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A historical perspective on Dewar's landmark contribution to organometallic chemistry

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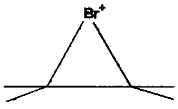
Abstract

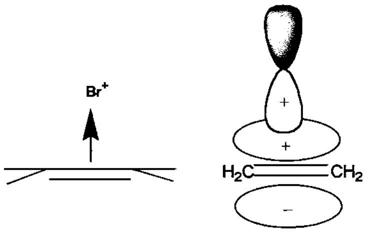
A historical background to Dewar's development of a bonding model for metal–alkene complexes in 1951 is reviewed and its implications described. Chatt and Duncanson's subsequent contribution is also reviewed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Dative bond; Coordinate link; Synergic bonding; Dewar–Chatt–Duncanson; Bonding in π-complexes

At the end of April 1950 a *Colloque International* was held in Montpellier, France, primarily for organic chemists, and Michael Dewar presented a review paper entitled 'A review of π-complex theory'. The papers and the discussions which arose from the presentations were published in *Bulletin de Société de Chimie France* in 1951 [1,2]. A small section of Dewar's review and a question stimulated by Winstein [3] was to have a profound effect on the development of organometallic chemistry. These fragmentary comments were to develop into what has come to be referred to as the Dewar–Chatt–Duncanson model in organometallic chemistry [4]. In this special issue we celebrate the 50th anniversary of Dewar's profound insight into chemical bonding and have collected a series of papers, which illustrate the widespread impact of this bonding model. This introductory paper aims to provide a historical introduction to the development of the model and provide an insight into why Dewar's contribution represented such an outstanding leap of the imagination. Secondly, I hope to trace the more complex evolution of the Dewar model into the Dewar–Chatt–Duncanson model in many organometallic chemists' vocabulary and hopefully provide some insight into the social and scientific interactions, which may contribute to the association of a theoretical model with the names of specific scientists [5]. Finally, I hope to indicate why the Dewar–Chatt–Duncanson model has survived the test of time so effectively and indeed has been applied to systems far from those originally envisaged. The origins of the model can be associated with the proposal that in the *trans*-addition of electrophilic reagents X_2 and XY to alkene the bromonium–alkene cations (I) were present as intermediates. Such cyclic intermediates (or π-complexes) which could be represented by conventional valencies were proposed originally by Roberts and Kemball in 1937 [6].



(I)



(II)

The more radical idea that alkenes might be able to donate their π-electrons to form dative bonds, a property usually associated with lone-pair donors, was first suggested by Dewar in 1945 [7,8], who used the formalism illustrated in (II) for the bromonium ion intermediate. Clearly, this formalism derived from molecular orbital theory could be extended to other electrophiles and therefore an alkene may be viewed as a base which

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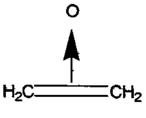
was analogous to classical Lewis bases such as amines, ethers, etc. This view was not readily accepted by organic chemists who were still wedded to formulating their ideas in terms of a valence bond formalism. Winstein expressed his reservations in 1951 as follows: "Dewar has advocated a π-bond formula (II), but there seems to be no special need for it, since it depends on the assumption that a halogen can only form a simple covalent bond" [3].

As early as 1947 Walsh [9] had proposed similar π-complex structures (III), (IV) and (V) for ethylene oxide, silver–alkene complexes and cyclopropane.



