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Dipole Moments and the Structure of π-Complexes of Metals

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Information on the dipole moments of π-complexes of metals is surveyed and systematised in this article: cyclopentadienyl, arene, alkene, carbonyl, and polymetallic complexes. The possibility of using the dipole moments method for finding the geometric structure of the π-complex molecules, the spatial position of the ligands, and the nature and polarity of the bonds which arise in complex formation has been shown. The results obtained in measurements of dipole moments are compared with data from infrared and NMR spectra, X-ray diffraction, and the chemical properties of the π-complexes. There is a bibliography of 298 references.

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I. INTRODUCTION

There is now an ever-increasing interest in the study of the structure of coordination compounds, in which the bond of the metal with the ligand is delocalised and brought about by interaction of the molecular π-orbitals of the ligand with the corresponding orbitals of the metal.

A series of monographs[1-4] and reviews[5-12] have generalised and systematised the information on the properties and structure of the π-complexes; these publications consider the results obtained by the methods of vibrational and NMR spectra, magnetochemistry, X-ray diffraction, and electron diffraction.

However, in none of these, nor in any of the other monographs[13-15] of a more general nature, is sufficient attention paid to the results of investigations of the polar properties of the π-complex molecules. Nevertheless a considerable number of papers has now been published[16-17] on the study of the structure and properties of coordination compounds by the dipole moment method, which gives valuable information on the geometrical structure of the molecules of the complexes, the spatial position of the ligands, the nature and polarity of the bonds arising in complex formation.

Interpretation of the values of the dipole moments does not require complicated mathematical equipment needed for dealing with the results from several other methods. However, it should be noted that the dipole moments method and vector calculations cannot always give an unambiguous characterisation of the structure of a complex molecule containing several polar groups. Because of this a knowledge of the value of the dipole moment is especially convenient when it is necessary to find which of several probable structures (*cis*- or *trans*-, centrosymmetric or otherwise) truly corresponds with the physical and chemical properties of the complex. The results obtainable on measuring the dipole moments are of special interest and cannot be replaced by X-ray structural investigations, since unlike the latter they characterise the structure of individual molecules in solution and not in a condensed phase.

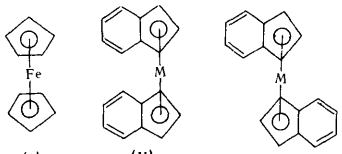
The present review surveys material (up to 1968) on the study of polar properties and the structure of coordination compounds of the transition metals and the halides of the elements of Groups III–V with unsaturated and aromatic and nitrosyl complexes. We usually compare the conclusions nitrosyl complexes. We usually compare the conclusions drawn from the values of the dipole moments with the results of other methods of investigation (infrared and NMR spectroscopy, X-ray diffraction, etc.) and also from certain data on the chemistry of the π-complexes.

The methods of determining dipole moments and the problem of estimating and calculating atomic polarisation are not examined in this review as these problems were discussed earlier[16,18-24].

II. CYCLOPENTADIENYL, ARENE, AND CYCLOALKENE COMPLEXES OF THE TRANSITION METALS

1. Cyclopentadienyls and Cyclopentadienides

Even in the first paper[25] devoted to the study of the structure of biscyclopentadienyliron, synthesised by Kealy and Pauson[26], on the basis of the zero value of the dipole moment and the results of other methods of investigation the now generally accepted structure (I) was proposed for ferrocene†:



(I) (II) (III) M = Fe, Ru.

The zero value of the dipole moment was subsequently used as an unambiguous criterion of the high symmetry and sandwich structure of various cyclopentadienyl complexes of transition metals (Table 1).

Of the data given in Table 1,[25,28-42] attention may be paid to the different values of the atomic polarisation (P_A) at which the values of the dipole moments of the complexes reach zero. Taking into account that the ratio $(P_A + P_E)/P_E$ ‡ is a unique criterion of the "ionicity" of the bonds in the complexes[43], conclusions can be drawn about the largest ionicity of the cyclopentadienyl derivative of magnesium. This conclusion is also confirmed by the results of an investigation of magnesium biscyclopentadienide by mass spectroscopic and X-ray diffraction methods[6].

The different nature of the bond in cyclopentadienyl complexes can be observed not only from the values of P_A, but also from the changes in the values of the dipole moments of the complexes in different solvents[32]. Whereas in *cyclopentadienyls* with a pure covalent bond and low values of P_A (ferrocene, nickelocene, etc.) the dipole moment hardly changes on going from heptane to dioxan, for the "ionic" magnesium and manganese cyclopentadienyls it increases by 1.9 and 2.3 D respectively[32].

In addition to the *dipole-free* cyclopentadienyl complexes there is a group of compounds with a dipole moment different from zero: these are the derivatives of beryllium, tin, bismuth, lead[29,31], manganese[32], mercury[34], and also tantalum, niobium[38], molybdenum[39], and lutetium[36]. The explanations for the polarity of these derivatives are contradictory. Whereas in the early studies[29] suggestions are advanced concerning the organometallic nature of these complexes with an angled position for the σ-bound rings, it was subsequently shown that the $Pb(C_5H_5)_2$ and $Sn(C_5H_5)_2$ molecules are "sandwich" with non-parallel cyclopentadienyl rings[6,31,34,42,44]. An investigation of the structure of the metal biscyclopentadienyls using gas electron diffraction leads to the same conclusion[8,11].

Nevertheless, on the basis of the infrared and NMR spectra Fritz[44,45] does not rule out the possibility of σ-bonding of one of the five-membered rings in $Pb(C_5H_5)_2$ and $Pb(C_5H_4CH_3)_2$.

We see[46] that the cyclopentadienyl rings are also non-parallel in the $Zn(C_5H_5)_2$ molecule. Moreover, an angular arrangement of the σ-bound nuclei has been demonstrated[47] for $Hg(C_5H_5)_2$ with dipole moment 1 D.[34]

† The electronic structure of ferrocene has been discussed by Shustorovich and Dyatkina[27] and also by several other foreign authors[4].

‡ P_E is the electron polarisation.

The dipole moment (~ 2.5 D) of $Be(C_5H_5)_2$ was at first attributed to the presence in its molecule of π- and σ-bound cyclopentadienyl rings[31,34,35]. However, an investigation of the structure of biscyclopentadienylberyllium in the gas phase by electron diffraction shows the free motion of the Be ion in the cell formed by the five-membered rings, and explains the value given above for the moment by the possibility of the metal's being situated at a different distance from the π-cyclopentadienyl nuclei[8,48]. The last feature leads to the polar C_{5v} symmetry[48]. An examination of its infrared spectrum shows that $Be(C_5H_5)_2$ also has an asymmetric sandwich structure[49].

Table 1. Dipole moments of the cyclopentadienyl complexes of metals.

Compound	Name *	Solvent **	P_A, % of P_E	Dipole moment μ, D	Reference
$[\pi\text{-}C_5H_5]_2Fe$	bis-(π-cyclopentadienyl)iron(II) (ferrocene)	B	6	0	25, 28
		CCl_4	—	0	29, 30
$[\pi\text{-}C_5H_5]_2Ni$	bis-(π-cyclopentadienyl)nickel(II) (nickelocene)	B	2.5	0±0.33	31
		D		0	
$[\pi\text{-}C_5H_5]_2Co$	bis-(π-cyclopentadienyl)cobalt (cobalticene)	B	5.1	0±0.38	31
$[\pi\text{-}C_5H_5]_2Ru$	bis-(π-cyclopentadienyl)ruthenium (ruthenocene)	B	5.2	0±0.23	31
$[\pi\text{-}C_5H_5]_2Os$	bis-(π-cyclopentadienyl)osmium (osmocene)	B	1.6	0±0.30	31
$[\pi\text{-}C_5H_5]_2V$	bis-(π-cyclopentadienyl)vanadium	B	2.2	0±0.34	31
$[\pi\text{-}C_5H_5]_2Cr$	bis-(π-cyclopentadienyl)chromium (chromocene)	B	15	0±0.41	31
		D		0.6	32
$[C_5H_5]_2Mg$	magnesium cyclopentadienide	B	31	0±0.35	31
		D		2.7	32
$[C_5H_5]_2Mn$	manganese cyclopentadienide	H		1.0	
		B		1.0	32
		D		3.3	
$[C_5H_5]_2Sn$	bis(cyclopentadienyl)tin	B	10	1.09±0.06	29
		H	—	0.9	32
		C	15	0.96±0.1	31
		D	—	1.2	32
		CS_2		1.49±0.06	33
$[C_5H_5]_2Pb$	bis(cyclopentadienyl)lead	B	10	1.63±0.06	29
		D		1.0	34
				2.16	32
		C	15	1.29±0.04	31
		CS_2	10	1.49±0.06	33
$[C_5H_5]_2Be$	bis(cyclopentadienyl)beryllium	C	15	2.24±0.09	32, 35
		B	15	2.46±0.06	31
		D		2.6	32
$[\sigma\text{-}C_5H_5]_2Hg$	bis-(σ-cyclopentadienyl)mercury	B		1.0	34
$[C_5H_5]_3Bi$	tris(cyclopentadienyl)bismuth	B	15	1.17	31
$[C_5H_5]_3Lu$	tris(cyclopentadienyl)ruthenium	B	—	0.86±0.05	36
$[C_5H_5]_4U$	tetrakis(cyclopentadienyl)uranium	B	—	0	37
$[C_5H_5]_4Ta$	tetrakis(cyclopentadienyl)tantalum	B		4.09±0.03	38
$[C_5H_5]_4Mo$	tetrakis(cyclopentadienyl)molybdenum	B	—	2.61±0.15	39
$[\pi\text{-}C_5H_5]_2ReH$	bis-(π-cyclopentadienyl)rhenium hydride	B	15	1.17	31
$[\pi\text{-}C_5H_5]Cr$ $[\pi\text{-}C_7H_7]$	π-cyclopentadienyl-(π-cycloheptatrienyl)-chromium	B		0.79±0.05	40
				0.73±0.05	41
$Co_2C_{25}H_{34}$	2,4-bis(cyclopentadienylcobaltcyclopentadien)yl-cyclopenta-2,4-diene	B		0	29
$[C_5H_5]_3Y$	tris(cyclopentadienyl)yttrium	B		1.46	42

* Given by Wilkinson and Cotton[6].

** B = benzene, D = dioxan, C = cyclohexane, H = heptane.

Similar considerations explain[41] the polarity (μ = 0.8 D)[40,41] of cycloheptatrienyl(cyclopentadienyl)chromium $C_5H_5Cr^0C_7H_7$. Clearly the complex $C_5H_5V^0C_7H_7$,[50] in which according to X-ray diffraction data the metal is found at a different distance from the planes of the cyclopentadienyl (1.9 Å) and cycloheptatrienyl (1.5 Å) rings[51], should also be polar.

