139. The Variation of Bond Type in Cyclopentadienyl–Metal Compounds.

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The variation of bond type in cyclopentadienyl–metal compounds with the nature of the central element is reviewed. Compounds from the elements of Groups I to IV are compared with those of the transition elements; the bonding is considered in terms of a purely ionic model, a delocalized π-complex and a localized σ-complex model. Consideration of promotion energies, group-overlap integrals, and electron-transfer energies leads to the view that the elements of Groups Ia and IIa form compounds with pronounced ionic character whereas those of Groups Ib and IIb will tend to form σ-complexes. With regard to Group IIIb and IVb it is more tentatively suggested that the thallium and indium compounds possess more covalent character than hitherto considered; for biscyclopentadienyl-lead and -tin the σ-complex is indicated. The relative success of simple molecular orbital theory in explaining the electronic structure of the transition metal–biscyclopentadienyl compounds is due, in part, to the lower promotion energies of the π-structure valency states than of the σ-structure states.

THE isolation [1] of ferrocene (biscyclopentadienyl-iron) in 1951 was followed by a rapid extension of the series $M(C_5H_5)_2$, M = metal, to many elements of the three transition series, and simple molecular-orbital-theory [2,3] has provided a reasonable explanation of bonding in such compounds. This explanation is, of course, not quantitative but the central feature seems correct; namely, that overlap of partially filled central metal d-orbitals with the π-orbitals of the cyclopentadienyl radicals causes considerable stabilization of the molecule $M(C_5H_5)_2$. Estimates of the energies of the respective orbitals in the isolated systems in terms of ionization potentials and promotion energies then provide a basis from which semiquantitative estimates of bond energies can be made in certain cases.[5] In addition to the transition metals, other elements form cyclopentadienyl compounds,[4] *e.g.*: triscyclopentadienylmetal compounds $M(C_5H_5)_3$, formed by lanthanides and

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[1] Kealy and Pauson, *Nature*, 1951, **168**, 1039; Miller, Teboth, and Tremaine, *J.*, 1952, 632.

[2] Moffitt, *J. Amer. Chem. Soc.*, 1954, **76**, 3386; Jaffé, *J. Chem. Phys.*, 1953, **21**, 156.

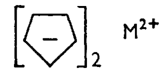
[3] Dunitz and Orgel, *J. Chem. Phys.*, 1955, **23**, 954.

[4] Fischer and Fritz, " Advances in Inorganic and Radiochemistry," Academic Press New York, 1960, Vol. I, p. 55; Cotton and Wilkinson, " Progress in Inorganic Chemistry," Interscience Publ. Inc., New York, 1960, Vol. I, p. 1.

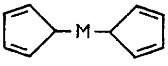
[5] Cotton and Reynolds, *J. Amer. Chem. Soc.*, 1958, **80**, 269.

actinides (these will not be considered in this paper); and the elements of Group Ia and b, Group IIa and b, Group IIIb, and Group IVb, $M(C_5H_5)_2$ or $M(C_5H_5)$.

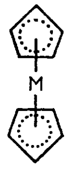
In general, a complex $M(C_5H_5)_2$ or $M(C_5H_5)$ may be envisaged as comprising (*a*) ionic bonding, (*b*) localised covalent bonds (σ-bonded complex), or (*c*) delocalized covalent bonding with D_{5d} sandwich structure (π-bonded complex) (cf. Fig.); this classification has also been discussed by Fischer and Fritz.[4]



(*a*)



(*b*)



(*c*)

In this paper we examine, on simple theoretical grounds, the variation of bond type of the cyclopentadienyl complexes of the above groups and suggest, where possible, the most probable structure for each case. We discuss first the theoretical basis, then some of the general conclusions, and, finally, compare the theoretical results in detail with the experimental data.

Molecular orbital theory does not yield satisfactory quantitative data for, *e.g.*, bond energies and electronic levels except in very simple cases. Ideally, it is necessary, for the above complexes to set up a variational treatment and to solve the resulting secular equation:

$$|H_{ij} - S_{ij}E| = 0$$

where H_{ii}, H_{jj}, H_{ij} are the coulomb terms of the *i*th and *j*th orbital and the resonance integral between the *i*th and *j*th orbital respectively, the summation being taken over the *s*-, *p*-, and *d*-atomic orbitals of the central atom and the π-orbitals of the cyclopentadienyl radical or, in the case of a σ-complex, simply over the σ-orbital of a carbon atom of the cyclopentadienyl ring. In a satisfactory quantitative treatment it must be possible to calculate the above terms with reasonable accuracy; unfortunately, with the present development of theory, only semi-empirical methods are available. Detailed semi-empirical calculations [3] have been confined to ferrocene; these gave coulomb terms from observed ionization potentials, resonance integrals from calculated group-overlap integrals, and the promotion energy of the central atom to the correct valency state for combination with the cyclopentadienyl radicals from observed term spectra of the free atom. However, satisfactory agreement between calculated and measured bond energies on such semi-empirical models only confirms the correctness of the empirical parameters employed. Comparison between different central atoms on such a model is very difficult, indeed almost impossible, since an empirical parameter relating H_{ij} to S_{ij} may not be transferable from one element to another. In view of these uncertainties, we have restricted the argument to a consideration of valency-state promotion energies, ionization potentials, and overlap integrals as criteria for determining the most probable structure for a complex of a given element.

For an ionic compound $M^{n+}(C_5H_5^-)_n$, the energy (W) required to transfer n electrons from the central atom to the cyclopentadienyl radicals is given by the expression:

$$W = -\sum^{n} I_n + nE_{e_1} + \Delta = E_i + \Delta$$

where I_n is the nth ionization potential of the central atom, E_{e_1} is the electron affinity of the e_1-orbital of the cyclopentadienyl radical, and Δ is the difference in energy between the cation and anion, in the gas phase and the ions either in the crystal or in solution.

