THEORY OF BONDING IN YLIDES, ACETYLACETONATES AND π-CYCLOPENTADIENYL COMPOUNDS[a]

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Abstract—The theory of bonding in ylides and their oxides, acetylacetonates and π-cyclopentadienyl complexes has been discussed from the viewpoint of hypervalent bonding. The existing ylides and acetylacetonates are discussed and new ones are proposed. The π-cyclopentadienyl complexes are only speculative.

INTRODUCTION*

The octet theory of chemical bonding was first presented by Lewis in 1916 and Langmuir in 1919 although the key ideas had already appeared in a memorandum of Lewis' of 1902.† This numerological theory‡ was later easily incorporated into quantum mechanics by Heitler, London. E. Hueckel, Pauling and Hellmann§ by allowing singly occupied electron orbitals to bind with other singly occupied electron orbitals. This accounted for the p-electron bonding in Groups V–VII, the s-electron bonding in Groups I–II and the inertness of the rare-gas atoms. Hybridization among the energetically inequivalent

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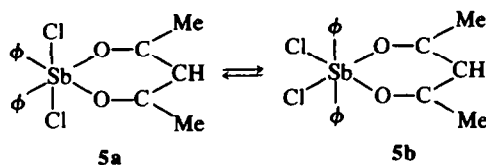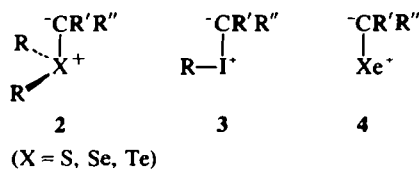[a] This paper is dedicated to the memory of Charles A. Coulson.

*The van't Hoff-Le Bel contribution memorialized in this volume is well-discussed in W. G. Palmer, *The History of the Concept of Valence to* 1930. Cambridge Univ. Press (1965) and J. Harley-Mason, *Palestine Chemists' Organization*, Jerusalem Branch 3, 1 (1945), the latter being written for the 75th van't Hoff-Le Bel memorial. The van't Hoff article was published privately in Dutch in September 1874 prior to the generally cited article of 1875 [*Bull. Soc. chim.* **23**, 295 (1875), a reference which does not appear in Palmer]. The Le Bel article was published in November 1874 [*Bull. Soc. chim.* **22** 337 (1874)]. Van't Hoff (1852–1911) received the first Nobel Prize in Chemistry in 1901. Le Bel (1847–1930) was never so honored.

†The octet theory was developed into an extended-octet theory in the 1960's by R. J. Gillespie, *Angew. Chem. Int. Ed.* **6**, 749 (1967). The "lone pairs" of this theory are the *lower* lying non-bonding orbitals, the LOMO's. These are entirely different from the ordinary "lone pairs" which are the *highest* lying non-bonding orbitals, the HOMO'a.

‡The octet theory may well have eliminated further development of non-octet organic chemistry such as that of iodine(III) initiated by C. Willgerodt, *Ber. Dtsch. Chem. Ges* **25**, 3494 (1892) and that of selenium(IV) on which a single paper was written by R. Lesser and R. Weiss, *Ibid.* **42**, 2510 (1914).

§For a discussion of Hellmann's fate see J. I. Musher, *Amer. J. Phys.* **34**, 267 (1966).

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s- and p-electrons, one p-electron in Group III and two in Group IV, was all that was needed for quantum mechanics to provide an octet rule plus α-orbitals. In 1957 Gillespie and Nyholm presented the complete theory of transition metal and main-group element bonding, including the non-octet molecules, using s, p and d hybridized atomic orbitals. It was assumed that the ultimate theory had been obtained.