The polarity of tetrakis(cyclopentadienyl)tantalum[38] and tetrakis(cyclopentadienyl)molybdenum[39] is explained by the participation in the formation of their molecules of σ- and π-bonded cyclopentadienyl rings, and that of manganese cyclopentadienide by the high "ionicity" of the bonds in this complex[32].

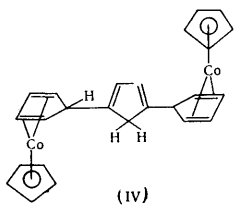
In connection with what has been stated it must be borne in mind that the values of the dipole moments cannot be an unambiguous criterion allowing the π-cyclopentadienyls to be distinguished from the usual organometallic compounds: the zero value of the moment shows the high symmetry of the molecule, but the appearance of polarity is not necessarily due to a change in the nature of the bonding. Therefore the conclusions concerning the type of bonds in the cyclopentadienyl complexes of metals drawn solely on the basis of values of dipole moments must be approached with caution.

The values of the dipole moments have been used to determine the possibility of free rotation of the cyclopentadienyl rings of disubstituted ferrocenes. Richmond and Freiser [52], who determined the dipole moments of the monoacetyl- (3.02 D) and diacetyl- (4.23 D) ferrocenes, concluded there was free rotation of the acetylcyclopentadienyl rings around an axis perpendicular to these nuclei [52]. However, these quantities can also be consistent with a restrained configuration [5].

A similar conclusion is also valid for *p*-chlorophenylferrocene [53]: the value found for its dipole moment (3.12 D) agrees best with those calculated for the 1,1′-prismatic (3.12 D) or antiprismatic (2.97 D) models. The value of the dipole moment calculated assuming free rotation of the *p*-chlorophenylcyclopentadienyl rings is 2.2 D. [53,54]

It is now assumed that whereas for ferrocene itself free rotation is only slightly restricted [3,4,6,55], bulky substituents can significantly inhibit it [54,56,57].

The bis(indenyl) derivatives of iron [31] and ruthenium [29] can be considered to belong to this class of compounds. These are extremely interesting as compounds having different structures in the crystalline state and in solution. The X-ray diffraction results show the asymmetric *cis*-position of the indenyl rings (II) in relation to the metal [58] and the zero value of the dipole moment gives a basis for attributing to the bis(indenyl) compounds the symmetric structure (III) with *trans*-arrangement of the ligands [31]. A study of the NMR spectra of indenyl complexes leads to the same conclusion [59]. The determination of the dipole moments of derivatives of ferrocene [60] and biferrocenyl [61], for which X-ray diffraction studies have been made [62-64] is of considerable interest in this connection.



(IV)

An interesting cyclopentadienyl derivative of a metal is the dinuclear complex $Co_2C_{25}H_{24}$. The structure first proposed for this compound, pentakis-(π-cyclopentadienyl)-dicobalt $(C_5H_5)Co_2$ in which each cobalt atom forms a trigonal prism surrounded by three cyclopentadienyl rings [29], was subsequently disproved [65-69]. It has now been found [69] that the molecule of this complex, which is 2,4-bis-(π-cyclopentadienylcobaltcyclopentadien)ylcyclopenta-2,4-diene, is constructed from two sandwich fragments connected through a planar cyclopentadiene bridging ring (IV). This structure agrees with the low polarity of complex (IV). [29]

2. Arene Complexes

The absence of a dipole moment was an important argument in support of a highly symmetric sandwich structure for bis(benzene)chromium [70] and several of its derivatives [29,31,71]. Just as for ferrocene, the atomic polarisation for the arene complexes of chromium is not more than 5–10% of the electronic polarisation; this has been shown not only by calculation [29] but also by the infrared spectra: P_A for bis(benzene)chromium is 3.3 ± 1 cm³ and that for bis(mesitylene)chromium [72] is 3.2 ± 0.7 cm³. In relation to these compounds the high dipole moments of bis(hexamethylbenzene)cobalt $Co[C_6(CH_3)_6]_2$, 1.78 D [73]— and the analogous chromium derivative (1 D) [74] seem extremely strange. The values given for the moments refute a centrosymmetric structure [73] but the reason for the polarity of these complexes is still not clear§.

This type of compound also includes the arenechromiumcyclopentadienyls [31], which do not have a dipole moment.

Determination of the dipole moment makes it possible to find certain details in the structure of heteroangularly substituted bis(benzene)chromium complexes. Thus the absence of dipole moments shows the *trans*-position of the substituents in the arene nuclei of bis(toluene)- and bis-(xylene)-chromium [31].

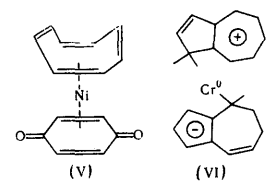
3. Cycloalkene Complexes

A large number of π-complexes of the transition metals with cycloalkenes [76-78], *p*-quinones [79,80], and acyclic alkenes [10,81] is now known.

Unlike the cyclopentadienyl and arene compounds, the cycloalkene complexes of metals are usually polar. Cycloheptatriene(cyclopentadienyl)chromium(0) $C_7H_8CrC_5H_5$ has a dipole moment of 1.1 D, [77] 1,3,5-cyclo-octatriene(cyclopentadienyl)chromium(0) 1.4 D. [77] The low dipole moment of (1.2 D) of π-cycloheptadienyl(cyclopentadienyl)nickel $C_5H_5NiC_5H_7$, which was initially given the structure of bis(cyclopentadienylnickel) [76] in error, agrees well with its unsymmetrical structure.

For the same reason allyl(cyclopentadienyl)palladium (μ = 1.5 D) [82] is polar. Nevertheless among similar complexes compounds with zero dipole moments are encountered, for example, benzene(cyclohexa-1,3-diene)-iron(0). [78]

π-Complexes of nickel with duroquinone and cyclooctatetraene (V), bicyclo[2,2,1]hepta-2,5-diene, bicyclopentadiene, and cyclo-octa-1,5-diene exhibit high dipole moments (3.5–4.3 D), due, evidently, to the high contribution of the polar structures [79,80].



(V) (VI)

It has been found that the value of the dipole moment depends on the polarity of the π-alkene bond and varies symbathically with the donor strength of the alkene ligand [80].

Of the cycloalkene π-complexes the bis(azulene) derivatives of chromium (VI) and iron [83,84] are of considerable

§ Nicholson and Longuet-Higgins [75] explain this anomaly by the Jahn-Teller effect.

interest. The slight polarity (1.18 D) of the chromium complex can scarcely serve as a basis for the structure proposed for it (VI). Here the polar properties are possibly connected with a difference in the distance of the metals from the planes of the azulene rings[8].

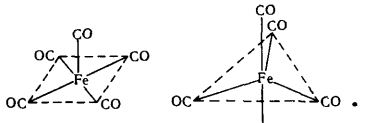
III. CARBONYLS AND NITROSYLS OF METALS

A series of detailed reviews[3,6,10,85,86] have dealt with the nature of the bonds, the methods of preparation, and properties of the carbonyls and the related nitrosyl, isonitrile, and cyano-complexes, but have not, however, considered the polar properties of these compounds.

1. Mononuclear Carbonyls and Nitrosyls

The absence of a dipole moment[87,88] shows the symmetrical nature of the tetracarbonylnickel molecule and can be consistent with planar, square, or tetrahedral configurations. This conclusion is not contradicted by the data obtained in investigating $Ni(CO)_4$ by other physical methods: study of the Raman spectra shows a planar configuration[89], but the infrared spectra[89,91] and electron diffraction[92] allow this complex to be assigned a tetrahedral structure.

The dipole moment for pentacarbonyliron $Fe(CO)_5$, determined by various authors, varies within the range 0–0.8 D. On the basis of the values first obtained for the moment (0.64 [92] and 0.81 D [93]) a square-pyramidal structure (VII) was proposed for $Fe(CO)_5$ and the non-polar configuration of a trigonal pyramid (VIII) was rejected. The non-zero values of the dipole moments were contradicted, however, by the results of an investigation of $Fe(CO)_5$ by vibrational spectroscopy[13,91,94] and by electron diffraction[95], according to which a trigonal bipyramidal structure was proposed for this complex:



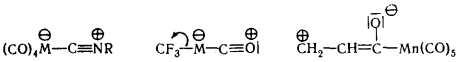
(VII) (VIII)

Later investigations made by Weiss[96] showed that on taking account of the atomic polarisation (20% of the electronic) the value of the dipole moment is close to zero. A definitive solution of the problem in support of structure (VIII) gives a zero value to the dipole moment of $Fe(CO)_5$ obtained by a microwave method[97]. This conclusion is confirmed by the similarity in the values found experimentally for the entropy[98] and those calculated from spectroscopic data, and also by the X-ray diffraction results[99,100].

Carbonyls in which CO groups have been replaced by nitrosyl ligands have dipole moments extremely close to zero. Tricarbonylnitrosylcobalt $Co(CO)_3(NO)$ exhibits a moment of 0.4 D ($P_A = 20\% P_E$) and that of dicarbonyldinitrosyliron $Fe(CO)_2(NO)_2$ is 0.7 D.[96]

The low polarity of the carbonylnitrosyls[96], hydrogen pentacarbonylmanganate[101], and alkyl and aryl pentacarbonylmanganates (at an atomic polarisation equal to 20% of the electronic their dipole moment is 0–0.5 D[102,103]) gives a value of 0.5–0.8 D for the moment of the M–Co bond[96,104,105]. Measurements of the dipole moments of the cyclopentadienylcarbonyl complexes lead to the same value¶.

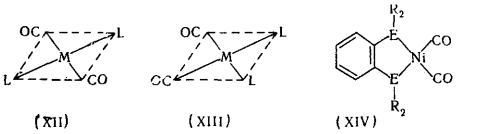
The introduction of polar groups into the complexes leads to a sharp rise in their dipole moments. The moment of $Fe(CO)_4(CNCH_3)$ is 5.07 D.[96] This value cannot be explained by the polarity of the isocyanide with dipole moment 2.5 D [106] and is connected with the high polarisation of the donor–acceptor bond (structure IX).



(IX) (X) (XI)

Analogous polar structures are proposed to explain the dipole moments of the complexes $CF_3Mn(CO)_5$ (X) 3.6 D and $RCOMn(CO)_5$ (R = Alk, 2.3 D; CF_3, 3.5 D; Ar, 2.3 D) and also of acrylic acid derivatives (XI) 2.4 D.[103] Similar dipole moments are possessed by the rhenium carbonyls $CH_3CORe(CO)_5$ 2.5 D and $C_6H_5CORe(CO)_5$ 2.6 D [103] and also the nickel complexes[105,107] $Ni(CO)_3PAr_3$ 3.84 D and $Ni(CO)_3AsAr_3$ 3.59 D.