The values of I_n are readily available for all the elements concerned. The electron affinity of the e_1-orbital of the cyclopentadienyl radical has been estimated by Moffitt[2] to be approximately 8 ev. It is very difficult to estimate Δ, which, in the case of the solid state, represents the lattice energy of a cyclopentadienylmetal. One would expect this quantity to be fairly small since the anion will consist of unit negative charge spread over a ring and, for a given cation, the lattice energy decreases with increasing anion size of constant charge. Thus, for the alkali-metal complexes we should expect Δ to be much less than for the alkali iodides (6—7 ev). In general we shall assume Δ to be about 2—3 ev, with the consequence that only if E_i, which we shall tabulate, is appreciably negative may we then safely conclude that ionic character is unlikely.*

For our discussion of the covalent structures (π- and σ-type), we require a knowledge of both the valency-state promotion energies and the relevant overlap integrals. The valency-state promotion energy P is the energy required to convert the free atom in its ground state to the valency state compatible with bonding interaction with the cyclopentadienyl group, for the particular model to be considered; the promotion energy varies, therefore, considerably throughout the series and we shall consider each group briefly in turn.

For the π-model, interaction in the D_{5d} group (or C_{5v} for $M{\cdot}C_5H_5$) will be of a type previously considered.[3,5,6] The main bonding interactions will be of the form $(e_{1g}nd_{xz,yz})$ or $(e_1nd_{xz,yz})$ and $(e_{1u}np_{xy})$ or (e_1np_{xy}) where n denotes the principal quantum number of the atomic orbital of the central atom. To anticipate somewhat, we note that for Groups I—IV it is the second of the above groups of interaction which is important, in contrast to the position for the transition metals where, although there is appreciable interaction with the np-orbitals,[6] it is the former group which is dominant. The valency states of the elements of Group I (Table 1) simply involve promotion of an electron from an ns-orbital to np- or nd-orbitals and are obtained directly from the observed spectral data.[7] The elements of Group II may attain the valency state $nd^2(V_2)$ or $np^2(V_2)$ corresponding to the two groups of interaction above. The promotion energies of the latter state are available from the work of Pritchard and Skinner,[8] and spectroscopic data give no evidence for the nd^2-state below the first ionization potential; the values are again given in Table 1. In the case of elements of Group III, the most probable valency-state appears to be that suggested by Cotton and Reynolds[5] in which two electrons are paired in a s/p_z hybrid orbital directed away from the ring, leaving an empty s/p_z hybrid to overlap the filled totally symmetric π-orbital of the ring and with one electron in a $p_{x,y}$ orbital overlapping with the doubly degenerate e_1-orbital of the ring and containing three electrons. Such an electronic arrangement raises the problem of assessing the valency-state promotion energy for a configuration involving hybridized orbitals; the problem has been discussed in detail for a few special cases involving s- and p-orbitals[9] and for a wide range of hybridization of s-, p-, and d-orbitals of the first transition elements.[10] In the cases considered in this paper, however, the extent of mixing of s- and p-orbitals is not known exactly and so we have not attempted to carry out the above procedure; for example, in the case above it does not follow that equal participation of the s- and p-orbitals will occur in the two hybrids. The statement is also true of many of the valency-states of the elements when prepared for σ-bonding as discussed below. In the case of uncertain mixing of s- and p-orbitals we have therefore followed Moffitt's method[11] of estimating the approximate electron configuration s^qp^r (where q and r may be fractional) of the valency state; the

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* The reliability of such conclusions is strengthened by the fact that the value of 8 ev assigned to E_{e_1} is probably too large. I thank the Referees for drawing my attention to this point.

[6] Brown, *J. Chem. Phys.*, 1958, **29**, 1086.

[7] Moore, "Atomic Energy Levels," N.B.S. Circular 467, U.S. Government Printing Office, Washington D.C., Vols. I—III.

[8] Pritchard and Skinner, *Chem. Rev.*, 1955, **55**, 745.

[9] Van Vleck, *J. Chem. Phys.*, 1934, **2**, 22.

[10] Skinner and Sumner, *J. Inorg. Nuclear Chem.*, 1957, **4**, 245.

[11] Moffitt, *Proc. Roy. Soc.*, 1950, *A*, **202**, 534.

promotion energy may then be assigned within limits, albeit rather wide limits, from Pritchard and Skinner's tables.[8] On this basis it can be shown that the above arrangement gives rise to the configuration $sp^2(V_1)$, the promotion energies being given in Table 1. It is again estimated that the state $spd(V_1)$ lies above the first ionization potential. The elements of Group IV possess the low-lying valency state $s^2p^2(V_2)$ which is directly suitable for the π-bonding through the interaction $(e_{1u}np_{xy})$. The promotion energies of the states $s^2pd(V_2)$ and $s^2d^2(V_2)$ are again estimated from spectral data and given in Table 1. The promotion energies of the first transition elements are also given in Table 1 and are taken

