TILDEN LECTURE

Valence in Transition-metal Complexes

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1 Preamble

The past ten years have seen, by common consent, a consolidation of the early systematization of those areas of inorganic chemistry in which the crystal-field theory played such a significant role. But the interplay between experiment and theory has been both qualitatively and quantitatively different for a number of reasons. Diffraction methods have provided accurate structural results for molecules of increasing complexity; spectroscopic methods have become increasingly powerful, the latest developments in induced emission spectroscopy providing energy level data which are stringent tests for any valence theory; organometallic chemistry has become an increasingly strong wing of inorganic chemistry. The inorganic chemist was required, in short, to turn to more flexible theories of the chemical bond in inorganic molecules.

It is a matter of individual prejudice, if not ignorance, as to which particular areas of the subject are highlighted in an attempt to describe some of the progress which has been made in this connection. The focus of attention has undoubtedly been transition-metal—rather than main-group—chemistry. Here, such topics as metal clusters, stereochemical non-rigidity of complexes in solution, metal complexes with high co-ordination numbers, metal-carboranes, dinitrogen complexes, electron delocalization in metal–sulphur complexes, catalytically active compounds, and many others jostle for our attention and emphasis. But in many ways the search in all of these has been for an economical and a reasonable, if not rigorous, view of what a particular equilibrium arrangement of atoms in a molecule implies for a valence theory and what information spectroscopy can provide on the intramolecular charge distribution and its time dependence (if any).

So far as the interpretation of equilibrium structures of transition-metal complexes is concerned, two extreme situations can be delineated usefully if not exactly. The first refers to those metal complexes where deductions of the nature of the metal–ligand bond are based on interpretations of a metal–ligand bond length. Here one is referring to ligands such as ammonia, tertiary phosphines and, only slightly less exactly, acetylacetone and related unsaturated ligands where there are negligible changes in ligand geometry following co-ordination to a metal. The second refers broadly to those unsaturated ligands, co-ordinated in

particular to metals in formally low oxidation states, whose geometries are modified drastically by co-ordination.

2 The Bond between Transition Metals and Unsaturated Ligands

Until 1961, no unambiguous evidence was available to prove that major changes of stereochemistry of unsaturated ligands occurred on co-ordination, although it was clear from studies of catalysis that a metal may bring about modification of the electron density on a ligand. Infrared data suggested a lengthening of the carbon–oxygen bond of carbon monoxide after co-ordination to a metal but results based on diffraction analysis were hardly accurate enough at that time to offer substantial confirmation of this view. In any event, the interpretation of the i.r. data for carbonyls was ambiguous, for, in spite of general assertions, the observed reduction of stretching frequency following co-ordination could be interpreted in terms of the carbon 'lone pair' orbital having some bonding character with respect to the carbon–oxygen bond rather than necessarily supporting a valence model based on metal-to-ligand π-bonding. A cause célèbre, if it may be called that, centred on the bonding in bis(benzene)chromium, for an early X-ray analysis[1] had suggested that its symmetry was D_{3d} rather than D_{6h}. Longuet-Higgins *et al.*,[2] using theoretical ideas which are enlarged upon below, pointed out that this result was difficult to understand on the grounds that no electronically excited state of benzene having threefold symmetry was low-lying enough to be 'mixed in' to the ground state to any substantial extent as a result of the presence of the metal. Here was the first application of second-order Jahn–Teller theory to organometallic molecules and it was more successful than was thought at the time, for Cotton, Dollase, and Wood, and others, showed later that benzene undergoes little change in its geometry on co-ordination.[3-5]

Since then, much structural data has been accumulated on the geometries of co-ordinated carbocyclic ligands[6] but the nature of metal-induced changes of stereochemistry can readily be appreciated by looking at structural results for dioxygen, carbon disulphide, acetylene, and olefin complexes of various metals in low oxidation states. For the iridium(I) complexes of dioxygen,[7] the valence-bond model which so usefully accounts for bond lengths in many dinuclear cobalt(III) complexes is clearly of little value as a basis for explaining an 0—0 bond length of 1.6 Å. In the case of carbon disulphide,[8] acetylene,[9] and olefin

[1] F. Jellinek, *Nature*, 1960, **185**, 871.

[2] D. H. W. den Boer, P. C. den Boer, and H. C. Longuet-Higgins, *Mol. Phys.* 1962, **5**, 387.

[3] F. A. Cotton, W. H. Dollase, and J. S. Wood, *J. Amer. Chem. Soc.*, 1960, **85**, 1543.

[4] J. A. Ibers, *J. Chem. Phys.*, 1964, **40**, 3129.

[5] E. Kevelen and F. Jellinek, *J. Organometallic Chem.*, 1966, **5**, 490.

[6] M. R. Churchill and R. Mason, *Adv. Organometallic Chem.*, 1967, **5**, 93.