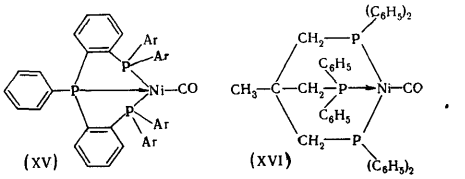
The values of the dipole moments of the planar dicarbonyl complexes of the type $L_2M(CO)_2$ are determined by their stereochemistry: the *trans*-isomers (XII) should not have dipole moments but the *cis*- (XIII) should exhibit considerable polarity:



(XII) (XIII) (XIV)

where E = As or P.

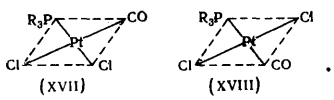
The moment of bis(chlorocarbonyl)platinum is 3.65 D [104] and therefore the complex is ascribed the *cis*-structure (XIII; M = Pt, L = Cl). $Ni(CO)_2(AsAr_3)_2$ with dipole moment 3.34 D and $Ni(CO)_2(PAr_3)_2$ with 3.82 D have the *cis*-configuration[105]†. The *cis*-structure seems the only possibility for complexes (XIV): their dipole moments lie in the range 5–5.5 D.[105,107] Taking into account that the Ni–C–O group is of low polarity (0.5 D) the authors estimate the moments of the Ni–P and Ni–As bonds to be 3.4 and 3.2 D respectively[105]. The same value for the Ni–P bond is also obtained from the value of the dipole moments for the monocarbonylphosphinic complexes (XV, $\mu = 5.18$ D) and (XVI, $\mu = 4.95$ D):[109]



(XV) (XVI)

For the same reason the Fe–P bond should also exhibit considerable polarity, since the dipole moment of $Fe(NO)_2[P(C_6H_5)_3]_2$ is 4.99 D.[110]

Chatt and coworkers investigated the polar properties of monocarbonylphosphinic complexes of platinum(II) chloride[111]. On the basis of the high values of the dipole moments (~ 10 D) and the infrared spectra the *cis*-structure (XVII) is ascribed to these complexes: the *trans*-isomers (XVIII) should have lower moments[111]:



(XVII) (XVIII)

¶ For more details about these complexes, see below.

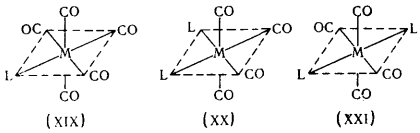
† For $Ni(CO_2)(PEt_3)_2$ of the same structure $\mu = 4.4$ D.[108]

The polar properties of the metal carbonyls and nitrosyls $M(CO)_5L$, $M(CO)_4L_2$, $M(CO)_4L$, $M(CO)_3(NO)L$, $M(CO)_2(NO)L$, and $M(CO)_2L$, where L is a *p*-electron donor, and M the metal, depend on both the geometry of the molecule and the polarity of the M–L bond.

The high value of the dipole moment is characteristic for the halogenopentacarbonyls of manganese $Mn(CO)_5L$ (for the bromo-derivative $\mu = 3.2$ D [103] or 3.99 D, [112] for the iodo-derivative 3.25 D [103]) and for the derivatives of chromium, molybdenum, and tungsten with nitrogenous bases (L = pyridine, quinoline, piperidine, and aniline 6–7 D [113]). For all these complexes structure (XIX) is assumed and the formula

$$\mu_{M-L} = \mu_{expt} - \mu_{M-Co} - \mu_L$$

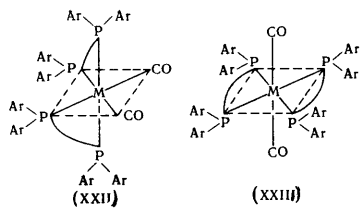
can be used to determine the partial dipole moment of the M–C bond [113]. For $Cr(CO)_5L$ and $Mo(CO)_5L$ the latter lies within the limits 3.6–4.1 D; for $W(CO)_5L$ it is higher by 0.7 D and only depends slightly on the nature of the donor [113]. It is somewhat lower (2.5–3.3 D) only for complexes with acetonitrile, benzonitrile, and aniline [113].



(XIX) (XX) (XXI)

For complexes of the $M(CO)_4L_2$ type *cis*- (XX) and *trans*- (XXI) configurations are possible and the values of the dipole moments can vary from 10 (XX) to 0 (XXI) D. The values of the dipole moments of the *cis*-phosphinic derivatives of the tetracarbonyls of chromium, molybdenum, and tungsten lie within the limits 7–8 D. [114] $Mo(CO)_4 \cdot 2Py$ has a moment of 9.3 D, the analogous tungsten complex 10.3 D, [113] and $Cr(CO)_4[P(C_6H_5)_3]_2$ and $Cr(CO)_4 \cdot 2$(cyclohexylnitrile), which have been assigned the *trans*-structure, do not possess dipole moments [115].

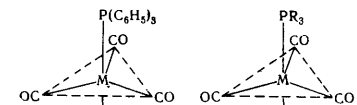
The calculated dipole moment for the *trans*-structure is zero, and that for the *cis*- can be calculated by the formula $\mu_{cis} = \mu_{mono}\sqrt{2}$ (for a regular octahedron), where μ_{mono} is the moment of the complex $M(CO)_5L$ with the same donor, and agrees satisfactorily with the values obtained experimentally [113]. It should be noted that only the *cis*-isomers of the above Mo and W complexes have been isolated, whereas both configurations are known for the chromium compounds [114]. Similar regularities are also observed for the dicarbonyl complexes of the Group VI metals with bidentate phosphines [114]. For $[Cr(CO)_2\{C_2H_4(PAr_2)_2\}_2]$ both the *cis*- (XXII; $\mu = 6.2$ D) and the *trans*- (XXIII; $\mu = 6.95$ D) isomers are known but the similar molybdenum and tungsten complexes with dipole moments 6.15 and 6.7 D respectively, have only the *cis*-octahedral structure (XXII). [114]



(XXII) (XXIII)

The dipole moment of *cis*-$Fe(CO)_4 \cdot (HgCH_3)_2$ is extremely low—2.1 D. [116] There may be an equilibrium of the *cis*- and *trans*-isomers in solution here.

The reasons for the considerable differences in the values of the dipole moments of triphenylphosphineirontetracarbonyl $Fe(CO)_4 \cdot P(C_6H_5)_3$, 5.1 D [110] and of the analogous manganese derivative $Mn(CO)_4 \cdot P(C_6H_5)_3$‡, 1.1 D [117] and mononitrosyltriphenylphosphinemanganesetricarbonyl $Mn(NO)(CO)_3P(C_6H_5)_3$, 4.9 D, [110] to which is assigned a trigonal bipyramidal structure (XXIV): [110,117,118]

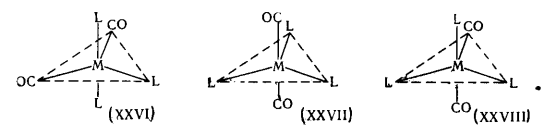


(XXIV) (XXV)

are not understood.

Attempts to explain these differences by the large contribution of the polar form $\bar{M} \leftarrow \overset{+}{P}(C_6H_5)_3$ do not appear to be very convincing in relation to the nitrosyl complex $Mn(NO)(CO)_3 \cdot P(C_6H_5)_3$. [110] The anion $[Mn(CO)_4(PAr_3)]^-$ is assigned a trigonal bypyramidal structure on the basis of the identical values of the dipole moments (5.1 D) of $HMn(CO)_4PAr_3$ and $Fe(CO)_4PAr_3$. [119] However, such a comparison can scarcely be considered an unambiguous criterion in the solution of structural problems particularly as the octahedral complex $CH_3Mn(CO)_4PAr_3$ has a moment (4.9 D), extremely close to that given above [119]. Dipole moments close to zero suggest for the complexes $Fe(CO)_3[P(C_6H_5)_3]_2$, [120] $Mn(CO)_2(NO)[P(C_6H_5)_3]_2$, and $Mn(CO)_2(NO)[P(C_6H_{11})_3]_2$ [110] the trigonal bipyramidal model (XXV) with *trans*-PR_3 groups. As Hieber and Tengler [110] consider, the tetragonal pyramidal and trigonal bipyramidal structures with *cis*-arrangement of the PR_3 ligands which are formally possible here should have a dipole moment of ~ 5 D. [110] In this instance it is not clear what structure is characteristic for $Fe(CO)_3[P(OC_6H_5)_3]_2$ with a moment 2.31 D. [121]

The high value of the dipole moment (4.97 D) allows tris(triphenylphosphine)irondicarbonyl to be assigned the structure of a trigonal bipyramid with CO groups lying at the vertices of the triangular base (XXVI). [121] The possible structure (XXVII), is rejected on the basis of the infrared spectra, and (XXVIII) should have a dipole moment of ~ 7 D: [121]



(XXVI) (XXVII) (XXVIII)

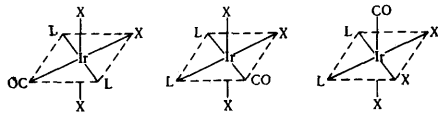
A structure analogous to (XXVI) is proposed starting from the values of the dipole moments and the results of studies of the infrared spectra, for the phosphine derivative of the dicarbonyl halides of cobalt(II) [122] and also for $IMn(NO)_2[P(C_6H_5)_3]_2$ with moment 3.19 D. [123]

For the triphenylphosphinedinitrosyliron halides, $Fe(NO)_2P(C_6H_5)_3X$, it was noted [124] that there is an increase in the dipole moment with increase in the atomic weight of the halogen (X = Cl, $\mu = 6.78$ D; Br, $\mu = 7.02$ D; I, $\mu = 7.21$ D). The same regularity was observed earlier for the analogous complexes of cobalt [125]. However, the increase in the moment in the last instance is insignificant (Cl 6.79 D, Br 6.83 D, I 6.89 D [125]), as it is for the halogen derivatives of pentacarbonylmanganese [103]. More significant changes in the values of μ are characteristic

‡ According to Sidgwick's rule this compound should be a dimer and consequently diamagnetic. However, published data [117] show it to be paramagnetic (1.86 μ_B) and monomeric ($M_{exp} = 420$; $M_{calc} = 429.2$).

for the complexes being considered on replacing the phosphorus by other elements of Group V: whereas the dipole moment of $Co(NO)_2P(C_6H_5)_3Br$ is 6.83 D, that for the analogous manganese derivative is 6.4 D and that for antimony 5.26 D.[125] The phosphine-substituted complexes $Co(NO)(PAr_3)_3$ and $Co(NO)(CO)_2PAr_3$ should have similar dipole moments for a tetrahedral configuration. Actually, if the atomic polarisation is not taken into account, then for $Ar = C_6H_5$ the moments of these complexes amount to 4.27 and 4.56 D respectively, and for $Ar = OC_6H_5$ 2.38 and 2.27 D.[125] However, at $P_A = 20\% P_E$ the values of the dipole moments in the first instance differ by 1.2 D, but in the second, by 0.5 D.[125] The reasons for these differences are, in the opinion of these authors[125], connected with the distortion of the valence angle of the tetrahedron under the influence of the bulky PAr_3 groups.