TABLE 1. *Promotion and ionization energies.*

Element	Electron confign.	Valency state	Promotion energy (ev)	E_i (ev)	Element	Electron confign.	Valency state	Promotion energy (ev)	E_i (ev)
Li	$2p$		1·85	+2·61	Si	$3s^23d^2$	$s^2d^2(V_2)$	>8·15	
	$3d$		3·88			$3s^23p^2$	$s^{4/3}p^{8/3}(V_2)$	<6·0	
Na	$3p$		2·10	+2·86	Ge	$4s^24p^2$	$s^2p^+p^-(V_2)$	0·31	−7·81
	$3d$		3·62			$4s^24p4d$	$s^2pd(V_2)$	∼6·10	
K	$4p$		1·61	+3·66		$4s^24d^2$	$s^2d^2(V_2)$	>7·88	
	$4d$		3·40			$4s^24p^2$	$s^{4/3}p^{8/3}(V_2)$	<7·0	
Rb	$5p$		1·56	+3·82	Sn	$5s^25p^2$	$s^2p^+p^-(V_2)$	0·50	−5·97
	$5d$		3·19			$5s^25p5d$	$s^2pd(V_2)$	∼5·40	
Be	$2p^2$	$p^2(V_2)$	7·30	−11·53		$5s^25d^2$	$s^2d^2(V_2)$	>7·34	
	$3d^2$	$d^2(V_2)$	>9·32			$5s^25p^2$	$s^{4/3}p^{3/8}(V_2)$	<7·0	
	$2s2p$	$sp(V_2)$	∼3·36		Cu	$4p$		3·78	+0·28
Mg	$3p^2$	$p^2(V_2)$	6·87	−6·67		$4d$		6·19	
	$3d^2$	$d^2(V_2)$	>7·64		Ag	$5p$		3·66	+0·43
	$3s3p$	$sp(V_2)$	∼3·12			$5d$		6·04	
Ca	$4p^2$	$p^2(V_2)$	4·84	−1·98	Zn	$4p^2$	$p^2(V_2)$	9·99	−11·35
	$4d^2$	$d^2(V_2)$	>6·11			$4d^2$	$d^2(V_2)$	>9·39	
	$4s4p$	$sp(\mathrm{V}_2)$	∼2·15			$4s4p$	$sp(V_2)$	4·49	
Sr	$5p^2$	$p^2(V_2)$	4·45	−0·72	Cd	$5p^2$	$p^2(V_2)$	9·41	−9·90
	$5d^2$	$d^2(\mathrm{V}_2)$	>5·69			$5d^2$	$d^2(V_2)$	>8·99	
	$5s5p$	$sp(V_2)$	∼2·04			$5s5p$	$sp(V_2)$	4·26	
B	$2s2p^2$	$sp^2(V_1)$	∼6·58	−0·30	Ti	$3d^24s^2$	$d^2s^2(V_2)$	0·50	−4·46
	$2s2p3d$	$spd(V_1)$	>8·30			$3d^4$	$d^4(V_2)$	5·35	
	$2s2p^2$	$s^{3/2}p^{3/2}(V_1)$	<6·58		V	$3d^34s4p$	V_5	∼5·0	−4·94
Al	$3s3p^2$	$sp^2(V_1)$	∼5·03	+2·02		$3d^34s^2$	$d^3s^2(V_3)$	1·47	
	$3s3p3d$	$spd(V_1)$	>5·98			$3d^5$	$d^5(V_5)$	4·04	
	$3s3p^2$	$s^{3/2}p^{3/2}(V_1)$	<5·03		Cr	$3d^44s4p$	V_6	∼7·0	−7·25
Ga	$4s4p^2$	$sp^2(V_1)$	∼6·15	+2·00		$3d^54s$	$d^5s(V_6)$	1·91	
	$4s4p4d$	$spd(V_1)$	>6·00			$3d^7$	$d^7(V_4)$	5·57	
	$4s4p^2$	$s^{3/2}p^{3/2}(V_1)$	<6·15		Mn	$3d^54s4p$	V_7	∼8·0	−7·07
In	$5s5p^2$	$sp^2(V_1)$	∼6·30	+2·25		$3d^54s^2$	$d^5s^2(V_5)$	2·21	
	$5s5p5d$	$spd(V_1)$	>5·79			$3d^7$	$d^7(V_7)$	7·52	
	$5s5p^2$	$s^{3/2}p^{3/2}(V_1)$	<6·30		Fe	$3d^64s4p$	V_6	∼7·0	−8·08
C	$2s^22p^2$	$s^2p^+p^-(V_2)$	0·32	−19·64		$3d^8$	$d^8(V_2)$	4·8	
	$2s^22p3d^2$	$s^2pd(V_2)$	∼9·70		Co	$3d^74s4p$	V_5	∼7·0	−8·91
	$2s^23d^2$	$s^2d^2(V_2)$	>11·26			$3d^74s^2$	$d^7s^2(V_3)$	∼1—2	
	$2s^22p^2$	$s^{4/3}p^{8/3}(V_2)$	<9·85		Ni	$3d^84s4p$	V_4	∼6·0	−9·78
Si	$3s^33p^2$	$s^2p^+p^-(V_2)$	0·21	−8·49		$3d^84s^2$	$d^8s^2(V_2)$	∼1—2	
	$3s^23p3d$	$s^2pd(V_2)$	∼5·60						

from the results of Shustorovich and Dyatkina;[12] discussion is deferred. It remains now to consider the promotion energies for the valency states required for the σ-bonded structure (*c*). The valency states of the elements of Group I are identical, of course, with those of the π-complex case. The elements of Group II require a configuration in which the *ns*- and *np*-orbitals are hybridized to give orbitals *ns*/*np* directed towards a localized σ-orbital of a carbon atom. In this case, the electrons occupy singly the above hybrid orbitals and it can be shown that such an arrangement is based on the configuration $sp(V_2)$; the values in Table 1 are taken from Pritchard and Skinner's results.[8] The elements of Group IIIb possess a ground state which is compatible with direct σ-bonding between the central np_σ-orbital and the σ-orbital localized on the carbon atom of the

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[12] Shustorovich and Dyatkina, *Zhur. neorg. Khim.*, 1958, **3**, 2721.

cyclopentadienyl system. It is also possible to consider the arrangement $(ns/np)^2(ns/np)^1$, where ns/np denotes a linear hybrid of the ns- and the np-orbital and it can be shown that such an arrangement is based on the configuration $s^{3/2}p^{3/2}(V_1)$. The indices of this configuration will depend on the extent of mixing of the ns- and the np-orbitals in the above hybrids and since we are unable to assess the degree of mixing accurately we assign a promotion energy to the above state as intermediate between that of $s^2p(V_1)$ and $sp^2(V_1)$; the energy is expressed, therefore, as an inequality in Table 1. A similar problem arises with the elements of Group IVb. The ground state $ns^2np^2(V_2)$ is again compatible with direct σ-bonds. Promotion to the configuration $(tr)^1(tr)^1(tr)^2$, where tr denotes a trigonal hybrid, leads to the intermediate configuration $s^{4/3}p^{8/3}(V_2)$. The value listed in Table 1 for the promotion energy to the above valency state is again expressed as an inequality for the same reasons as for Group III.