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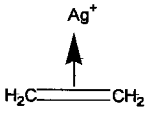

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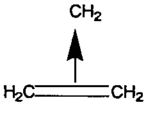
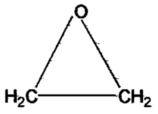


(V)

From the point of view of an organometallic chemist, this represented the first example of anyone proposing a dative bond between an alkene and a metal ion, and Walsh supported the proposal by noting that the ionisation energy of the ethylene π-bond (10.45 eV) is virtually identical to that of ammonia and thereby undermining the conservative view that a dative bond could only originate from a lone pair. However, Walsh's proposal attracted strong criticism from no less a personage than Sir Robert Robinson [10] and also the doyen of theoretical chemistry Coulson [11]. Walsh reacted by re-formulating his model for cyclopropane in terms of delocalised molecular orbitals — a model, which has proved to be enduring and remains associated with his name [12]. Interestingly, Chatt noted Walsh's suggestion for silver–alkene complexes and drew attention to it as early as 1947 as a footnote added at the proof stage in his review in the 1946 Annual Reports [13]. This also led Chatt to study the possibility of adduct formation between ethene and BX_3 Lewis acids, which were known to form stable adducts with ethers and amines.

Chatt's research between 1946 and 1951 was driven by a mission to understand the bonding in metal–alkene complexes and more specifically Zeise's salt $K[PtC_3(C_2H_4)]$ which had been first identified in 1825 [14–17] but was still poorly understood. Indeed in a later paper he noted:"Since the electronic theory of valency these substances have held great theoretical interest because they, together with perhaps with the corresponding, though as yet poorly defined, complexes of the acetylenes represent the only definite exceptions to the lone-pair theory of the coordinate bond." [18].

In their separate fields Dewar and Chatt had identified the underlying difficulty of the Walsh π-donation model. Dewar noted that the chemistry of ethylene oxide and cyclopropane corresponded well to that expected for strained three-membered rings, i.e. **(VI)** and **(VII)**;



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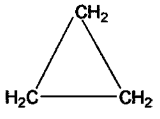


(VII)

While the silver–alkene formulation **(IV)** is unreactive to nucleophiles unlike the bromonium–alkene ions **(I)**. Since these species can be represented as π-complexes why did they fail to behave accordingly [18,19]? Chatt noted in 1951 [20]. "It seems highly probable that donation of electrons in any manner from the ethylene molecule to the metal cannot, of itself, be responsible for the coordination of ethylene. There is some other mechanism or additional condition, which can be satisfied by platinous chloride but not trimethylboron" (which represented a classical Lewis acid in his eyes).

Indeed Chatt linked for the first time CO, PF_3 and C_2H_4 as a distinct and new class of ligands in a paper titled 'The Coordinate Link in Chemistry' (*Nature* 1950) [21]. They all formed the dihalide addition products $COCl_2$, PF_3Cl_2 and $C_2H_4Cl_2$ and behaved as anomalous ligands which formed no or very weak complexes with BX_3 or BR_3 Lewis acids, but formed stable complexes with platinum(II) salts. He also noted that these ligands also shared the common property of exhibiting strong *trans*-effects in square-planar platinum(II) complexes, whereas more conventional lone-pair donors such as NH_3 exhibited *cis*-effects.

Drawing on the earlier proposal by Hieber [22] and the ubiquitous Linus Pauling [23], that the unusual behaviour of CO could be attributed to simultaneous donation from the lone pair on carbon and back donation from the metal d electrons to the carbonyl, he suggested that phosphines with electronegative substituents may exhibit similar properties by a back donation process involving the transfer of metal d electrons to empty 3d orbitals on phosphorus. He underlined this important suggestion by synthesising the complex $[PtCl_2(PF_3)_2]$ [24] (analogous to Schützenberger's $[PtCl_2(CO)_2]$ and predicted $[Ni(PF_3)_4]$, which was subsequently made by Wilkinson in 1951) [25].

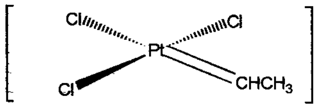
He was clearly still perplexed by alkene complexes and he hints at the retro-dative bond "A bond which is typified by olefins where it appears that d electrons from the metal as well as two electrons from the ligand are required." [21]. Unfortunately, his lack of knowledge of the symmetry aspects of molecular orbital theory prevented him from taking the next logical step required to complete the model. One does not come much nearer than "It is not how the two atoms of the ethylene molecule can be bound by a π-bond to a platinum atom, but the mechanism of bonding has undoubtedly many similarities to that of the carbonyl".