[7] J. A. McGinnety, N. C. Payne, and J. A. Ibers, *J. Amer. Chem. Soc.*, 1969, **91**, 6301 (and references therein).

[8] R. Mason and A. I. M. Rae, *J. Chem. Soc. (A)*, 1970, 1767.

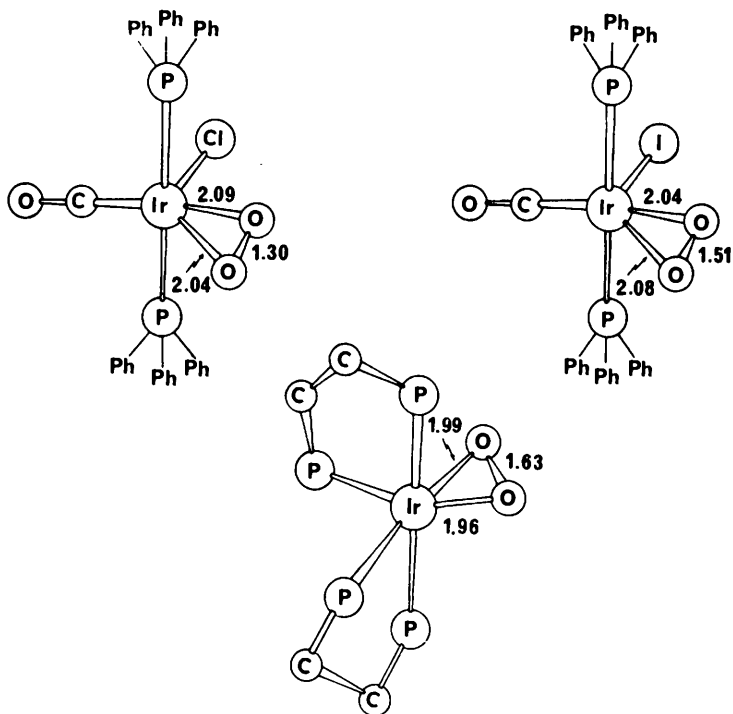[9] R. Mason, *Nature*, 1968, **217**, 543 (and references therein).

Figure 1 *The oxygen–oxygen and metal–oxygen bond lengths (in Å) in three di-oxygen complexes of iridium*(I) *(after ref. 7 and references therein)*

complexes,[10,11] some feel for stereochemical changes at the co-ordinated carbon atoms can be obtained from simple valence ideas involving σ-bond formation between the metal and carbon and consequent rehybridization of the carbon atom. But, as in the oxygen complexes, such a simple view is too inflexible to account for the dependence of carbon–carbon and oxygen–oxygen bond lengths on the formal oxidation state of the metal, the substituents on the hydrocarbon, or the remaining ligands in the molecule. The Chatt–Dewar model,[12] a knowledge of ligand ground- and excited-state geometries, and the second-order Jahn–Teller effect offer us the basis of a more complete discussion.

The Chatt–Dewar model is a combination of symmetry rules and the Pauling Electroneutrality Principle. Although it was much used by inorganic chemists for qualitative discussions on, for example, the stabilization of low oxidation states of metals by ligands with low-lying unfilled orbitals, it needed closer examination

[10] L. Manojlović-Muir, K. W. Muir, and J. A. Ibers, *Discuss. Faraday Soc.*, 1969, No. 47, p. 84.
[11] L. J. Guggenberger and R. Cramer, *J. Amer. Chem. Soc.*, 1972, **94**, 3779 (and references therein).
[12] M. J. S. Dewar, *Bull. Soc. chim. France*, 1951, **18**, C71; J. Chatt, *J. Chem. Soc.*, 1953, 2939.

before its general implications for the geometries of co-ordinated ligands were appreciated. What is almost intuitively obvious—that the σ–π bonding model
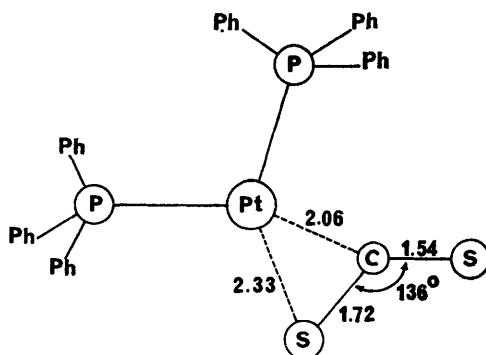

Figure 2 *The stereochemistry of bis(triphenylphosphine)platinum carbon disulphide (after ref. 8). Lengths are in* Å

implies, within a 'molecules in molecules' scheme, that the molecular wave-function contains electronically excited wavefunctions of both the metal and ligand—was quantitatively developed only recently.[13] The essential point to
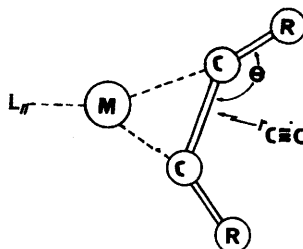