The calculation of the group overlap integrals for the π-complex is quite straightforward and requires little comment. We have used simple Slater-type atomic orbitals for the central element and calculated the screening constants according to Slater's rules.[13] The bond distances between the ring carbon atoms and the central atom were calculated from the covalent radii of the central elements taken from Pauling's data [14] for twelve-fold co-ordination together with the normal radius of the carbon atom. This procedure is very approximate, but since we are interested only in comparing the values of overlap integrals it seems a consistent method for the calculation of distance. The geometry of the molecule $M(C_5H_5)_2$ or $M(C_5H_5)$ was then calculated with the above M–C distance and with the dimensions of the C_5H_5 ring assumed identical with those of the C_5H_5 ring in ferrocene.[15] The distances in ferrocene and nickelocene are known from accurate X-ray studies, and those of the biscyclopentadienyl compounds from chromium, vanadium, and cobalt are known approximately.[16] The normal parameters p and t which define the overlap integrals [20] are readily calculated and are given in Table 2. The formulæ for the group overlap integrals have been given previously,[3,5,6] but for convenience we list them:

$$\begin{aligned}
S(a_{1g}ns) &= \sqrt{10}\cos\theta S(2p_\sigma ns)\\
S(a_{1u}np_z) &= \sqrt{10}[S(2p_\sigma np_\sigma)\cos^2\theta - S(2p_\pi np_\pi)\sin^2\theta]\\
S\begin{pmatrix}e_{1g}nd_{xz}\\ \phantom{e_{1g}nd}yz\end{pmatrix} &= \sqrt{5}[\sqrt{3/2}S(2p_\sigma nd_\sigma)\sin 2\theta\cos\theta + S(2p_\pi nd_\pi)\cos 2\theta\sin\theta]\\
S(e_{1u}np_{x,y}) &= \sqrt{5}\sin\theta\cos\theta[S(2p_\sigma np_\sigma) + S[2p_\pi np_\pi)]
\end{aligned}$$

These formulæ apply to $M(C_5H_5)_2$ with D_{5d} symmetry; the five-fold axis of symmetry is the z-axis, and θ denotes the angle between this axis and the metal–carbon vectors. For the monocyclopentadienyl complex, $M(C_5H_5)$, which has only C_{5v} symmetry the g,u classification is removed and it is necessary to divide the above formulæ by $\sqrt{2}$. The formulæ are not corrected for overlap between the π-orbitals of the rings since it is comparative values in which we are interested in this treatment. The majority of the constituent overlap integrals required in the above formulæ have been tabulated,[17,18] but unfortunately, in the case of the integrals $S(2p_\sigma 3d_\sigma)$, $S(2p_\pi 3d_\pi)$ and those involving wave functions of principal quantum number five, the published tables contain intervals in p and t which are often too large for satisfactory interpolation, even for a comparative study. Accordingly, the latter integrals were calculated from the master formulæ for the nearest set of parameters p and t to those calculated above for which the auxiliary functions $A_m(p)$ and $B_n(pt)$ were available. The Swedish tables [19] of $A_m(p)$ for

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[13] Slater, *Phys. Rev.*, 1930, **36**, 57.
[14] Pauling, *J. Amer. Chem. Soc.*, 1947, **69**, 542.
[15] Dunitz, Orgel, and Rich, *Acta Cryst.*, 1956, **9**, 373.
[16] Weiss and Fischer, *Z. anorg. Chem.*, 1954, **284**, 69.
[17] Mulliker, Recke, Orloff, and Orloff, *J. Chem. Phys.*, 1949, **17**, 1248.
[18] Jaffé and Doak, *J. Chem. Phys.*, 1953, **21**, 196; Jaffé, *ibid.*, p. 258.
[19] Flodmark, " Table of Molecular A and B Functions," Inst. Theoretical Physics, Stockholm, **1957**.

$m = 0, 1, \ldots 8$ and $0 < p \leqslant 50$ and $B_n(pt)$ for $n = 0, 1, \ldots 8$ and $0 < pt \leqslant 50$ proved invaluable. The integrals involving wave functions of principal quantum number four may be obtained, with one exception, from master formulæ and tables now available as the result of two independent studies of this group.[6,20] The master formula for the one exception, $S(2p_\pi 4d_\pi)$, is derived in the Appendix. The evaluation of the integral

TABLE 2. *Group overlap integrals for systems* $M(C_5H_5)_2$ *and* $M(C_5H_5)$.

M	Electron confign.	p	t	$S(a_{1g}ns)$ $[S(a_1ns)]$	$S(a_{1u}np_z)$ $[S(a_1np)]$	$S(e_{1g}nd_{xz})$ $[S(e_1nd)]$	$S(e_{1u}np_{x,z})$ $[S(e_1np)]$
Li	$2p(2s)$	4·987	0·429	0·274	0·201	—	0·229
	$3d$	4·658	0·529	—	—	0·035	—
Na	$3p(3s)$	5·942	0·378	0·205	0·243	—	0·171
	$3d$	4·934	0·660	—	—	0·004	—
K	$4p(4s)$	6·544	0·464	0·072	0·058	—	0·072
	$4d$	5·586	0·715	—	—	−0·009	—
Rb	$5p(5s)$	6·681	0·494	0·027	0·005	—	0·046
	$5d$	5·759	0·733	—	—	−0·007	—
Be	$2s^2$	4·653	0·250	0·606	—	—	—
	$2p^2$	,,	,,	—	0·255	—	0·511
	$3d^2$	3·892	0·494	—	—	−0·112	—
Mg	$3s^2$	5·764	0·262	0·472	—	—	—
	$3p^2$	,,	,,	—	0·261	—	0·345
	$3d^2$	4·868	0·494	—	—	0·095	—
Ca	$4s^2$	6·203	0·357	0·119	—	—	—
	$4p^2$	,,	,,	—	0·053	—	0·151
	$4d^2$	5·363	0·569	—	—	0·009	—
Sr	$5s^2$	6·447	0·390	0·138	—	—	—
	$5p^2$	,,	,,	—	0·111	—	0·136
	$5d^2$	5·619	0·595	—	—	0·030	—
B	$2s2p^2$	4·839	0·111	0·491	0·144	—	0·295
	$2s^23d$	5·129	0·048	0·486	—	−0·080	—
	$(2p^23d)$	3·239	0·660	—	0·191		0·276
Al	$3s3p^2$	5·810	0·163	0·389	0·306	—	0·298
	$3s^23d$	6·038	0·119	0·410	—	−0·063	—
	$(3p^23d)$	4·070	0·660	—	0·337		0·301
Ga	$4s4p^2$	6·127	0·092	0·395	0·304	—	0·313
	$4s^24d$	6·323	0·058	0·414	—	−0·024	—
	$(4p^24d)$	3·901	0·715	—	0·334		0·316
In	$5s5p^2$	6·604	0·130	0·337	0·323	—	0·252
	$5s^25d$	6·810	0·096	0·357	—	−0·018	—
	$(5p^25d)$	4·307	0·733	—	0·354	—	0·257
C	$2s^22p^2$	4·729	0	0·708	0·013	—	0·564
	$2s^22p3d$	4·765	0·018	0·760	0·009	−0·147	0·561
		2·849	0·660				
		5·020	0·058				
	$2s^23d^2$	3·165	0·494		—	−0·298	—
Si	$3s^23p^2$	5·931	0·081	0·619	0·460	—	0·330
	$3s^23p3d$	6·162	0·040	0·627	0·479	−0·059	0·321
		3·861	0·660				
	$3s^23d^2$	4·289	0·494		—	0·009	—
Ge	$4s^24p^2$	6·364	0·031	0·611	0·480	—	0·463
	$4s^24p4d$	6·556	0				
		3·826	0·715	0·624	0·508	−0·037	0·459
	$4s^24d^2$	4·182	0·569		—	−0·068	—
Sn	$5s^25p^2$	6·638	0·070	0·543	0·492	—	0·403
	$5s^25p5d$	6·829	0·040	0·559	0·525	−0·024	0·405
		4·098	0·733				
	$5s^25d^2$	4·453	0·595		—	−0·054	—
Cu	$4p(4s)$	5·077	0·238	0·216	—	—	0·243
	$4d$	3·666	0·715	—	0·021	−0·027	—
Ag	$5p(5s)$	5·332	0·275	0·148	—	—	0·182
	$5d$	3·920	0·733	—	0·010	−0·025	—
Zn	$4p^2(4s^2)$	5·690	0·160	0·468	0·288	—	0·414
	$4d^2$	4·207	0·569	—	—	−0·066	—
Cd	$5p^2(5s^2)$	5·932	0·198	0·350	0·257	—	0·335
	$5d^2$	4·886	0·595	—	—	−0·043	—