On the basis of dipole moments the configuration of the isomeric carbonyl complexes of the type $IrX_3(CO)(ER_3)_2$, where X = Cl, Br; E = P, As, Sb, and R = Alk, Ar, and of the iridium carbonyl hydride $IrHCl_2(CO)[P(C_2H_5)_2C_6H_5]_2$ was established[126]. For these complexes with X = Cl, E = P, and $R = C_2H_5$, two, (XXIX) and (XXX), of the three possible isomers, (XXIX)–(XXXI), were isolated and all three of the analogous butyl derivatives: (XXIX) 2.35 D, (XXX) 9.55 D, (XXXI) 12.35 D.[126]



(XXIX) (XXX) (XXXI)

Two isomers, (XXIX) and (XXX), are observed for the phosphinic complex $IrCl_3CO[P(C_2H_5)_2(C_6H_5)]_2$ with dipole moments 3.3 and 9.65 D, for the analogous arsenic derivatives 2.95 and 9.8 D, and also the carbonyl hydrides $IrHCl_2(CO)[P(C_2H_5)_2(C_6H_5)]_2$ 1.2 and 5.1 D.[126] The complexes $IrBr_3(CO)[P(C_2H_5)_2(C_6H_5)]_2$ and $IrCl_3(CO)[Sb(C_3H_7)_3]_2$ are assigned the configuration (XXIX) (their dipole moments are 3.4 and 2.4 D respectively), but $IrCl_3(CO)[As(C_2H_5)_3]_2$ with moment 9.65 D and the bromo-derivative of the above carbonyl hydride (5.35 D) the configuration (XXX).[126]

From the dipole moments (2.5–3.5 D) the *trans*-structure can be assigned to complexes of the general formula $Rh[(XC_6H_4)_3M]_2(CO)Cl$, where M = P, As, and X = H, CH_3, Cl, OCH_3.[127]

Analogous results were obtained for the carbonyl-phosphinic derivatives of rhenium and manganese[120,128]. For $Re(CO)_3[P(C_6H_5)_3]_2I$ *cis*- and *trans*-isomers were observed[128] with dipole moments of 7.6 and 3.0 D respectively but for $Re(CO_3)[P(OC_6H_5)_3]_2I$ only the *cis*-isomer (5.7 D). The carbonyl hydride derivatives of manganese $HMn(CO)_3[[(C_6H_5)_3]_2$ with dipole moment 0.58 D and $HMn(CO)_3.[P(OC_6H_5)_3]_2$ with 2.09 D[120] analogous to the rhenium complex $HRe(CO)_3.[P(C_6H_5)_3]_2$ with 2.5 D,[128] and also carbethoxybis(triphenylphosphine)tricarbonylmanganese (1.7 D),[129] have the *trans*-structure. In this connection the dipole moment of the recently synthesised[130] *cis*-isomer $HMn(CO)_3.[P(OC_6H_5)_3]_2$ is of definite interest.

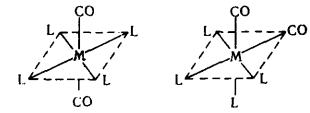
The dipole moment values allow the isomers of halogenophosphinic derivatives of manganese carbonyls to be distinguished[112]. The complex $Mn(CO)_3[P(OC_6H_5)_3]_2Br$ with dipole moment 4.78 D is ascribed the *cis*- and the compound with $\mu = 3.52$ D the *trans*-structure[112].

$$Re(CO)_3[(C_6H_5)_3PO]_2X$$

(X = Cl, Br, I; $\mu = 8$–10 D) has the *cis*-structure[131].

Similar conclusions concerning the structure of complexes of the $L_3MN(CO)_3X$ type follow from their infrared spectra[130,131].

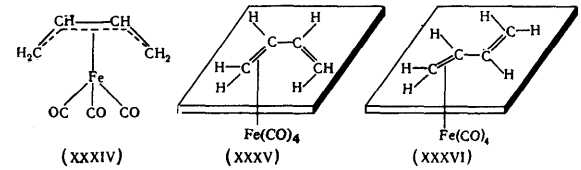
Structural problems similar to those described above also arise in solving problems of the configuration of complexes of type $M(CO)_2L_4$.[132] Here, in addition to an isomer without a dipole moment (XXXII) with *trans*-arrangement of the CO groups (D_{4d} symmetry), a polar *cis*-form should exist (XXXIII, C_{2v}).



(XXXII) (XXXIII)

2. Diene- and Polyene-carbonyls

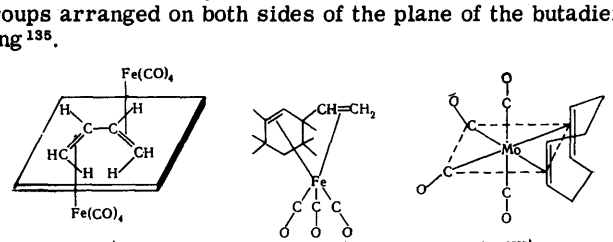
The simplest complexes of this type are the butadieneirontri- and tetracarbonyls[133–136]. Undoubtedly these compounds are of the π-complex type[10,136]. Hallam and Pauson[134] proposed structure (XXXIV) for butadieneirontricarbonyl, and this was confirmed[10,137] by X-ray structural data[138] and chemical properties. The infrared spectrum of butadieneiron tetracarbonyl shows that complex formation takes place through only one π-bond[135].



(XXXIV) (XXXV) (XXXVI)

It seems probable that there are two structures with *cis*- (XXXV) or *trans*- (XXXVI) arrangement of the butadiene fragment (analogous structures can also be postulated for butadieneirontetracarbonyl). The dipole moment method was used to distinguish these structures[135]. However, the values of the dipole moments 2.15 D (for butadieneirontetracarbonyl) and 1.94 D (for the tricarbonyl analogue) did not permit *cis–trans* isomers to be distinguished[135].

More definite information was obtained for butadienylironoctacarbonyl, which on the basis of its low polarity ($\mu \simeq 0.9$ D) was assigned structure (XXXVII) with $Fe(CO)_4$ groups arranged on both sides of the plane of the butadiene ring[135].



(XXXVII) (XXXVIII) (XXXIX)

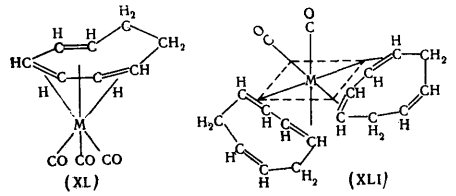
Complexes (XXXV)–(XXXVIII) are evidently the only exceptions among the carbonyl–alkenes where the diene occupies one coordination site: in all the other instances the diene acts as a bidentate ligand.

In the 3-vinylcyclohexeneirontricarbonyl complex the alkene is coordinated by both π-bonds with the formation of the complex (XXXVIII) with $\mu = 2.94$ D.[1]

On the basis of the dipole moment (4.9 D),[139] and the infrared[139] and NMR[140] spectra the (cyclo-octa-1,5-diene) metaltetracarbonyls are assigned the structure (XXXIX) with a boat conformation of the cycloalkene.

Clearly, an analogous structure can be assumed for cyclo-octa-1,5-dieneirontricarbonyl with dipole moment 3.1 D,[139] the infrared spectra[141] being consistent with this structure.

The comparatively high value of the dipole moment of cyclo-octatrienemolybdenumtricarbonyl $C_8H_{10}Mo(CO)_3$, 4.1 D, shows the coordination of the cycloalkene as 1,3,5-cyclo-octatriene (XL) and the displacement of the electron density from the cyclo-octatriene ring to the metal and further towards the carbonyl groups[142]. The lower moment for bis(cyclo-octatriene)molybdenumdicarbonyl $(C_8H_{10})_2Mo(CO)_2$, 1.96 D, can be explained by the participation of the 1,3,6-isomer in the complex formation[142]. Fischer and coworkers assume that the *trans*-arrangement of the 1,3-diene system is improbable. However, because of its comparatively low dipole moment (~ 2 D) the compound has been assigned the structure (XLI):[142]

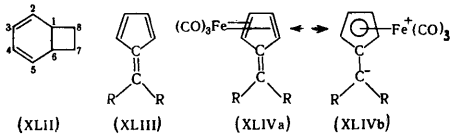

(XL) (XLI)

where M = Mo or W.

Two alkene carbonyl complexes of iron were also obtained by the reaction of a mixture of cyclo-octatriene isomers with $Fe(CO)_4$: a yellow liquid and red crystals[142]. By analogy with the molybdenum complexes the liquid product (dipole moment 2.37 D) was assigned the structure of a 1,3,6-cyclo-octatriene complex.

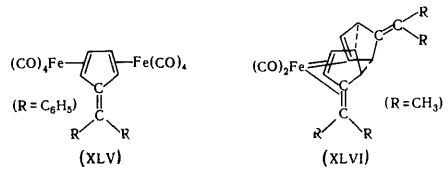
The solid, with a higher dipole moment (3.66 D) was assigned a structure with 1,3,5-configuration of the cyclo-octatriene ligand[142]. Later investigation of the chemical properties[143,144] and the infrared[144] and NMR[145] spectra showed that any isomerisation of cyclo-octatriene with iron carbonyls leads to bicyclo[4,2,0]octa-2,4-diene (XLII) of which the complexes under consideration are derivatives[143].

The π-system of the cyclopentadiene ring of the diphenylfulvenes was found to be convenient for the formation of alkene(carbonyl) complexes[146].


(XLII) (XLIII) (XLIVa) (XLIVb)

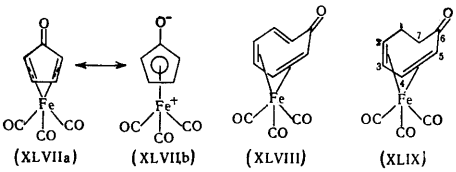
The values of the dipole moments of the diphenylfulvene-irondi- and tricarbonyls reach 2.5–3.5 D[146] whereas diphenylfulvene itself (XLIII; R = C_6H_5) has a moment of 1.34 D[147] and its *p*-chlorophenyl derivative (XLIII, R = *p*-ClC_6H_4) 0.68 D.[18] These values of the dipole moments are connected with the contribution of the polar structures (XLIVb), which is especially significant for the *p*-chlorophenyl derivatives[146]. Weiss and Hübel[146] consider that the realisation of structure (XLIVb) is confirmed by the marked rise in dipole moment (XLIVa, R = *p*-ClC_6H_4) in comparison with the initial fulvene and complex (XLIVa, R = C_6H_5), whereas electron-withdrawing substituents in the phenyl nuclei of the ligand decrease the moment[146].