Figure 3 *Schematic stereochemistry of acetylene co-ordinated to a low-valent metal.* $r_{C \equiv C}$ *is usually* 1.35 ± 0.05 Å; θ *is usually* 140 ± 8°

emerge was that, for π-complexes with small intermolecular overlap, the wave-function describing the Lewis acid–base pair is that described by Mulliken twenty years ago. With large overlap between donor and acceptor orbitals—such as we have in organometallic π-complexes—the Mulliken charge-transfer functions are supplemented by wavefunctions which can be recognized as the electronically excited states of the donor and acceptor in the various possible spin states. The admixture of excited-state wavefunctions into the ground state has consequences on the equilibrium geometry of the ligand, and the extent to which it takes place will depend on the amount of transfer between the

[13] R. McWeeny, R. Mason, and A. D. C. Towl, *Discuss. Faraday Soc.*, 1969, No. 47, p. 21.

metal and ligand (and *vice versa*), which in turn will reflect the energies of the various donor and acceptor orbitals. Qualitatively, the 'mixing in' of neutral excited states can be expected to be important relative to the ionic wavefunctions of Mulliken only when, in the spirit of the Electroneutrality Principle, little or no net migration of charge from the ligand to the metal takes place—in other words, when we have metals in low oxidation states ($+ 1$ to $- 1$) and neutral ligands.

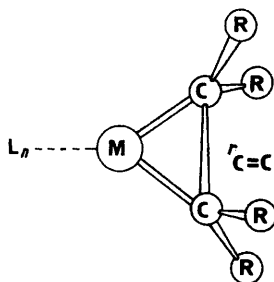The effect of the admixture of electronically excited states on the energy of a

Figure 4 *Stereochemistry of substituted-olefin complexes of metals. $r_{C=C}$ ranges from 1.35 to 1.53 Å; the dihedral angle between the planes containing MCC and CCR vary in the range 99—115° (see ref. 10)*

molecule's ground state can be evaluated by the pseudo-Jahn–Teller effect. The wavefunction of a molecule, ψ, corresponding to a new nuclear arrangement which is consequent upon the admixture of a k'th excited-state wavefunction, ψ_k, into the undistorted molecular wavefunctions, ψ_0, is given by

$$\psi = \psi_0 + \sum_k \frac{Q < \psi_0 \,|\, \dfrac{\partial U}{\partial Q} \,|\, \psi_k > \psi_k}{(E_0 - E_k)}$$

with a related energy E,

$$E = E_0 + Q \left\langle \psi_0 \frac{\partial U}{\partial Q} \psi_0 \right\rangle + \frac{Q^2}{2} \left\langle \psi_0 \left| \frac{\partial^2 U}{\partial Q^2} \right| \psi_0 \right\rangle + \frac{\left[Q \left\langle \psi_0 \left| \dfrac{\partial U}{\partial Q} \right| \psi_k \right\rangle \right]}{(E_0 - E_k)}$$

U is the nuclear–nuclear and nuclear–electron potential energy and Q is a normal co-ordinate of the molecule. Expectedly, admixture is inversely proportional to the energy level differences ($E_0 - E_k$) and the expressions also guide us as to which distortions are impossible for symmetry reasons, since we require that the direct product of the representations of the ground and excited states be the same as the normal co-ordinate, Q, leading to the distortion. But broadly speaking, our knowledge of molecular force-constants and energy levels is too imprecise to take a positive, *a priori* view on what molecular distortions will take place in ligands following co-ordination. It is true that den Boer, den Boer, and

Longuet-Higgins[2] could offer the quantitative suggestion that reduction in symmetry of dibenzenechromium from D_{6d} to D_{3h} was unlikely; such a distortion would require an excited singlet state lying at only *ca.* 0.2 eV above the ground state and would require an even lower-lying triplet state which, unless unreasonable assumptions were made, would be inconsistent with the diamagnetism of the molecule. But in their theoretical investigations of bis(hexamethylbenzene)cobalt, Nicholson and Longuet-Higgins[14] were only able to provide several alternative structures of low symmetry which could be produced through the operation of the second-order Jahn–Teller effect and which could account for the observed dipole moment of the molecule. This particular problem is representative also of those relatively few organometallic compounds of the later transition elements which do not, at first sight, obey the rare-gas or eighteen-electron rule. Craig and Doggett showed[15] why the rule will be followed when metal-to-ligand charge-transfer supplements electron donation from the ligand, for it is only then that the radial and angular dependence of the potential experienced by the metal 'd'-orbitals approaches that in the adjacent rare gas. Electron occupancy of ligand antibonding orbitals may have significant structural implications in a way which we can anticipate from the Walsh Rules,[16] and Parr *et al.* have recently demonstrated[17] the relation between the eighteen-electron rule and Walsh's recipes. But while all of these views dovetail together in a reassuring way, we are left in structural organometallic chemistry with, at best, persuasive *ex-post facto* arguments.[18] We are prevented from making confident predictions about twenty-electron structures such as $(\pi\text{-}C_5H_5)_2Ni$ and twenty-one-electron complexes like $(\pi\text{-}C_6H_6)_2Co$ through the absence of quantitative spectroscopic data. The available structural data demonstrate that first-row transition metals induce major ligand distortions in only relatively strong Lewis acids such as butadiene, cyclopentadienone, and other unsaturated ligands with strongly electronegative substitutent groups. Second- and third-row metals, with their higher-lying valence orbitals, are needed to distort unsubstituted arenes when, in particular, the total electronic energy of the system may be reduced by antibonding electrons on the metal being transferred to the ligand, with a consequent low-energy-mode deformation of the ligand. Two structural analyses illustrate this proposition. Hexakis(trifluoromethyl)benzene-π-cyclopentadienylrhodium[19] and bis(hexamethylbenzene)ruthenium[20] are both formally twenty-electron structures, but Figure 5 shows that an effective eighteen-electron environment of the metal is achieved by the stabilization of a non-planar arene ring. It is very unlikely that this arrangement will be found in bis(hexamethylbenzene)cobalt or indeed in the iron and manganese complexes. It seems much more probable that these structures will be distorted from D_{6h} symmetry in