Most significantly he did propose for the first time in this paper that CO, PF_3 and C_2H_4 were all capable of forming a 'dative π-bond' and that their complexes with platinum(II) was the result of a 'dative double bond'.

Chatt's papers of this time show that he is much attracted by Hel'man's [26] proposal that Zeise's salt owed its stability to the donation of two electrons from platinum(II) to the olefin thereby causing a putative oxidation to platinum(IV) followed by donation of an electron pair from the olefin to platinum, but unfortunately was unable to reformulate it in a modern orbitally based model.

He clearly still had Walsh's [9] dative model in mind when he wrote [18] "Difficult to visualise in terms of modern theory, as π-bonding from two carbon atoms of an olefin to the d orbitals of the metal appears to be impossible except by a structure closely related to that proposed by Walsh for cyclopropane and ethylene oxide. Serious objections have been made to this structure by Coulson [11], whereas π-bonding to a single atom as in carbonyls is feasible".

The final point made in this paragraph, the observation made earlier by Anderson [27] that Zeise's salt hydrolysed on heating to acetaldehyde and other related experimental observations led Chatt to propose quite erroneously that ethylene must be bonded to platinum asymmetrically and bonded to platinum by a π-dative bond to one carbon. Thus, he proposed the ethylidene structure shown below (VIII) [28].

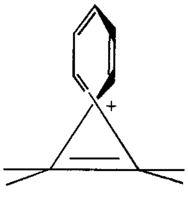


(VIII)

In a more recent interview Chatt suggested that he abandoned this structure after some critical discussions with Ingold [29].

Dewar in collaboration with Longuet–Higgins was enthusiastic to introduce molecular orbital concepts to develop a semi-quantitative theory of organic chemical reactivity [30]. His 1951 review provided an opportunity for him to illustrate the wide applicability of the concepts. He recognised that the π-bonding could occur between filled p or d orbitals on the Lewis acid (X^+) and the empty antibonding orbital of the alkene. The alkene and the acceptor are thus doubly linked by two opposed dative bonds, which is in line with earlier suggestions by Chatt, Hieber and Pauling. However, he was able to specify precisely the symmetry properties of the orbitals involved and demonstrate that the two components were distinguishable in terms of their symmetries.

In the main part of the review he illustrated these ideas by reference to the π-complex between ethylene and the phenyl cation (IX), where interactions between ethylene π* and filled π-orbitals of the phenyl ring are responsible for the retro-dative bond.

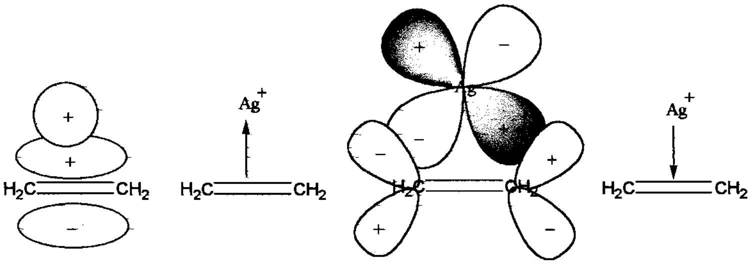


(IX)

The review also mentions the possibility of filled d orbitals back donating to the ethylene π*- in complexes of silver, copper nickel and platinum.

This suggestion was taken up in the discussion and led to the following detailed and complete development of the synergic bonding model for metal–alkene complexes which all organometallic chemists are familiar with.

"The d electrons in heavy metals, bromine, etc. have the correct symmetry to interact with the antibonding π-molecular orbital of an olefin, in π-complexes formed from the olefin and the heavy atom. If the latter carries d-electrons, it can therefore form a second dative molecular bond with the vacant antibonding π-molecular orbital, opposite in direction to the normal molecular bond. This is illustrated diagrammatically below, the phases of the lobes of the orbitals being identified to show the symmetry properties. The s orbital of Ag^+ has the wrong symmetry for interaction with the antibonding π-molecular orbital. The two molecular orbitals are therefore distinct.



