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# CONDITIONS FOR THE FORMATION AND STABILISATION OF THE CARBON–TRANSITION METAL σ BOND

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## I. INTRODUCTION

The organic chemistry of the transition metals is a new, rapidly developing branch of chemistry, which already forms the subject of hundreds of investigations, and a large number of complexes of different types have been prepared. Following the discovery of ferrocene and other metallocenes there was the discovery of the analogously constructed sandwich bisarene complexes, cyclopentadienylcarbonyl and arenecarbonyl complexes were obtained, and from about 1957 the area was considerably extended owing to the use of a wide range of alkenes, both cyclic and acyclic. The existences of complexes containing alkenes from ethylene to tropylene suggests that from two to seven carbon atoms from a single molecule can be bonded simultaneously with a metal atom. The best combinations of ligands in such complexes, which make them the most stable, are the combinations of alkenes with CO groups, phosphines, amines, sulphides, acetylacetone, or simple electronegative atoms, such as halogen. Recently, purely alkene complexes have also been obtained and shown to be considerably less stable than the mixed complexes. It was found that all transition metals — without exception — are able to form π-complexes with alkenes. Usually the Dewar–Chatt scheme [1,2] is employed to explain the structure of these compounds. Several reviews and monographs devoted to this field have appeared, among which can be recommended the reviews of Wilkinson and Cotton [3] and Dyatkina [4] on the cyclopentadienyl and arene complexes, Nesmeyanov and Perevalova [5] and Rausch [6] on ferrocene chemistry, Bennett [7], Guy and Shaw [8], the monograph of Fischer and Werner [9] on alkene and alkyne π complexes of the transition metals, the review of Treichel and Stone [10] on fluoroalkyl derivatives of metals. The review article of Fritz [12] is devoted to spectroscopic results, and the theoretical side of the problem has been stated in the books by Orgel [13] and Ballhausen [14], both of which have been published in Russian.

Simultaneously with the study of the conditions for the formation of π complexes many of the conditions for the formation and stabilisation of covalent σ-bonded derivatives of the transition metals were found and although the problem of the carbon–transition metal bond has not been solved completely, the empirical data which have been accumulated allow some conclusions to be drawn. Besides the preparation of many mixed complexes which include a σ-bound organic group, the conditions for the σ derivative →

→ π complex transition and the reverse are now known. A repeat study of some structures showed that in several instances where the π complex structure has been proposed earlier, actually there is the addition of metal to a system of double bonds of the Diels–Alder type and the bonding with the organic molecule is effected by one π and two σ bonds. A large group of fluorocarbon σ complexes of various types has been obtained. Besides comparatively old reviews, a book [15], and Cotton's review [16], the material on the σ-bonded derivatives of the transition metals has not been surveyed. The review we offer is an attempt at such a survey and embraces the literature up to December 1964. The tables do not exhaust the available information, but only illustrate it.

## II. THEORETICAL PREMISES

The problem of the transition metal–carbon covalent bond remained an enigma for a long time. As is well known, the hydrocarbon σ derivatives of most transition metals are almost impossible to isolate in a pure state; they are unstable, exist only at low temperatures, are sensitive to oxygen and atmospheric moisture. The latter is inherent, however, in an alkyl derivative of certain non-transition metals, for example, the alkali metals, but is not characteristic of derivatives of Hg, Sn, Pb, etc. Furthermore, the alkyl derivatives of the main groups have a considerably better thermal stability than their transition metal analogues.

The strength of a covalent bond depends on the extent of the overlap of the valence orbitals of both atoms. The instability of the covalent derivatives of the transition metals is connected with insufficient overlap of the completed 3*d*, and also the 4*s* and 4*p* orbitals of the metal in the first transition series with the typical σ orbitals of the ligands, owing to the small dimensions of these orbitals of the metal. Confirmation of the correctness of this conclusion is provided by the fact of the formation of alkyl derivatives of metals with *d* orbitals of the largest dimensions. However, it was acknowledged that the difference in the size of the overlap integrals is not very great and possibly the difficulty of obtaining these compounds is explained, not by their thermodynamic instability, but by their high reactivity. If that is so, when the covalent bond is formed as a donor–acceptor bond, the great strength of the bond facilitates a greater polarisability of the donor molecule and the great affinity of the acceptor ion for an electron. With increase in the charge on the metal ion, its electronegativity, within the limits of a single period of the Periodic System, and also the polarisability of the ligand, the covalency of such ordinary bonds should increase [13].

The transition metal–carbon bond can be either a simple ordinary bond or a bond of multiple character. Carbonyls, cyanides, etc. are examples of comparatively stable and long-known carbon derivatives of the transition metals. The order of the metal–carbon bond in the compounds of these classes is greater than unity, thanks to additional overlap of symmetry-suitable filled orbitals of the metal and free orbitals of the ligand. Fig. 1 shows the different ways of representing the increase in the multiplicity of the metal–carbon bond in carbonyls.

The additional overlap is termed a π bond or dative component of the bond. Usually π bonding, and consequently the formation of bonds of significant multiplicity is an

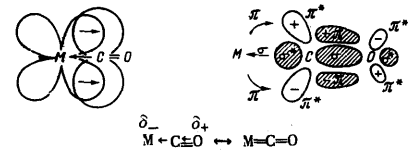



Fig. 1. Different methods of representing the increased multiplicity of the metal–carbon bond in metal carbonyls.

ability of an electronegative atom in the vicinity of carbon, such as oxygen in carbonyls, nitrogen in cyanides, etc. In explaining the properties of the derivatives of transition metals, the π component of the bond plays an important part. The excess of negative charge is removed from the metal with its aid to the ligand and double-bond character appears, which in total leads to the strengthening of the bond and increases the stability of the molecule as a whole. Actually, without such an assumption of reverse transfer of electrons from the metal to the ligand it would be difficult to understand why in the majority of their most stable derivatives transition metals have an electron configuration of a noble gas, that is, they receive from 8 to 15 electrons, which generally is not characteristic of metals. The reverse transfer does not occur with simple alkyl derivatives, since they do not have low-lying free orbitals. Furthermore, the establishment of a cyclic configuration due to σ groups alone is evidently impossible from even steric considerations.

All this does not explain, however, why the alkyl derivatives of transition metals should be less stable than the alkyl analogues with non-transition metals and why just carbon is so poorly bonded with the transition metal. As will be shown below with the help of experimental data, the transition metals can under certain conditions form stable σ bonds with carbon. In such molecules, in addition to the σ bound group stabilising ligands are present — carbonyl, phosphine, cyanide, or cyclopentadienyl groups. These mixed complexes are often very stable and represent a contrast to the extremely unstable simple organic derivatives of the $MR_n$ type.

Chatt and Shaw [17,18] consider that the peculiarity of the transition metals is that the *d* orbitals of the penultimate layer are energetically close to their *s* and *p* valence orbitals. This creates the possibility of easy transition of non-bonding electrons from the higher occupied *d* orbital to the antibonding orbital of the metal–carbon bond. When the *d* orbital is vacant then the reverse transition from the orbital of the metal–carbon bond to this vacant orbital is possible. One or the other should weaken the M–C bond, the transfer of electrons is the first stage in the rupture of this bond. Fig. 2 shows the scheme of the energy levels of the vacant and occupied orbitals of the metal atom. To form a stable complex the energy difference of the highest occupied and the lowest vacant orbital $\Delta E$ should be greater than some critical value. Chatt and coworkers made several alkyl and aryl derivatives of the metals of Group VIII, stabilised by tertiary organic phosphines. The authors connect the stabilising role of the ligands with the fact that their addition to the metal allows $\Delta E$ to be increased. This is brought about by the formation of a strong dative bond with the metal as the result of the involvement of the non-bonding electrons of the highest occupied level in the formation of a bond with this ligand

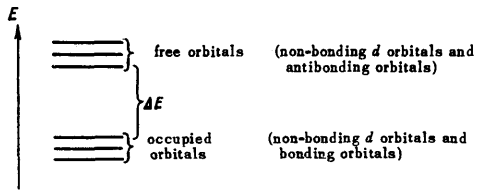



Fig.2. Suggested condition of stability of covalent organic derivatives of the transition metals.

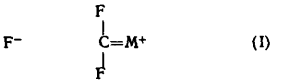
which leads to the lowering of the level, that is, to an increase in $\Delta E$. In square-planar and octahedral complexes the stabilising influence of such ligands is greater than in tetrahedral. With the heaver transition metals the splitting of the orbitals is greater than in the lighter ones and there is a greater capability to form dative bonds. Therefore the heavy metals should give more stable organic σ derivatives, which is what occurs in reality. This is the reverse of what is observed for all the other elements of the Periodic System, where the heaviest element in each subgroup forms the least stable organic derivatives. The zinc group is an exception, where there is no true relationship: the mercury derivatives are thermally more stable, but the chemical reactivity is completely the reverse. Chatt considers that in the zinc group there is still a shade of transition metal character.

The cleavage of the metal–carbon bond is irreversible and it is evident, therefore, that as a result a very active particle is produced — a radical or carbanion. Unlike this, the metal–halogen bond, for example, can be broken reversibly since the halide anion is stable and can exist until it is possible for the broken bond to be reformed.

Behaviour towards oxygen and moisture, that is, towards chemical reaction, also enters into the concept of stability — which is generally not very definite. Apparently, complexes which have available free or only partly occupied orbitals will be sensitive to nucleophilic attacks.

Jaffé and Doak [19] calculated the bond energy in alkyl and aryl derivatives of transition metals and drew the following conclusions about the reasons for the instability of these compounds: (1) the bonds with transition metals have only one-third of the energy of ionic resonance which makes stable the alkyl derivatives of the alkali metals, (2) they have only one-half of the covalent energy which makes stable bonds with all the other elements. The aryl σ derivatives are somewhat more stable than the σ alkyl derivatives. This is due to the increase in the *s* character of the bonds formed by the $sp^2$ orbitals in comparison with the $sp^3$ orbitals, which is favourably reflected in the ionisation potential, the overlap integral, and the ionic resonance energy of the M–C bond, and also the large electronegativity of the $sp^2$ orbitals of carbon compared with the $sp^3$ orbitals. The same conclusions are drawn in respect of the vinyl and ethynyl derivatives and are also confirmed experimentally.

Starting from Jaffé and Doak's conclusions that the instability of the simple transition metal–carbon bond can be linked with the low ionic resonance energy, a group of investigators [20,21] concluded that σ-bound fluorocarbon derivatives of the transition metals should exist. The effective electronegativity of the $CF_3$ group is ~ 3.3 on the Pauling scale and is situated between those for fluorine (4.10) and chlorine (3.0) [22]. The effective electronegativity of the $C_6F_5$ group is approximately equal to that for bromine (2.8). Therefore the ionic character of the metal–carbon bond should increase on going from hydrocarbon to fluorohydrocarbon derivatives. And although fluoroalkyls — like alkyls — cannot participate in π bonding, the metal–fluoroalkyl bond should be considerably more stable. The bonding electrons of such bonds are drawn out towards the fluorocarbon group, decreasing the charge on the metal. The spectroscopic data for them confirm the essential importance of structure (I):



The preparation of a large number of fluorocarbon derivatives of different type, the ease with which they are obtained, and the stability (both thermal and chemical) of most of them confirms the general correctness of the premises.

Hence the stability of a complex depends on various factors, the influence of which is not always understood and cannot *a priori* be predicted and explained. We will turn therefore to the experimental data, classified according to the groups of the Periodic System. Fluorinated σ complexes will be considered in parallel.

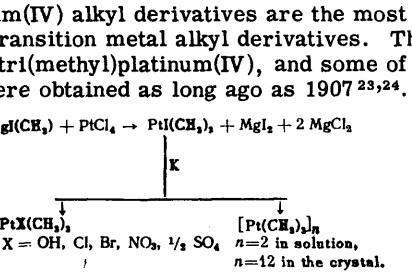
As a review on a similar theme by Razuvaev and Latyaeva was recently published [11], which described in detail the chemistry of organotitanium compounds†, we exclude Group IV from consideration. The copper subgroup is also not considered here, as there is already a sufficiently complete review [15].

## III. EXPERIMENTAL DATA

### 1. Group VIII

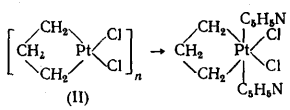
Platinum, palladium, nickel. In addition to the comparatively stable alkyl derivatives of platinum of composition $PtXR_3$, $PtR_4$, $[PtX_2R_2]_n$, the following types of mixed complexes have been obtained for this group of metals: $PtX_2R_2L_2$, $MXRL_2$, $MR_2L_2$, $MXR_fL_2$, and $MR_{f2}L_2$, where M = Pt, Pd, Ni; L is a unidentate ligand of the organic phosphine type; X halogen; R alkyl or aryl; $R_f$ a fluorocarbon radical; Ni-($\pi$-$C_5H_5$)R($PR_3$), Ni-($\pi$-$C_5H_5$)$R_f$(CO), $K_2M(C{\equiv}CR)_4$, and $K_2M(C{\equiv}CR)_2$ for all three metals. A systematic comparison of the stability was made for the example of square-planar phosphine complexes $MR_2L_2$, and it was shown that their stability varies in the order: $NiR_2L_2 < PdR_2L_2 < PtR_2L_2$.