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[20] Leifer, Cotton, and Leto, *J. Chem. Phys.*, 1958, **28**, 364.

involving the fourth quantum group is again not always satisfactory from the published tables and the procedure adopted was to evaluate the integral from the master formula for the two nearest and surrounding values of p for which $A_n(p)$ are available, the final integral being then obtained by interpolation. This procedure is different from that employed above since the $A_n(p)$ are tabulated, for non-integral n, over much larger intervals of p than in the case of integral n. In view of the uncertainties in the metal–carbon distances the above procedure seems satisfactory. The values of the group overlap integrals are given in Table 2; the integrals tabulated for the elements of Groups I and III apply, of course, to the monocyclopentadienyl compound and for this reason each column is assigned the two symbols appropriate to D_{5d} or C_{5v} symmetry. For comparison, we give in Table 3 the values of some of the group overlap integrals for the elements of the first transition series. A rigorous application of Slater's rules has been made for the 3*d*- and 4*s*-orbitals of this group since there is some evidence [21] from spectral parameters that this procedure is justifiable, at least for the free atom.

TABLE 3. *Group overlap integrals for transition elements and Groups* Ib, IIb. Systems $M(C_5H_5)_2$ and $M(C_5H_5)$.

Element	Principal quantum no. (n)	$S(a_{1g}ns)$	$S[a_{1g}(n-1)d_{z^2}]$	$S[e_{1g}(n-1)d_{xz}]$
Ti				
V		0·266	0·036	0·401
Cr	4	0·283	0·027	0·404
Mn		—	—	—
Fe		0·347	0·011	0·320
C		0·434	0·027	0·243
Ni		0·503	0·027	0·182
Cu	4		—	0·143
Ag	5	—	—	0·338
Zn	4		—	0·128
Cd	5		—	0·247

The calculation of the relevant overlap integrals for a σ-complex is much simpler since overlap now occurs between the 2*s*- and the 2*p*-orbitals of the ring carbon atom and the *ns*- and the np_σ-orbital of the central atom. We shall not assume that the carbon orbital is a pure tetrahedral hybrid although this is probable, nor shall we consider that the *ns*- and *np*-orbitals assume a particular state of hybridization. Instead, the individual overlap integrals, $S(2sns)$, $S(2snp_\sigma)$, $S(2pns)$, $S(2p_\sigma np_\sigma)$ are evaluated as described above and tabulated in Table 4. For the σ-bonded model, we have calculated the interatomic distances from Pauling's single-bond covalent radii, except for the first transition series where, for the direct comparison with the known π-complex structure, the distance was taken as identical with that observed in the π-complex. We have not attempted to calculate overlap integrals involving atomic orbitals of principal quantum six, although the method used by Brown [6] and by Leifer *et al.*[20] is equally applicable to this group.

Craig *et al.* considered the overlap criterion to be a better measure of interaction between two orbitals than the maximum extension of a given orbital.[23] Nevertheless, it provides no direct estimate of the *energy* of interaction of two orbitals; in general, theory is incapable of determining this energy. We are forced to rely on the overlap integral as a measure of chemical bonding, and these rather unsatisfactory foundations render it unwise to theorise too extensively; nevertheless, it is reasonable to suppose that trends in the overlap integrals should reveal trends in bond character, provided that the differences are considerable. With this qualification we shall now consider the results tabulated.

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[21] Brown, *J. Chem. Phys.*, 1958, **28**, 67.

[22] Craig, Maccoll, Nyholm, Orgel, and Sutton, *J.*, 1954, 332.

[23] Pauling, " The Nature of the Chemical Bond," Cornell Univ. Press, New York, 1944, p. 76.

It follows from the extremely small values of the integral $S(e_1nd)$ (Table 2) that promotion to valency states involving outer *d*-orbitals is not likely to lead to appreciable bonding for elements in the Group Ia, IIa, IIIb, or IVb. This conclusion is supported by the relatively large promotion energies (Table 1) for the corresponding valency states of these elements. It at once differentiates these elements from those of the first transition series for which the integral $[S(e_{1g}3d)]$ is the primary bonding interaction and is of reasonable magnitude throughout the series (Table 3). The relative inefficiency of *d*-orbital overlap in these groups, compared with those of the transition elements, is due to the greater screening of *d*-electrons by the remaining electrons.