[14] B. J. Nicholson and H. C. Longuet-Higgins, *Mol. Phys.*, 1965, **9**, 461.
[15] D. P. Craig and G. Doggett, *J. Chem. Soc.*, 1963, 4189.
[16] A. D. Walsh, *J. Chem. Soc.*, 1953, 2260, 2266, 2296, 2301.
[17] Y. Takahata, G. W. Schnuelle, and R. G. Parr, *J. Amer. Chem. Soc.*, 1971, **93**, 784.
[18] D. M. P. Mingos, *Nature Phys. Sci.*, 1971, **229**, 193.
[19] M. R. Churchill and H. Mason, *Proc. Roy. Soc.*, 1966, A292, 61.
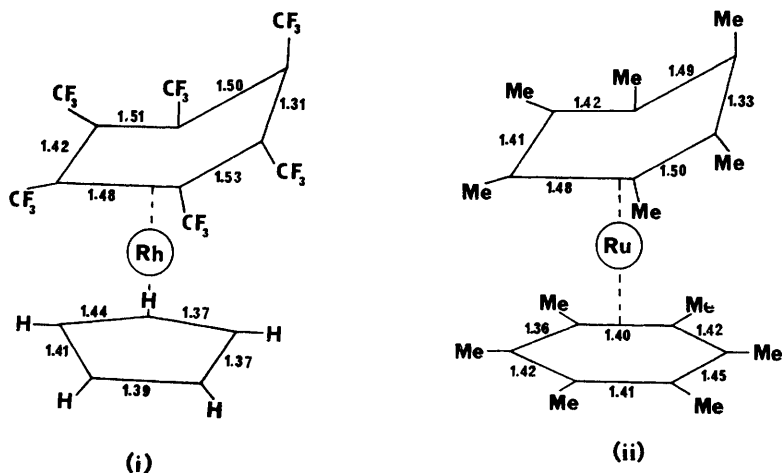[20] G. Huttner, S. Lange, and E. O. Fischer, *Angew. Chem. Internat. Edn.*, 1971, **10**, 556.

Figure 5 *The structures of* (i) *hexakis(trifluoromethyl)benzene-π-cyclopentadienyl-rhodium*[19] *and* (ii) *bis(hexamethylbenzene)ruthenium*[20]

one of two other ways – either *via* an A_{2u} deformation mode (asymmetric metal to ring stretching) or, more likely in my view, *via* an E_{1u} mode which will produce a wedge-like arrangement such as is found in $(\pi\text{-}C_5H_5)_2MoH_2$.[21] But one has clearly struck a note of uncertainty which can only be resolved by further structural analyses coupled with the characterization of molecular energy levels through photoelectron spectroscopy.

The alternative to a perturbation theoretical account of co-ordinated ligand geometries is to use something like a non-empirical molecular orbital theory and then show, by some variational calculation, that the observed equilibrium geometry corresponds to a minimum in the total energy. But this is not feasible in that present computational facilities and methods restrict non-empirical calculations to molecules or complexes containing not more than fifty electrons or so; even these are very demanding of time, and to systematically explore the molecule's potential energy surface as a function of various distortions is for the future.

We are in need of other experimental data to supplement the inferences which have been drawn from crystallographic studies. Cook *et al.*[22] have described ESCA studies of several low-valent complexes of platinum; the chemical shifts of the platinum $4f_{7/2}$ level suggest that, in the complexes $(PPh_3)_2PtL$, the state of oxidation of the platinum increases in the ligand (L) series $PPh_3 < PhC_2Ph < C_2H_4 < CS_2 < O_2 < Cl_2$. The interpretation of the chemical shifts depends on the assumption that the charge on the metal in $(Ph_3P)_2PtCl_2$ is $+2$ and is 0

[21] M. Gerloch and R. Mason, *J. Chem. Soc.*, 1965, 296.
[22] C. D. Cook, K. Y. Wan, V. Gelius, K. Namrin, G. Johannson, E. Olsson, H. Siegbahn, C. Nadling, and K. Siegbahn, *J. Amer. Chem. Soc.*, 1971, **93**, 1904.