The platinum(IV) alkyl derivatives are the most stable of the known transition metal alkyl derivatives. The first of these, iodotri(methyl)platinum(IV), and some of its derivatives were obtained as long ago as 1907 [23,24].




† The review mentioned [11] covers the covalent organometallic compounds of the transition metals of Groups IV–VIII (Ed. of Translation).

Subsequently, in the repetition of this work[25-27], in addition to iodotri(methyl)platinum(IV) and tetramethylplatinum(IV), diiododi(methyl)platinum(IV), triiodo(methyl)-platinum, etc. were isolated. There are also other paths for obtaining iodotri(methyl)platinum(IV), for example, the alkylation of tetrachloro-dipyridino-*cis*-platinum(IV) with a Grignard reagent[28] or the reaction of methylmagnesium iodide with Zeise's salt‡ or with $Na_2PtCl_4$ in the presence of an excess of methyl iodide[2,29]. Gilman and coworkers found[25,26] that tetramethylplatinum(IV), isolated originally as a side-product, can be obtained satisfactorily from iodotri(methyl)platinum(IV) and methylsodium. It is crystalline and without a definite melting point or decomposition temperature. Tetramethylplatinum, etc. are of special interest because of their tetrametric structure[30], which is shown in Fig. 3. The bridge function of the methyl groups is unusual, although also not unprecedented. Halogen, sulphur, or phosphorus atoms, which have free electron pairs, are most often encountered in such a role. The formation of the tetramer, and also the solvation and association in solutions reflect the coordination unsaturation of the platinum atoms and the tendency to add on more than four groups. In these compounds, and also in alkylacetylacetonatomethylplatino and similar dimers[31-34] platinum tends to become 6-coordinate. Unlike these complexes, cyclopentadienyltri(methyl)platinum(IV) is monomeric[35]. Chatt and coworkers isolated the polymeric trimethyleneplatinum complex(II) from the reaction between $H_2PtCl_6$ and cyclopropane[36]. The polymerisation is effected by means of halogen bridges, as was confirmed by the breaking down of the polymer with amines. Phosphines replace the trimethylene ligand, both in the polymeric complex and in the pyridine-containing monomer.

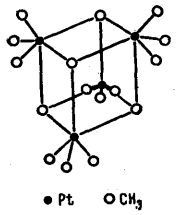


(II)

Platinum(IV) derivatives are also obtained by addition of alkyl halide to certain platinum(II) complexes or by oxidation of the latter with halogens[17]:

$$PtI(CH_3)(PR_3)_2 + CH_3I \rightarrow PtI_2(CH_3)_2(PR_3)_2,$$
$$Pt(CH_3)_2(PR_3)_2 + Cl_2 \rightarrow PtCl_2(CH_3)_2(PR_3)_2.$$

σ-arylphosphine complexes are obtained similarly. Derivatives of the $PtAr_4$ type have not been obtained pure, although there are indications that a mixture of phenyl derivatives is formed in the reaction of $PtCl_4$ with bromo(phenyl)magnesium[27].



● Pt ○ $CH_3$

Fig. 3. Structure of tetramethylplatinum, after Rundle[30].

‡ $K[PtCl_3(C_2H_4)]$ (Ed. of Translation).

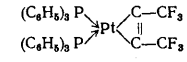
The simplest platinum(II) derivatives $PtR_2$ are unknown, but platinum(II) complexes are easily alkylated, giving stable crystalline square-planar complexes, which exist as *cis*- and *trans*-isomers[17,37]:

$$PtX_2(PR_3)_2 + 2MgXR' \text{ or } 2LiR' \rightarrow PtXR'(PR_3)_2 \text{ or } PtR'_2(PR_3)_2.$$

The alkyl groups of such complexes are detached by the action of acids or salts like magnesium iodide[17]. Analogous aryl and ethynyl complexes are obtained which are usually more stable than the alkyl complexes.

Halogeno(alkyl)phosphine complexes of platinum and palladium are known to undergo the reaction termed carbonylation, in which CO from the gas phase is inserted at the R–M bond[38]. This interesting reaction, characteristic of many complexes, will be considered in detail below. In the present example, typical acyl derivatives capable of the reverse, decarbonylation, with recovering of the initial substance, are obtained.

As is well known, the reaction of platinum derivatives with alkynes leads to the formation of π complexes of the Zeise's salt type, where acetylene is present instead of ethylene. Such a structure is confirmed by the infrared spectra, in which there are frequencies of coordinated triple bonds, and also the regeneration of acetylene as a result of various effects. Perfluorobut-2-yne is an exception, and is reported[39] to add on by two σ bonds, giving (III):



(III)

Yet another type of alkyne derivative of platinum, palladium, and nickel is obtained — acetylido-complexes, for example, $K_2Pt(C{\equiv}CR)_4$, which are non-explosive, diamagnetic complexes, which on reduction give pyrophoric $K_2Pt(C{\equiv}CR)_2$, readily oxidised to tetraalkynylplatinates[40].

The simplest organic derivatives of palladium and nickel have not been described although attempts to obtain them have been made[16] and there is indirect confirmation of their existence. Just as for platinum, square-planar mixed complexes of composition $MR_2L_2$ or $MXRL_2$ are characteristic for palladium, where R can be alkyl, aryl, or ethynyl[41]. For nickel, only aryl and ethynyl derivatives have been obtained[42,43]. Only the *trans* forms of these Pd and Ni complexes have been isolated. Aryl derivatives of nickel exhibit moderate stability with the exception of those whose aryl groups have *ortho*-substituents. For example, $[NiBr\{2,4,6\text{-}(CH_3)_3C_6H_5\}\{P(C_2H_5)_3\}_2]$ sublimes in the atmosphere at ~ 160° at normal pressure.

The general theory of stability and the stabilising effect of some ligands were considered above. Fig. 4 shows the splitting of the levels of the *d* orbitals in planar complexes of type $d^8$ analogous to the organometallic derivatives being considered[44]. The stability of these complexes thus depends on the difference in the energy of the least stable $d_{x^2-y^2}$ orbital and $d_{xy}$ orbital lying in the plane of the molecule. Evidently in alkyl phosphine derivatives of nickel, the splitting of the *d* levels is insufficient to stabilise them and the necessary value is reached only in aryl complexes. Unsubstituted phenyl groups are capable of free rotation around the metal–carbon bond; in this, their π orbitals overlap with the $d_{xy}$, $d_{xz}$, and $d_{yz}$ orbitals, somewhat lowering all these levels and increasing $\Delta E$ the more so. In this way the metal–phenyl bond acquires some degree of multiplicity, making worse the mesomeric electron displacement from the metal to the phenyl group.

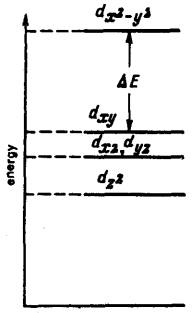



Fig. 4. Scheme of energy levels of the *d* orbitals for square planar configuration.

This makes them more stable in comparison with the alkyl derivatives. With *ortho*-substituted aryl derivatives, bulky substituents prevent free rotation, the aryl group is held in the plane perpendicular to the plane of the complex. In that position the $\pi$ orbital of the aryl group should react preferentially with the $d_{xy}$ orbital, hence $\Delta E$ will be greater than when there is free rotation. The increase $\Delta E$ prevents the thermal dissociation of the complex, leading to breaking away of the free radical and the screening of the metal atom by the ortho-substituents hinders the attack by chemical reagents. *Meta*- and *para*-substituted aryl complexes are analogous to the unsubstituted phenyl and — depending on the substituent — somewhat increase or decrease $\Delta E$.

All these complexes are obtained from metal halogeno--complexes and Grignard reagents or alkyllithiums, some of which are shown in Table 1.

A recent paper by Yamazaki and Hagihara[45] describes the production of the first $\sigma$ alkyl complexes of nickel which contain $\pi$-cyclopentadienyl and phosphine groups in the molecule:

$$NiCl(\pi\text{-}C_5H_5)P(C_6H_5)_3 + MgIR \rightarrow NiR(\pi\text{-}C_5H_5)P(C_6H_5)_3,$$

where R = $CH_3$, $C_2H_5$, $C_6H_5$, C≡CH, etc. The least stable of these are again those with alkyl groups. They are all comparatively difficult to decompose by heating, but the solutions are unstable, especially in air. It is interesting to note that attempts to obtain $NiR(C_5H_5)(CO)$ did not give a positive result, although the formation of a labile non--isolable methyl derivative was proved spectroscopically.

Hence the combination of $\pi$-cyclopentadienyl and phosphine is so effective that it allows stable alkyl derivatives of nickel to be obtained.

The high electronegativity of $R_f$ groups is due to the pseudo-halogen nature of the perfluoroalkyl iodides. In

TABLE 1. $\sigma$ derivatives of platinum, palladium, and nickel.

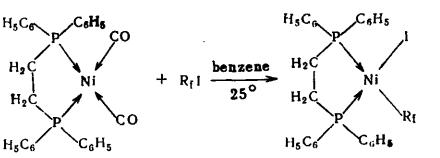
| Derivative* | Colour | M.p., °C | Reference | | | |
|---|---|---|---|---|---|---|
| | | | preparation | infrared spectra | NMR | dipole moment |
| $(CH_3)_4$ Pt | white | — | 26 | — | — | — |
| $(CH_3)_3$ PtI | orange-yellow | 195—200 (decomp.) | 26 | — | — | — |
| $(CH_3)_2$ $PtI_2$ | black | — | 26 | — | — | — |
| $CH_3PtI_3$ | » | — | 26 | — | — | — |
| $(CH_3)_3$ PtI (pyridine)$_2$ | white | 168 | 28,31 | — | — | — |
| $[(CH_3)_3$ Pt(acetylacetone)$]_2$ | » | 200 (decomp.) | 31,32 | — | — | — |
| $[(CH_3)_3$ Pt $(CH_3CH_2CO)_2$ $CH_2]_2$ | » | 190 (decomp.) | 32 | — | — | — |
| $[(CH_3)_3Pt]_2$ | pale yellow | explodes | 26 | — | — | — |
| $[(CH_3)_3$= $PtCl_2]_n$ | yellow | 148 (decomp.) | 36 | 36 | 36 | — |
| $(CH_3)_2$ = $PtCl_2$(pyridine)$_2$ | white | 140—145 | 36 | 36 | 36 | — |
| $(CH_3)_3$ $PtC_6H_5$ | » | 65 | 35 | — | 35 | — |
| $(CH_3)_2$ Pt (Cl)$_2$ [P $(C_2H_5)_3]_2$ | » | 114—117 | 17 | — | — | 17 |
| $(C_6H_5)_2$ (Cl)$_2$ Pt [P $(C_2H_5)_3]_2$ | » | 153—155 | 17 | — | — | 17 |
| *cis*-$(CH_3)_2$ Pt [P $(C_2H_5)_3]_2$ | » | 81—82 | 17 | 37 | — | 17 |
| *trans*-$(CH_3)_2$ Pt [P $(C_2H_5)_3]_2$ | » | 76—79 | 17 | — | — | 17 |
| *trans*-$(C_6H_5)_2$ Pt [P $(C_2H_5)_3]_2$ | » | 176—180 | 17 | — | — | 17 |
| *cis*-$(CH_3)$ Cl Pt [P $(C_2H_5)_3]_2$ | » | 113—116 | 17 | 37 | — | 17 |
| *trans*-$CH_3$ (SCN) Pt[P$(C_2H_5)_3]_2$ | » | 93—95 | 17 | 37 | — | 17 |
| *trans*-$(C_6H_5)_2$ Pt [As $(C_2H_5)_3]_2$ | » | 138—141 | 17 | — | — | 17 |
| *trans*-(*o*-Tolyl)$_2$ Pt [P $(C_2H_5)_3]_2$ | » | 192—196 | 17 | — | — | 17 |
| *cis*-(Metsityl) BrPt [P $(C_2H_5)_3]_2$ | » | 182—185 | 17 | — | — | 17 |
| *trans*-(CH≡C)$_2$ Pt [P $(C_2H_5)_3]_2$ | » | 62—63 | 17 | — | — | 17 |
| *trans*-$(C_6H_5C\equiv C)_2$ Pt [P $(C_2H_5)_3]_2$ | » | 186—187 (decomp.) | 17 | — | — | 17 |
| $CH_3COPt$ (Cl) [P $(C_2H_5)_3]_2$ | pale yellow | 70—71 | 38 | 38 | — | 38 |
| $C_6H_5COPt$ (Cl) [P $(C_2H_5)_3]_2$ | ditto | 87—89 | 38 | 38 | — | 38 |
| *trans*-$(CH_3)_2$ Pd [P $(C_2H_5)_3]_2$ | — | — | 41 | — | — | — |
| *trans*-$CH_3$ (Br) Pd [P $(C_2H_5)_3]_2$ | white | 73—74 | 41 | — | — | — |
| *trans*-$(C_6H_5)_2$ Pd [P $(C_2H_5)_3]_2$ | — | 95 (decomp.) | 41 | — | — | — |
| $[(CH_3)_2$ $NC_6H_4]_2$ Pd [P $(C_2H_5)_3]_2$ | — | 99—100 | 41 | — | — | — |
| *trans*-$(C_6H_5C\equiv C)_2$ Pd [P $(C_2H_5)_3]_2$ | — | 164—166 | 41 | — | — | — |