TABLE 4. *Constituent overlap integrals for σ-bonded systems* $M(C_5H_5)_2$ and $M(C_5H_5)$.

Element	n	p	t	$S(2sns)$	$S(2snp\sigma)$	$S(2p\sigma ns)$	$S(2p\sigma np\sigma)$
Li	2	4·535	0·429	0·333	0·477	0·153	0·187
Na	3	5·146	0·378	0·308	0·458	0·098	0·112
K	4	5·726	0·464	0·241	0·345	0·120	0·022
Rb	5	6·000	0·494	0·186	0·296	0·005	−0·003
Be	2	4·618	0·250	0·341	0·463	0·253	0·272
Mg	3	5·766	0·262	0·292	0·430	0·160	0·208
Ca	4	6·200	0·357	0·246	0·381	0·080	0·105
Sr	5	6·450	0·390	0·221	0·348	0·053	0·070
B	2	4·660	0·111	0·365	0·430	0·332	0·308
Al	3	5·810	0·163	0·294	0·417	0·208	0·269
Ga	4	6·102	0·092	0·307	0·444	0·213	0·261
In	5	6·438	0·130	0·291	0·431	0·174	0·228
C	2	4·729	0·000	0·341	0·368	0·368	0·329
Si	3	5·514	0·080	0·322	0·395	0·265	0·304
Ge	4	5·926	0·031	0·331	0·447	0·253	0·251
Sn	5	6·229	0·070	0·245	0·448	0·210	0·262
Cu	4	5·084	0·238	0·355	0·513	0·123	0·117
Ag	5	5·325	0·275	0·319	0·469	0·080	0·079
Zn	4	5·558	0·160	0·344	0·481	0·178	0·195
Cd	5	5·947	0·198	0·316	0·475	0·138	0·182
Ti	4	—	—	—	—	—	—
V	4	5·470	0·292	0·181	0·457	0·099	0·112
Cr	4	5·363	0·271	0·326	0·478	0·107	0·118
Mn	4	—	—	—	—	—	—
Fe	4	5·062	0·232	0·362	0·516	0·134	0·125
Co	4	5·391	0·213	0·344	0·493	0·141	0·151
Ni	4	5·654	0·195	0·332	0·474	0·156	0·179

In contrast, the integral $S(e_{1u}np)[S(e_1np)]$ is of reasonable size for most of the members of the above groups and, taken together with the lower promotion energies of the required valency state, indicates that it is the *np*-orbitals which will be responsible for any covalent bonding on the π-complex model for the cyclopentadienyl compounds of the elements of these groups.

Moreover, for all the elements considered in Table 2 there is a decrease in a given overlap integral on descent of a given Periodic Group, particularly for the elements of Groups Ia and IIa. It follows that increased ionic character will be expected for a given complex on increasing the atomic number of the central atom; a conclusion consistent with experiment.

From Table 4, it is noticeable that in general the admixture of the np_σ-orbital with the *ns*-orbital of the central atom leads to increased overlap with the carbon 2*s*- and 2*p*-orbitals; however, there are some exceptions. It follows that *s*/*p* hybridization of the central atom will lead to increased overlap, but that the extent of hybridization may well vary considerably within the groups under consideration. Finally, in the formation of a σ-complex a cyclopentadienyl radical (configuration $a_1^2e_1^3$) is converted into a system in which conjugation is limited to only four carbon atoms. The loss in conjugation energy per ring is about 1·4β, on the simple Hückel molecular-orbital theory, where β is the resonance integral between adjacent carbon $2p\pi$-orbitals. In other words, where the σ- and the π-model appear to be of very similar stability, the above effect may be especially important.

After the above general conclusions we shall discuss the known cyclopentadienyl complexes of these groups in terms of the theoretical results given in Tables 1—4.

Group I.—All the alkali metals, except francium, are known to form cyclopentadienyl compounds $M(C_5H_5)$. Columns 5 and 10 of Table 1 show that the transfer of an electron from an alkali metal to a cyclopentadienyl radical is energetically favoured and we should expect, therefore, that these compounds will be largely ionic in character owing mainly to the low first ionization potentials of the alkali metals. However, the promotion energy of the ns-electron to an np_σ-orbital is quite low and the overlap integrals on both σ- and π-complex models are considerable, at least for the early members of the Group, and so some covalent character is indicated for monocyclopentadienyl-lithium and -sodium. It is impossible to conclude with our approximations which of the two models is to be preferred for covalent bonding. Experimentally,[4] it is found that these compounds are colourless salts which decompose immediately in air but dissociate in polar solvents. The sodium compound has been estimated to possess 50% ionic character.[24]

The subgroup elements, copper and silver, might be expected to form complexes exhibiting some ionic character in view of the results given for these elements in Table 1; the formation of ions is possible on energetic considerations. The covalent π-complex model shows quite reasonable overlap for the quantity $S(e_1np)$ but considerable overlap also occurs of the type $S[e_1(n-1)d]$ between the filled $(n-1)d$-orbitals of these elements and the e_1-cyclopentadienyl orbitals. Thus both bonding and anti-bonding interactions will occur between the e_1-orbital and the orbitals of the central atom; this is likely to render the complex unstable. The covalent σ-complex model suffers no such disadvantage and exhibits overlap integrals of reasonable magnitude (Table 4); moreover the promotion energies are fairly small and, indeed, s/p hybridization would lower these energies. It follows then that we should predict the monocyclopentadienyl compounds of Group Ib to show some ionic character but to be largely σ-bonded and covalent in structure. To date, no simple cyclopentadienyl complex of this subgroup has been obtained but copper(I) yields the white, crystalline cyclopentadienyl triethylphosphine complex C_5H_5Cu,PEt_3, which is stable to water and is apparently a σ-bonded complex.