In 1951 Pimentel[1] proposed a qualitative theory of three-center-four-electron (3c–4e) bonding, mentioning a xenon(II) compound, and Rundle[2] presented a similar theory but restricted explicitly to polyiodide ions claiming that the s,p,d-hybridization theory adequately explained the interhalogens. The dramatic synthesis of XeF_4 by Claassen, Selig and Malm[3] in 1962 reminded chemistry world of the 1810 synthesis of PCl_5 by Davy, the 1814 synthesis of ICl_3 by Gay-Lussac and the 1818 synthesis of $SeCl_4$ by Berzelius, and therefore of the gap that had existed for the previous 150 years. This led Pimentel[4] to remind people of his theory by describing the unfortunate example of HeF_2, and led Rundle[5] to rewrite his theory to include main-group elements with monofunctional ligands. The critical argument was given by Pitzer[6] and Musher[7] who showed this type of chemical bonding required the low ionization potential of the main-group atom and the electronegativity of the ligands. The qualitative 3c–4e bonding theory and its more complex derivatives for 5- and 6-coordinate systems are now widely accepted as one of the alternatives to the traditional s,p,d-hybridized theory and to the popular expanded-octet theory. Its use remains, however, explicative and not predictive.

The theory of hypervalent bonding, following its brief introduction in 1963 was developed using localized bond-orbitals in 1969.[8] The straightforward molecular orbital description was presented in 1972[9] and speculative articles on new molecules[10-12] were presented in 1969–71. This work led to the

preparation of iodine(III) compounds by Agosta,[13] of iodine(III),[14] tellurium(IV)[15] and xenon(II)[16] polymers, with Livingston, and of the first xenon compound that was neithter a fluoride nor an oxide, xenon bis-trifluoroacetate, by Musher.[17] Related predicted compounds in sulfur[18-20] and selenium[21,22] chemistry have recently been prepared by several authors.

The present article gives a brief introduction to the theory of hypervalent molecules and then discusses the applications of this theory to bonding in ylides, acetylacetonates and a novel type of π-cyclopentadienyl compounds. Several examples will be given of unusual new structures which might well be prepared in the future.

Theory of molecular bonding

I consider single bonding in molecules to be best and most simply described in terms of bond orbitals of three types utilizing only the s and p electrons that lie within the valence shells of the atoms. These are

(a) ordinary or covalent bonds in which the singly occupied p-orbital of the heteroatom or carbon is bonded to singly occupied atomic orbitals from the ligands;

(b) hypervalent-I bonds in which one or more doubly-occupied p-orbitals of the heteroatom are bonded with *two* singly occupied atomic orbitals from two colinear ligands; the molecular orbital description of this three-center four-electron process involves a *single* doubly-occupied *bonding* orbital and a *single* doubly-occupied *non-bonding* orbital; as the three-center bonds are by no means homopolar it is a mistake to assume the bonding to take place between a positively charged heteroatom and two half-negatively charged ligands; and

(c) hypervalent-II bonds in which the heteroatom or carbon attains its highest valence by utilizing the doubly-occupied s-orbitals to form s–p hybridized molecular orbitals; these orbitals are no longer directed along the near-perpendicular axes of the heteroatom or carbon p-orbitals, but by mixing with the s-orbitals take up the most symmetrical geometry available.

All main group elements cannot expand their val-

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*In my view emphasis has long been incorrectly placed on the role of d-orbitals which are therefore not considered explicitly here. Recent *ab initio* calculations on a variety of systems including SO_4^{2-}, thiophene, SF_6, ClO_4^- and PF_5 show explicitly that the inclusion of d-orbitals always involves small perturbation theoretic corrections *raising* almost all the orbital energies [H. Nakatsuji and J. I. Mussher, *Chem. Phys. Letters* 24, 77 (1974)]. In the PF_5 calculation the fraction of the changes in the orbital energies and total energy when d-orbitals are added are 3.2×10^{-3} (average) and $2.4 = 10^{-4}$ respectively.