The combination of these two oppositely directed dative molecular bonds should leave the olefin much less charged than it would have be in a normal π-complex; this would account for the low reactivity of the π-complexes from olefins with metals, where the binding energy of the d-electrons is low, and also for the differences in reactivity of different metals since the stabilities of the two bonds will be affected differently by changes in overall structure."

He then proceeds to give a description of the effects of substituents on the olefin and the metal, which would be recognisable to a modern organometallic chemist as the synergic bonding model [1,2]. Some have suggested that Dewar's discussion contribution has been undervalued because he did not seek to establish the experimental evidence for his model in subsequent publications [5]. However, in a review written in the following year [31] he notes that the structure of $Ag(C_6H_6)ClO_4$ reported by Rundle and Goring [32] in 1950 provides the necessary experimental confirmation.

"The Ag^+ ions associated with a given benzene molecule are attached to opposite edges on opposite sides of the plane of the ring. Arguments based on resonance theory had predicted that Ag^+ would be attached symmetrically to the midpoint of the ring. The observed lateral attachment had been correctly predicted from molecular orbital considerations".

Significantly, the Rundle paper notes that the structure is interesting "due to possible implications in organic reaction mechanisms" and refers to Dewar's book published in 1949. Dewar, Rundle and Chatt in common with other chemists of their generation were not to know that metal π-complexes were about to take a major leap forward and they still considered the area to be a relative backwater of chemistry.

Dewar seems not to have been aware that his model for alkene complexes of silver was also supported by Raman studies by Taufen et al. [33] which had been completed a decade previously. These studies clearly established that the alkene remained largely unchanged in coordination to Ag^+ but the C=C bond was weakened slightly by the formation of the complex. However, Dewar had satisfied himself that the silver alkene complexes formed just part of a bigger picture and he had provided the necessary theoretical model and established that the experimental evidence was consistent with that model. He returned to his major passion of developing a semi-quantitative theory of organic chemistry.

Chatt was aware of the Raman studies in 1950, if not earlier, because he submitted a review on the mercuration of olefins at that time [34]. It is also clear from this review that Chatt had developed in his own mind a distinction between silver and platinum alkene complexes — "These silver-ion complexes are often compared with the platinous, palladous and cuprous chloride olefin complexes, *but this comparison does not seem to be valid*. In the former case the silver-ion appears to be essential and the more ionised salts, such as perchlorate, from the greater variety of olefin compounds. In the case of platinous olefin compounds the metal is certainly not present as an ion but in a covalent state and the oxy-salts form less stable olefin complexes than does chloride. The presence of filled d-orbitals on the metal atom seems to be essential for the formation of platinous complexes. *The Pitzer* [35,36] *structure may be correct for the silver-ion complexes and for the mercurium ion* but not for the platinous and similar complexes with olefins."