TABLE 1 (contd).

| Derivative* | Colour | M.p., °C | Reference | | | |
|---|---|---|---|---|---|---|
| | | | preparation | infrared spectra | NMR | dipole moment |
| $CH_3CO$ (Cl) Pd [P $(C_2H_5)_3]_2$ | pale yellow | 65—67 | 38 | 38 | — | 38 |
| (Bipyridyl) Pd $(n\text{-}C_3H_7)_2$ | ditto | 180—181 | 50 | 50 | — | — |
| (Bipyridyl)Pd $(CH_3)$ $(n\text{-}C_3H_7)$ | yellow | 206—207 (decomp.) | 50 | 50 | — | — |
| $(C_6H_5)_2$ Ni [P $(C_2H_5)_3]_2$ | pale yellow | 125—130 (decomp.) | 43 | — | — | — |
| (Mesityl)$_2$ Ni [P $(C_2H_5)_3]_2$ | ditto | 148—150 (decomp.) | 43 | — | — | 42 |
| (*o*-Tolyl)(Cl) Ni [P $(C_2H_5)_3]_2$ | orange-red | 75—77.5 | 43 | — | — | 43 |
| (Mesityl)) (Br) Ni [P $(C_2H_5)_3]_2$ | cinnamon brown | 159—160 | 42,43 | — | — | 42,43 |
| $(C_6Cl_5)$ (Cl) Ni [P $(C_2H_5)_3]_2$ | ditto | 156—158 | 43 | — | — | 42,43 |
| (Naphthyl)(Br) Ni [P $(C_2H_5)_3$] | » | 150—152.5 (decomp.) | 43 | — | — | — |
| *trans*-$(HC\equiv C)_2$ Ni [P $(C_2H_5)_3]_2$ | pale yellow | 36—36,5 | 42,43 | — | — | 42 |
| *trans*-$(C_6H_5C\equiv C)_2$ Ni [P $(C_6H_5)_3]_2$ | orange | 170—172 (decomp.) | 42,43 | — | — | 42,43 |
| $CH_3$ Ni (CO) $C_5H_5$ | — | — | 48 | 48 | — | — |
| $CH_3$Ni [P $(C_6H_5)_3$] $C_5H_5$ | dark green | 115—118 (decomp.) | 45 | — | 45 | — |
| $C_2H_5$Ni [P $(C_6H_5)_3$] $C_5H_5$ | ditto | 90—110 (decomp.) | 45 | — | 45 | — |
| $C_6H_5$Ni [P $(C_6H_5)_3$] $C_5H_5$ | » | 137—139 | 45 | — | — | — |
| $HC\equiv CNi$ [P $(C_6H_5)_3$] $C_5H_5$ | » | 111.5—112.5 | 45 | 45 | — | — |
| $C_6H_5C\equiv CNi$ [P $(C_6H_5)_3$] $C_5H_5$ | » | 135 | 45 | 45 | — | — |
| $(C_6F_5)_2$ Ni [P $(C_2H_5)_3]_2$ | pale yellow | 213--214 | 47 | 47 | — | — |
| $(C_6F_5)_2$ Ni (bipyridyl) | dark yellow | 255 (decomp.) | 47 | 47 | — | — |
| **$(C_6F_5)$ (Br) Ni [P $(C_6H_5)_3]_2$** | yellow | 199—200 (decomp.) | 47 | 47 | — | — |
| **$(C_6F_5)$ (SCN) Ni [P $(C_2H_5)_3]_2$** | » | 149—150 | 47 | 47 | — | — |
| **$(C_2F_5)$ (I) Ni [P $(C_6H_5)_2$ $CH_3]_2$** | red-brown | (decomp.) >260 | 46 | — | — | — |
| **$(n\text{-}C_3F_7)$ (I) Ni [P $(C_6H_5)_2$ $CH_3]_2$** | ditto | 220—222 (decomp.) | 46 | — | — | — |
| **$CF_3$Ni (CO) $C_5H_5$** | red | liquid | 48 | 48 | 48 | — |
| **$C_2F_5$Ni (CO) $C_5H_5$** | purple | » | 48 | 48 | 48 | — |
| **$n\text{-}C_3F_7$Ni (CO) $C_5H_5$** | » | » | 48 | 48 | 48 | — |
| **$CF_2$=CF—$CF_2$Ni (CO) $C_5H_5$ + + $CF_2$—CF=CFNi (CO) $C_5H_5$** | dark red | » | 48 | — | 48 | — |
| **$C_2F_5$Ni [P $(C_2H_5)_3$] $C_5H_5$** | dark green | 164—165 | 48 | 48 | 48 | — |
| **$CF_2$=CF—CF=CFNi [P $(C_6H_5)_3$] $C_5H_5$** | ditto | 114—115 | 48 | 48 | 48 | — |

* Because of the number of complexes involved, no attempt has been made to rearrange the formulae in the tables into the IUPAC form (Ed. of Translation).

relation to the transition metals this is expressed in their ability to displace some of the carbonyl groups or carbonyl complexes from carbonyls or carbonyl complexes just as elemental iodine does. This reaction, which occurs under exceptionally mild conditions, is one of the methods of making perfluoroalkyl derivatives of transition metals (Method A). McBride and his coworkers [46] used it for nickel; they obtained iodo(perfluoroalkyl)nickel complexes containing the desired diphosphines, as diamagnetic crystals with a square-planar arrangement of the ligands — examples of complexes in which the effective atomic number rule is not obeyed. Nevertheless they are stable substances, with decomposition temperatures > 200°, which is very remarkable considering that the analogous alkyl derivatives are incapable of existence:



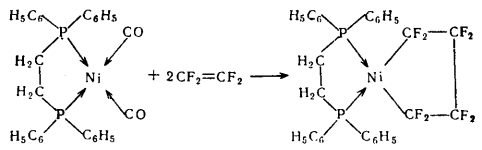

The perfluoroaryl complexes $NiAr_{f2}(PR_3)_2$ and $NiXAr_f.(PR_3)_2$ are stable even in solution [47]. Many of them

melt without decomposition and can be melted a second time.

Dimeric cyclopentadienylcarbonylnickel also decomposes readily under the action of perfluoroalkyl iodides, to form cyclopentadienylperfluoroalkylcarbonyl complexes[48]:

$$[Ni(C_5H_5)(CO)]_2 + R_fI \xrightarrow[25^\circ]{\text{benzene}} Ni(C_5H_5)R_f(CO) + NiI(C_5H_5)(CO).$$

Carbonyls and carbonyl complexes of some metals react with perfluoroethylene, some of the carbonyl groups being replaced. The expected $\pi$ complexes are not formed, however, but $\sigma$ heterocycles with the metal atom in the ring. This is one of the methods of obtaining stable perfluorinated $\sigma$ derivatives of nickel, cobalt, and iron (Method B)[49]:



Single examples of perfluoroalkyl derivatives of platinum and palladium are known. Thus in the treatment of bipyridyldimethylpalladium with perfluoropropyl iodide replacement of one or both of the methyl groups occurs[50]:

$$Pd(C_{10}H_8N_2)(CH_3)_2 + CF_3CF_2CF_2I \xrightarrow[20^\circ]{\text{tetrahydrofuran}} Pd(C_{10}H_8N_2)(C_3F_7)_2.$$

There is a reference to the bis(perfluoroethyl)platinum complex $Pt(C_2F_5)_2\{P(C_2H_5)_3\}$ obtained by the addition of perfluoroethylene to a fluoro-complex in hydrogen fluoride medium[10].

The example of nickel is a clear, convincing illustration of the stabilising influence of fluorine on the transition metal–carbon $\sigma$ bond.

Iron, ruthenium, osmium. Numerous attempts to bring about reaction between a Grignard reagent and iron(II) or iron(III) halides have ended in the reduction of the metal and the formation of the dimer of the radical of the arylating agent:

$$2MgBr(C_6H_5) + FeCl_2 \rightarrow C_6H_5C_6H_5 + Fe + MgBr_2 + MgCl_2.$$

The dimerisation was subsequently used as a method of preparation, and, as is well known, one of the two discoveries of ferrocene is connected with an attempt to obtain biscyclopentadienyl from bromo(cyclopentadienyl)-magnesium and iron(III) chloride. On the other hand this reaction was considered to be a measure of the stability of the $\sigma$ derivative formed as an intermediate and all the metals of Group VIII have been studied from this viewpoint in terms of reaction with phenylmagnesium bromide[27,51]. When the yield of biphenyl is taken as a measure of the instability of the $\sigma$ derivative, then it must be concluded that the phenyl derivatives of iron, cobalt, nickel, ruthenium, rhodium, and palladium are evidently completely unstable and exist only briefly. As shown above, platinum gives stable methyl derivatives. Probably its phenyl derivatives are also fairly stable, since under comparable conditions only traces of biphenyl are formed. The low yield of biphenyl is also found with osmium(III) and iridium(III) chlorides, and their phenyl derivatives evidently exhibit moderate stability. The catalytic reaction of dimerisation, which takes place in the presence of non-stoichiometric amounts of transition metal salt, was studied by Kharasch and coworkers[52-56], and it was shown that $CoCl_2$ exhibits the greatest activity of them all. The mechanisms advanced for different types of R took into account the strength of the metal–carbon bond in the hypothetical $MR_n$.

Subsequently the formation of unstable derivatives in the first stage was used in the original synthesis of $\pi$ alkene complexes by Fischer and coworkers[57-60], for example:

$$FeCl_3 + 3MgBrPr^i \xrightarrow{\text{ether}} [FePr^i_3(\text{ether})_n] \longrightarrow$$

$$\xrightarrow[35^\circ,\ \text{ultraviolet}]{2C_6H_5} \pi\text{-}C_6H_6FeC_6H_5\text{-}\pi + C_3H_8 + C_3H_6 + H_2.$$

The labile ethereal complex of triisopropyliron decomposes when irradiated and the vacated coordination sites are occupied by the alkene. If the geometrical or electronic properties of the alkene structure do not match up to the metal then there is a simultaneous rearrangement of the alkene, in the present example dehydrogenation. In this way otherwise unobtainable pure alkenic $\pi$ complexes of iron, ruthenium, osmium, and chromium of low stability were prepared.

The polymerisation of acetylene in the presence of derivatives of chromium, nickel, etc. is apparently brought about by an analogous mechanism. Hence because of their reactivity the unisolable, unstable $\sigma$ derivatives of the transition metals play an important part in the intermediate stages of many processes.

In addition to these organic derivatives of iron, ruthenium, and osmium, which apparently exist in solutions but cannot be isolated pure, several completely stable mixed complexes have been obtained. For iron there are first of all derivatives of cyclopentadienyldicarbonyliron and corresponding dinuclear complexes, some tetracarbonyl-complexes and their fluorinated analogues and also complexes of the $MR_2L_2$ type, although the last are evidently the least characteristic. For ruthenium and osmium only the four-coordinated complexes of composition $MXRL_2$ are known.

Derivatives of cyclopentadienylcarbonyls are obtained by two main methods (C) and (D), developed by Piper and Wilkinson[61]:

$$\left.\begin{array}{l} C_5H_5M(CO)_nNa + RCl \\ MX(C_5H_5)(CO)_n + MgXR \end{array}\right] \rightarrow M(C_5H_5)R(CO)_n \qquad \begin{array}{l}\text{(Method C)}\\ \text{(Method D)}\end{array}$$

A method which has limited application for obtaining only methyl derivatives is the methylation of hydro(cyclopentadienyl)carbonyl complexes with diazomethane[61,62]:

$$C_5H_5M(CO)_nH + CH_2N_2 \rightarrow C_5H_5M(CO)_nCH_3 + CO. \qquad \text{(Method E)}$$

Method C forms the basis of the preparation of dinuclear complexes[63,64], dihalides being used. Acyl and fluorocarbon derivatives are also obtained by Method B. It has been shown that trimethylsulphonium iodide can be used as a methylating agent in Method B.[65] The yields in all three methods vary considerably. Table 2 gives the physical properties of some representatives of this class of complexes. Usually the isoalkyl derivatives are considerably less stable than the n-alkyl. Many of these are liquids which are readily oxidised even at low temperatures.

