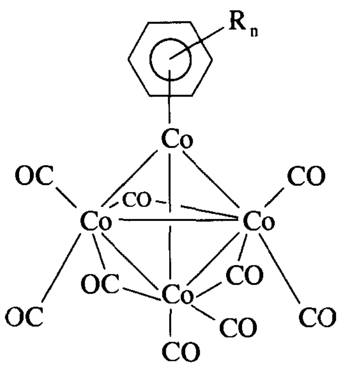


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Table 1
Reaction times and yields of the complexes $(arene)Co_4(CO)_9$ (**1**)

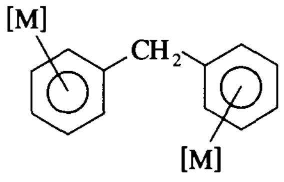
No.	Arene	Time of reaction (h)	Yield (%)
1a	$1,3,5\text{-}Me_3C_6H_3$	22	55
b	C_6Me_6	14	60
c	Ph_2	16	18
d	Ph_2CH_2	22	31
e	Ph_3CH	22	10
f	*p*-$C_6H_4(CH_2)_{10}$	22	48
g	$Mes(CH_2)_3Mes$	14	52
h	$PhCH{=}CH_2$	16	35
i	$Ph(CH_2)_2CH{=}CH_2$	14	55
j	$Ph(CH_2)_3CH{=}CH_2$	14	44
k	$PhCH{=}CHPh$	32	16
l	$Ph(CH_2)_2Br$	14	42
m	$Mes(CH_2)_2OH$	14	25 [a]
n	$C_6Me_5CH_2OH$ [b]	14	36 [a]
o	Ph_2O	30 [c]	16
p	$Mes(CH_2)_3COOEt$	7	36
q	$PhCH_2CH_2CN$ [de]	–	–
r	$MesCH_2CN$ [bd]	–	40
s	Ph_2SiMe_2	24 [c]	28
t	*cis*-$(PhMeSiO)_3$	16	23
u	*trans*-$(PhMeSiO)_3$	16	16
v	$PhCH_2Fe(CO)_2Cp$	22	41
w	$Ph(CH_2)_2Fe(CO)_2Cp$	22	37
x	$Ph_2Cr(CO)_3$	24	2
y	$Ph_2CH_2Cr(CO)_3$	24	9
z	$Ph_3CHCr(CO)_3$	24	2.5
a′	$Mes(CH_2)_3MesCr(CO)_3$	22	30
b′	$Ph_2SiMe_2Cr(CO)_3$	24	1.3
c′	$[Mes(CH_2)_2MesMn(CO)_3]BF_4$ [e]	–	–
d′	$Ph_2Co_4(CO)_9$	32	6
e′	$Ph_2CH_2Co_4(CO)_9$ [b]	32	10
f′	$Ph_3CHCo_4(CO)_9$	32	5
g′	$Mes(CH_2)_3MesCo_4(CO)_9$	24	15
h′	$PhCH(OH)C_5H_4FeC_5H_5$ [b]	22	38
i′	$PhCH(OH)C_5H_4RuC_5H_5$	16	14
j′	$PhCH(OH)C_5H_4OsC_5H_5$	16	13
k′	$PhCH_2CH_2CNOs_3(CO)_{11}$	6	14
l′	$MesCH_2CNW(CO)_5$ [e]	–	–
m′	$MesCH_2CNMn_2(CO)_9$ [e]	–	–
n′	$[MesCH_2CNFe(CO)_2Cp]PF_6$ [e]	–	–
o′	$Ph_2SiMe_2Co_4(CO)_9$	24	17

[a] For crystallized product.
[b] X-ray analysis is available.
[c] In hexane–heptane (2 : 1).
[d] The complex is obtained by an indirect route.
[e] Identification by IR spectrum.