Group II.—Of the main-group elements, beryllium, magnesium, and calcium form dicyclopentadienyl compounds.[25-27] It follows from our measure of ionic character that considerable energy is required for the transfer of electrons from the central atom to the cyclopentadienyl radicals. This quantity decreases markedly down the Group and only for the beryllium complex does ionic character appear to be really improbable. Both covalent π- and σ-complex models show considerable overlap which decreases down the series; however, such overlap is achieved by the π-model at the expense of considerably more promotion energy (p^2V_2) than in the σ-model case (spV_2). It is tempting to conclude that for the higher members of this group the σ-complex is the more likely, but this is not necessarily correct, for the following reasons. First, there is loss of resonance energy of the cyclopentadienyl rings on σ-complex formation and, secondly, there is additional stabilization for the π-complex model of the type ($a_{1g}ns$) which, as column 5 of Table 2 indicates, is considerable. These additional factors which increase the stability of the π-complex make the position ambiguous; we shall note similar ambiguity for Group III. It follows from our theoretical considerations that the calcium complex will be largely ionic, the magnesium complex ionic with some covalent character, and the beryllium complex mainly covalent; it is difficult to predict which of the covalent models will be favoured

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[24] Weise and Cohen, *Chem. Abs.*, 1957, **51**, 8664.
[25] Fischer and Hofmann, *Chem. Ber.*, 1959, **92**, 482.
[26] Cotton and Wilkinson, *Chem. and Ind.*, 1954, 307.
[27] Ziegler and Froitzheim, *Chem. Ber.*, 1956, **89**, 434.

although it appears that where ionic character is most unlikely the σ-bonded structure is the more probable since the difference in promotion energies is then greater. The beryllium compound [25] is a white compound, easily hydrolysed and oxidized, and has a finite dipole moment; Fischer and Hofmann suggested that it is a genuine σ-complex. The magnesium compound [26] appears to possess a sandwich structure both in the vapour state and in solution, as shown by the infrared spectrum and zero dipole moment; it is generally regarded as an ionic compound but since the overlap integrals on both σ- and π-models † are considerable some covalent contribution is to be expected. The calcium compound [27] has not been obtained pure.

In the subgroup of Group II both zinc and mercury form biscyclopentadienyl compounds. Columns 5 and 10 of Table 1 show that ionic compounds are most unlikely in view of the large energies involved. The covalent π-complex model is again improbable for reasons analogous to those given for Group Ib, namely, that although the overlap integral $S(e_{1u}np)$ (Table 2) is of reasonable magnitude so too is the integral $S[e_{1g}(n-1)d]$ (Table 4). It follows that the bonding interactions of the former type will be counteracted by the anti-bonding interactions of the latter type owing to the completely filled $(n-1)d$ orbitals. Again the σ-complex possesses no such disadvantages and we should predict, therefore, that zinc and mercury will form σ-complexes, especially in view of the much lower valency-state promotion energies involved $[sp(V_2) < p^2(V_2)]$. It is observed that both biscyclopentadienyl-mercury and -zinc are relatively unstable; the infrared spectrum of the former is most consistent with a σ-complex structure.[28]

Group III.—The elements indium and thallium form monocyclopentadienyl compounds [29] of the type $M(C_5H_5)$ although indium also forms an intermediate $In(C_5H_5)_3$ which on being heated decomposes to give the mono-complex. Table 1 indicates that the formation of ionic compounds is energetically possible for all the members of the group. The π-complex model, however, indicates considerable overlap (Table 2) for most of the members of Group III so that some covalent character cannot be excluded. With the electron configuration ns^2np^1, both bonding (e_1np) and anti-bonding $(a_1ns)^*$ types of interaction will occur, whereas promotion to the valency state $(sp)^0(sp)^2(sp)^1$, in which sp denotes linear hybrids directed towards and away from the ring, should lead to completely bonding interactions. The use of the latter valency state requires, however, considerable promotion energy as shown by the inequalities in Table 1. In contrast, the σ-model may be based on direct interaction between the $np\sigma$-orbital of the central atom and a carbon σ-orbital of the ring; in this case the valency state will lie close to the ground state with a relatively low promotion energy. However, as in Group II the σ-complex is formed at the expense of ring conjugation energy and without the additional stabilization of the a_1-orbital which occurs with the π-complex formed from the second valency state above. The situation is again ambiguous. If the sum of the loss in conjugation energy and the stabilization of the a_1-orbital is greater than the difference in promotion energies between the valency states appropriate to the σ- and the π-model, then the π-complex will be favoured as the covalent structure. Experimentally, it is found that both the indium and the thallium compound are insoluble in water and that the indium is more readily oxidised than the thallium compound. It now seems well established that the thallium compound possess C_{5v} symmetry since the microwave spectrum [30] of the vapour gives unequivocal proof of this and also leads to a Tl–C bond distance of about 2·4 Å. It was suggested by Cotton and Reynolds [5] that the thallium complex was largely ionic, but this was due to a numerical error † and the correct values given in Table 2 show some

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† Dr. Cotton, in a personal communication, has informed the author that the data in ref. 8 are incorrect because of a numerical error.

[28] Piper, Hafner, and Wilkinson, *J. Inorg. Nuclear Chem.*, 1956, **2**, 82.
[29] Fischer and Hofmann, *Z. angew. Chem.*, 1957, **69**, 639.
[34] Meister, *ibid.*, p. 533.
[30] Tyler, Cox, and Sheridan, *Nature*, 1959, **183**, 1182.

covalent bonding for both monocyclopentadienyl-indium and -thallium. It is implicit in the above argument of course that the overlap integrals for the thallium complex will be only slightly smaller than those calculated for the indium complex. The additional fact that the thallium compound is stable in the vapour phase at 100° seems to suggest some covalent character in the molecule.

Group IV.—Tin and lead form biscyclopentadienyl compounds.[31] The energies required for the formation of ions (columns 5 and 10, Table 1) indicate that ionic character is not likely to be important in this Group, in contrast to Group III. The symmetrical π-complex (D_{5d}) is also unlikely. The bonding effect which arises from the overlap between the half-filled cyclopentadienyl (e_{1u}) orbitals with the singly occupied p_xp_y-orbitals of the central atom will be offset by the anti-bonding effect of overlap of the filled a_{1g} cyclopentadienyl orbitals with the filled ns-orbital of the central atom; Table 2 indicates that both interactions are considerable for the elements of Group IV. It follows that the D_{5d} model is unlikely. It has recently been suggested [32] that an angular sandwich model may occur in this Group; the central atom is considered to be in a valency state $(nsnp^2)^1(nsnp^2)^1(nsnp^2)^2$ with overlap between the singly occupied trigonal hybrids and the symmetric cyclopentadienyl a_1-orbitals. This model requires both promotion of the π-electrons of the cyclopentadienyl ring to the state $a_1e_1{}^4$ and considerable promotion of the central atom to the above valency state (Table 1). In contrast, direct σ-bonding is possible on the basis of the ground-state configuration, $s^2p^+p^-(V_2)$, of the central atom, and the overlap integrals are of reasonable magnitude (Table 4). It is, of course, possible that some mixing of the s- and p-orbitals of the central atom may occur, with a consequent increase in promotion energy, and the observed dipole moments suggest that this is so. The experimental evidence is not yet unambiguous, as admitted by Dave *et al.*; [32] the interpretation of the nuclear magnetic resonance spectrum does not rule out the σ-complex, and the infrared spectrum provides the sole evidence for the angular π-complex.