Diphenylfulvenedi-ironoctacarbonyl $C_{18}H_{14}Fe_2(CO)_8$ has moment 1.73 D, not greatly above that of free diphenylfulvene (1.34 D). Therefore the complex under consideration is assigned the structure (XLV) with symmetrically arranged $Fe(CO)_4$ groups, each of which is coordinated with one double bond of the diene ligand.


(XLV) (XLVI)

A quite unusual structure (XLVI) in which the exocyclic double bond of fulvene is utilised, is assigned to bis(dimethylfulvene)irondicarbonyl $[(CH_3)_2C{=}C_5H_4]_2Fe(CO)_2$ on the basis of the dipole moment (2.88 D)[148] and infrared spectra[146].

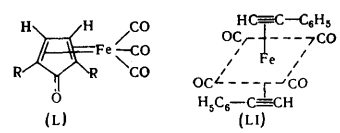
In the formation of mixed carbonyl complexes cyclopentadienone and tropolones can act as π-ligands[148–151]. The high values of the dipole moment of complex (XLVIIa), 4.4 D,[150] taken in conjunction with the infrared spectra[148,149] show the polarisation of the carbonyl group and the significant contribution of the polar structure (XLVIIb):


(XLVIIa) (XLVIIb) (XLVIII) (XLIX)

The ability of the iron cyclopentadienonecarbonyls to form adducts with acids and phenols of general formula $(CO)_3FeC_5H_4O.HX$, where X = Cl, Br, I, OAr and to give a negative reaction, characteristic of ketones, with phenyl- and 2,4-dinitrophenyl-hydrazines agrees with these suggestions[150].

However, this explanation can hardly be completely correct since the analogous complexes of tropoloneirontricarbonyl (XLVIII) with dipole moment 4.3 D show reactions typical of the keto-group[151]. The product of the non-polar hydrogenation of complex (XLVIII), cyclohepta-2,4-dienoneirontricarbonyl (XLIX) exhibits the same properties: at a high value of the dipole moment it forms the stable 2,4-dinitrophenylhydrazone[151] and has a C=O stretching frequency of 1661 cm^{-1}; the carbonyl group probably does not coordinate with the metal atom.

The reaction of pentacarbonyliron with phenylacetylene yields 2,5-diphenylcyclopentadienoneirontricarbonyl (L) with dipole moment 3.1 D.[152,153] This value eliminates the centrosymmetric structure (LI) suggested earlier[10,152]:

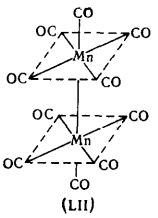

(L) (LI)

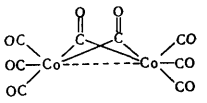
where R = C_6H_5.

3. Polynuclear Carbonyls and Nitrosyls

The dipole moments of the dinuclear carbonyls of rhenium and manganese of composition $M_2(CO)_{10}$, determined in benzene, dioxan, and cyclohexane, have values close to 1.0 D,[103] although according to the infrared spectra[12,154–157]

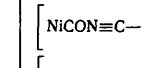
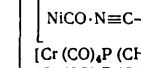
and X-ray structural investigations[158,159] these complexes should have a symmetric structure[86].


(LII)


(LIII)

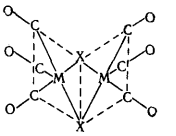
In this connection the assumption is made that the atomic polarisation should constitute 20–30% of the electronic: the dipole moment of both complexes should then become close to zero[103]. To explain the polarity (μ = 1.29 D)[160] of octacarbonyldicobalt $Co_2(CO)_8$ it was assumed that the CO bridges connecting the cobalt atoms are curved (LIII; C_{2v} symmetry)[14,154].

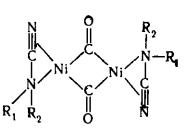
Table 2. Dipole moments of doubly charged complexes.

No.	Compound	Dipole moment in benzene, at 25°C, μ, D	Reference
1	$[Fe(CO)_3S]_2$	1.63	161
2	$[Fe(CO)_3Se]_2$	2.20	161
3	$[Fe(CO)_3SC_2H_5]_2$	2.69	161
4	$[Fe(CO)_3NH]_2$	3.28	162
5	$[Fe(CO)_3P(CH_3)_2]_2$	3.1	166
6	$[Fe(CO)_3P(C_2H_5)_2]_2$	3.6	166
7	$[Fe(CO)_3As(CH_3)_2]_2$	3.8	166
8	$[Fe(CO)_3Tep\text{-}C_6H_4OCH_3]_2$	3.00	124
9	$[Fe(CO)_4P(CH_3)_2]_2$	4.2	166
10	$[Fe(CO)_4Sn(C_4H_9)_2]_2$	0.8	116
11	$[Fe(NO)_2SC_2H_5]_2$	1.88	165
12	$[Fe(NO)_2SeC_2H_5]_2$	0.92	165
13	$[Fe(NO)_2P(C_6H_5)_2]_2$	2.53	164
14	$[Co(NO)_2Cl]_2$	1.04	165
15	$[Co(NO)_2Br]_2$	1.02	165
16	$[Co(NO)_2P(C_6H_5)_2]_2$	1.67	164
17	$[Mn(CO)_4P(OC_6H_5)_2]_2$	2.67	117
18	$[Mo(CO)_4P(CH_3)_2]_2$	1.9	167
19	$[Mo(CO)_4P(C_2H_5)_2]_2$	0.9	161
20	$[Mo(CO)_4As(CH_3)_2]_2$	0.9	161
21	$[Mo(CO)_5P(CH_3)_2]_2$	4.8	167
22	$[Mo(CO)_5P(C_2H_5)_2]_2$	3.9	161
23	$[NiCO\cdot N{\equiv}C{-}N(CH_3)_2]_2$	1.08	168
24		2.12	168
25		1.57	168
26	$[Cr(CO)_4P(CH_3)_2]_2$	1.0	167
27	$[Cr(CO)_4P(C_2H_5)_2]_2$	1.4	161
28	$[Cr(CO)_5P(CH_3)_2]_2$	4.6	167
29	$[W(CO)_4P(CH_3)_2]_2$	1.2	167
30	$[W(CO)_4P(C_2H_5)_2]_2$	0.6	161
31	$[W(CO)_4As(CH_3)_2]_2$	1.1	161
32	$[W(CO)_5P(CH_3)_2]_2$	3.9 4.6	161 167
33	$[W(CO)_5P(C_2H_5)_2]_2$	3.7	161
34	$[W(CO)_5As(CH_3)_2]_2$	3.9	161

Not only CO but also other groups (NH, SC_2H_5, SeC_2H_5, PMe_2,[161,162] PR_2,[163,164] and AsR_2 [163]), halogen atoms[165], and sulphur and selenium atoms[161], and also SnR_2 [116] can act as bridging ligands in polynuclear carbonyls. Table 2 gives the values of the dipole moments of complexes with these groupings.

Model (LIV), in which the two bridging groups and two iron atoms do not lie in the same plane, was proposed to explain the polarity of the externally non-symmetric carbonyls of the $[FeX(CO)_3]_2$ type[161]. This model has C_{2v} symmetry. A similar symmetry is evidently characteristic for $[Fe(NO)_2(SC_2H_5)]_2$,[165] the halogeno(nitrosyl) complexes of cobalt[165], and the tungsten and molybdenum carbonyls of general formula $[M(CO)_4ER_2]_2$.[117,161,167] X-ray diffraction showed a similar structure for $[Fe(CO)_3(SC_2H_5)]_2$.[169] In all the complexes considered the presence of bridging groups creates a certain rigidity of structure and increases their symmetry. In those dinuclear carbonyls where the dimerisation occurs through a metal–metal bond (Table 2, compounds 21–23, 32–34) there arises the possibility of free rotation around this bond, which leads to a decrease in the symmetry of the molecule and the appearance of a comparatively high dipole moment[161,167].

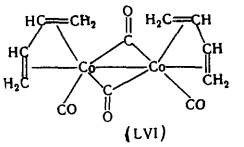

(LIV)

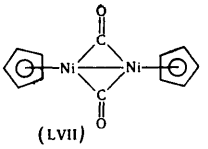

(LV)

The presence of bridging CO groups was suggested on the basis of results obtained in the determination of dipole moments and investigations of the infrared spectra for the dialkylcyanoamido-complexes of nickel carbonyl (LV). The lone pair of electrons of the amine nitrogen and the π-electrons of the nitrile group take part in the formation of these complexes; the values of the dipole moments (1.5–2.0 D) are consistent with C_{2h} molecular symmetry[168].

The determination of dipole moments was an important tool for finding the structure of the polynuclear carbonyls containing organic π-ligands.

The high polarity (μ = 3.39 D) allows bis(butadiene-cobalt-tricarbonyl) to be assigned the structure with *cis*-arrangement of the CO ligands (LVI):[1,170] the dipole moment for the *trans*-configuration should be close to zero.

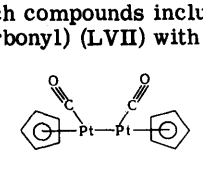

(LVI)

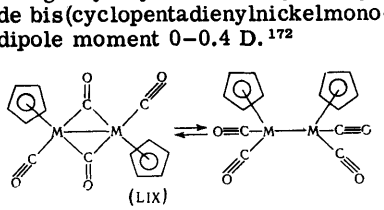

(LVII)

The considerable value of the dipole moment (3.02 D) of the compound bis(cyclo-octa-1,3,6-trienecobaltdicarbonyl) is connected with the angular structure of this complex[171].

The dipole moment method has proved extremely useful for solving problems of the presence or absence of carbonyl bridges in a series of dimers of cyclopentadienylmetalmonocarbonyls of general formula $[C_5H_5M(CO)]_2$. Two groups of complexes can be distinguished among these compounds: (1) those with a dipole moment close to zero, and (2) those which are polar, with a moment of ~ 2.0–3.0 D.