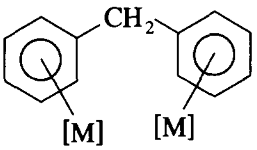
An analogous structure has also been found for the complex with triptycene [31]. Later, more detailed X-ray investigations were carried out for some of the complexes that we synthesized, in particular complexes $(CO)_9Co_4C_6Me_5CH_2OH$ (**1n**) and $(CO)_9Co_4MesCH_2CN$ (**1r**) [23], $(CO)_9Co_4PhCH(OH)C_5H_4FeC_5H_5$ (**1h′**) [18] and also the bicluster complex $Ph_2CH_2[Co_4(CO)_9]_2$ (**1e′**) [32]. It was found that the plane of the aromatic ring in all cases is virtually parallel to the plane of the cluster's base to that the complexes $(\eta^6\text{-arene})Co_4(CO)_9$ can be considered as a kind of sandwich compound, where one cobalt atom is bonded with an arene ligand on one side and with the tricobalt metallocycle on the other [32]. The geometry of these compounds can be described as a distorted tetrahedron or as a trigonal pyramid. The latter is in agreement with the marked shortening of the Co–Co bond lengths (by ca. 0.04 Å) in the base of the tetrahedron in comparison with the lateral bonds. This phenomenon can be also caused by the tightening effect of the bridging carbonyl groups.

One more geometric peculiarity of the clusters **1** becomes apparent in a difference of the length of the bonds to equatorial and axial CO groups. The lengthening of axial bonds in comparison with equatorial bonds (0.016–0.032 Å) is not large but is clearly expressed in all the structures studied.

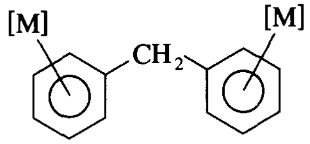
To conclude the discussion of X-ray data it is appropriate to note that at least three versions of the conformation of the bicluster derivative of diphenylmethane $(CO)_9Co_4C_6H_5CH_2C_6H_5Co_4(CO)_9$ (**1e′**) had to be taken into account as shown where **A** is *S-cis-S-trans*, **B** is *S-cis-S-cis* and **C** is *S-trans-S-trans*.



A



B



C

The X-ray investigation has shown that for the complex **1e′** in the crystal the conformation **C** (*S-trans-S-trans*), which was the least spatially hindered, is realized [32]. It is interesting that the same type of conformation was found also for the bischromiumtricarbonyl complex of diphenylmethane, $(CO)_3CrC_6H_5CH_2C_6H_5Cr(CO)_3$ [32], for which the conformation of the type A had been proposed earlier [33]. Thus, the *S-trans-S-trans* conformation is realized in a crystal independently of the size of the metal-containing group, $Cr(CO)_3$ or $Co_4(CO)_9$ [32]. In addition it should be noted that the geometry of the diphenylmethane ligand in both complexes almost coincides with that of free diphenylmethane [34].

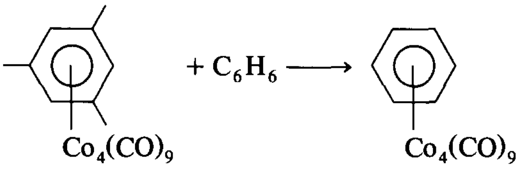
The compounds **1** are, as a rule, dark-green, almost black crystalline solids, stable in air and soluble in organic solvents, resulting in dark-green or brown–green solutions. The stability of these clusters is connected with the rule of a 60-electron configuration for tetrahedral clusters.

It is interesting that in spite of the considerable size, the cluster with a mesitylene ligand (**1a**) proved to be suitable for the formation of an inclusion compound with γ-cyclodextrin [35].

Finally, it should be noted that the stable and accessible cluster **1a** was the compound most often used for the investigation of the properties of these compounds [16,17,36,37].

3. Arenetetracobaltnonacarbonyls as arene π-complexes

In considering arenetetracobaltnonacarbonyls **1** as arene π-complexes, it is useful to compare their properties with those of mononuclear arene π-complexes. Thus, for example, under thermal conditions the aromatic ligand in **1** can be replaced by another arene [16,17], as it can in arenechromium tricarbonyls:



1a

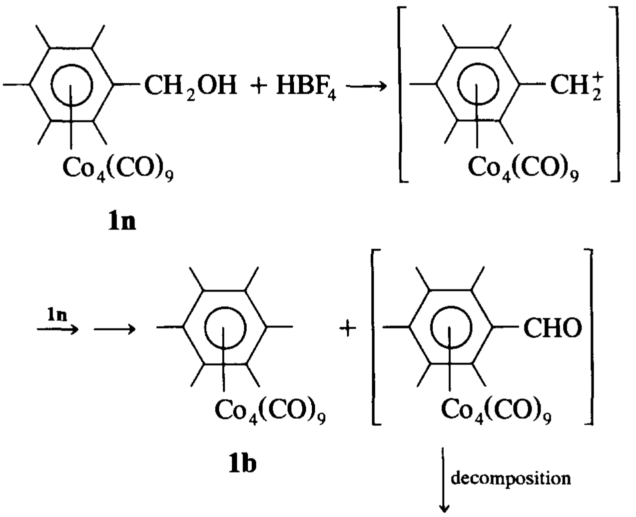
The study of the thermochemistry of complexes **1** with benzene, mesitylene and hexamethylbenzene ligands has shown that the enthalpy of the arene–Co bond increases in the same sequence. This shows that the stability of complexes **1** increases with the introduction of additional methyl substituents into the benzene ring [38].

The thermal reaction of complexes **1** with phosphines leads only to rupture of the Co–arene bond, whereas with phosphites $P(OR)_3$ substitution of one CO group in the cluster framework occurs [15]. At temperatures > 70°C in heptane the arene ligand can also be substituted by CO, which is typical of mononuclear arene complexes.

The interaction with electrophiles was studied with the complexes **1a** and **b** with mesitylene and hexamethylbenzene ligands [17]. Unlike arenechromiumtricarbonyl analogues, the complexes **1** are less strong bases and do not undergo protonation by trifluoroacetic acid in CH_2Cl_2, their IR spectra in the metallocarbonyl region remaining unchanged. Complexes **1a** and **b** react slowly with $HgCl_2$ at room temperature, and a light-grey adduct precipitates after 20–30 min of refluxing in CH_2Cl_2 [17]; under the action of $SnCl_4$ on **1a** and **b**, a light-blue adduct precipitates after 4–5 min. It should be noted that arenechromiumtricarbonyls react with Lewis acids at approximately the same rate (see, for example, Ref. [39]).

Nucleophiles such as alkalies or amines decompose the complexes **1** even at room temperature [16], i.e. the Co–arene bond proved to be considerably less resistant towards the action of nucleophiles than the Cr–arene bond in arenechromiumtricarbonyls [40,41].

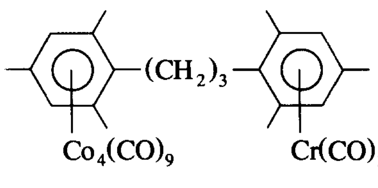
The study of the chemical properties of complexes **1** containing functional groups in a side-chain is also interesting [17]. First we investigated the possibility of stabilization of the neighbouring carbocationic centre by the tetrahedral cluster fragment $Co_4(CO)_9$ and compared the results with the stabilization by the $Cr(CO)_3$ group [42]. The complexes **1** with benzyl or 3,5-dimethylbenzyl alcohols proved to be insufficiently stable, and therefore the formation of the α-carbocation was studied with the more stable complex **1n** with pentamethylbenzyl alcohol [17]. Its protonation has shown that, unlike carbocations with the $Cr(CO)_3$ group [42], the carbocation generated is unstable and, just as the cation $C_6Me_5CH_2^+$ of the free ligand [43], it disproportionates easily, presumably according the following scheme:

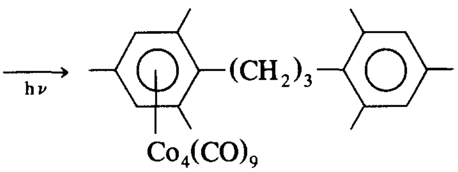

1n

1b

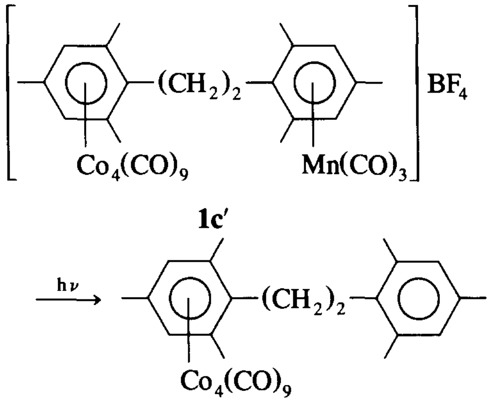
The only product isolated after this reaction was the complex **1b** [17]. Probably the complex with an aldehyde group decomposes rapidly, being very unstable, like the derivatives of benzophenone and ethyl benzoate mentioned above. Thus, it can be concluded that the $Co_4(CO)_9$ group, in contrast to the $Cr(CO)_3$ group, does not stabilize the neighbouring cationic centre. This observation, together with the sensitivity to the action of nucleophiles and indifference to CF_3COOH described above, and also the instability of the complexes containing electron-withdrawing groups, points to a greater accepting strength of the $Co_4(CO)_9$ group in comparison with the $Cr(CO)_3$ group. The NMR spectra also support that assumption. In the ^1H NMR spectrum of the complex **1a** the signals of the aromatic and even the methyl protons were observed further downfield than those of mesitylenechromiumtricarbonyl [17,44]. This effect may be connected with the conclusion about the stronger accepting ability of $Co_4(CO)_9$ group compared with the $Cr(CO)_3$-group mentioned above, although, of course, differences in anisotropy of the metal–arene bond in these compounds cannot be completely excluded.