First Transition Series.—Table 1 shows that, with the possible exception of titanium and vanadium, considerable energy is required for the formation of an ionic compound. The promotion energies listed for the valency states appropriate to the π-complex are taken from the calculations of Shustorovich and Dyatkina [12] and the wide range of some of them merits comment. Unfortunately, there is considerable uncertainty in the nature of the valency state of the central metal atom in the biscyclopentadienyl compounds of the transition elements, as it is difficult to assess the degree of mixing of the $3d$- and $4s$-orbitals. If the configuration $3d^n$ is chosen, thereby leaving the $4s$-orbital empty but involving considerable promotion energy, a stable bonding interaction of the type $(a_{1g}4s)$ will occur throughout the series (compare overlap integrals in Table 3). However the configuration $3d^{n-2}4s^2$, requiring a much lower promotion energy (as given by the lower limit in Table 1), leads to anti-bonding interactions $(a_{1g}4s)^*$, and not simply to the absence of the above bonding $(a_{1g}4s)$ as suggested by the Russian workers.

The group overlap integrals for the π-complex are similar throughout the series, on the assumption that Slater's rules are applicable. The possible σ-complex, although having reasonable overlap integrals, requires promotion energies that are always greater than for the π-model. From this difference and from the loss of ring conjugation energy on σ-complex formation it follows that the π-complex model is generally to be preferred to the σ-complex for the biscyclopentadienyl compounds of the transition metals. As suggested by Shustorovich and Dyatkina,[12] ionic character is especially likely for the manganese compound in view of the exceptionally large upper limit to the range of promotion energies. The titanium, vanadium, and chromium compounds may also be expected to show some ionic character in view of the similarity of the promotion energies

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[31] Fischer and Grubert, *Z. Naturforsch.*, 1956, **11b**, 423; *Z. anorg. Chem.*, 1956, **286**, 237.

[32] Dave, Evans, and Wilkinson, *J.*, 1959, 3684.

to the energy of electron transfer: in fact, both the vanadium and the chromium compound form ammoniates and with ferrous chloride in tetrahydrofuram yield ferrocene.[4]

This comparison between the compounds of the transition metals and of the elements of Groups I—IV, showing that promotion energies of the former on the π-complex model are always lower than those on the σ-complex model, has allowed a fairly secure theory to be constructed for the transition series. However, no such clear difference exists for elements of Groups I—IV and it is harder to predict the type of covalent complex most likely for a given Group.

Conclusions.—Our general conclusions may be summarised as follows: Groups Ia and IIa, especially the lower members, will exhibit pronounced ionic character. Groups Ib and IIb will tend to form σ-bonded complexes. Group IIIb will form complexes of mixed ionic–covalent character, and probably of π-complex type. Group IV will form neither ionic nor simple π-complexes, but the structure of the covalent complex is probably based on the σ-model. The experimental evidence is still not clear.

APPENDIX

Evaluation of Overlap Integral $S(2p_\pi 4d_\pi)$.—We use the functions:

$$\psi_{2p_\pi} = \frac{(\alpha_{\mathrm{A}})^{5/2}}{(\pi)^{1/2}} \cdot r_{\mathrm{A}} \exp\,(-\alpha_{\mathrm{A}} r_{\mathrm{A}}) \sin\theta_{\mathrm{A}} \cos\phi$$

$$\psi_{4d_\pi} = \frac{(2\alpha_{\mathrm{B}})^{4\cdot2}}{(4\pi)^{1/2}} \cdot \frac{(15)^{1/2}}{(7\cdot4!)^{1/2}} \cdot r_{\mathrm{B}}{}^{2\cdot7} \exp\,(-\alpha_{\mathrm{B}} r_{\mathrm{B}}) \sin\theta_{\mathrm{B}} \cos\theta_{\mathrm{B}} \cos\phi$$

With the usual notation for the evaluation of overlap integrals [17] and on transformation to spheroidal co-ordinates ζ, η, and ϕ we obtain the expression:

$$S(2p_\pi 4d_\pi) = N_{24} \int_1^\infty \int_{-1}^{+1} (\zeta - \eta)^{1\cdot7}(\zeta + \eta)(\zeta\eta - 1)(\zeta^2 - \zeta^2\eta^2 + \eta^2 - 1)\,,\, \mathrm{e}^{-p\zeta}\mathrm{e}^{-p\eta t}\mathrm{d}\zeta\mathrm{d}\eta$$

where $N_{24} = p^{6\cdot7}(1 + t)^{2\cdot5}(1 - t)^{4\cdot2}(15)^{1/2}/2^{3\cdot5}(7\cdot4!)^{1/2}$

On expansion of the above expression and term-by-term integration we obtain the final expression:

$$N_{24} \sum_{i=0}^{\infty} \binom{1\cdot7}{i}(-1)^i[(A_{5\cdot7-i} - 2A_{3\cdot7-i} + A_{1\cdot7-i})(B_{i+1} - B_{i+3}) + (A_{4\cdot7-i} - A_{2\cdot7-i})(2B_{2+i} - B_{4+i} - B_i)]$$

$$A_n(p) = \int_1^\infty x^n \mathrm{e}^{-px}\mathrm{d}x$$

$$B_m(pt) = \int_{-1}^{+1} x^m \mathrm{e}^{-ptx}\mathrm{d}x$$

The numerical values of these functions are available from Flodmark's tables.[19]

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