Table 1 Phosphorus $(2p)$ and metal binding energies (eV) in substituted-olefin complexes of platinum(0) and iridium (I)

Level	$(Ph_3P)_2PtC_2H_4$	$(Ph_3P)_2PtC_2Cl_4$	$(Ph_3P)_2PtC_2F_4$	$(Ph_3P)_2Pt\{C_2(CN)_4\}$
$P(2p)$	131.7	131.7	131.6	131.8
Pt $\{4f_{7/2}$	73.0	73.2	73.0	73.2
$\;\;\;4f_{5/2}$	76.1	76.5	76.2	76.5

Level	$Ir(CO)(PPh_3)_2ClCO$	$Ir(CO)(PPh_3)_2Cl(C_2F_4)$	$Ir(CO)(PPh_3)_2Cl\{C_2(CN)_4\}$
$P(2p)$	132.0	131.2	131.4
Ir $\{4f_{7/2}$	62.1	62.4	63.4
$\;\;\;4f_{5/2}$	64.7	64.9	65.9

in $(PPh_3)_4Pt$, and that a linear relation exists between metal charge and binding energy. The Electroneutrality Principle would suggest that this range is too great but, at first sight, the relative Lewis acidity ordering of the ligands seemed sensible. It seems worthwhile, therefore, to examine the ESCA spectra of several complexes bearing a closer structural relationship to one another. The results are collected in Table 1, together with those for several iridium(I)–olefin complexes.

The energy-level data are identical to those of Cook *et al.*[22] in that they show a constancy of the $P(2p)$ binding energies—notwithstanding the fact that there are significant differences in the various metal–phosphorus bond lengths (see p. 443). In the case of the platinum(0)–olefin complexes, our results are different from those reported earlier in that there is no significant difference between the metal binding energies in $(Ph_3P)_2Pt(C_2H_4)$, in the substituted-olefin complexes, and those observed in complexes such as $(Ph_3P)_2PtCl_2$ where the formal charge on the metal is $+2$. The energy-level data for the olefin adducts of iridium(I) show significant differences which reflect, in a semi-quantitative way, the Lewis acidity of the olefin. The conclusions are obvious; the Lewis basicity of the bis(triphenylphosphine)platinum moiety is so high that olefin substituents play but a minor role (if any) in determining the extent of metal-to-ligand charge transfer; the chloro-iridium complex has a much lower basicity, and electronegative subtituents on the olefin bring the ligand antibonding orbitals much more effectively into the intramolecular bonding scheme. The available bond-length and equilibrium-constant data for these complexes bear out these remarks.[23]

One has not done much more here than use ESCA results in almost a phenomenological way but both low- and high-energy photoelectron spectroscopy are becoming valuable, in spite of a number of shortcomings and difficulties (for example, inadequate resolution in the high-energy case; the assumption of the validity of Koopmans' theorem), to the assessment of quantitative theories of charge density.

The history of the application of molecular orbital theory to inorganic complexes can be sketched by reference to the results which have appeared during the past twenty years or so on the permanganate ion and on tetracarbonylnickel(0) and hexacarbonylchromium(0). Since the Dahl–Ballhausen review[24] of the results of 'approximate' calculations on MnO_4^-, results which well illustrate the lack of agreement on energy assignments, three recent non-empirical calculations[25–27] are in general accord with each other and with the available spectroscopic data[28] although the results based on the most extended orbital basis set[26] do not give a calculated stability to the complex with respect to the sum of individual atomic energies!

[23] R. Mason, D. M. P. Mingos, G. Rucci, and J. A. Connor, *J. C. S. Dalton*, 1972, 1729.
[24] J. P. Dahl and C. J. Ballhausen, *Adv. Quant. Chem.*, 1968, **4**, 170.
[25] I. H. Hillier and V. R. Saunders, *Chem. Phys. Letters*, 1971, **9**, 219.
[26] P. D. Dacre and M. Elder, *Chem. Phys. Letters*, 1971, **11**, 377.
[27] K. H. Johnson and F. C. Smith, *Chem. Phys. Letters*, 1971, **10**, 219.
[28] For example, P. Day, L. Di Sipio, and L. Oleari, *Chem. Phys. Letters*, 1970, **5**, 533.