The following methods for obtaining $\sigma$ alkyl and aryl derivatives involves the decarbonylation of the corresponding $\sigma$ acyl derivatives:

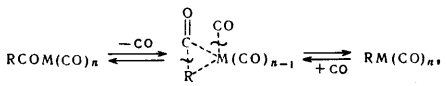
$$M(RCO)(C_5H_5)(CO)_n \rightarrow MR(C_5H_5)(CO)_n + CO. \qquad \text{(Method F)}$$

TABLE 2. $\sigma$ derivatives of iron, ruthenium, and osmium.

| Derivative | Colour | M.p., °C | Reference | | | |
|---|---|---|---|---|---|---|
| | | | preparation | infrared spectra | NMR | dipole moment |
| $(C_6Cl_5)_2$ Fe [P $(C_2H_5)_2$ $C_6H_5]_2$ | yellow | 135—142 (decomp.) | 72 | — | — | — |
| $CH_3Fe$ $(CO)_2$ $C_5H_5$ | » | 78—82 | 61,65 | 61 | 61 | — |
| $C_2H_5Fe$ $(CO)_2$ $C_5H_5$ | » | liquid | 61 | 61 | 61 | — |
| $\sigma$-$C_6H_5Fe$ $(CO)_2$ $C_5H_5$-$\pi$ | orange | 46 | 61 | 61 | 61 | — |
| $C_6H_5Fe$ $(CO)_2$ $C_5H_5$ | yellow | 35—36 | 61,69 | 61,69 | 61,69 | — |
| $CH_2$=$CHFe$ $(CO)_2$ $C_5H_5$ | orange | liquid | 69 | 69 | 69 | — |
| HC≡$CCH_2$—Fe $(CO)_2$ $C_5H_5$ | orange-red | 96—96.5 | 188 | 188 | 188 | — |
| $CH_2$=CH—$CH_2$—Fe $(CO)_2$ $C_5H_5$ | amber | b.p. $45/10^{-3}$ | 68 | 68 | 68 | — |
| n-$C_3H_7$—Fe $(CO)_2$ $C_5H_5$ | » | liquid | 186 | 186 | 186 | — |
| $(CH_3)_2$ CD—Fe $(CO)_2$ $C_5H_5$ | — | — | 186 | 186 | 186 | — |
| $(CH_3)_2$ C—Fe $(CO)_2$ $C_5H_5$ | yellow | liquid decomp. >20 | 186 | 186 | 186 | — |
| CNCH$_2$Fe $(CO)_2$ $C_5H_5$ | orange-yellow | 123 | 190 | 190 | 190 | — |
| $CNCH_2CH_2Fe$ $(CO)_2$ $C_5H_5$ | ditto | 29.5 | 190 | 190 | 190 | — |
| $CH_3CH$ (CN) Fe $(CO)_2$ $C_5H_5$ | orange-red | 86—87 | 190 | 190 | 190 | — |
| $CH_3OOC$—(Fe(CO)$_4$)—$COOCH_3$ | yellow-orange | 57 | 71 | — | 71 | — |
| $(CH_2)_3$ [Fe $(CO)_2$ $C_5H_5]_2$ | orange | 103—135 | 63 | 63 | 63 | — |
| $CH_3C$≡$CCH_2$ [Fe $(CO)_2$ $C_5H_5]_2$ | » | — | 63 | 63 | 63 | — |
| $CH_3COFe$ $(CO)_2$ $C_5H_5$ | » | 56—57 | 64 | 64 | 64 | — |
| $C_2H_5COFe$ $(CO)_2$ $C_5H_5$ | orange-red | liquid | 67 | 67 | 67 | — |
| $C_6H_5COFe$ $(CO)_2$ $C_5H_5$ | orange | 59—62 | 69 | 69 | 69 | — |
| $CH_2$=$CHCOFe$ $(CO)_2$ $C_5H_5$ | » | liquid | 69 | 69 | 69 | — |
| $(CH_3)_2$ NCO—Fe $(CO)_2$ $C_5H_5$ | » | 111—112 | 64 | 64 | 64 | — |
| CO $(CH_2)_3$ CO [Fe $(CO)_2$ $C_5H_5]_2$ | » | 110—111.5 | 64 | 64 | 64 | — |
| $CF_3Fe$ $(CO)_4$ I | orange-red | 94 (decomp.) | 74 | 74 | — | — |
| $C_2F_5Fe$ $(CO)_4$ I | dark red | 15—16 | 74 | 21,74 | 81,69 | — |
| $C_6F_5Fe$ $(CO)_4$ I | ditto | 74 | 77 | 77 | — | — |
| [$C_2F_5Fe$ $(CO)_2$ I]$_2$ | » | 110—112 (decomp.) | 74 | 74 | — | — |
| [$C_3F_7Fe$ $(CO)_2$ I]$_2$ | pale orange | 140—142 (decomp.) | 74 | 74 | — | — |
| $(CF_2)_4$ = Fe$(CO)_4$ | white | 77 | 21,80 | 21 | 21 | — |
| $(C_2F_5)_2$ Fe$(CO)_4$ | pale yellow | 62—63.5 | 74,75 | 74 | 81,69 | — |
| (n-$C_3F_7)_2$ Fe $(CO)_4$ | ditto | 88—89 | 74 | 74 | 81,69 | — |
| n-$C_3F_7Fe$ $(CO)_3$ (I) P $(C_6H_5)_3$ | pale brown | 125 (decomp.) | 82 | 82 | — | — |
| n-$C_3F_7Fe$ $(CO)_2$ (I) (pyridine) | cinnamon brown | 123 | 82 | 82 | — | — |
| (n-$C_3F_7)_2$ Fe $(CO)_2$ (pyridine)$_2$ | pale brown | 138 | 82 | 82 | — | — |
| $CF_3Fe$ $(CO)_2$ $C_5H_5$ | pale yellow | 137—139 | 69 | 69 | 69 | — |
| $C_2F_5Fe$ $(CO)_2$ $C_5H_5$ | orange | 43—45 | 69 | 69 | 69 | — |
| $CF_3CF$=$CFFe$ $(CO)_2$ $C_5H_5$ | yellow-orange | 69.5—70.5 | 74,75,76 | 74, 76 | 74, 76 | — |
| $(CF_2)_3$ [Fe $(CO)_2$ $C_5H_5]_2$ | yellow | 168—172 | 75 | — | — | — |
| $C_6F_5Fe$ $(CO)_2$ $C_5H_5$ | yellow-orange | 144.5—145 | 78,79 | 79 | 78,79 | — |
| p-$HC_6F_4Fe$ $(CO)_2$ $C_5H_5$ | » | 128—130 | 79 | 79 | 79 | — |
| p $CF_3C_6F_4Fe$ $(CO)_2$ $C_5H_5$ | ditto | 119—120 | 79 | 79 | 79 | — |
| $CF_3COFe$ $(CO)_2$ $C_5H_5$ | orange | 33—34 | 69 | 69 | 69 | — |
| $C_2F_5COFe$ $(CO)_2$ $C_5H_5$ | » | liquid | 69 | 69 | 69 | — |
| CO $(CF_2)_3$ CO [Fe $(CO)_2$ $C_5H_5]_2$ | » | 112—113 | 64 | 64 | 64 | — |
| $C_2H_5CORu$ $(CO)_2$ $C_5H_5$ | pale yellow | liquid | 67 | 67 | 67 | — |
| $CH_3$ (H) Ru [$CH_2P$ $(C_6H_5)_2]_2$ | colourless to pale yellow | (decomp.) | 73 | 73 | — | — |
| $C_2H_7$ (H) Ru [$CH_2P(C_6H_5)_2]_2$ | colourless to pale yellow | 120—220 | 73 | 73 | — | — |
| $CH_3$ (Cl) Ru [$CH_2P$ $(C_6H_5)_2]_2$ | — | 312 (decomp.) | 18,73 | — | — | 18 |
| $C_2H_5$ (Cl) Ru [$CH_2P$ $(C_6H_5)_2]_2$ | — | 330 (decomp.) | 18,73 | — | — | 18 |
| $CH_3$ (Cl) Os [$CH_2P$ $(C_6H_5)_2]_2$ | — | 295—296 (decomp.) | 18 | — | — | 18 |
| $C_2H_5$ (Cl) Os [$CH_2P$ $(C_6H_5)_2]_2$ | — | 310—314 (decomp.) | 18 | — | — | 18 |

This method is widely used in the chemistry of the carbonyl complexes of manganese and cobalt, where the acyl derivatives are more accessible than the alkyl derivatives. The decarbonylation of manganese and cobalt acylcarbonyls proceeds very easily on heating. It is often so easy that even at room temperature and normal pressure an equilibrium mixture of the alkyl and acyl derivatives is formed. However, when there is only one phosphine or cyclopentadienyl group in the complexes then the decarbonylation is greatly hindered. Thus although a series of acyl derivatives of cyclopentadienyldicarbonyliron was obtained[64,66,67], they could not be decarbonylated just so long as the change from σ allyl to π allylcyclopentadienylcarbonyl complexes did not succeed[68].

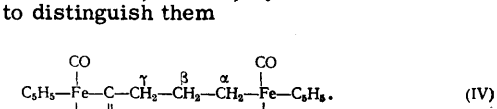
Radiochemical methods were used to show[66] that the reversible carbonylation–decarbonylation process takes place by the mechanism:



that is, it is not the acyl carbonyl that is detached, but one of the CO groups of the carbonylmetal moiety. The reverse reaction of carbonylation of the alkyl complex proceeds in such a way that the CO entering bonds only with the metal, and the acyl group is formed by an inner-sphere rearrangement. Therefore the success of the decarbonylation of acylcarbonyls probably depends on how strongly the carbonyl groups of such complexes are bound to the metal, which can be judged from the ease with which they are replaced by a phosphine. King and Bisnett found[69] that decarbonylation of acyls is facilitated by ultraviolet irradiation, just as the replacement of CO by phosphine is sometimes facilitated. A synthesis path was worked out for certain previously inaccessible alkyl complexes, for example, cyclopentadienylvinyldicarbonyliron. All this relates also to cyclopentadienylperfluoroacyl complexes. They are obtained by Method C; when the acyl halides are gaseous, the anhydrides of the perfluoro-acids are used. The yields of perfluoroacyls are usually about 10% low and in the reactions a large quantity of the dimer of cyclopentadienyldicarbonyliron is always obtained. Acyl derivatives of unsaturated acids also give low yields.

It has been repeatedly noted[64,69] that in the nuclear magnetic resonance spectra of the complexes $FeR(C_5H_5)(CO)_2$ the position of the signals of the ring protons depends on the nature of R. Thus when R = alkyl it is ~ 5.27 τ, with R = acyl ~ 5.17 τ, with R = perfluoroacyl ~ 5.04 τ, and with R = I 4.93 τ, that is, the displacement varies inversely with the electronegativity of R. The shifts for ring protons in fluoroalkyls and fluoroacyl complexes are very similar.

The displacements for the α and β protons of an alkyl chain are almost the same, that is, by the NMR method it is impossible to distinguish them



(IV)

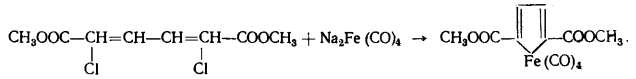
In the acyl groups two types of protons are evident, corresponding to the γ and β positions. Non-symmetrical doubly-charged complexes of type (IV) have two ring proton signals associated with the different electronegativity of the groups attached to the iron.

Quite recently a new reaction between the σ complexes of iron with liquid $SO_2$ was discovered. Analogously to carbon monoxide, $SO_2$ is inserted at the R–Fe bond. The reaction proceeds easily at -40° to -60° immediately the complex is dissolved in liquid $SO_2$:[70]

$$Fe(C_5H_5)R(CO)_2 + SO_2 \rightarrow Fe(C_5H_5)(SO_2R)(CO)_2,$$

where R = $CH_3$, $C_2H_5$, or $C_6H_5$.

A derivative of the so-called ferrole — a five-membered unsaturated heterocycle with iron in the ring — is obtained by the reaction of dihalogenoalkenes with $Na_2Fe(CO)_4$:[71]



It is crystalline, m.p. 57°, and capable of being chromatographed under the usual conditions.

The ferrole motiv is repeated in a series of complexes obtained from iron carbonyls and alkynes, which will be considered below.

Hydro-complexes are capable of addition to alkenes, and this reaction is one of the paths for the synthesis of σ derivatives (Method G). In the group of metals now being considered addition to the butadiene system takes place:[68]

$$FeH(C_5H_5)(CO)_2 + CH_2{=}CH{-}CH{=}CH_2 \rightarrow Fe(CH_2{-}CH{=}CH{-}CH_3)(C_5H_5)(CO)_2.$$

The sole example of a four-coordination iron complex — bis(pentachlorophenyl)bis(diethylphenylphosphine)-iron — is crystalline, with decomposition temperature ~ 130°.[72] The analogous complexes of ruthenium and osmium usually contain only one alkyl group and a halogen atom, which can be reduced and the corresponding hydro(alkyl) complexes obtained. Unlike all the others, the square complexes of ruthenium and osmium are obtained by the action of trialkylaluminium on dihalogeno--complexes[73]. Judging by the decomposition temperature, the least stable complexes of this group are those of iron.

It was shown above that perfluoroalkyl halides displace the carbonyl groups in carbonyl complexes of nickel. Pentacarbonyliron also reacts under mild conditions at 25–70° with perfluoroalkyl halides, giving a mixture of derivatives of composition $FeIR_f(CO)_4$ and $[FeIR_f(CO)_3]_2$.[21,74] The latter is dimerised by means of halogen bridges. On heating, the monomeric complexes lose CO, being converted into dimers.