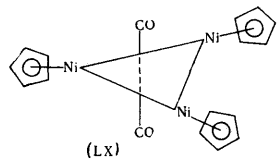
The first type of complex is credited with a rigidly symmetric structure, the dimerisation in which occurs by an M–M bond, and the "rigidity" by two carbonyl bridges. Such compounds include bis(cyclopentadienylnickelmonocarbonyl) (LVII) with dipole moment 0–0.4 D.[172]

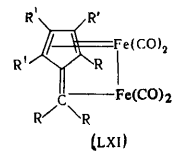

(LVIII)


(LIX)

The appearance of polarity in the second group of complexes is connected with dimerisation solely by the M–M bond, around which free rotation is possible. The infrared and NMR spectra are inconsistent with carbonyl bridges and a symmetrical arrangement of the C=O groups in bis(cyclopentadienylplatinum-monocarbonyl)(LVIII) with dipole moment 2.6 D.[173]

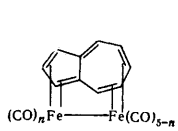
Other relationships are observed between the values of the dipole moments and structure of the dimers of cyclopentadienylmetaldicarbonyls $[C_5H_5M(CO)_2]_2$. In this instance the complexes with the pure M–M bond (M = Os)[174] and the compounds with an M–M bond fixed by carbonyl bridges (M = Fe)[175] have appreciable dipole moments, respectively 2.6 and 3.1 D, due to the breaking of the carbonyl bridges in the solution and the formation of polar *cis*-structures (LIX), observed in detailed infrared spectroscopic investigations[176].

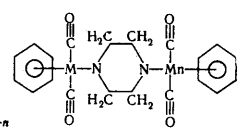

(LX)


(LXI)

The zero value of the dipole moment of the polynuclear nickel complex, $(C_5H_5)_3(Ni_3(CO)_2$, indicated the centrosymmetric structure (LX),[172] and this was also confirmed by X-ray diffraction[15].

The complexes of $Fe_2(CO)_9$ with substituted fulvenes obtained by Weiss and Hübel are interesting, the fulvenes evidently acting as bidentate ligands. The polarity (3.5–4 D)[146] and the absence from the infrared spectra of bands for carbonyl bridges suggests that the probable structure for this group of complexes is (LXI). However, the number of CO groups at the iron atoms (3 : 3 or 4 : 2, as in (LXI) —remains uncertain[146].


(LXII)


(LXIII)

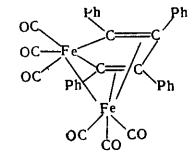
Azulene can also take part in the formation of similar complexes[177]. On the basis of the considerable polarity (μ = 3.97 D) and absence of absorption in the region for bridging CO groups, Wilkinson and coworkers ascribed the structure (LXII) to the complex with general formula $C_{10}H_8Fe_2(CO)_5$.[177]

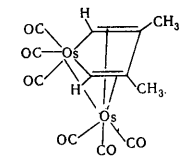
The low dipole moment (~ 1 D) of the complex (LXIII) agrees well with its symmetric structure[178].

The reaction of acetylene[10,175,179] and its derivatives with iron carbonyl is very interesting. Two centrosymmetric structures were proposed for the products of the reaction of iron tetracarbonyl with acetylene and diphenylacetylene, of general formula[180]:

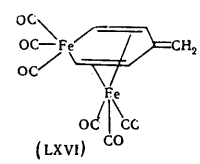
$$Fe_2(CO)_6(RC{\equiv}CR)_2.$$

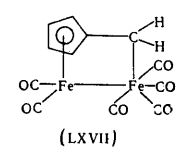
However, the high values of the dipole moments of these complexes (μ = 2.86 D for R = H;[175] μ = 3.3 D for R = C_6H_6 [180]) are against their symmetric structure. It transpired that it is more correct to regard these compounds as derivatives of tricarbonyl(ironcyclopentadienyl)irontricarbonyl (LXIV),[180] particularly as structures similar to (LXIV) have been demonstrated by X-ray diffraction for a series of reaction products of acetylenes with iron[181–183] and osmium[182] (LXV) carbonyls.


(LXIV)


(LXV)

A non-zero value of the dipole moment allows conclusions to be drawn about the absence of a centre of symmetry for compounds[175] of the general formula $(C_2H_2)_3Fe_2(CO)_6$. One of these with dipole moment 1.7 D was given the structure (LXVI) because of its paramagnetism[175]; its isomer with a higher dipole moment (3.41 D) was assigned the structure (LXVII).[175]

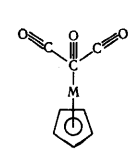

(LXVI)

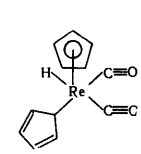

(LXVII)

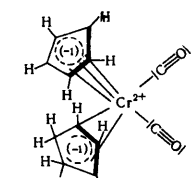
4. Cyclopentadienyl and Arenecarbonyl Compounds

The values of the dipole moments of the monocyclopentadienylmetal carbonyls lie within the range 2.9–3.5 D and to a first approximation vary little with the number of carbonyl groups in the complex[96,184,185]. The value of the moment also varies little on replacing the carbonyl groups by nitrosyl: cyclopentadienylchromiumdicarbonylmononitrosyl π-$C_5H_5Cr(CO)_2(NO)$ has μ = 3.2 D.[96]

These values of the dipole moment allow the M–C_5H_5 bond moment of the bond to be estimated as ~ 2.0–2.5 D,[96] if it is assumed that the moment of the M–C–O fragment does not exceed 0.5–0.8 D.[96,105] The high polarity of the π-complexes of this type is connected with the asymmetry of their structure, for example (LXVIII).[1,6,86]


(LXVIII)


(LXIX)


(LXX)

The dipole moments of the π-cyclopentadienylmetalcarbonyls are almost independent of the solvent, which is explained by the coordination saturation of the metal atom in these compounds[185]. Bis(cyclopentadienyl)rheniumdicarbonyl hydride $(C_5H_5)_2ReH(CO)_2$, which belongs to this type of complexes, was assigned structure (LXIX) with π- and σ-bonded cyclopentadienyl rings on the basis of its high polarity (μ = 3.85 D)[31,186,187] and NMR and infrared spectra[188]. Structure (LXX), in which the CO groups are

Table 3. Dipole moments of arenemetaltricarbonyls.

No.	Formula	Arene	Solvent	P_A, % of P_E	μ, D	Reference
1	$C_6H_6Cr(CO)_3$	benzene	B	15	5.08	193
			B	15	4.92	31
				15	4.81	191
			C	15	4.31	31
			H	15	4.38	191
			D	15	5.33	191
2	$C_7H_8Cr(CO)_3$	toluene	B	—	5.26	193
			B	15	5.20	31
			B	—	5.12	191
			H		4.38	191
			D		5.40	191
3	$C_8H_{10}Cr(CO)_3$	*p*-xylene	B	—	5.52	193
			B	15	5.39	31
			H	—	4.95	191
			B	—	5.41	191
			D	—	5.55	191
4	$C_8H_{10}Cr(CO)_3$	*o*-xylene	B	15	5.41	31
5	$C_8H_{10}Cr(CO)_3$	*m*-xylene	B	15	5.37	31
6	$C_9H_{12}Cr(CO)_3$	mesitylene	B	—	5.52	193
			B	15	5.56	31
			B	—	5.59	191
			H	—	5.22	191
			D	—	5.72	191
7	$C_{10}H_{14}Cr(CO)_3$	1,2,4,5-tetramethylbenzene	B	—	6.04	193
8	$C_{12}H_{18}Cr(CO)_3$	hexamethylbenzene	B	—	6.48	193
			B	15	6.22	31
			B	—	6.27	191
			H	—	5.94	191
			D	—	6.35	191
9	$C_{10}H_8Cr(CO)_3$	naphthalene	B	15	6.33	31
			B	—	5.02	191
			B	—	5.13	194
			H	—	4.86	191
			D	—	5.00	191
10	$C_{12}H_{10}Cr(CO)_3$	biphenyl	B	—	5.33	193
11	$C_{14}H_{10}Cr(CO)_3$	anthracene	B	—	5.20	195
12	$C_{14}H_{10}Cr(CO)_3$	phenanthrene	B	—	5.03	195
13	$HOC_6H_5Cr(CO)_3$	phenol	B	15	5.13	31
14	$CH_3OC_6H_5Cr(CO)_3$	anisole	B	—	5.43	193
			B	15	5.26	31
15	$H_2NC_6H_5Cr(CO)_3$	aniline	B	15	5.40	31
16	$(CH_3)_2NC_6H_5Cr(CO_3)$	dimethylaniline	B	—	6.30	193
17	$ClC_6H_5Cr(CO)_3$	chlorobenzene	B	—	5.08	193
			B	—	4.21	192
			B	—	4.53	196
18	$IC_6H_5Cr(CO)_3$	iodobenzene	B	—	4.59	196
19	$BrC_6H_5Cr(CO)_3$	bromobenzene	B	—	4.65	196
20	$pCl_2C_6H_4Cr(CO)_3$	*p*-dichlorobenzene	H	—	3.72	191
			B	—	4.00	
			D	—	4.20	
21	$FC_6H_5Cr(CO)_3$	fluorobenzene	B	—	4.91	193
			B	15	4.75	31
			B	—	4.51	196
22	$F_2C_6H_5Cr(CO)_3$	*p*-difluorobenzene	H	—	3.97	191
			B	—	4.40	
			D	—	4.67	
23	$CH_3O_2C—C_6H_5Cr(CO)_3$	methyl benzoate	B	15	4.47	31
24	$p(CH_3O_2C)_2C_6H_4Cr(CO)_3$	dimethyl terephthalate	B	—	3.52	192
25	$p(CH_3)_2C_6H_4Mo(CO)_3$	*p*-xylene	H	—	5.75	191
			B	—	6.06	
			D	—	6.25	
26	$p(CH_3)_2C_6H_4W(CO)_3$	*p*-xylene	H	—	5.86	191
			B	—	6.23	
			D	—	6.53	
27	$SeC_4H_4Cr(CO_3)$	selenophen	B	—	5.55	196
28	$2.5\text{-}(CH_3)_2SeC_4H_2Cr(CO)_3$	2,5-dimethylselenophen	B	—	6.00	196
29	$SC_4H_4Cr(CO)_3$	thiophen	B	—	5.54	196

arranged in the *cis*-position in relation to one another and the coordination number of the chromium is seven, is proposed[189] for cyclopentadienyl(cyclopentenyl)chromium-dicarbonyl $(C_5H_5)(C_5H_7)Cr(CO)_2$, from consideration of the vibrational and NMR spectra and the value of the dipole moment (3.5 D).

Arenechromiumtricarbonyls§ of the general formula $XArCr(CO)_3$, in distinction from the bisarene complexes of chromium, exhibit considerable polarity (the values of their dipole moments vary within the range 4.5–6.5 D, see Table 3). This value cannot be connected with a small moment of the C–O group (0.8 D) and it is explained by the polarisation of the metal–arene bond[31,71,191,192].

It was logical to assume that the presence of this polarisation should lead to an increase in the dipole moment of the arenechromiumtricarbonyls containing electron-donating substituents in the benzene rings and a decrease in polarity when the substituents are electron-withdrawing[31,191,193]. The values of the dipole moments of the complexes with electron-donating (compounds 2–16, Table 3) and electron-withdrawing (compounds 17–22) substituents confirm the hypothesis and there is a satisfactory correlation between Hammett's σ constants, the dipole moments, and the displacements of the C–O stretching frequencies[192].