For the two metal carbonyls, Hillier and Saunders[29] have completed all-electron *ab initio* SCF-MO calculations in a better than minimal basis set of atomic orbitals. In $Ni(CO)_4$, the highest lying t_2 and e molecular orbitals contain 74% and 90% metal character respectively while the $2t_{2g}$ MO of $Cr(CO)_6$ has 75% metal $3d$ character; this is an interesting commentary on the value of the crudest electrostatic description of the chemical bond in organometallic π-complexes. Equally, the calculated nickel and chromium charges of $0.47e$ and $+0.70e$ illustrate how well—there being only one or two apparent exceptions[30] —the most precise calculations vindicate the Electroneutrality Principle, even where, as in MnO_4^- and CrO_8^{3-},[31] the metal ion has a very high formal charge. The calculated (arbitrarily scaled by a small normalization factor to allow for orbital relaxation effects) and experimental vertical ionization potentials of the carbonyls agree to within *ca.* 1 eV, and it may be that this result does not reflect the approximation of the still restricted basis set but rather a further lack of understanding of the effects of orbital relaxation following ionization; the agreement of the results obtained from the calculations with the observed ESCA core energy shifts is better.

The Chemist has a neo-genetic attachment to orbitals for the description of valence; and yet it is unreasonable to believe that SCF-MO theory in anything like its present form can be applied to those second- and third-row transition-metal complexes of such interest today. It may be that new and rational core electron approximations will emerge as the result of the present non-empirical calculations on simpler molecules. Even so, it would be sensible to enquire further into what limitations (if any) are present in alternative methods for the calculation of molecular eigenvalues. The scattered-wave model calculation[27] for MnO_4^- produced accurate eigenvalues in a very small fraction of the time needed to complete an *ab initio* SCF-MO calculation. It is a method which takes us away from concepts which have proved of immense value, but it is not severely restricted by the number of electrons and could be of particular interest to a discussion of the bonding in cluster complexes; it should not be impossible to determine how the calculated eigenvalues could be 'made up' from the more common orbital description.

3 Metal–Ligand Bond Lengths and Related Matters

The interaction of metals with saturated ligands or those ligands such as phosphines with rather imprecisely defined and/or high-lying virtual orbitals is, perhaps paradoxically, more difficult to define. Tertiary arsines and phosphines are often taken to be fairly good Lewis acids with respect to metals in low oxidation states on the simplest line of evidence—the existence of such complexes as tetrakis(triphenylphosphine)platinum(o)! Spectroscopic and crystallographic (bond length) data on these complexes are difficult to interpret directly so far as defining the relative σ- and π-contributors to the metal–ligand bond is concerned.

[29] I. H. Hillier and V. Saunders, *Mol. Phys.*, 1971, **22**, 1025.
[30] B. L. Kalman and J. W. Richardson, *J. Chem. Phys.*, 1971, **55**, 4443.
[31] P. D. Dacre and M. Elder, *J. C. S. Dalton*, 1972, 1426.

The point, so far as the molecular stereochemistry is concerned, is that the ligands undergo little change in their geometries on co-ordination, so that our earlier discussion becomes irrelevant. To discuss the make-up of, say, a metal–phosphorus bond, we are forced to resort to an examination of its length and then try to delineate the various factors which may affect this value.

For carbon–ligand bonds, three factors evidently determine the departure of the length from the sum of respective covalent radii. The electronegativity of the ligand determines the extent of admixture of ionic structures into the covalent canonical form and the Schomaker–Stevenson equation tells us that differences of up to *ca.* 0.1 Å between observed and calculated covalent distances may be anticipated. Only slightly smaller variations are to be expected for those bonds between atoms of similar electronegativity but where, say, the carbon atom changes its hybridization state. For carbon–carbon single bonds, Coulson[32] accounted nicely for the variation in bond lengths between atoms of different hybridizations by suggesting that the covalent radius of an atom corresponds to the centroid of its electron density,

$$\bar{r} = \int r \, \psi_H{}^2 \, d\tau$$

and then showed that for hybrid orbitals, $\bar{r}$ varied from 0.73 Å ($H = sp$) to 0.77 Å ($H = sp^3$). The recognition of this dependence allowed a much clearer definition of the bond order–bond length relationship.

Transition-metal complexes containing, for example, single bonds between the metal and a chlorine atom demonstrate an additional factor, that the M—Cl bond length may vary by up to 0.25 Å in a way which depends, in planar and octahedral complexes, on the nature of the ligand *trans* to that bond. Fortunately, this *trans*-influence of ligands can be discussed from the standpoint of simple perturbation theory.[33,34] One can return to an examination of the other factors and do so by discussing the bond lengths in third-row complexes, *trans*-(Me$_2$ PPh)$_2$MCl$_4$ (M = W^{IV}, Re^{IV}, Os^{IV}, Ir^{IV}, and Pt^{IV}), a series which illustrates also the value of accurate crystallographic analysis on closely related species. The metal ions have essentially D_{4h} local symmetry; the metal–phosphorus bond lengths change rapidly with electronic configuration whereas the metal–chlorine bond lengths are constant to within 0.02 Å.[35]