Unlike the cyclopentadienylperfluoroacylcarbonyls, which are decarbonylated only under ultraviolet irradiation[64,69], perfluoroacylcarbonyls of iron are decarbonylated apparently quite readily, since when perfluoroacyl chlorides and $Na_2Fe(CO)_4$ react, only bisperfluoroacylcarbonyls can be isolated[74,75]. In this respect they are more similar to the acyl derivatives of cobalt and manganese. It should be noted, however, that the replacement of even one of the carbonyl groups by a phosphine makes the acyl derivatives stable to thermal decarbonylation. Decarbonylation of perfluoroacyl derivatives gave complexes of the type $Fe(C_5H_5)R_f(CO)_2$,[69] with different $R_f$, shown in Table 2. Some of these can also be obtained by Method C[74,76] (see p. 173). The perfluoroaryl complexes are obtained with yields of 2–7% by the action of pentafluorophenyllithium[77] or bromo(pentafluorophenyl)magnesium[78] on the corresponding halogen derivatives.

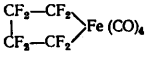
Nucleophilic replacement of fluorine by other groups is characteristic for highly fluorinated aromatic hydrocarbons. King and Bisnette[79] used this feature to obtain fluorinated aromatic σ derivatives of iron. On heating fluorobenzenes in tetrahydrofuran with $Na[Fe(C_5H_5)(CO)_2]$, fluorine is replaced by the cyclopentadienyl dicarbonyliron cation:

$$C_6F_5R + Na[Fe(C_5H_5)(CO)_2] \rightarrow [Fe(C_5H_5)(p\text{-}RC_6F_4)(CO)_2],$$

where R = H, or $CF_3$.

With octafluorotoluene in this reaction, fluorine is displaced from the benzene nucleus, not the side-chain, 1,2,3,4-tetrafluorobenzene gives $[Fe(C_5H_5)(2,3,6\text{-}C_6H_2F_3).(CO)_2]$ that is, the C–Fe bond is bound in such a way that both *ortho*-positions are occupied by fluorine. The yields in these reactions reach 30–50%, but the method is not applicable to $Na_2[Fe(CO)_4]$, $Na[Mo(C_5H_5)(CO)_3]$, and some other carbonylmetalates. The complexes obtained are stable on heating and against oxidation, melt without decomposition, and can be chromotographed on $Al_2O_3$.

Yet another type of iron complexes — heterocyclic complex (V), obtained by Method B[21,80] originally was thought to be a π perfluoroethylene complex — is the substance



(V)

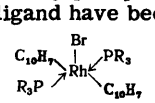
stable in all respects.

It is not decomposed by bromine, phosphines do not displace the perfluorohydrocarbon and only prolonged thermal treatment (120 h at 70°) leads to the detachment of perfluorocyclobutane.

As Table 2 shows, fluorocarbon complexes do not differ from the hydrocarbon analogues in ability to exchange ligands. One or two of their carbonyl groups can be replaced by phosphines or amines[82]. NMR data for the fluorocarbon complexes have been given by Pitcher and coworkers[81].

Cobalt, rhodium, iridium. It has been reported[83,84] that organometallic derivatives of the composition $CoX_3(C_{10}H_7)$ and $CoX_2(C_{10}H_7)_2$ are obtained by the action of halogeno(naphth-2-yl)magnesiums on ethereal solutions of cobalt salts. But since data about their composition, hydrolysis products, and thermal decomposition are insufficient, it is impossible to consider the existence of the simplest σ derivatives of cobalt as proved. Those classes of derivatives which contain carbonyls or phosphines, etc. instead of σ groups have been more thoroughly studied. Quite recently a new class of stable organic derivatives was discovered — the alkylpentacyanocobaltates. Perfluorinated analogues of some of these complexes have been obtained. Cobalt, like the other elements of Group VIII, is capable of forming four-coordinated complexes of *trans*-configuration $CoAr_2L_2$, where Ar is a bulky aromatic radical of the mesityl type[72]. They are all crystalline and melt with decomposition above 100°. They are somewhat less stable than the analogous derivatives of Pt, Pd, and Ni, which Chatt explains by a tetrahedral (instead of planar) arrangement of the ligands. The stabilising action of the phosphine groups is less in such a configuration.

**Five**-coordinated arylphosphine complexes (VI), having halogen as a fifth ligand have been obtained for rhodium[85]:

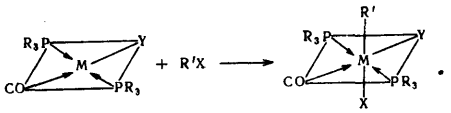


(VI)

In these compounds the rhodium(III) — usually six-coordinated — is coordinatively unsaturated and it could be expected that these substances would be unstable towards nucleophilic attack; however, they are completely stable. This is explained by the almost spherical structure formed by the bulky ligands which compactly surround the metal and shield it from the attacking agent.

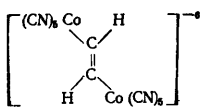
A preliminary communication that complexes of the type $MR_2L_2$ are obtained has been published[18].

Six-coordinated σ complexes of iridium(III) and rhodium(III) have been obtained[86]. They are formed as a result of the addition of active organic halides to some planar complexes of iridium(I) and rhodium(I):



During this, the metal is oxidised to the tervalent state. Table 3 lists some of the complexes obtained in this way. They are all crystalline, high-melting materials, stable in air.

Griffith and Wilkinson[87] observed, as long ago as 1959, that aqueous solutions of a pentacyanocobaltate absorb acetylene. They isolated a crystalline, diamagnetic salt of composition $K_6[Co_2(CN)_{10}(C_2H_2)].4H_2O$, which has been ascribed the structure (VII) on the basis of infrared and NMR analyses:



(VII)

The *trans*-configuration was chosen arbitrarily, as there are no analogues for these compounds and the available data are insufficient to settle the question of configuration conclusively. It was later shown[88] that aqueous solutions of $[CoH(CN)_5]^{-3}$ and $[Co(CN)_5]^{-3}$ absorb perfluoroethylene at atmospheric pressure. Salts of the composition $K_3[Co(CN)_5(CF_2CF_2H)]$ and $K_6[(CN)_5Co(CF_2CF_2)Co(CN)_5]$ were isolated. Unlike (VII), which is of comparatively low stability, decomposes slowly in air and rapidly in a vacuum at 70°, the fluorinated complex salts are stable to oxidation and thermally up to 300°. The reaction with perfluoroethylene goes so easily and unambiguously, that, in the authors' opinion, it can be used analytically for determining metal–hydrogen bonds when the latter cannot be observed by NMR analysis.

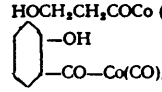
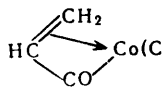
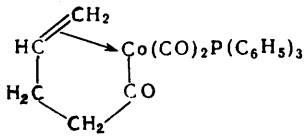
A variant of the synthesis of this class of complexes consists of the reactions of pentacyanocobaltates with alkyl halides[89]. It is possible to start from a mixture of $CoCl_2$ and NaCN:

$$2[Co(CN)_5]^{-3} + C_6H_5CH_2Br \rightarrow [Co(CN)_5(C_6H_5CH_2)]^{-3} + [CoBr(CN)_5]^{-3}.$$

Methyl, ethyl, and n-propyl derivatives are obtained analogously. The most stable of these are the benzyl complexes, which are slowly decomposed in air, split off bibenzyl when heated in a vacuum, and are decomposed by acids and mercury(II) chloride.

Many investigations have been devoted to acyl and alkyl derivatives of cobalt carbonyls. The interest in them is undoubtedly connected with explaining the mechanism of

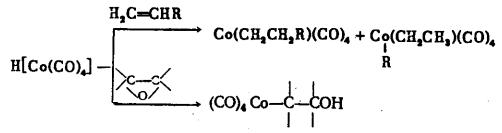
TABLE 3. $\sigma$ derivatives of cobalt, rhodium, and iridium.

| Derivative | Colour | M.p., °C | Reference | | | |
|---|---|---|---|---|---|---|
| | | | preparation | infrared spectra | NMR | dipole moment |
| $CH_3Co(CO)_4$ | yellow | exists <—80 | 91,112 | 91,112 | — | — |
| $C_6H_5Co(CO)_3P(C_6H_5)_3$ | » | 140 | 106 | 106 | — | — |
| $CH_3COCo(CO)_4$ | – | — | 99 | 99 | — | — |
| $C_6H_5COCo(CO)_4$ | – | — | 99 | 99 | — | — |
| $HOCH_2CH_2COCo(CO)_3P(C_6H_5)_3$ | yellow-brown | 95—100 (decomp.) | 93 | 93 | — | — |
|  | pale yellow | — | 93 | — | — | — |
| $CH_2=CHCH_2COCo(CO)_3P(C_6H_5)_3$ | yellow | 82(decomp.) | 90 | 90 | — | — |
|  | » | 106—107 (decomp.) | 90 | 90 | — | — |
|  | slightly coloured | 106.5—107 | 90 | 90 | — | — |
| $CH_2=CH(CH_2)_3COCo(CO)_3P(C_6H_5)_3$ | yellow-brown | 90.5—93 (decomp.) | 96 | 96 | — | — |
| $(CH_3)_3COCOCo(CO)_3P(C_6H_5)_3$ | — | (decomp.)>100 | 105 | — | — | — |
| *trans*-(Mesityl)$_2$Co[$P(C_2H_5)_3$]$_2$ | yellow | 113—116 (decomp.) | 72 | — | — | — |
| *trans*-(2-$C_6H_4C_6H_5$)$_2$Co[$P(C_2H_5)_2C_6H_5$]$_2$ | » | 115—119 (decomp.) | 72 | — | — | 72 |
| *trans*-(2-Methyl-1-naphthyl)$_2$Co[$P(C_2H_5)_2C_6H_5$]$_2$ | » | 144—146 (decomp.) | 42,72 | — | — | 42,72 |
| *trans*-($C_6Cl_5$)$_2$Co[$P(C_2H_5)_2C_6H_5$]$_2$ | lemon-yellow | 224—228 (decomp.) | 72 | — | — | 45 |
| $CF_3Co(CO)_4$ | amber | 13.31/28 mmHg | 107,108 | 107,108 | 107 | — |
| $C_2F_5Co(CO)_4$ | » | b.p. 32/16 mmHg | 106,107 | 106,107 | 107 | — |
| $n\text{-}C_7F_{15}Co(CO)_4$ | yellow-brown | 30 | 106 | 106 | — | — |
| $CF_3Co(CO)_3P(C_6H_5)_3$ | pale yellow | 168 | 108 | 108 | — | — |
| $C_2F_5Co(CO)_3As(C_6H_5)_3$ | dark yellow | 134 | 106 | 106 | — | — |
| $C_2F_5Co(CO)_3Sb(C_6H_5)_3$ | yellow-brown | 120 | 106 | 106 | — | — |
| $C_2F_5Co(NO)_2P(C_6H_5)_3$ | violet-brown | 65 | 106 | 106 | — | — |
| $(CO)_4CoCF_2CF_2Co(CO)_4$ | orange | 70 (decomp.) | 80 | 80 | 80 | — |
| $CF_3COCo(CO)_4$ | yellow | 4 | 108 | 108 | — | — |
| $CF_3COCo(CO)_3P(C_6H_5)_3$ | » | 172 | 108 | 108 | — | — |
| $C_2F_5COCo(CO)_3P(C_6H_5)_3$ | » | 138 | 106 | — | — | — |
| $CF_3(I)Co(CO)C_5H_5$ | black | 145 (decomp.) | 110 | 111 | 111 | — |
| $n\text{-}C_3F_7(I)Co(CO)C_5H_5$ | » | 121 | 110 | 111 | 69,81 | — |
| $(CF_2)_4=Co(CO)C_5H_5$ | yellow | 106 | 109 | 109 | 109 | — |
| $(C_6F_5)_2Co[CH_2P(C_6H_5)_2]_2$ | » | 186 (decomp.) | 47 | | — | — |
| $CH_3Rh(Cl)(I)(CO)[P(n\text{-}C_4H_9)_3]_2$ | pale yellow | 85—86 | 86 | 86 | — | — |
| $C_6H_5CH_2Rh(Cl)(Br)(CO)[P(n\text{-}C_4H_9)_3]_2$ | ditto | 109—110.5 | 86 | 86 | — | — |
| $CH_3CORh(I_2)(CO)[P(n\text{-}C_4H_9)_3]_2$ | orange | 76—78 | 86 | 86 | — | — |
| (Naphth-1-yl)$_3$Rh(Br)[$P(C_3H_7)_3$]$_2$ | white | 137—139 | 85 | — | — | 85 |
| $CF_3Rh(I)(CO)C_5H_5$ | red | 168—169 | 111 | 111 | 111 | — |
| $C_2F_5Rh(I)(CO)C_5H_5$ | » | 145—147 | 111 | 111 | 111 | — |
| $C_3F_7Rh(I)(CO)C_5H_5$ | » | 118—119 | 111 | 111 | 111 | — |
| $CH_3Ir(Cl)(I)(CO)[P(C_6H_5)_3]_2$ | pale yellow | 268—269 (decomp.) | 86 | — | — | — |
| $CH_3OOCCH_2Ir(Cl)(I)(CO)[P(C_6H_5)_3]_2$ | ditto | 248—249 | 86 | — | — | — |
| $CH_2=CHCH_2Ir(I_2)(CO)[P(C_6H_5)_3]_2$ | red-brown | 214 | 86 | — | — | — |

the oxo-synthesis. Alkylcarbonylcobalts can be obtained from alkyl halides and sodium carbonylcobaltates[90,91]:

$$Na[Co(CO)_4] + XR \rightarrow RCo(CO)_4, \qquad \text{(Method H)}$$

or by addition of hydrogen tetracarbonylcobaltate(-1) to alkenes[92] or epoxy-compounds[93,94]:



Alkylcobaltcarbonyls evidently exist in equilibrium with an acyl form. This is suggested

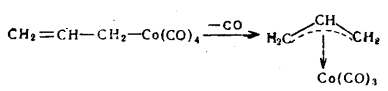
$$RCo(CO)_4 \rightleftarrows RCOCo(CO)_3 \overset{CO}{\rightleftarrows} RCOCo(CO)_4$$

by the existence of a 5.8 $\mu$ band in the spectra of alkylcarbonyls in the gas phase and in solutions. The ease of the reciprocal changes and the instability of one or the other often does not allow them to be isolated in a pure state. This applies especially to the alkylcarbonyls. Irrespective of the nature of R they can be characterised only in the form of acylcarbonylphosphine complexes. This is because during the treatment of the alkylcarbonyl with phosphine the CO being displaced does not depart to the outer sphere, but is inserted at the R–Co bond, with formation of an acyl complex:

$$RCo(CO)_4 + PR'_3 \rightarrow RCOCo(CO)_3PR'_3.$$

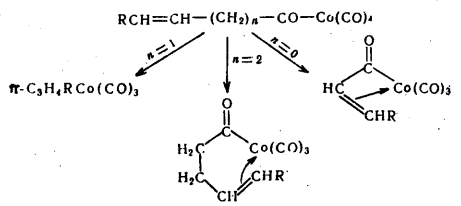
Hence the acyl complex is obtained directly by Method H in the presence of phosphines.

When R is an unsaturated radical the molecule is stabilised by rearrangement into a $\pi$ complex. For example, the stage of the $\sigma$ allyl derivative could not be isolated since on heating it is converted into the $\pi$ allylcarbonyl[90,95]:



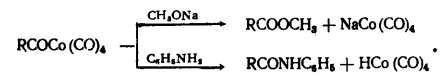
The special nature of the bond in a $\pi$ allyl complex makes it incomparably more stable compared with the $\sigma$ complex, although in either the metal has a closed electron configuration of krypton and the same stabilising ligands. When phosphines act on it, one of the carbonyl groups is replaced, but acyl complexes are not thus obtained.

Acylcarbonyls of cobalt are obtained by the carbonylation of alkylcarbonyls or by Method H. When the acyl radical has an unsaturated chain, reaction H takes place with liberation of CO, but the products obtained contain an acyl group. It is thought that one of the CO groups of the carbonyl residue is displaced by the carbon–carbon double bond and a $\sigma\pi$ complex is obtained:



The intermediate acyltetracarbonyl complexes are not usually isolated, but sometimes their crystalline phosphine derivatives can be obtained[90,96,97].

The acylcarbonyls readily react with various nucleophilic reagents[98]:

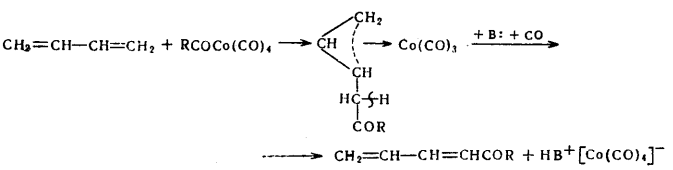


Like the alkyl compounds they are extremely unstable thermally. Thus methyltetracarbonylcobalt exists as yellow crystals at -80° and decomposes at higher temperatures, but the acyltetracarbonylcobalt is a crystalline substance with m.p. -33° and decomposition temperature -20°. The combination of the properties described for the acyl and alkyl derivatives of cobalt carbonyl determines their role in catalytic processes, and in turn in hydroformylation.

Analogous syntheses and transformations are also possible for manganese carbonyl. Here also the reversible reaction of carbonylation–decarbonylation is characteristic, but both the alkyl and the acyl derivatives of manganese carbonyl are considerably more stable and can be isolated.

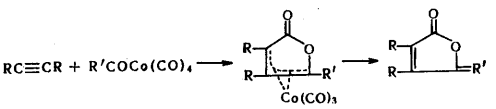
Phosphines replace one of the carbonyl groups of acyl complexes[98-100]. Some sterically strained tertiary phosphites are capable of displacing one, two, and even three carbonyl groups, but the phosphito(acyl) complexes thus obtained are unstable to oxidation[101].

Heck[102-104] observed an interesting ability of acylcarbonyls to add to a diene system or acetylene. With the former, substituted $\pi$ allylcarbonyls are obtained, which under the action of nitrogenous bases decompose with the liberation of acyldienes:



Since the acyl complex is always found in equilibrium with the alkyl, the same result is obtained on starting from the alkylcarbonyls, or what is even simpler, on taking a mixture of the sodium salt of a carbonyl, an alkyl halide, diene, and amine.

The addition of acylcarbonyls to the acetylenes leads to a complex type of $\pi$-enyl, the formation of which is confirmed spectroscopically, and also the liberation of phosphine derivatives. An intermediate complex, by breaking down in the presence of amine, gives an unsaturated lactone:



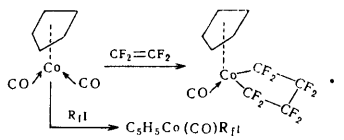
Some examples are known of perfluoroalkylcarbonyl-cobalt complexes, obtained by Method H[106-108] (see above). In attempts to use this method to obtain perfluoroacylcarbonyls, decarbonylation took place simultaneously. However, when the reaction is carried out below room temperature perfluoroacylcarbonyls can be isolated[106,108]. If then one of their carbonyl groups is replaced by a phosphine, then acyl derivatives completely stable to decarbonylation are obtained[106,108]. Both types of $\sigma$ complex are considerably more stable than their hydrocarbon

analogues. It should be noted that the back reaction of carbonylation of the perfluoroalkylcarbonyls evidently occurs with greater difficulty than for the alkylcarbonyls, since during reaction with phosphines, arsines, or stibines CO is liberated and an acyl complex is not obtained.

Cobalt carbonyl in tetrahydrofuran under very mild conditions at room temperature reacts with perfluoroethylene, which is inserted between the two metal atoms, giving a dinuclear σ complex[80]:

$$Co_2(CO)_8 + CF_2{=}CF_2 \rightarrow (CO)_4CoCF_2CF_2Co(CO)_4.$$

Under somewhat more severe conditions, in an autoclave at 160° perfluoroethylene reacts with cyclopentadienyldicarbonylcobalt, one of the carbonyl groups being replaced by a perfluorinated ring[109]:

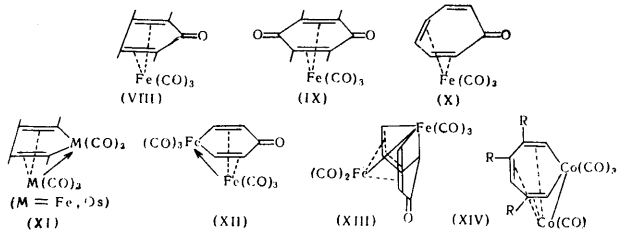


Finally, one of the carbonyl groups can be displaced by a perfluoroalkyl iodide[110]. Cyclopentadienyldicarbonylrhodium behaves analogously[111].

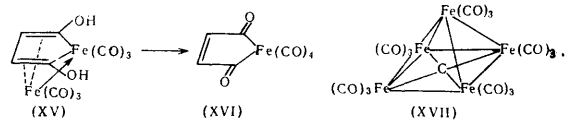
Table 3 contains some examples of σ complexes of cobalt. rhodium, and iridium.

Products of the reaction of alkynes with carbonyls and carbonyl complexes of Group VIII metals. Diels–Alder type of metal addition. The variety of complexes obtained from acetylenes and carbonyls or carbonyl complexes may be recalled again. Although the structure of many of these is not indisputable, continuing study of them led to an interesting hypothesis and paths for future investigation were noted.

Acetylene, as such, hardly ever participitates in the formation of π complexes, although acetylenic π complexes are evidently the first stage in the reaction and can be isolated when platinum is involved. Among the products of the reaction of iron and cobalt carbonyls with acetylene, two classes of derivatives (in addition to others) have been isolated: (1) carbonyl complexes of unsaturated ketones, obtained as the result of the cyclic polymerisation of several acetylene molecules, with the participation of carbon monoxide, (VIII), (IX), (X), etc.; (2) five-, six-, and seven-membered heterocycles with metal atoms in the ring (XI), (XII), (XIII), (XIV)[113-119]. For the structure of (XIV), however, see Mills and Robinson[120].

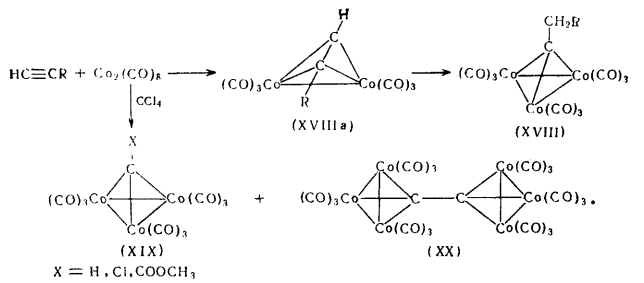


The formation of heterocycles is thus brought about by σ bonding with the metal. The molecules are stabilised by the attachment of a second carbonylmetal grouping of the π complex formation type. Their structure was confirmed by chemical destruction and also by X-ray analysis. Most of them are sufficiently stable thermally to be isolated in a pure state. The chemical stability is confirmed by such facts as, for example, the possibility of replacing the CO groups by other ligands, in particular, $SO_2$ [121], or by the oxidation (XV) → (XVI) with retention of the ring structure[122]:



The reaction of $Fe_3(CO)_{12}$ with some substituted acetylenes leads to the formation of (XVII) together with other complexes. The substance is diamagnetic, does not have bridging CO groups, and X-ray structural analysis has shown it to be a tetragonal pyramid at the apices of which tricarbonyliron groups are situated, and a single carbon atom lies in the base of the pyramid[123].

The analogous carbide-like compounds (XVIII), (XIX), and (XX) (if the carbon of the CO groups is not considered) are also obtained from octacarbonyldicobalt and monosubstituted acetylenes[114,124,125] carbon tetrachloride, or bromoform[126]:

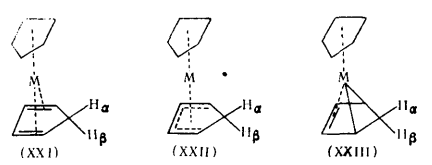


Structures of type (XVIIIa) have been proposed for the products of the reaction of $Hg[Co(CO)_4]_2$ and disubstituted acetylenes[127,128] and also for some derivatives of cyclopentadienylcarbonylnickel[129]. All are crystalline, often deeply coloured substances, sometimes with high melting points (~ 200°) and stable in air.

Hence the transition metal–carbon σ bond is widely used in complex molecules.

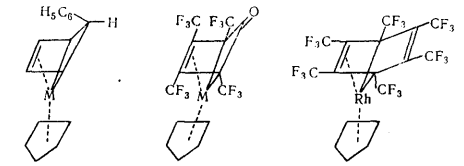
Within the last two years a series of crystallographic investigations made in England by Churchill and coworkers have been published, and these have changed some former concepts about the structure of several complexes and the nature of the bonds.