†The amusing xenonium fluorenyl ylide was suggested some time ago.[17]

ence by forming hypervalent bonds with monofunctional ligands even though, without numerical calculations, *qualitative* bonding molecular orbitals can be written for *all* of them. The essential criterion for the stability of hypervalent bonds is that the heteroatom or carbon be sufficiently electropositive to donate electrons to the bond and that the ligands be sufficiently electronegative to attract electrons to the bond. It is important to note that electropositive and electronegative are *relative* terms and that net transfer of charge is not always required to go in the indicated direction. Experiment shows that the strength of a hypervalent bond depends critically on the nature of the heteroatom, being strongest for C among group IV atoms, for P among V atoms, probably for S among group VI atoms, for I among group VII atoms and for Xe among group VIII atoms.

The relative bond strengths are clearly such that a covalent bond is stronger than half of a (3-center) hypervalent-I bond as it involves two bonding electrons rather than one. The hypervalent-II bond strengths are somewhat in between the two, as the hypervalent-II bonding averages the two types of p-bonding with s-bonding. All hypervalent-II bonds in a given molecule do not have the same energies, reactivities, etc., since clearly the colinear bonds in PF_5 or IF_7 must be exceedingly different electronically, if not energetically, from the 3- or 5-coplanar bonds.

Bonding in ylides and their oxides

An ylide is a hypervalent molecule in which a 3-center bond is reduced to a 2-center bond using a single orbital from the hypervalent atom and formally transferring one electron from the main-group atom to the ylide carbon or nitrogen. Thus when the bonding is to carbon the structure can be written as

$$R_nX = CR'R'' \leftrightarrow R_nX^+C^-R'R''$$
$$\textbf{1a} \qquad\qquad \textbf{1b}$$

where the single X^+C^- bond, approximately described by the localized orbital

$$\psi = \psi_X + \lambda\psi_C \qquad (1)$$

is doubly occupied. Depending on the value of λ this bond can go a long way to reduce the formal polarity of the single bond. Since d-orbitals make essentially no contribution to the bonding in hypervalent molecules,* ylides of all rows of the periodic table can be considered together.

There are clearly two types of ylides and their oxy-ylides since there are two types of hypervalent bonds.[23,24] The HV_1 ylides utilize only p-orbitals from the heteroatom, model examples of which are **2** of Group VI, **3** of Group VII and **4** of Group VIII, for the latter of which there are no known examples.† These are drawn in a way that emphasizes the near-perpendicular character of the bond-

2   **3**   **4**

(X = S, Se, Te)

**5a**   **5b**

R = C₆H₅, t-Bu

6

ing observed in the stable sulfonium[23,25,26] and selenonium[23,27] ylides. The structure of the iodonium[28,29]* ylides is unknown. It might also be possible to prepare higher HV_I ylides such as $RI(CR'R'')_2$, $Xe(CR'R'')_2$ and $Xe(CR'R'')_3$ and oxy-ylides such as $RI(CR'R'')O$, $Xe(CR'R'')_2O$ and $Xe(CR'R'')O_2$.

The best known ylides are the HV_{II} phosphonium ylides, first named by Wittig, in which the phosphorus s-orbital must be utilized to provide the pentavalent bonding. There are also numerous ylides of nitrogen, arsenic, antimony and bismuth. HV_{II} ylides of Group VI atoms are, however, restricted to oxy-ylides of sulfur, $R_2S(CR'R'')O$, which should clearly not be written as $R_2S^{+2}(C^-R'R'')O^-$ as implied by the arrow to the oxygen in the literature, and the di-imines of sulfur. It might be possible to prepare sulfonium diylides, $R_2S(CR'R'')_2$† from *cis*-R_2SF_4 compounds or even from an oxy-ylide, iodonium triylides, $RI(CR'R'')_3$, and xenonium tetraylide $Xe(CR'R'')_4$ as well as all of their oxides. It is worth noting that the most general asymmetric di-, tri- and tetra-ylide can be schematically written as R_nXQ_m where R_n indicates the R groups for the usual valence of the heteroatom, X, and Q_m indicates the set of ylide ligands being CR'R'', NR''' and O. In this sense, oxides are ylides in that they utilize the same type of bonding as do carbon ylides and imines.