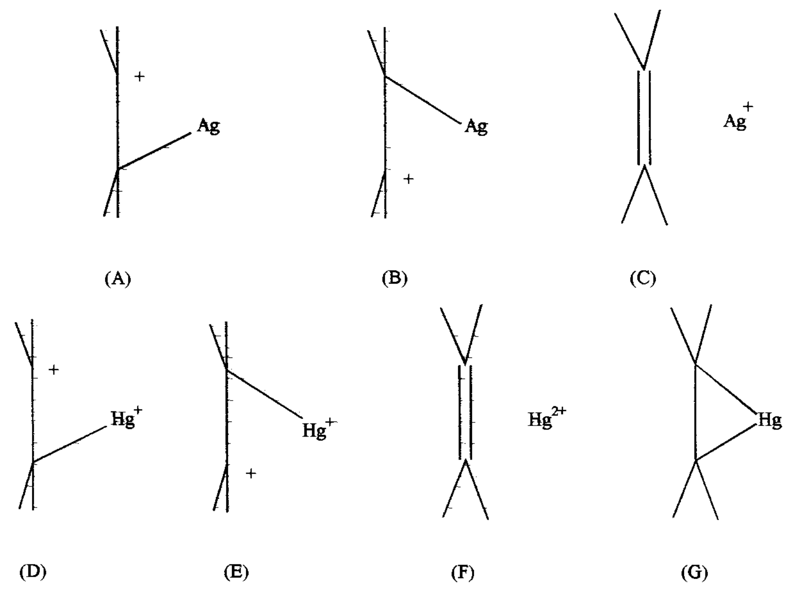
Therefore, Chatt clearly believed that for Ag^+ and Hg^{2+} the d shell was core like and not available in the manner necessary to stabilise Pt(II) alkene complexes. In this paper, which was published at the same time as Dewar's *Bull. Chim. Soc. Fr.* paper Chatt remain equivocal concerning the bonding in alkene complexes: [34]

"The electronic structure of the mercurinium ion cannot be regarded as settled but is probably related to that of the silver-ion complexes which have been investigated more thoroughly [35,36]." A study of the Raman spectra of a number of unsaturated compounds dissolved in solutions of silver salts (reference to Taufenn et al.) shows a lowering of the strong double-bond frequency consistent with the view that the complex is stabilized by resonance of the forms (A), (B) and (C) which should be compared with (D) (E) (F) + (G) and the Pitzer structure for diborane.

Interestingly, modern molecular orbital calculations on silver(I) and copper(I) complexes have indicated that there is much less back donation between these metals and the alkene than in the corresponding platinum complexes, and that the interaction might be primarily electrostatic. However, this does not carry a structural implication which would justify Chatt's distinction.

This diffidence and confusion between the alkene complexes of Ag^+/Hg^{2+} and Pt^{2+}/Pd^{2+} seem to have been resolved by Chatt between 1951 and 1953 when the highly cited Chatt–Duncanson paper was published [37]. The procurement of the infrared spectrometer at the ICI laboratories enabled Duncanson to record infrared spectra on a range of platinum(II) alkene complexes and thereby disprove conclusively the earlier Chatt proposal based on an ethylidene moiety (VIII) [28]. Chatt's preparative skills were to make a significant contribution because he had developed improved routes to platinum(II) alkene complexes and extended the range which enabled Duncanson to study a series of five related complexes. This was a significant advantage because Zeise's salt showed only a very weak ν(C=C) mode and the more telling information arose from the related propene complexes.

It is clear from the acknowledgements to the 1953 paper [37] and a subsequent interview with Chatt [29], that Chatt had discussed the bonding in Zeise's salt with both Dewar and Orgel between 1951 and 1953 and had taken on board the elegantly developed dative