If we take the tungsten–phosphorus and tungsten–chlorine bond lengths of 2.550 and 2.339 Å respectively, the difference of 0.21 Å is almost exactly matched by the prediction of the Schomaker–Stevenson equation [$X_W{}^{IV} = 2.0$, $X_P = 21.0$, $X_{Cl} = 3.0$; $r_{cov} (P) = 1.05$ Å and $r_{cov} (Cl) = 1.00$ Å]; the same procedure gives a calculated difference for the Pt^{IV} bonds as zero compared with an observed difference of 0.06 Å. A major objection to this calculation is that it is based on the assumptions that the metal uses equivalent hybrid orbitals for forming σ-bonds with the chlorine and phosphorus atoms and that there is little or no chlorine

[32] C. A. Coulson, 'Victor Henri Memorial Volume', Desoer, Liège, 1948, p. 15.
[33] R. Mason and A. D. C. Towl, *J. Chem. Soc. (A)*, 1970, 1601.
[34] A. D. C. Towl, Ph.D. Thesis, University of Sheffield, 1969.
[35] L. Aslanlov, R. Mason, A. G. Wheeler, and P. O. Whimp, *Chem. Comm.*, 1970, 30.

to metal π-bonding (it is safe to assume no metal to phosphorus π-bonds in complexes containing metals in $+4$ formal oxidation states). A more flexible approach is needed, therefore, which will also make an attempt at the estimation of absolute covalent radii of the metals. This was developed[36] through the definition of covalent bond radii as corresponding to the distance from the nucleus to the overlap density centroid,

$$\bar{r} = \frac{\int \psi_L r \psi_M d\tau}{\int \psi_L \psi_M d\tau}$$

where ψ_L and ψ_M are appropriate ligand and metal wavefunctions.

The agreement between observed and calculated metal bond radii was found to be better than 0.005 Å; the different behaviour of the metal–phosphorus and metal–chlorine bond lengths with electronic configuration was shown to originate in the very different character of the two symmetry-distinct metal σ-bonding orbitals; ϕ_{axial}, contributing to the metal–phosphorus bonds, possesses much metal 's' character compared with its equatorial counterparts.

The nuclear quadruple resonance data[37] are consistent with this observation but they have not been analysed in the detail which Brown *et al.*[38] have provided for some of the third-row hexahalogeno-complexes MCl_6^{2-}. Leigh and Bremser[39] have studied the X-ray photoelectron spectra of the complexes and these are summarized in Table 2, together with the results for the hexahalogeno-species.

Table 2

		Complex	
Metal Level		MCl_6^{2-}	$MCl_4(PMe_2Ph)_2$
W $\begin{cases} 4f_{5/2} \\ 4f_{7/2} \end{cases}$		36.8	36.5
		35.1	34.3
Re $\begin{cases} 4f_{5/2} \\ 4f_{7/2} \end{cases}$		46.9	46.3
		44.5	43.8
Os $\begin{cases} 4f_{5/2} \\ 4f_{7/2} \end{cases}$		56.4	55.5
		53.7	53.2
Ir $\begin{cases} 4f_{5/2} \\ 4f_{7/2} \end{cases}$		66.0	66.5
		63.2	63.7
Pt $\begin{cases} 4f_{5/2} \\ 4f_{7/2} \end{cases}$		78.8	78.4
		75.6	75.8

In hexahalogeno-complexes, the $Cl(2p_{3/2})$ binding energy is 199.1 eV ($\sigma = 0.2$ eV); in the tertiary phosphine complexes it is also 199.1 eV ($\sigma = 0.3$ eV) and the phosphorus binding energies are essentially constant [all the binding energies are relative to $C(1s) = 285.0$ eV]. Even in the complexes *mer*-[$MCl_3(PMePh)_3$],

[36] R. Mason and L. Randaccio, *J. Chem. Soc. (A)*, 1971, 1150.
[37] J. A. S. Smith, personal communication, 1970.
[38] T. L. Brown, W. G. McDugle, and L. G. Kent, *J. Amer. Chem. Soc.*, 1970, **92**, 3645.
[39] G. J. Leigh and W. Bremser, *J. C. S. Dalton*, 1972, 1216.

where the chemically non-equivalent metal–chlorine and metal–phosphorus bond lengths differ by as much as 0.1 Å,[35] the ESCA experiment affords no resolution of the ligand ionization peaks. These results, taken with the earlier ones, suggest strongly that, in general, studies of ligand ionization energies by ESCA methods will prove of little value in the present state of instrumental development; that for σ-bond species, metal binding energies will show considerable ($\gtrsim 1$ eV) shifts only when the formal oxidation state is changed; but that with π-acceptor ligands, a good deal of useful information can be derived from a study of both ligand and metal ionization energies.