The theoretical distinction between HV_I and HV_{II}

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*These are called betaines in the Russian and Latvian literature since the compounds were originally written as
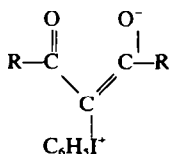
where the CIC right angle is not intended to be taken as structural.

†Such a diylide is likely to have two *geometrically* non-equivalent CR'R'' groups for structural reasons. There would thus be not only the rotation about the X = CR'R'' "double bond" as in ordinary ylides (~ 10 kcal/mole and < 7 kcal/mole for sulfonium[26] and selenonium[27] ylides, respectively) but also the site-exchange between the two CR'R'' groups.

‡The usual description of acetylacetonates of transition metals, with the negative charge arbitrarily delocalized along the carbon chain, differs from the organic chemist's picture which has a carbonium ion along the carbon chain and a negative charge localized at the heteroatom. For this reason I do not specify charge in the pictures.
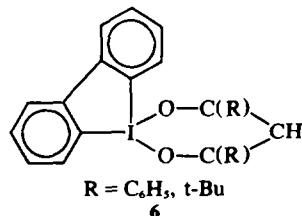
ylides might well have some important consequences both for structural chemistry and for chemical reactivity, and it should be worthwhile looking for these.

Bonding in acetylacetonates

Main-group acetylacetonates are known only for antimony[30,31] as in **5**‡ and in the unique iodine compound,[32] **6**, whereas there are numerous acetylacetonates of Group IV atoms. Although the structure of **6** is not known, it can be assumed to be as drawn with one of the I–C bonds along the bisector of the O–I–O angle. This is because we envisage the acetylacetonate group occupying the remaining portion of the T-shaped structure of the trivalent iodine.

The bonding in these hypervalent systems is unique in that only *one* electron pair is used to bond *two* ligands to the heteroatom. There are thus, effectively, two *half*-bonding X–O linkages. This bonding may be most easily visualized as a linear combination of two valence-bond structures **7a** and


7a   **7b**
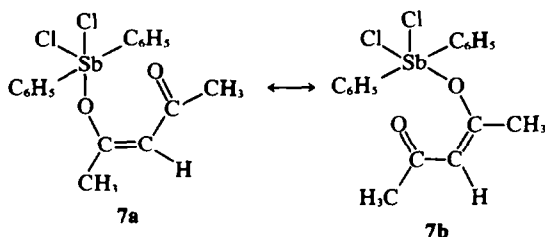
7b. A bond orbital description for **5** can be written roughly as

$$\psi = \psi_{Sb} + 2^{-1/2}\lambda(\psi_{0.1} + \psi_{0.2}) \qquad (2)$$

where ψ_{Sb} is an antimony orbital, essentially of the ground-state $sp^{3/2}$ configuration, pointing along the bisector of the OSbO angle. This three-center bond is itself a hypervalent bond which is likely to be no stronger than 50 kcal/mole (although no values are as yet available) and so that the half-bonding X–O bond is likely to be unusually weak.

There are no known diacetylacetonates of hypervalent molecules, several attempts to make such from selenium(IV) compounds gave only the ylides. By utilizing the trans-orientation of the two chlorine atoms in $(CH_3)_3SbCl_2$ it might be possible to prepare **8** whose two acetylacetonate groups might be sterically unable to combine. Another more speculative possibility would utilize a bridged double acetylacetonate in the hope that the tricyclic system would prove more stable than the ylide, or that there would be no mechanism whereby to attain the ylide. It should, of course, be possible to make numerous monoacetylacetonates of all the higher main-group elements such as **9**, and perhaps even all the higher acetylacetonates of Se and I, such as $SeF_5(acac)$, $IF_4(acac)$ and $IF_6(acac)$, plus an acetylacetonate of Xe, $FXe(acac)$.