Randel and Sutton[193] determined the dipole moments of a group of arenechromiumtricarbonyls containing from one to six methyl groups in the benzene nucleus and concluded that the moments found experimentally (in benzene) agree satisfactorily with the values calculated by the formula $\mu = \mu_0 + 0.23n$ (where μ_0 is the moment of benzenechromiumtricarbonyl and n the number of methyl groups). It was shown later that for other solvents also similar relations can be found: $\mu = \mu_0 + 0.26n$ (heptane) and $\mu = \mu_0 + 0.20n$ (dioxan)[191]. However, if it is remembered that the dipole moment values of the methyl-substituted arenechromiumtricarbonyls obtained for one or another solvent by different authors vary by 0.2–0.3 D (Table 3), the above relations must be considered to be extremely approximate. With the arenechromiumtricarbonyls the solvents have a considerable effect on the value of the dipole moment: the greatest moment is observed in solvents such as dioxan and the least in heptane; benzene occupies an intermediate position[191]. This peculiarity in the behaviour of the arenechromiumtricarbonyls, the aromatic rings of which can behave as potential acceptors of electrons is thought by Strohmeier to be explained by the formation of donor–acceptor compounds between the complex and the solvent[191]. Such an explanation agrees well with the fact that the difference in the values of the dipole moments ($\Delta\mu$) determined in dioxan and in heptane gradually decreases with increase in the number of electron-donating groups in the aryl nuclei of the complexes and reaches a minimal value for hexamethylbenzenechromiumtricarbonyl[191]. Furthermore, from this position it is not clear why $\Delta\mu$ decreases, not increases, for arenechromiumtricarbonyls with electron-acceptor substituents in the aryl nuclei (chlorine, fluorine[191], and especially an ester group[194]), and why the value of $\Delta\mu$ for naphthalenechromiumtricarbonyl is extremely low (0.14 D).[191,195]

A comparison of the dipole moments of the *p*-xylenetricarbonyl complexes of chromium, molybdenum, and tungsten (Table 3) shows that in the series Cr → Mo → W the values of the moments increase with increasing acceptor strength in the order $Cr(CO)_3$, $Mo(CO)_3$, $W(CO)_3$.[191]

The dipole moments of the cyclopentadienyl and arenemetal carbonyls of the general formula $RM(CO)_2L$, where M = Cr and L is a nitrogen base, $P(C_6H_5)_3$, are $SO_2(CH_3)_2$ groups[115], and also π-ligands (alkenes, alkynes)[197] have been determined. The results have been used to calculate

§ A review on substituted carbonyls of the metals of Group VIb appeared recently[190].

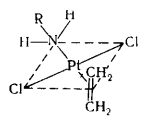
the partial dipole moments μ(M–L) of the metal–donor bond and to establish a correlation between these quantities and the stretching frequencies of the carbonyl groups of the complexes[197].

IV. COMPLEXES OF METAL SALTS WITH UNSATURATED HYDROCARBONS

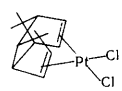
1. Complexes of Alkenes

The dipole moments of the purely alkenic complexes bis(ethyleneplatinum chloride) $(C_2H_4PtCl_2)_2$ [198] and bis-(ethylene) platinum(II) dichloride[199] have not been measured.

In 1947 Syrkin and Shidlovskaya[200] determined the dipole moment of the simplest representative of the alkene complexes (LXXI; R = H) of platinum(II) chloride $C_2H_4PtCl_2NH_3$, which was investigated in detail later by Chatt and coworkers[198,199].



(LXXI)



(LXXII)

The values obtained for complexes of the type (LXXI) (for R = p-$CH_3C_6H_4$ the dipole moment is 2.35 D; for R = p-ClC_6H_4, 1.79 D) correspond to the difference in moments $\mu_{(N-Pt)} - \mu_{(C_2H_4-Pt)}$ and since $\mu_{(N-Pt)}$ has been evaluated[201] as ~ 6 D the moment $\mu_{(C_2H_4-Pt)}$ should be 4 D.[186] Evidently this value characterises a donor–acceptor bond produced by the bonding of the π-orbital of ethylene and the dsp^2-orbitals of platinum. A bond of this type is extremely polar, therefore the comparatively low value of the dipole moment is explained by the formation of an additional dative bond from the Pt atom to the antibonding π^*-orbital of the alkene ligand[198].

This treatment of the nature of the metal–alkene bond¶, which is confirmed by X-ray diffraction[204,205] and electron diffraction investigations[206], by the prominant trans effect of the alkenes[203,207] and also by calculated data[208], is now widespread.

Determination of the dipole moment of the complex of platinum(II) chloride with bicyclopentadiene led to a conclusion about the coordination at the π-bond of the alkene[209]. For 50 years this compound had been ascribed a structure with a C–M σ-bond[210] and it was only in 1956 on the basis of the considerable dipole moment (μ = 13 D) and the infrared spectra that it was given structure (LXXII).[209]

The complexes of $PtCl_2$ with hexa-1,5-diene (6.1 D) and cyclo-octatetraene (7.0 D)[211] should probably also have structures similar to (LXXII). In the latter instance the appreciable value of the dipole moment is thought by Jensen[211] to be connected with the fact that the cyclo-octatetraene in the complex has the "boat" conformation and this is also detected in the spectroscopic investigations[212]. According to the results of crystal-chemical investigations[213] dipenteneplatinum dichloride $C_{10}H_{16}PtCl_2$, norbornadiene palladium dichloride[214] $C_7H_8PdCl_2$, and dimeric cyclo-octa-1,5-dienerhodium chloride[215] have structures similar to (LXXII).

In connection with the increasing interest in the mechanism of cationic polymerisation[216,217] papers devoted to a study of the polar properties of complexes of tin(IV) chloride with unsaturated compounds[218,219] have recently appeared.

¶ The earlier work of Gel'man[202,203] is interesting in this connection.

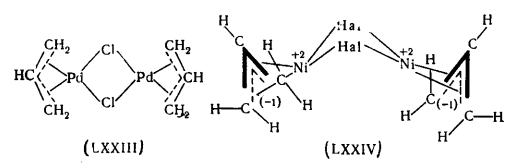
Using a method of dielectrometric titration Gol'dshtein and coworkers determined the values of the dipole moments of complexes of tin(IV) chloride with styrene (0.73 D), stilbene (0.75 D), and 1,1'-diphenylethylene (1.09 D).[218,219] The dipole moments of such complexes of $SnCl_4$ with alkenes are distinguished from the moments of the free ligands by 0.4–0.7 D and it was concluded that the products of the reaction of tin(IV) chloride with unsaturated hydrocarbons are π-complexes[218].

The existence of such complexes was shown not only in the determination of the dipole moment but also by a spectroscopic method[220,221]. Furthermore it must be borne in mind that the interpretation of the values of the dipole moments of these complexes in benzene is difficult, since according to some data $SnCl_4$ itself has a moment of 0.8–0.95 D in this solvent[16,17].

2. π-Allyl Complexes

The structure of the π-allyl complexes of the transition metals has now been adequately studied[222,223]. The largest number of dipole moment data are for bis(allylpalladium chloride) $(C_3H_5PdCl)_2$,[224,225] its methylallyl $(C_4H_7PdCl)_2$ [226] and phenyl $(C_9H_9PdCl)_2$ [227] analogues, and bis-(π-allylnickel halides) $(C_3H_5NiX)_2$.[228,229] The participation of the π-electrons of the allyl radical in the formation of such complexes is now no longer open to doubt[230–233]: it has been demonstrated in the study of the infrared[234] and NMR [235] spectra of the allyl complexes of palladium chloride, by X-ray structural investigations[236–238], and in other ways.

The dimeric nature of these complexes[225] and the results of X-ray structural analyses[236–238] allow structure (LXXIII) with μ-halogeno bridges to be ascribed to complexes of this type.



(LXXIII)

(LXXIV)

For the strictly planar structure of type (LXXIII) the dipole moment should be close to zero. Starting from this assumption, Syrkin and coworkers assumed that the non-zero value of the dipole moment of bis-(π-allylpalladium chloride) 2.23 D (for the α form) and 3.4 D (for the β) belong to the monomer[225]. However, other authors[226] state that the moment of 2.2 D obtained for bis-(π-methylallylpalladium chloride) relates to a dimer. A similar opinion is also expressed for the allyl complexes of the nickel halides[229]: the dipole moment of 1.62 D for bis-(π-allylnickel iodide) and 1.31 D for bis-(π-allylnickel bromide) are connected with dimeric molecules which exist in benzene and cyclohexane solutions.

The question naturally arises as to the reason for the polarity of the externally symmetrical dimeric π-allyl complexes of the metal halides.

The hypothesis of the donor–acceptor interaction of the molecule of the complexes (LXXVII) with the π-system of the solvent, which could have a considerable effect on the value of the moment, is improbable here, since in cyclohexane the dipole moment of this type of compound is considerable (for example, for bis-(π-allylnickel iodide) it is 1.48 D.[229] Fischer considers that to explain these values of the dipole moments of the dimeric π-allylnickel halide molecules they must have the structure (LXXIV) in

which the halogen bridges cause curvature of the molecule, destroying its symmetry[229].

Similar ideas could evidently be extended to the butadiene complexes of palladium and platinum chlorides, the structure of which has been little studied.

The dipole moments (~ 3.5 D) of the π-allyl complexes of rhodium and palladium of the type

$$[E(C_6H_5)_3]Cl_2M\text{-}\pi\text{-}C_4H_7,$$

where E = P, As, Sb, have also been determined (~ 3.5 D).[239]

In conclusion it must be noted that the structural assignment of the products of the reaction of metal chlorides with allyl hydrocarbons is of considerable importance for finding the mechanism of oxidation of alkenes[240] and for various polymerisation processes[231].

V. COMPLEXES OF THE HALIDES OF THE ELEMENTS OF GROUPS III–V WITH AROMATIC HYDROCARBONS

Interest in the complexes of metal halides with aromatic hydrocarbons has arisen in connection with the study of the mechanisms of a large number of catalytic reactions which take place with participation of aluminium chloride[241,242] and the halides of other metals[243].

A principal part in solving the problem of the existence of metal halide complexes with aromatic hydrocarbons and of their nature was played by dipole moment studies on halides in various solvents. Even in the first papers of Ulich and Nespital it was shown that aluminium bromide, which is almost non-polar in carbon disulphide, has a high dipole moment (4.9–5.2 D) in benzene[244,245]. It was found later that in aromatic solvents (benzene, toluene, *p*-xylene) the dipole moments of aluminium bromide reach values of ~ 5–6 D[248] whereas in cyclohexane[249], carbon disulphide, bromine[248], and also the melt[246], the values of μ are close to zero. These results agree with ideas about the dimerisation of $AlBr_3$ in these solvents. X-Ray structural[250], electron diffraction[251,252], and spectroscopic[253] investigations lead to the same conclusion.