As long ago as 1959, Wilkinson[130] proposed three possible structures, (XXI), (XXII), and (XXIII), for compounds of the general formula $C_5H_5MC_5H_6$:



The NMR spectra, which are consistent with structure (XXIII), do not, however, agree with the infrared results, and it was impossible to settle the question in favour of one of these structures. A structure analogous to (XXIII) was

also proposed for the tetrakis(trifluoromethyl)(cyclopentadienone)tricarbonyliron [131]. The proximity of $H_\alpha$ to the central atom and the interaction with non-bonding electrons of the metal explained its mobility and spectroscopic characteristics. The absence of the characteristic $H_\alpha$ bands from complexes substituted in the methylene group is considered a sign that the $H_\alpha$ and not the $H_\beta$ is substituted and that the substituent is therefore in the *endo*-position [132,133]. However, as an X-ray study of cyclopentadienyl(phenylcyclopentadiene)cobalt has shown [134-136], in fact addition occurs to the cyclopentadiene ring of type (XXIII), but the $CHC_6H_5$ group departs from the plane of the remaining part of the ring to the side opposite from the metal and the phenyl occupies the *exo*-position (XXIV):



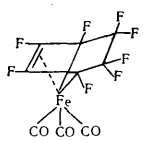
(XXIV) M = Co
(XXVII) M = Rh



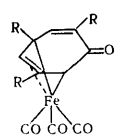
(XXV) M = Co
(XXVI) M = Rh



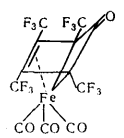
(XXVIII)



(XXIX)



(XXX)
R = H, $C_6H_5$

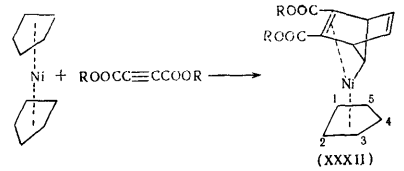


(XXXI)

A quasi-Diels–Alder addition of metal to a diene system, and consequently the rehybridisation of the carbon atoms of the ring which take part in the σ bonding, is shown by X-ray diffraction also for (XXV) [135,137], (XXVI) [138,139], (XXVII) [140], (XXVIII) [138,139,141], (XXIX) [142], (XXX) [143], (XXXI) [144]. The bond lengths, ring conformations, and bond angles show that the bond of the metal with the diene moiety in these molecules consists of one μ and two σ bonds. (XXVIII) is the first example of a localised addition of a transition metal to the benzene ring, as a result of which the planarity and the aromaticity of the ring are completely destroyed. It is thought [142] that the structure of butadienetricarbonyliron, which according to the most recent information [145] contains a delocalised system, should be studied more thoroughly.

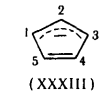
Both the metal ion and the other ligands bonded with it play a part in determining the degree of σ bonding. The formation of a localised bond also depends on the fall in the delocalisation energy under the influence of electronegative substituents, such as the $CF_3$ group. Bailly and coworkers [144] think that the departure from planarity should be taken as a measure of the σ bonding rather than the bond lengths, the difference in which is generally not significant. The greater departure of the ketone group in cyclopentadiene complexes shows the greater $sp^2 \rightarrow sp^3$ rehybridisation of neighbouring carbon atoms. According to Dahl and Smith's results [146] cyclopentadienyl(tetramethylcyclopentadienone)cobalt has, unlike (XXV), a levelled system [sic]§ and as it were a sandwich type of bond. However, the insignificant departure of the carbonyl group which is observed can also be considered as an indication of some localisation of the bond. The localisation energies at appropriate carbon atoms have been calculated [144].

The examples mentioned above showed the possibility of the localised addition of metal to a diene system. The possibility of a greater or less distortion of the delocalisation in a cyclopentadienyl ligand is also not excluded. Dahl and Chin Hsuan Wei [147] first drew attention to this, by studying the structure of the product of the addition of an ester of acetylenedicarboxylic acid to nickelocene (XXXII) [148]:



(XXXII)

The Ni–C and C–C distances in the cyclopentadienyl ring show partial delocalisation in the adduct with a μ bond from $C_{(1)}$–$C_{(2)}$ and a σ bond from $C_{(4)}$. It is thought that this type of bond with cyclopentadienyl is possible in rhodium(I) and nickel(I) complexes. An approximate calculation [149] shows that the structure (XXXIII) is possible for the cyclopentadienyl ring, where the bond order in the $C_{(1)}C_{(2)}C_{(3)}$ group of atoms is relatively lower than in the $C_{(4)}C_{(5)}$ group which is confirmed crystallographically for several complexes which do not possess cylindrical symmetry. The $C_{(1)}C_{(2)}C_{(3)}$ group is always in the *trans*-position to the ligand with the stronger field.



(XXXIII)

Despite the distortion of the delocalisation in the cyclopentadienyl ligand its aromatic nature is evidently unchanged, as in the NMR spectra there is, as before, a single signal for the ring protons [147,148]. This is explained by the dynamic effect of internal rotation.

## 2. Group VII. Manganese, Rhenium

See Cotton [16] for the early attempts to obtain organic derivatives of manganese and rhenium. Subsequently, iodo(methyl)manganese, dimethylmanganese, and diphenylmanganese, which are unstable to oxidation and insoluble in ether, were obtained [150,151]. With an excess of organolithium reagent they form colourless amorphous insoluble salts of composition $LiMnR_3$. The salts also decompose in air but more slowly than the initial dialkyl derivatives [150]. Dicyclopentadienylmanganese [152] and bis(methylcyclopentadienyl)manganese [153] have been obtained, and their properties show the ionic nature of the bonds in the molecules. These compounds have low oxidation resistance, the first of them burning in air with an explosion. Water and acids immediately destroy it with liberation of cyclopentadiene.

Complexes of the type $MR(CO)_5$, where R represents alkyl, aryl, the corresponding acyl, or fluorinated analogues, are more characteristic derivatives for manganese and rhenium. They are obtained by Method H [20,64,95,154-158] (p. 178), and dinuclear complexes $(CO)_5Mn(CH_2)_nMn(CO)_5$ are obtained by the same method. Features of the structure of some of them are discussed by King [64]. The methyl

§ There is delocalisation of the four π electrons of the tetramethylcyclopentadienone and the CO is tipped out of the plane of the other atoms by 9° away from cobalt (Ed. of Translation).

derivative is also obtained by Method E [159] (p. 173). Some derivatives with an unsaturated σ ligand are obtained by Method F [95] (p. 173), in which, just like the hydrocarbonyls, already prepared $MnR(CO)_5$ can be attached to the diene, to form new derivatives [160]. As for cobalt, here transitions of the σ allyl → π allyl type are characteristic [20,95], and others, but the σ derivatives of manganese are much more stable thermally, and can be isolated and characterised.

The acylcarbonyls of manganese and rhenium are, from their ability to reversible decarbonylation, analogues of the acyl derivatives of carbonylcobalt, although here also great stability is noted. See elsewhere [90,161-163] for the mechanism and kinetics of these changes.

As was recently reported [164], the cations of the carbonyl complexes of manganese and rhenium in alcoholic alkali undergo an interesting transformation into neutral σ carboalkoxycarbonyl complexes:

$$[Mn(CO)_4L_2]^+ + RO^- \underset{HCl}{\rightleftharpoons} ROOC{-}Mn(CO)_3L_2,$$

where L = phosphine, etc.

In this the carbonyl group of the complex is converted into σ bound carbonyl. The reaction is reversible: acid splits off the ester group and the original cation returns.

The preparation of some σ derivatives of dicyclopentadienylrhenium, formed as a result of the addition of dicyclopentadienyl hydride to substituted alkynes, has been described [165].

Perfluoro-alkyl or -aryl and perfluoroacyl derivatives of the carbonyls of manganese and rhenium have been obtained by Methods H [20,64,76,77,107,154] and D [78] (pp. 178 and 173). Perfluoroalkyl derivatives can also be obtained by decarbonylation of perfluoroacyls above 80° for manganese and above 120° for rhenium [20,64,107,154], or by the addition of $MnR(CO)_5$ to fluoroethylenes [75,166-168]. The addition to non-symmetrical fluoroethylenes of the type $CF_2{=}CFCl$ and $CF_2{=}CCl_2$ depends on the reaction conditions. Usually the more fluorinated end of the molecule adds on to the metal, but with ultraviolet irradiation a mixture of products in which the $-CFCl-Mn$ derivative predominates is obtained [167,168]. The irradiation facilitates the addition of methyl- and phenyl-carbonylmanganese to fluoroethylenes.

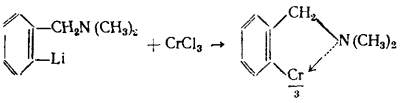
Table 4 contains examples of all classes of the σ derivatives of manganese and rhenium.

### 3. Group VI. Chromium, Molybdenum, Tungsten

We will not dwell on the well-known history of the phenyl derivatives of chromium, but note only that certain covalent derivatives, stabilised by the addition of solvent molecules — Lewis bases, or carbanions — were isolated in a pure state. First of all, there is $Cr(C_6H_5)_3.3THF$, a red crystalline substance which decomposes at 85° and the product of the addition to it of magnesium salts $Cr(C_6H_5)_3.3THF.3(MgBrCl.THF)$ [169]. In solutions they exist briefly, regrouping into π complexes, and are instantly decomposed by water and mercury(II) chloride. The stabilising action of the tetrahydrofuran molecule is clearly demonstrated by the decomposition of the complex on drying.

The phenylation of chromium(III) chloride with an excess of phenyllithium in ether leads to the formation of $Li_3[Cr(C_6H_5)_6].2\frac{1}{2}(ether)$ [170], which later results [171] suggest should be $Li_3[Cr(C_6H_5)_6].4(ether)$. It consists of orange-yellow crystals, sensitive to oxygen and atmospheric moisture, capable of being reduced to the monohydride. Corresponding salts of substituted phenylchromium [172] and phenyltungsten [173] have been obtained.

There is proof of the formation of benzyl derivatives of chromium: $[Cr(C_6H_5CH_2)(H_2O)_5]^{2+}$, [174] $[Cr(C_6H_5CH_2)_3]$, and $CrCl(C_6H_5CH_2)_2$, [171] which contain solvent molecules, etc. (XXXIV) has been briefly described — an amino-σ-aryl chelate complex, obtained [175] thus:




(XXXIV)

— as have the alkynyl derivatives $K_3[Cr(C{\equiv}CR)_3(CO)_3]$ [176]. We will not dwell on the role of this kind of chromium derivative in catalytic processes.

By the reaction of molybdenum(V) chloride with an excess of cyclopentadienylsodium, Fischer and Hristidu [177] obtained tetrakiscyclopentadienylmolybdenum. This diamagnetic substance, which is extremely sensitive to oxygen, has one π and three σ cyclopentadienyl groups, according to the authors' results.

General methods for obtaining cyclopentadienylcarbonyl σ complexes (Methods C, D, and E, p. 173) [61] are applicable to various extents to the Group VI metals. Table 5 shows derivatives obtained in this way and some of their fluorinated analogues [69,178]. Among them, the instability of molybdenum compounds of type $Mo(RCO)(C_5H_5)(CO)_3$ has been repeatedly noted. Attempts to obtain them often end in the formation of a dimer cyclopentadienyltricarbonylmolybdenum. Even their perfluorinated analogues are 50–80% decarbonylated during isolation. Unlike them, the analogous acyl complexes of tungsten are completely stable and are not decarbonylated even on irradiation.

The σ allyl derivatives of molybdenum and tungsten, like the iron analogues, are only converted into π allyl complexes on irradiation [179,180].

The interesting thermal decomposition of ethylcyclopentadienyltricarbonylmolybdenum has been described, in which such products as $[Mo(C_2H_5C_5H_4)(CO)_3]_2$ and $(C_5H_5)Mo(CO)_3Mo(CO)_3(C_5H_4C_2H_5)$ are obtained, that is, the ethyl group is transferred from the metal to the ring [181]. This is explained by the general nature of the ethyl–molybdenum bond.

### 4. Group V. Vanadium, Niobium, Tantalum

According to the results of Meijer and coworkers [182], dicyclopentadienylvanadium is capable of adding alkyl halides according to the equation:

$$2V(C_5H_5)_2 + RX \rightarrow VR(C_5H_5)_2 + VX(C_5H_5)_2.$$

Dicyclopentadienylvanadium dichloride and LiR also give alkyldicyclopentadienvylvanadium. In this way derivatives stable when solid were obtained, with $R = C_6H_5CH_2$ (m.p. 109°), $CH_3$ (decomp. 80–100°), and $C_2H_5$, still less stable.