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9
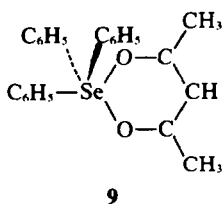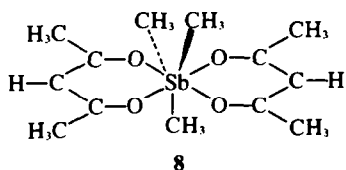
Bonding in π-cyclopentadienyl compounds

I speculate now on the preparation of hypervalent molecules analogous to ferrocene which contain the appropriate number of small organic ligands to provide the appropriate valency.

The theory of bonding is the same as for ordinary hypervalent molecules except that there is now a pseudo-three-center bonding orbital in which each of the π-cyclopentadienyl rings serves as a ligand. The hypervalent bonding orbital is written as

$$\psi = \psi_z + \lambda(\psi_a + \psi_b) \tag{3}$$

where ψ_z is the p-orbital of the central atom, and ψ_a and ψ_b are the totally symmetric combination of the five π-orbitals on the two cyclopentadienyl rings. Two electrons will occupy this orbital while two will occupy the non-bonding orbital $\psi_a - \psi_b$ containing no p-orbital contribution from the main-group atom. This orbital also mixes with the central atom's lower-lying s-orbital, but only lowers the total energy to second-order.[9]* The bonding dif-

fers from that of ferrocene since it is dominated by the hypervalent bonding p-orbital rather than the diffuse, weakly bonding 3d-and 4s-orbitals and the non-valence-shell 4p orbital of the iron atom.[†]

It might be possible to prepare some compounds of the series bis(pentahaptocyclopentadienyl)trimethyl antimony, $(CH_3)_3Sb(h^5-C_5H_5)_2$, **10**, bis-(pentahaptocyclopentadienyl)dimethyl selenium, $(CH_3)_2Se(h^5-C_5H_5)_2$, **11**, bis(pentahaptocyclopentadienyl)phenyl iodine, $C_6H_5I(h^5-C_5H_5)_2$, **12**, and bis(pentahaptocyclopentadienyl) xenon, **13**. In all of these it might be possible to replace one or both of the $h^5-C_5H_5$ groups by $h^5-NC_4H_4$ to increase the stability as in ferrocene itself. As with the spiro hypervalent sulfuranes and selenuranes, greater stability can be introduced by cyclization. This can be done either in the ordinary organic group as in **14** or in the cyclopentadienyl group or groups as in **15**. The geometrical constraints of **15** which do not permit the ideal orientation of the cyclopentadienyl groups will be more than compensated for by the stabilizing influence of the bridges.

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11   **12**

13   **14**   **15**
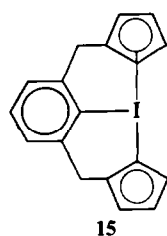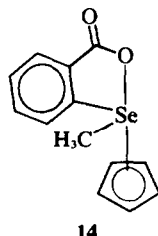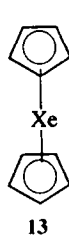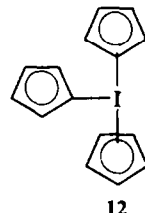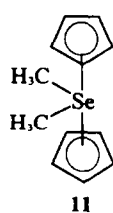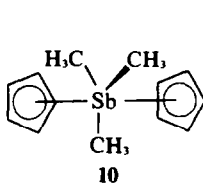
CONCLUSION

The theory of hypervalent bonding has been applied to ylides, acetylacetonates and π-cyclopentadienyl compounds, giving numerous chemical examples. The intent of this work has been to provoke new chemistry and not merely to explain existing results. I hope that I have succeeded in so doing. It might be desirable to replace the CH_2 group by a more electronegative group such as CF_2, $C{=}O$, or $C(CF_3)_2$.

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*See footnote on page 1748.
†It should be noted that the bonding in the recent *ab initio* calculation on ferrocene [M-M. Coutière, J. Demuynck and A. Veillard, *Theor. chim. Acta* **22**, 281 (1972)] is quite different from that in the popular literature.

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