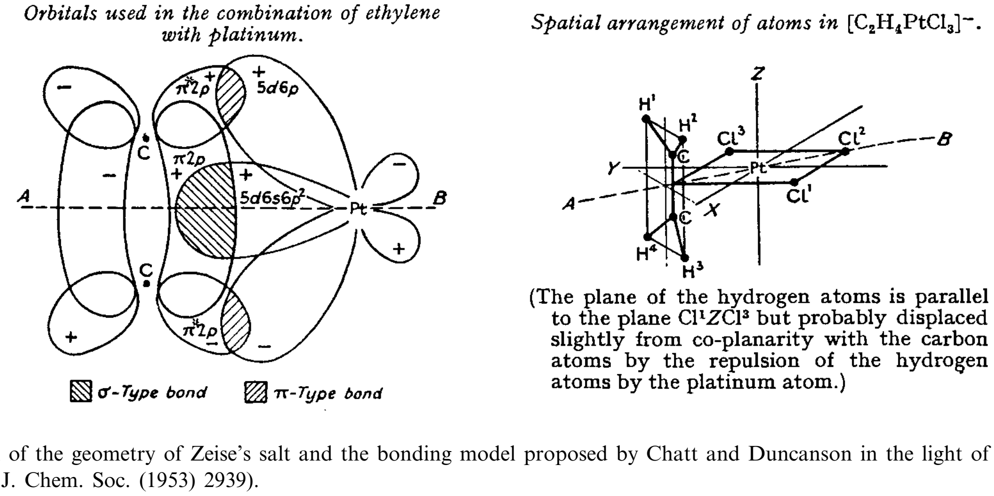


double bond model developed by Dewar for Ag^+/alkene complexes. Although, unfamiliar with the symmetry aspects of the molecular orbital picture Chatt would have been receptive to these ideas in view of his attraction to the earlier Hel'man proposals [26] and his own work on dπ–dπ back bonding in PF_3/Pt(II) complexes [21]. He has been convinced that silver and platinum alkene complexes showed the same basic structure. Thus, he was able to put his earlier ethylidene mistake behind him and go forward in the highly cited Chatt and Duncanson paper as follows: [37].

"Ethylidene structure for Zeise's Salt (*Research* 4 (1951) 180) proposed a second structure also satisfying these requirements, but without the objectionable feature of the migration of a hydrogen atom, was proposed at about the same time by Dewar (*Bull. Soc. Chim.*). It was proposed with particular reference to the silver-ion complexes, but its adaptation to the platinous complexes the σ-type bond would be formed by overlap of a 5d $6s6p^2$ hybrid orbital of the platinum atom with the π-orbital of the olefin, and the π-type bond by overlap of a filled 5d-orbital of the metal atom with the antibonding π-orbital of the olefin. The π-type bond would be strengthened, however, by hybridisation of the 5d-orbital with the vacant 6p-orbital of the platinum atom to give a dp hybrid more suitably shaped than the unhybridrised 5d orbital to provide a larger overlap with the antibonding orbitals of the coordinated olefin.

The new data we present here show the ethylidene structure is untenable but accord with the above structure (Fig. 1). A review of the properties of olefin–metal complexes, showing how they can all be correlated on the basis of Dewar's structure was given at a conference in March 1952. Only new data is presented in this paper."

Having rightly acknowledged the major contribution made by Dewar; Chatt and Duncanson and Chatt [37] independently in a separate review [38] showed how the model could be used not only to interpret the chemical


Orbitals used in the combination of ethylene with platinum.

Spatial arrangement of atoms in $[C_2H_4PtCl_3]^-$.

(The plane of the hydrogen atoms is parallel to the plane Cl^1ZCl^3 but probably displaced slightly from co-planarity with the carbon atoms by the repulsion of the hydrogen atoms by the platinum atom.)

Fig. 1. Illustration of the geometry of Zeise's salt and the bonding model proposed by Chatt and Duncanson in the light of Dewar's proposals (reproduced from J. Chem. Soc. (1953) 2939).

and physical properties of alkene complexes, viz. the dipole moment, chemical reactivity and oxidation state. Also drawing on the earlier Taufen et al. [33] work, they were able to conclude that the platinum(II) olefin complexes had the alkenes more strongly bonded than the silver(I) complexes because the decrease of ν(CC) was almost twice as large.

Since by their own admission the platinum(II)–alkene model presented by Chatt and Duncanson was based on Dewar's molecular orbital model and did not provide the first experimental evidence to support the model-Rundle's X-ray structure and Taufen et al.'s Raman studies had already provided justification for the model — it is difficult on these grounds to understand the extension of the Dewar model to the Dewar–Chatt–Duncanson model. Chatt's later suggestion that [29] "this was the first time that any structure for the olefin compounds has been suggested and reasonably proven. Of course there had been many others all suggestions are listed in Keller's review and in a review by Hel'man, none proven anymore than had been Dewar's proposed silver-ion olefin structure" remains difficult to maintain in view of the structural and spectroscopic work summarised above.