Useful information has been obtained in investigations of the behaviour of complexes with polyaromatic ligands. Thus, under UV irradiation in heptane or diethyl ether, the complex **1a**′, containing both $Co_4(CO)_9$ and $Cr(CO)_3$ groups, slowly loses the $Cr(CO)_3$ group [17]:

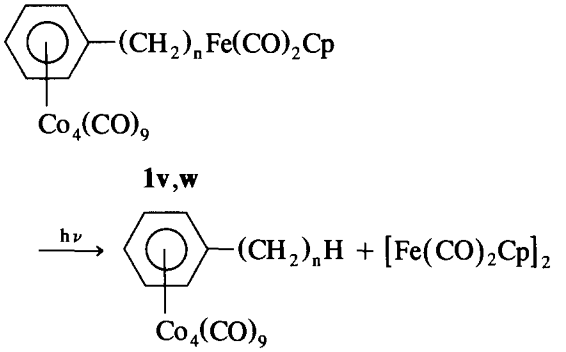

1a′


1g

This demonstrates the greater photochemical stability of the arene–$Co_4(CO)_9$ bond than the arene–$Cr(CO)_3$ bond. It should be remembered that the trend is the reverse with respect to the action of nucleophiles. The stability of the arene–$Co_4(CO)_9$ bond is also higher than that of the arene–$Mn(CO)_3$ bond. This has been shown by irradiation of the cationic complex **1c**′ [45]:


1c′

In this connection, it is not surprising that the arene–$Co_4(CO)_9$ bond proved to be more stable under UV irradiation than the C–Fe σ-bond in the side-chain [17]:


1v,w

4. Arenetetracobaltnonacarbonyls as carbonyl clusters

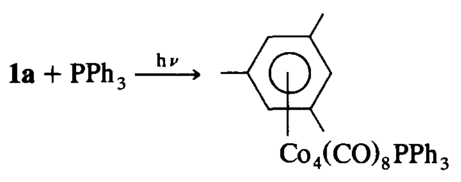
Being carbonyl complexes, the IR spectra of the clusters **1** show five bands in the region 1800–2100 cm^{-1}, one of which corresponds to the bridging carbonyl groups (in the region 1800–1850 cm^{-1}). The investigation of **1a** as an example of these complexes by ^{13}C NMR spectroscopy at room temperature shows that the signals of the carbonyl carbons appear as one singlet, indicating rapid interconversions between all the CO ligands [17]. At low temperature (−35 to −70°C), these spectra showed three signals of equal intensity corresponding to three kinds of CO ligands in the molecule, i.e. axial, equatorial and bridging [46,47]. The rapid interconversion at room temperature was also confirmed by ^{17}O NMR spectroscopy [44].

The specificity of the cluster core $Co_4(CO)_9$ in forming complexes with arenes was distinctly observed in a comparative study of the influence of various organometallic groups on the ring π-current in π-arene complexes with [10]paracyclophane as ligand [48]. Earlier, the investigation of mononuclear complexes of some paracyclophanes had shown the upfield shift of signals not only of the arene but also of the bridging CH_2 protons, and it was concluded that there was a decrease in the ring π-current upon η^6-coordination [49,50]. However, the study of the ^1H NMR spectrum of [10] paracyclophane$Co_4(CO)_9$ (**1f**) gave an unexpected result: an upfield shift was found only for the arene protons, whereas the signals of the bridging CH_2 groups moved downfield [48]. Of course, it cannot be concluded that there is an increase in the ring π-current on coordination, and it has been suggested that the theoretical concept regarding the ring π-current and the properties of the magnetic anisotropy cone throughout the space under and over the plane of the arene ring requires more detailed consideration [48].