The high values of the dipole moments of aluminium bromide in benzene[244–246,248] naturally raised the question of the reasons for its polarity in non-polar solvents.

The first attempt to explain this was made by Ulich and Nespital, who considered that in the benzene solution dissociation of the dimeric molecules of aluminium halides took place, leading to the appearance of non-symmetric monomers of $AlBr_3$ with a structure distorted under the influence of the solvent[244,245]. The appreciable dipole moment of aluminium iodide[246] and gallium chloride[254] in benzene (2.5 and 3.05 D respectively) responded to analogous treatment. In later investigations[246–248] although the dissociation of the dimeric molecules of aluminium halides in benzene was not contradicted, the high values of the dipole moments were connected with the formation of complexes of the monomeric molecules of the halides with the solvent.

Evidence in support of the existence of such complexes is provided by the results of the physicochemical analysis of the $AlBr_3$–C_6H_6 system[225] and the results of spectroscopic[256], thermochemical, and electrochemical[247] investigations.

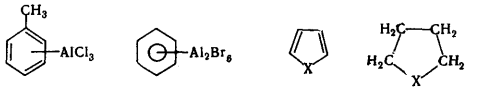
The high values of the dipole moments of antimony trichloride (~ 4.0 D)[257–259] and tribromide (3.28 D)[259] in benzene also show the interaction of SbX_3 with the solvent, leading to the formation of a complex, which is also observed by thermal analysis[260] and spectroscopy[261,262].

Similarly it is possible to explain the polarity of thallium(III) chloride (3.93 D)[263] and silver perchlorate (4.7 D)[264] in benzene, which in the last instance agrees with the existence of a molecular compound $AgClO_4.C_6H_6$[265] and also the appearance of non-zero moments for the symmetric molecules of tin(IV) chloride in benzene[266,267] and for the $SnCl_4$–naphthalene complex[268].

All the above results leave no doubt about the ability of aromatic hydrocarbons to form complexes with metal halides.

Many investigations[241,269–271] were made to explain the nature of these complexes and it became understandable only comparatively recently[271].

It is now generally accepted that aromatic compounds form π-complexes with metal halides owing to the interaction of the π-electrons of the aromatic system and the vacant orbitals of the metals. For example, the complex of toluene with aluminium chloride is ascribed the structure (XXV)[270]:



(LXXV) (LXXVI) (LXXVII) (LXXVIII)

where X = O, S.

Some recent investigations of the problem by Romm and Gur'yanova are of special interest[272]. They showed that in thoroughly dried benzene aluminium bromide keeps a dimeric structure and its dipole moment does not exceed 1 D. The authors consider that the π-complex of benzene with aluminium bromide has structure (LXXVI), and the high values of the dipole moments obtained earlier for $AlBr_3$ in aromatic solvents are connected with the formation of a ternary complex $Al_2Br_6.HBr.nAr$.[272] The results of this investigation, although not denying the possibility of the formation of π-complexes of the metal halides with aromatic hydrocarbons, merit critical examination of the values obtained earlier for the dipole moments of halides in aromatic solvents[16–17].

In determining the dipole moments of complexes of tin(IV) chloride with furan and thiophen (LXXVII) it was found that both the value of the moment of the complex and its increase during complex formation are considerably less than for saturated heterocycles (LXXVIII).[218,273] These results led to the conclusion that thiophen and furan form π-complexes with $SnCl_4$ (the dipole moment of the thiophen complex is 1.73 D, that of furan 0.99 D), but thiophan (5.0 D) and tetrahydrofuran (5.94 D) give complexes with a donor–acceptor bond owing to the *p*-electrons of the sulphur or oxygen atoms[273]. The infrared spectra of the complexes of $SnCl_4$ with thiophen and thiophan support these ideas[274].

It is remarkable that according to dielectric constant measurements of titanium(IV) chloride does not form π-complexes with benzene[275] and thiophen[276]. However, thermal analyses[277,278] and spectroscopic[278] and magnetic (EPR)[279] investigations show that $TiCl_4$ forms π-complexes with aromatic systems including benzene[279]. Therefore it must be borne in mind that in instances when the increase in dipole moment on going from the ligand to the complex is exceptionally small (< 0.5 D), the value of the moment cannot serve as a definite criterion for the absence of complex formation in the system. Only a combination of various physicochemical methods permits the behaviour of the compounds in solution to be judged.

In conclusion we note that not only metal halides but also a series of organometallic compounds are capable of

forming π-complexes with aromatic hydrocarbons. The same conclusion was reached from the results of Stromeier's work, which shows that the dipole moment of organometallic compounds in benzene is always greater than the value obtained in measurements in hexane, heptane, carbon disulphide, and other indifferent solvents [31,191,280,281].

VI. POLYMETALLIC $\pi\sigma$-COMPLEXES

Because of the rapid development of physicochemical and structural investigations in the field of bimetallic and polymetallic $\pi\sigma$-complexes [282,283], the polar properties of the organometallic compounds containing transition (M) and non-transition (M') metals are now being studied.

Kahn and Bigorgne [284,285] determined the dipole moments of bimetallic carbonyls of the type $(CO)_4Co.MX_3$, $(CO)_4Fe(MX_3)_2$, $[(CO)_4FeM'X_2]_2$, where M = Si, Ge, Sn, Pb; X = Cl, Alk, Ar, OMe.

From these results, detailed infrared investigations, and the assumption that the transition metal atom in these complexes is electrically neutral, the authors also determined the structure, found more accurately the nature of the M–M' bond [sic], and compared it with the bond in the $(CO)_4Fe–PX_3$ complexes.

On the basis of the dipole moments [286] of the recently prepared [287] carbonyl-π-cyclopentadienyls of the general formula $[\pi\text{-}C_5H_5Fe(CO)_2]_nSnX_{4-n}$, where X = Hal, Alk, Ar, conclusions were drawn about the monotonic increase in the moment with increase in the volume of X and the effect of the substituent on the polarity of the fragment $[\pi\text{-}C_5H_5Fe(CO)_2]$–Sn was discussed. This increase in the dipole moment is evidently connected with the approximation of the Fe–Sn–Fe angle to the regular tetrahedral angle (according to X-ray structural investigations [288–291] this angle is 124–126°).

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New information has recently appeared on the study of the structure of π-complexes by the dipole moment method. The value $\mu = 1$ D allows the *cis* structure to be ascribed to pentacarbonylbis(cyclopentadienyl)vanadium $(C_5H_5)_2V_2(CO)_5$; [292] the *trans*-configuration should be without a dipole moment. A centrosymmetric structure agrees with the insignificant value of the moment of the dimer of bis(cyclopentadienyl)platinum, $[Pt(C_5H_5)_2]_2$. [293]

The dipole moment method showed that the monocarbonyls [294] and mononitrosyls [295] of rhodium(I) and rhodium(III) of the general formulae $MX(CO)L_2$ and $MX_3(EO)L_2$ (where X = Cl, Br, I, SCN; L = PR_3, AsR_3) have the *trans*-structure. Analogous complexes of ruthenium have been isolated as *cis*- and *trans*-isomers [296].

A *trans*-arrangement of the PR_3 groups and *cis*-halogens is characteristic for dicarbonylphosphinic complexes $MX_2(CO)_2(PR_3)_2$ (M = Fe, Ru, Os), [297] but only the *cis*-structure for $[PtX_2CO(PR_3)]$. [298]

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Progress in the Synthesis of Perfumes Based on Pinenes†

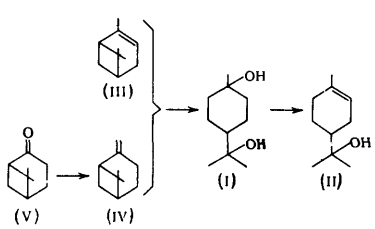
Y.-R.Naves

Turpentine was known in far antiquity. As is well known, it was obtained by steam distillation of various types of pine. Rosin and resins are obtained simultaneously.
All these products were used in the construction of ships. Turpentine was first produced in the XVIth century in North America, where there were vast areas of pine forests in North and South Carolina, Georgia, Alabama, and Virginia and where there was a market for these products, and they became widespread in the XVIIth century. The use of turpentine for the production of varnishes, paints, etc. began about 1830-1840.
There is a bibliography of 119 references.

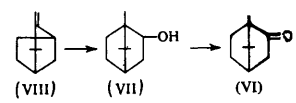
1. Turpentine and the Chemistry of Perfumes

Turpentine was first used as a raw material for the manufacture of perfumes at the end of the XIXth century. In 1827 Vogel obtained terpene (I), which Tilden in 1878 and Wallach in 1885 dehydrated to terpineol(II), and Flavitskii obtained terpineol directly from turpentine in 1879. In France the industrial production of terpineol was the consequence of work carried out by Bouchard and Bouari (1866) and Lafonte (1889).

The structure of α-pinene (III), the principal constituent of turpentine, was suggested by Wagner in 1894 and firmly established by Bayer two years later. The structure of β-pinene (IV) was established by Wallach in 1907 as a result of the synthesis of this terpene from norpinone (V). The first accurate analysis of a mixture of α- and β-pinenes was effected by Darmu in 1911 on the basis of measurements of optical rotatory dispersion.



Camphor (VI) was known in the Far East before recorded time. It was introduced into Europe by the Arabs. Reluz obtained it by the oxidation of borneol (VII) in 1841. At the end of the last century camphor became an important raw material for the manufacture of celluloid and smokeless powders. Bredt established the structure of camphor in 1893, but its synthesis, effected from the pinenes through the intermediate production of camphene (VIII), borneol, and isoborneol, was used industrially only until 1920.



Up to 1940 the pinenes were used for the production of terpineols, borneol, isoborneol, and their esters, and camphor. The position then changed sharply. This progress was due to the efforts of the producers of turpentine to increase its consumption and thanks to the wish of the synthetic perfumes industry to be freed from the use of natural ester oils, the difficulty of supply, variable quality, and high cost of which hindered the further development of this sector of industry.

I will not dwell on the papers dealing with the development of the chemistry of camphene, borneol, isoborneol, and camphor, and also terpenophenols, since most of the terpenophenols were first obtained in the USSR at the All-Union Scientific Research Institute for Synthetic and Natural Perfumes, where in this field also very interesting work is now being carried out.

This review will give the progress reached in effecting the opening of the bicyclic system of the pinenes and their derivatives into compounds of the monocyclic and aliphatic series.

The acid-catalysed decyclisation was effected even longer ago, since the production of terpineols was realised

† Paper read at the All-Union Scientific Research Institute of Synthetic and Natural Perfumes, Moscow, 1967.