Dewar was, in later life, clearly irritated by the Chatt–Duncanson extension and wrote in 1979: [19].

"It should also be noted that Chatt and Duncanson did not even 'adapt' the π-complex representation to the specific system considered by them since the original formulation explicitly referred to olefin complexes of transition metals in general.

Indeed, the orbital diagram given by Chatt and Duncanson is identical with the prototype, apart from the shapes of the stylised curves used to represent orbitals and the addition of specific quantum numbers. Since this application represents only a special case of a more general theory, it would seem more appropriate to refer to it as the 'π-complex theory of metal–olefin complexes' rather than to use any specific designation. However, if the latter is preferred, it seems inappropriate to include the names of Chatt and Duncanson in it."

The association of specific names with a theoretical model or specific compound is a complex phenomenon and not controlled by the individuals involved. It is a more wayward phenomenon which does not always accurately reflect the historically correct or appropriate designation of scientific priority or fair recognition of the relative contributions made by those who are cited. Wilkinson and Vaska were not the first to make the compounds which are named after them, but their names have become associated with the compounds because they developed a significant and important body of work around these compounds.

Chatt's association with the model certainly cannot be justified on the grounds that he made an important conceptual contribution to our theoretical understanding, but he did illustrate how the model could provide a valuable insight into a range of chemical properties associated with this exciting and expanding area of chemistry. The Chatt–Duncanson paper provided a convenient reference marker for those carrying out research in the area and those writing textbooks for the following reasons:

(1) Its publication in the *Journal of the Chemical Society* rather *than Bull. Soc. Chim. Fr.* made it more accessible to the chemical community.

(2) Graphically the bonding model for Zeise's salt was visually more attractive and economical than Dewar's separation of forward and back donation components in his original contribution. I suspect that the better resourced ICI laboratories made a significant and telling contribution to the final art work. Furthermore, although attention is not drawn to it in the Chatt–Duncanson paper the ethene molecule is shown to be perpendicular to the square-plane and this was noted in the three structural determinations of platinum and palladium olefin complexes published in 1955 [32,39–42]. These papers all make reference to the Chatt–Duncanson paper and the confirmation of this structural aspect of the model without reference to the Dewar paper. It must be recalled that at this time crystal structure determinations were still relatively crude and time consuming and more attention was paid to gross stereochemical features than details of metric parameters.

(3) Through the 1950s and 1960s infrared spectroscopy remained the primary and most routinely applied spectroscopic technique for synthetic inorganic chemists. Therefore, as more alkene complexes were discovered and reported in the literature it became customary to note the extent to which ν(C=C) was reduced and make reference to the earlier Chatt–Duncanson work. Raman studies did not become routine until the late 1960s when lasers became more readily available. It is perhaps significant that one of the most highly cited papers of the 1950s involved the distinguishing of the two isomeric forms of coordinated thiocyanate complexes.

(4) Since these changes in ν(C=C) were interpreted in terms of the relative contributions of the forward and back donation components those who did not read the literature carefully came to associate the phenomenon with Chatt and Duncanson rather than accurately noting Dewar's seminal contribution.

(5) Chatt incorporated the Dewar bonding model into a bigger picture which covered all aspects of synergic bonds and this major contribution was recognised by inorganic chemists. In a series of papers, which had the generic title 'Nature of the Coordinate Link', he developed the basic idea of synergic bonding to embrace not only ethene, CO and PF_3, but also extend it to the Class A and B classification of metal ions, the

trans-effect and more generally other concepts arising from ligand field theory to organometallic and coordination chemistry. For example, he interpreted the kinetic inertness of the metal alkyls, which he synthesised to a d-orbital splitting diagram for square-planar complexes. Not all of these applications of the synergic model have stood the test of time, but nonetheless they were at their most influential in the 1950s and 1960s. In contrast, Dewar neglected his child prodigy and did not follow it up in a significant fashion either experimentally or theoretically.