The specificity of the ^1H NMR spectra of tetracobaltnonacarbonyl derivatives of diphenyl-containing ligands Ph_2CH_2 [51] and Ph_2SiMe_2 [29] has also been noted. Thus, for example, coordination with a $Co_4(CO)_9$ group (complexes **1d** and **1e′**) moves the signal of the methylene protons of diphenylmethane in the opposite side in comparison with the chromiumtricarbonyl analogues ($\Delta = 0.29$ and -0.25 to -0.26 ppm, respectively) [51]. At the same time, the signal of silicon in the ^{29}Si NMR spectrum of the complex **1s** is moved in the same direction as that of the $Cr(CO)_3$ analogue, but much more markedly (4.46 and 3.67 ppm, respectively) [29].

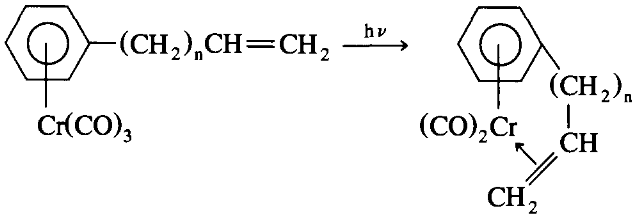
The study of the UV spectra of complexes **1** has shown that in these compounds a transfer of the charge occurs from the cobalt atom connected with arene to the three other cobalt atoms along the Co–Co bonds [24]. Clusters **1** exhibit reversible $1e^-$ reduction and irreversible $2e^-$ reduction by cyclic voltammetry, and also irreversible $1e^-$ oxidation [24].

The substitution of CO ligands in clusters **1** occurs differently from that in arenechromiumtricarbonyls, because here the arene and CO ligands are bonded with different metal atoms. The photochemical reaction of **1a** with PPh_3, unlike the thermal reaction described above, leads to the substitution of only one CO for the molecule of triphenylphosphine [17]:

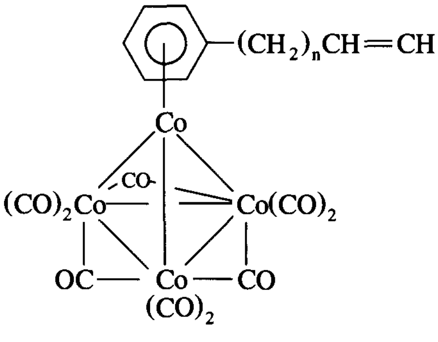


It is interesting that even after prolonged irradiation of **1a** in the presence of a tenfold excess of PPh_3, no product with two phosphine ligands in the molecule was detected. For the monophosphine derivative, in which the arene and the phosphine ligands are bonded with different cobalt atoms, the proton signal of the arene protons in the ^1H NMR spectrum is nevertheless shifted upfield by 0.13 ppm in comparison with the initial **1a**, indicating a weak but distinct transmission of the influence along the Co–Co bonds [17].

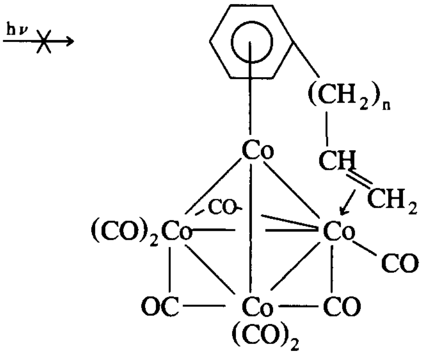
With the complexes **1i** and **j**, containing a double bond in the ω-position, an attempt was made to prepare the chelates analogously to those of the corresponding arenechromiumtricarbonyls [52], where the formation of chelates is well known with different bridge lengths ($n = 2$–4) between the arene ring and the unsaturated group:



In the case of clusters **1** it turned out that even prolonged irradiation of **1i** and **j** in heptane, benzene or diethyl ether did not lead to any novel products and only the starting compounds were recovered almost completely. At the same time, irradiation in THF leads to unusually vigorous decomposition [17]:



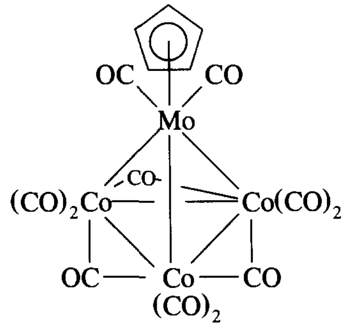
1i, n = 2
1j, n = 3



The instability of the generated chelate is probably due to the absence of CO groups available for substitution at the Co atom connected with arene. At the same time, the corresponding chelate is apparently formed on UV irradiation in THF of the complex **1p**, containing an ester group in the ω-position, since a band at 1590 cm^{-1} appears in the IR spectrum of the reaction mixture, which is observed together with the bands from the starting compound and can be ascribed to the coordinated ester group. However, an attempt to separate the product from the starting compound resulted in decomposition [17].

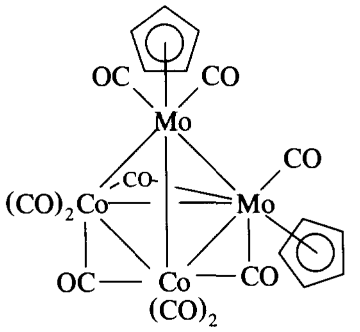
One of the most characteristic reactions of organometallic clusters is the replacement of a metal-containing top ML_n by another group $M'L_m$ [53]. It was found that the interaction of **1a** with the dimeric molybdenum derivative $[Mo(CO)_3Cp]_2$ in heptane under reflux led to the formation of the clusters **2** and **3**, corresponding to the replacement of one or two Co-containing tops in the initial complex [36]:

$$\mathbf{1a} + [Mo(CO)_3Cp]_2 \longrightarrow$$



2

+



3

However, after the action of $Mn_2(CO)_{10}$, $Fe_2(CO)_9$ or $[Fe(CO)_2Cp]_2$ under various experimental conditions, either the initial **1a** was recovered or, under more rigorous conditions, total decomposition occurred. The reaction with nickelocene led to complete declusterization [36]:

$$\underset{\mathbf{1a}}{2Me_3C_6H_3Co_4(CO)_9} + 6Cp_2Ni \xrightarrow{-2CO} 6CpCo(CO)_2 + 3[Ni(CO)Cp]_2 + 2Me_3C_6H_3$$

The structures of both compounds containing Co and Mo, **2** and **3**, were confirmed by X-ray analysis [36].

The complex **2** can also be prepared in higher yield by the interaction of $Co_2(CO)_8$ with $[Mo(CO)_3Cp]_2$. It is interesting that in this case the product **3** is formed only in a trace amount, i.e. in this reaction the direct addition of the cobalt carbonyl to the molybdenum dimer does not proceed, but their preliminary splitting to mononuclear fragments occurs. It is noteworthy that refluxing of a mixture of **2** and mesitylene in heptane results in a reaction which to some extent represents the reverse of the process by which **2** (and **3**) is formed and is some kind of disproportionation. The molecule of the arene seems to gather again to itself the tetrahedral cluster core $Co_4(CO)_9$ [36]:

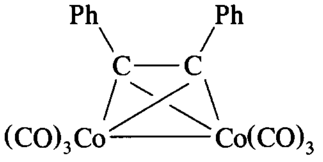
$$\mathbf{2} + Me_3C_6H_3 \longrightarrow \mathbf{1a} + [Mo(CO)_3Cp]_2$$

Hence the direction of this reaction depends on which reactant (Mo dimer or mesitylene) is in excess.

The complexes **1** do not exchange CO for tolane photochemically [17]. At the same time, the thermal interaction with PhC≡CPh on refluxing in heptane affords a mixture of products [37]:

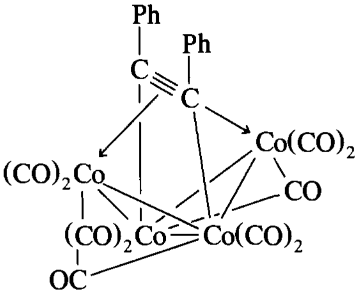
$$\mathbf{1a} + PhC{\equiv}CPh$$

$$\longrightarrow$$



4

+

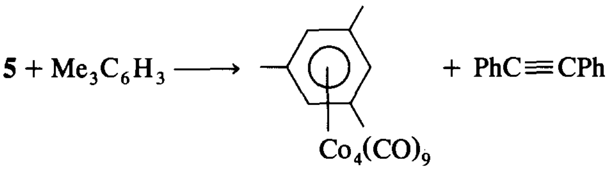


$$+ C_6Ph_6$$

5

After chromatographic separation of the reaction mixture, three main products were isolated: the binuclear complex **4**, the tetranuclear complex **5** with a "butterfly" structure and hexaphenylbenzene, formed as a result of the cyclotrimerization of tolane. Thus, the clusters **1**, and also arenechromiumtricarbonyls [54], are catalysts for the cyclotrimerization of tolane into hexaphenylbenzene (the same properties are typical also for cobalt carbonyls [55]). Both the isolated complexes, **4** and **5**, were known earlier, but have been prepared in this way for the first time. The formation of the cluster **5** shows that, after the cleavage of the weakest Co–arene bond in the initial compound, the $Co_4(CO)_9$ cluster core is partly retained and subsequently interacts with the triple bond of the tolane molecule. This addition, by virtue of the electronic requirements of the metal atoms, is accompanied by the rupture of one Co–Co bond in the tetrahedral cluster with transition to the "butterfly" structure and capture of one CO molecule from the decomposing part of the initial compound. In parallel, the cluster particle $Co_4(CO)_9$ partly decomposes into fragments, and its decomposition products form with tolane the complex **4**. If 1 equiv. of Ph_2C_2, not an excess, is used in the reaction, the products ratio changes in favour of complex **5** [37].

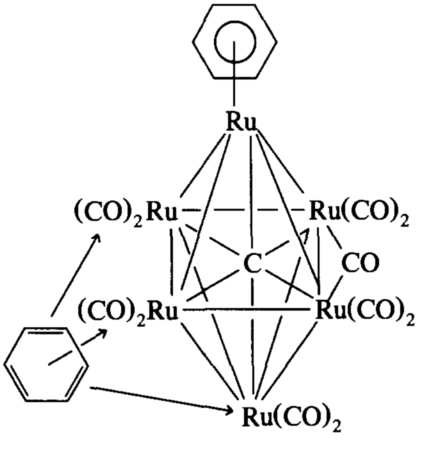
It was of interest to study the possibility of a reconversion of the cluster **5** into the initial compound **1**. In fact, if **5** is refluxed with mesitylene in heptane, the tetrahedral cluster **1a** is re-formed [37]:

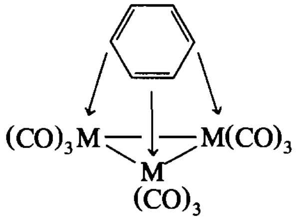


1a

This result shows once again that the structure of the tetrahedral cluster core $Co_4(CO)_9$ is readily restored in the presence of the arene. The direction of the reaction thus depends also in this case on the excess of the reactant employed (tolane or mesitylene).

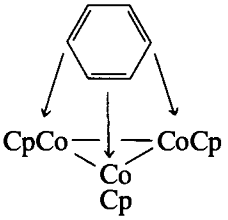
The most reinstable property of a number of arene clusters is the ability of some of them to give not only η^6-coordination of the arene ligand, when the arene ring is bonded only with one metal atom of the cluster fragment, but also $\eta^2:\eta^2:\eta^2$-coordination of an arene with three metal atoms. Such a result was obtained for the first time with carbonylcarbide octahedral clusters of ruthenium [56], and also with trigonal complexes of Ru and Os [56,57]:





M = Ru, Os

With regard to the cobalt clusters, $\eta^2:\eta^2:\eta^2$-coordination of an arene ligand was found only for 48-electron trigonal clusters with cyclopentadienyl ligands [58,59]:



In the case of 60-electron tetrahedral carbonyl cobalt clusters of the type **1**, such a coordination of the arene ligand has not yet been realized, but it is not excluded that it will be found in future.

5. Conclusion

The coordination of arenes with cobalt carbonyl tetrahedra, $Co_4(CO)_9$, gives stable 60-electron clusters, which make it possible to obtain a wide range of their derivatives. The properties of these compounds have still been little studied, but those data which are available show that they combine the properties of both π-arene complexes and clusters. In some cases their behaviour differs markedly from that of mononuclear π-arene complexes. These properties can be exploited in further investigations.

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