4 Metal–Metal Bonds in Cluster Complexes

Complexes containing metal to metal bonds have been studied intensively for the past fifteen years but quantitative theories of the factors determining their structures and properties are not available. The magnetic behaviour of weakly interacting metal ions cannot be interpreted unambiguously and the stereochemical data are not really valuable in the absence of well-defined bond order–bond length relationships, particularly in the region of unit bond order. The picture is clearer when the simplest of valence considerations indicates strong, multiple metal–metal bonds.

A metal–metal bond of order four was recognized first in the $Re_2Cl_8^{2-}$ ion, the criteria for multiple bonding being the bond length (2.24 Å compared with 2.75 Å in the metal) and the eclipsed rotameric conformation.[40,41] Within the limitations set by the available metal orbitals (s, p, and d) it is only by postulating substantial δ overlap that the second observation can be understood. Apart from those valence electrons associated with the rhenium–chlorine bonds, eight electrons are allocated to orbitals which are strongly bonding with respect to the metals and which have σ, π (twice), and δ symmetry. The geometries of the $Re_2Br_8^{2-}$ (ref. 42) and $Mo_2Cl_8^{4-}$, ions are consistent with this scheme and similarities are obvious for $Cr_2(CH_3)_8^{4-}$, $Cr_2(allyl)_4$, and $Mo_2(allyl)_4$;[43] the stereochemistry of the $Tc_2Cl_8^{3-}$ ion[40] indicates that the additional electron must be localized in an orbital which is essentially non-bonding with respect to the metal ions. A further and particularly informative series is represented by the M_2 $(O_2CR)_4L_2$ complexes (M = Cr, Mo, Re, Rh, and Cu),[44] where the carboxylate groups tend to impose the eclipsed configuration but also provide a framework where the metal–metal interactions can adjust themselves over a wide range of distances and bond orders. In $Cr_2(O_2CR)_4L_2$, $Mo_2(O_2CR)_4$, and $Re_2(O_2CR)_4X_2$, quadruple bonds appear which are similar to those in the rhenium and other species mentioned above. The addition of further electrons prompts the question of the nature of the orbitals which they occupy. The structure of $Rh_2(O_2CMe)_4$

[40] F. A. Cotton, *Accounts Chem. Res.*, 1969, **2**, 240.
[41] F. A. Cotton, *Inorg. Chem.*, 1963. **2**, 653.
[42] F. A. Cotton, B. G. de Boet, and M. Jeremic, *Inorg. Chem.*, 1970, **9**, 2143.
[43] F. A. Cotton and J. R. Pipal, *J. Amer. Chem. Soc.*, 1971, **93**, 5441.
[44] F. A. Cotton and J. G. Norman, *J. Co-ordination Chem.*, 1972, **1**, 95.

$(H_2O)_2$ serves partially to clarify the position, for an earlier discussion[45] was based on an X-ray analysis which has been superseded.[46]

Dahl and his co-workers have exploited systematic crystallographic analyses to detail the stereochemical consequences of valence-electron addition or removal in cluster complexes.[47-49] These authors have also done much to remind us that there is useful information to be obtained on the question of metal–metal bond interactions, from a consideration of the bond angle at a bridging ligand; when this is less than 90°, there is *prima facie* evidence for metal–metal interactions. In general terms, the structural analyses of dimethylberyllium[50] and beryllium dichloride[51] seem to have first prompted a consideration of the factors influencing the geometries of bridging groups and the closely associated metal–metal bond distance. These are additionally valuable because their simplicity quickly provides the symmetry and occupancy of the bridge molecular orbitals and hence a rationale[52] of their geometries; this rationale is quite different from that originally proposed since the underlying assumption,[51] namely that all of the bridge electrons in $BeCl_2$ would occupy orbitals which are bonding with respect to the metals, is not correct.

One is almost back full-circle in that for polynuclear complexes, particularly of the second- and third-row transition metals, useful bonding schemes are almost entirely based on symmetry arguments.[52] Whether quantitative models based on orbital theory become available in the near future is something about which one can afford to be at least sceptical. Applications of molecular orbital theory to 'superclusters' and chemisorption have been reported but are unconvincing; the challenge to theory is obvious and is unlikely to be met through the availability of larger and faster computers.

Many colleagues have shared my structural interests during the past few years, and my debt to them is considerable.

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[46] F. A. Cotton, B. G. de Boer, M. D. La Prade, J. R. Pipal, and D. A. Ucka, *Acta Cryst.*, 1971, **B27**, 1664.
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[48] C. E. Stronse and L. F. Dahl, *J. Amer. Chem. Soc.*, 1971, **93**, 6032.
[49] P. J. Vergamini, H. Vahrenkamp, and L. F. Dahl, *J. Amer. Chem. Soc.*, 1971, **93**, 6326.
[50] A. I. Snow and R. E. Rundle, *Acta Cryst.*, 1951. **4**, 348.
[51] R. E. Rundle and P. H. Lewis, *J. Chem. Phys.*, 1952, **20**, 132.
[52] R. Mason and D. M. P. Mingos, *J. Organometallic Chem.*, in the press.