Interestingly at this time the inorganic community was more receptive to new theoretical ideas than the organic community. Thus Annual Reports in 1951 and 1952 provide these contrasting statements: [43,44].

The Inorganic section celebrates:

“A growing number of simple and complex inorganic compounds in which the valencies of the constituent atoms are anomalous” and gives reference to a review by Klemm on anomalous valencies [45].

In contrast, the organic section (1952) reports [44] “M.J.S. Dewar has advocated a π-bond formula (for the ethene–bromonium ion) but there now seems to be no special need for it, since it depends on the assumption that a halogen can only form a single covalent bond.”

Indeed more than a decade was to pass before organic chemists would embrace fully molecular orbital ideas as a result of the orbital symmetry effects which have become associated with the names Woodward, Hoffmann and Fukui.

The synergic bonding models described above, electron-deficient compounds and hypervalent compounds and ligand field theory were to provide a more receptive audience for molecular orbital ideas in the inorganic chemical community.

From the earliest days inorganic chemists have not always given the appropriate recognition to Dewar for his contribution and although Coates and Glockling in their 1953 Annual Report [46] gives credit to Dewar for elucidating the symmetry aspects of the problem they also gave generous credit to Chatt and Duncanson since “all the properties of olefin complexes can be explained at least qualitatively in terms of this structure”. However, the drift towards Chatt as the prime contributor was recognisable in Mellor and Wunderlich’s 1955 suggestion [39,40] that their structural determination of Zeise’s salt “is in agreement with the geometry of the molecule as imposed by Chatt’s electronic model”. A view not dispelled in Chatt’s report on his contribution to the Symposium on Organometallic Compounds held in Manchester in April 1955 [47] which describes the electronic model and its chemical implications.

Inorganic and organometallic textbooks have noted that Chatt and Duncanson’s interpretation followed a proposal by Dewar. However, those who wish to retain the description Dewar–Chatt–Duncanson cannot rest their case on an assumption that Chatt and Duncanson ‘modified and elaborated’ Dewar’s idea — because this is difficult to sustain given the evidence presented above. It is more accurate to say that Chatt and Duncanson made it accessible to a wider chemical audience by demonstrating its implications for the interpretation of chemical properties of metal–olefin complexes.

The Dewar bonding model has proved to be so enduring not only because it incorporated the essential features of the interactions between transition metals and olefins (see for example the paper in this volume by Gernot Frenking) and it has been corroborated by numerous theoretical and experimental studies. Furthermore, it has proved to be sufficiently flexible to be extended to metal dihydrogen complexes and a consideration of the transition states and stereochemistries of oxidative addition reactions (see for example Kubas’ paper in this volume). Interestingly, in the seminal review [1] Dewar stated quite clearly that σ-bonds would not be capable of forming dative bonds (!), which just goes to show you cannot be right all the time.

1. Summary

Dewar’s paper has been important in the development of organometallic chemistry and perhaps his personal contribution has been undervalued by inorganic and organometallic chemists. I hope that this special volume will draw attention to a new generation of chemists his unique contribution and that they will in future reference his paper more often. I will not enter into the debate as to whether Chatt’s association with the model is justified. He provided the first infrared data to support the model and made the model more generally available to the inorganic community by illustrating its relevance to the interpretation of a wide range of properties. I know from personal experience in the context of polyhedral skeletal electron counting theories that the community has its own complex ways of deciding which contributor(s) should be associated with the generalisations and theoretical interpretations. However, I hope that I have provided a sufficiently accurate representation of the relevant papers and the historical background to make such a debate better informed. I would personally remain pleased if both of these outstanding chemists continue to be remembered by their association with the central concept in organometallic chemistry.

Acknowledgements

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