Quite recently, Juvinall [183] reported the production of the first alkyl derivatives of niobium and tantalum by the alkylation of the halides with diethylzinc:

$$2NbCl_5 + 3Zn(CH_3)_2 \rightarrow 2NbCl_2(CH_3)_3 + 3ZnCl_2.$$

TABLE 4. σ derivatives of manganese and rhenium.

| Derivative | Colour | M.p., °C | Reference | | | |
|---|---|---|---|---|---|---|
| | | | preparation | infrared spectra | NMR | dipole moment |
| $CH_3MnI$ | red-brown | liquid | 150 | — | — | — |
| $(CH_3)_2Mn$ | pale yellow | cryst. | 150,151 | — | — | — |
| $[(CH_3)_3Mn]Li$ | white | cryst. | 150,151 | — | — | — |
| $(C_6H_5)_2Mn$ | green | cryst. | 151 | — | — | — |
| $(C_6H_5)_2Mn$ | amber | 172—173 | 152 | 152 | 152 | 152 |
| $CH_3Mn(CO)_5$ | white | 94.5—95 | 155,159 | 108,154, 155 | — | 154 |
| $C_6H_5Mn(CO)_5$ | » | 54 | 155 | 154 | — | 154 |
| $C_6H_5CH_2Mn(CO)_5$ | pale yellow | 37.5—38.5 | 155 | 154,155 | — | 154 |
| $CH_2{=}CH{-}CH_2Mn(CO)_5$ | yellow | b.p. 45°/5 mmHg | 95 | 95 | 95 | — |
|  | white | 30 | 158 | — | — | — |
| $(CH_2)_3[MnCO)_5]_2$ | yellow | 64—65 | 64 | 64 | 64 | — |
| $C_2H_5OOC{-}Mn(CO)_3[P(C_6H_5)_3]_2$ | » | cryst. | 164 | 164 | — | 164 |
| $CH_3Mn(CO)_4P(C_6H_5)_3$ | pale yellow | 110 | 156,163 | 156,163 | — | — |
| $CH_3COMn(CO)_5$ | white | 54—55 | 155 | 108,155 | — | 154 |
| $C_6H_5COMn(CO)_5$ | » | 95—96 | 155 | 155 | — | 154 |
|  | yellow | 80.5—81 | 158 | — | — | — |
| $CH_3COMn(CO)_4NH_2C_6H_5$ | » | 83—84 | 161 | 161 | — | — |
| $CH_3COMn(CO)_4P(C_6H_5)_3$ | » | 98 | 163 | 163 | — | — |
| $CF_3Mn(CO)_5$ | white | 85 | 107,154 | 107,108, 154 | 107 | 154 |
| $C_2F_5Mn(CO)_5$ | » | 16 | 20 | 20 | 20,81 | — |
| $HCF_2CF_2Mn(CO)_5$ | pale yellow | 30.5—31.5 | 75,166 | 75,166 | 75,166 | — |
| $Cl(CF_2)_4Mn(CO)_5$ | ditto | b.p. 58/1 mmHg | 107 | 107 | — | — |
| $CHCl_2CF_2Mn(CO)_5$ | » | 69 | 166 | 166 | 166 | — |
| $(CF_2)_3[Mn(CO)_5]_2$ | white | 161 | 64 | 64 | 64 | — |
| $C_6F_5Mn(CO)_5$ | » | 121—122 | 77,78 | 77 | 77,78 | — |
| $CF_3CF{=}CFMn(CO)_5$ | » | 76—76.5 | 20,76, 107 | 76, 107 | 76, 107 | — |
| $CF_3COMn(CO)_5$ | orange-yellow | 57 | 107,154 | 107,108, 154 | — | 154 |
| $CF_3COMn(CO)_4P(C_6H_{11})_3$ | lemon-yellow | 98 | 156 | 156 | — | — |
| $(CF_2)_3(CO)_2[Mn(CO)_5]_2$ | pale yellow | 105—106 | 64 | 64 | 64 | — |
| $CH_3Re(CO)_5$ | white | 120 | 157 | 154 | — | — |
| $C_6H_5Re(CO)_5$ | » | 46—47 | 157 | 154 | — | 154 |
| $C_6H_5CH_2Re(CO)_5$ | yellow | 33—34 | 154 | 154 | — | — |
| $CH_3OOCCH{=}CH{-}Re(C_5H_5)_2$ | orange-brown | 161—162 | 165 | 165 | 165 | — |
| $CH_3CORe(CO)_5$ | pale yellow | 80—81 | 157 | 154 | — | 154 |
| $C_6H_5CORe(CO)_5$ | yellow | 120(decomp.) | 157 | 154 | — | 154 |
| $C_2F_5Re(CO)_5$ | pale yellow | 39—40 | 20 | 20 | 81 | — |
| $C_2F_5CORe(CO)_5$ | ditto | 81—83 | 20 | 20 | 81 | — |
| $n\text{-}C_3F_7CORe(CO)_5$ | » | 54 | 20 | 20 | 81 | — |

The reaction proceeds in pentane at -78°. The yellow, crystalline, trialkyl derivatives are monomers (from mass spectroscopic studies), volatile, decompose in a few hours at room temperature, but are fairly stable at -78° in the absence of water and oxygen. The tantalum analogue is less thermally stable. Their compositions were determined from the ratio of the products of alkaline hydrolysis.

Somewhat earlier, Fischer and coworkers [184] obtained complexes of composition $M(C_5H_5)_4$ by reaction of tantalum and niobium pentachlorides with cyclopentadienylsodium. These are extremely sensitive to oxygen, monomeric, and paramagnetic. From the infrared analysis, X-ray powder diagrams, and behaviour on hydrogenation, structures with two π and two σ-$C_5H_5$ groups are proposed.

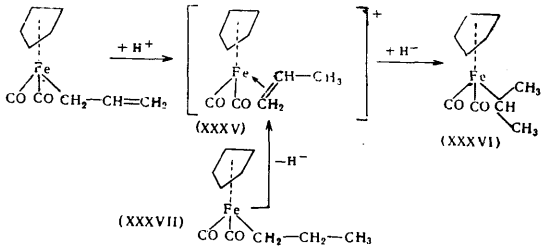
## 5. σ-Derivative → π-Complex Transitions and the Reverse

In conclusion we think it necessary to mention the interesting reaction, σ-derivative → π-complex and the reverse, which became known from the work of Green and Nagy. They showed that σ allyldicarbonyliron-

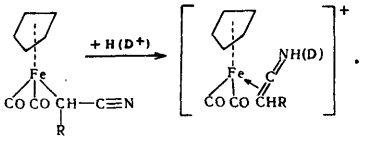
TABLE 5. σ derivatives of chromium, molybdenum, and tungsten.

| Derivative | Colour | M.p., °C | Reference | | |
|---|---|---|---|---|---|
| | | | preparation | infrared spectra | NMR |
| $CH_3Cr(CO)_3C_5H_5$ | yellow | cryst. | 61 | 61 | 61 |
| $CH_3Cr(NO)_2C_5H_5$ | dark green | 82.8—83.2 | 61 | 61 | 61 |
| σ-$C_5H_5Cr(NO)_2C_5H_5$ | cinnamon brown | 66.5—67.2 | 61 | 61 | 61 |
| $C_5H_5Cr(NO)_2C_5H_5$ | green | liquid | 61 | 61 | 61 |
| $CH_3Mo(CO)_3C_5H_5$ | yellow | 124 (decomp.) | 61 | 61 | 61 |
| $C_2H_5Mo(CO)_3C_5H_5$ | » | 77.5—78.5 | 61,180 | 61,180 | 61 |
| iso-$C_3H_7Mo(CO)_3C_5H_5$ | » | 29—30 | 61 | 61 | 61 |
| $CH_2$=CH—$CH_2Mo(CO)_3C_5H_5$ | pale yellow | —5 | 180 | 180 | 180 |
| $C_2H_5COMo(CO)_3C_5H_5$ | red | liquid | 67 | 67 | 67 |
| $CF_3Mo(CO)_3C_5H_5$ | yellow | 153 | 69 | 69 | 69 |
| $(CF_2)_3[Mo(CO)_3C_5H_5]_2$ | » | 200 (decomp.) | 69 | 69 | 69 |
| $HCF_2CF_2Mo(CO)_3C_5H_5$ | » | 53—54 | 75,178 | 178 | 178 |
| $CF_3COMo(CO)_3C_5H_5$ | » | 64—65 | 69 | 69 | 69 |
| $CH_3W(CO)_3C_5H_5$ | red-orange | 144.7—145.3 | 61,62 | 61 | 61 |
| $CH_2$=CH—$CH_2W(CO)_3C_5H_5$ | pale yellow | 24—26 | 179 | 179 | 179 |
| iso-$C_3H_7W(CO)_3C_5H_5$ | dark yellow | b.p. 40/$10^{-3}$ | 179 | 179 | 179 |
| $C_2H_5COW(CO)_3C_5H_5$ | orange | 5 | 67 | 67 | 67 |
| $CH_2$=$CHCOW(CO)_3C_5H_5$ | yellow | 57—59 | 69 | 69 | 69 |
| $CHF_2CF_2W(CO)_3C_5H_5$ | » | 65—65.5 (decomp.) | 178 | 178 | 178 |
| $CF_3COW(CO)_3C_5H_5$ | » | 80—82 | 69 | 69 | 69 |
| $C_2F_5COW(CO)_3C_5H_5$ | » | 53—55 | 69 | 69 | 69 |

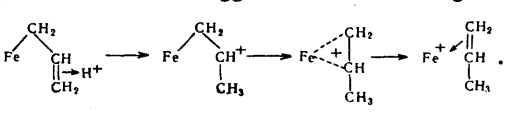
cyclopentadienyl is very easily protonated by gaseous HCl, giving the π propene complex cation (XXXV)[68,185,186]:



The protonation of σ-cyclopentadiene[187], σ-propargyl[188], and σ-cyanoalkyl[189,190] complexes of iron and the σ-allylcyclopentadienyltricarbonyl complexes of molybdenum[180] and tungsten[179] was then studied and it was shown that the reaction is general and always leads to a π-alkene complex cation. Although its products with the propargyl and cyanoalkyl complexes are more complicated there are results which confirm the allene and ketimine structure in the cations obtained:



Results with deuterium chloride show that the third carbon (or hetero-) atom of the ligand its protonated. The following mechanism was suggested for this change:



The reduction of the cations by the hydride reductants leads to neutral σ-alkyl complexes of iso-structure[191]. It was shown that the change (XXXV) → (XXXVI) does not exclude a hydro-complex stage with participation of the Fe–H bond.

The same authors[186,191,192] established the possibility of the change (XXXVII) → (XXXV) as a result of the detachment of the hydride ion from the σ-complex with salts of the triphenylmethyl cation. The change from n-propyl to isopropyl was brought about in this way. The mechanism of the hydride detachment is analogous to that of protonation. The structure of the cation obtained as a result of the hydride ion removal from $Fe(C_5H_5)CD(CH_3)_2(CO)_2$ shows that this occurs at the β carbon atom. In agreement with this is the fact that reaction does not occur with the methyl complex where there is no β carbon, or with the 2-cyanoethyl and 1,1,2,2-tetrafluoroethyl complexes, where such removal is hindered by the neighbouring electronegative groups. The detachment of the hydride ion from the σ ligand is evidently also general, like protonation. For example, it was observed[186] with ethylpentacarbonylmanganese, that is, it is present not only in cyclopentadienyl complexes. These reactions are considered to be models for understanding the mechanism of isomerisation of alkenes in chemisorption.

The following fundamental conclusions can be drawn on the basis of the experimental material considered: (1) comparatively stable carbon–transition metal covalent bonds are formed only in mixed complexes; (2) the observation of Sidgwick's rule in this is not obligatory. There are many examples of stable $MR_2L_2$ in Group VIII in which the metal is short of two to four electrons for the completed electronic configuration and on the other hand the extremely labile $CoR(CO)_4$ or $NiR(C_5H_5)(CO)$, etc., where this condition is observed, confirm this. These examples of planar complexes show what an important role the steric factors and the nature of the stabilising ligands play; (3) although fluorinated analogues have not yet been obtained for every σ-alkyl (aryl) derivative and the comparison of their stability is purely qualitative it

can be stated, however, that such thermal stability is less probable for σ carbon derivatives, than for σ fluorocarbons. Thus, $Co(CH_3)(CO)_4$ exists only at temperatures below 0° and $CF_3Co(CO)_4$ distils without decomposition at 91°; $Fe(C_2F_5)_2(CO)_4$ decomposes at ~ 100°; whereas $FeR_2(CO)_4$ could not be isolated; $Ti(C_5H_5)_2(C_6H_5)_2$ is stable in a vacuum up to 110° and decomposes at 150°, but $Ti(C_5H_5)_2 \cdot (C_6H_5)_2$ slowly decomposes at room temperature and rapidly at 100°. It must be mentioned, however, that in comparing the thermal stability it is thought that the decomposition mechanisms for the two classes of complexes are the same, although as far as we know there has not been any systematic investigation of the thermal dissociation of either class. Furthermore, in several instances there is no such sharp difference between the fluorinated and unfluorinated analogues.

Hence the factors which determine the stability of a σ derivative can be summarised as follows: (1) the valency state of the metal; (2) the nature of the ligands; (3) the electronegativity of the metal–ligand system (4) the electronegativity of the σ-bound group; (5) steric factors. Their role has been demonstrated, as far as is possible, by experimental data. The extent of the influence of the various factors cannot always be explained sufficiently satisfactorily and apparently it can be different in each particular instance. It is quite evident, however, that it is always necessary to take into account not any of the factors but all of them together.


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# MOLYBDENUM CHALCOGENIDES

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## 1. INTRODUCTION

The investigation of the chemistry of molybdenum can be said to have begun in the first half of the XIXth century, when Berzelius obtained and described some of the principal compounds of molybdenum. Both the metal itself and various of its compounds find wide and diverse applications in industry and in chemical technology. However, several molybdenum compounds of theoretical and practical importance have been studied far too inadequately. These include the molybdenum chalcogenides, that is, the compounds of molybdenum with sulphur, selenium, and tellurium.

It is well known that the most widely distributed molybdenum-bearing mineral — molybdenite — exhibits specific electrical and photoelectric properties and is a semiconducting material.

The field of use of semiconducting materials requires from them the most diverse properties. Therefore an intensive search for new semiconducting substances with various electrical characteristics is now being carried out. In particular, there is now interest in semiconductors which exhibit high thermoelectric characteristics and are suitable for efficient thermoelectric generation.

Because the higher the junction temperature the higher the efficiency of the thermoelement, there is special interest in those materials which exhibit the thermoelectric effect and retain its positive properties at high temperatures. These are, above all, high-melting-point compounds. It is also known that the best thermoelectric materials were obtained from chalcogenides, or combinations of them, which have as constituents metals of high atomic weight. What has just been said explains the special