Journal of Organometallic Chemistry, 82 (1974) 89—98

PHOTOELECTRON SPECTRA OF MOLECULES

VI*. HYPERCONJUGATION VERSUS p_π—d_π BONDING IN GROUP IVb COMPOUNDS

P.K. BISCHOF**, M.J.S. DEWAR, D.W. GOODMAN and T.B. JONES
Department of Chemistry, University of Texas at Austin, Austin, Texas, 78712 (U.S.A.)

(Received November 14th, 1973; in revised form June 28th, 1974)

Summary

Helium(I) photoelectron spectra have been obtained for the compounds $(CH_3)_3MPh$ and $(CH_3)_3MCH_2Ph$ (M = Group IV metal). The results have been partitioned by first order perturbation theory into hyperconjugation, induction and in the phenyl derivatives p_π—d_π bonding.

Introduction

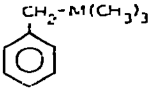
The electronic effects of substituents containing Group IVb elements have been the subject of much recent study [2] and attempts have been made to relate them to chemical reactivity [3, 4] or ^{19}F NMR chemical shifts [3, 5]. However, the most promising line of attack seems to be via comparisons of ionization potentials of the various metalloidal compounds with carbon analogs since these lead to direct estimates of the effect of the Group IVb element on the energies of the MOs. A number of studies of this kind have been reported, based on ionization potentials derived from charge transfer spectra of molecular complexes [6], from mass spectrometry [7] or from photoelectron spectroscopy [8] (PES) [9]. The results were interpreted in terms of σ—π hyperconjugation [10] or p_π—d_π bonding [11] but the relative importance of these and other possible factors has remained uncertain. Here we report a further study of this problem based on comparisons of the ionization potentials of the compounds

---

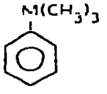
[*] For part V see ref. 1.

[**] Robert A. Welch Postdoctoral Fellow. Present address: Institut für Organische Chemie, Technische Hochschule, Darmstadt, (W. Germany).

Ia-d and IIa-d.



(I)



(II)

Ia M = C
Ib . M = Si
Ic M = Ge
Id M = Sn

IIa · M = C
IIb M = Si
IIc M = Ge
IIa M = Sn

Calculation of Ionization Energies

Ionization energies were calculated using the latest version (MINDO/3 [12]) of the MINDO [13] semiempirical SCF MO method. Parameters are available for silicon though without inclusion of *d* orbitals. The geometry of each molecule was calculated by minimizing the energy with respect to all geometrical variables, no assumptions of any kind being made, by means of a rapidly convergent minimization procedure [14] based on the Davidon—Fletcher—Powell alogorithm.

Experimental

The spectra were obtained on a high resolution photoelectron spectrometer using a 127° electrostatic cylindrical analyzer [15], similar to that described by Turner [16]. The compounds were prepared by published procedures (see Table 1) purified by distillation and, if necessary, by preparative GLPC. Purity was checked by GLPC, NMR, and mass spectroscopy.

Spectra were obtained at a resolution of 25-40 mV (argon half-height peak width). All samples were degassed thoroughly prior to ionization, repeated until consistent, and internally calibrated.

Results and Discussion

Figure 1 shows the He(I) photoelectron spectra of the molecules studied.

TABLE 1

FIRST IONIZATION POTENTIALS (eV)[a]

Molecule	Ref.	PES	MINDO/3
Benzene		9.24	9.22
Toluene		8.82	9.06
Ia		8.77	8.91
Ib	19	8.42	8 65
Ic	20	8.40	
Id	21	8.21	
IIa		8.83	8 96
IIb	22	9.05	9.05
IIc	23	9.00	
IId	23	8.94	

[a] First ionization potentials calculated assuming the validity of Koopmans' Theorem [24].

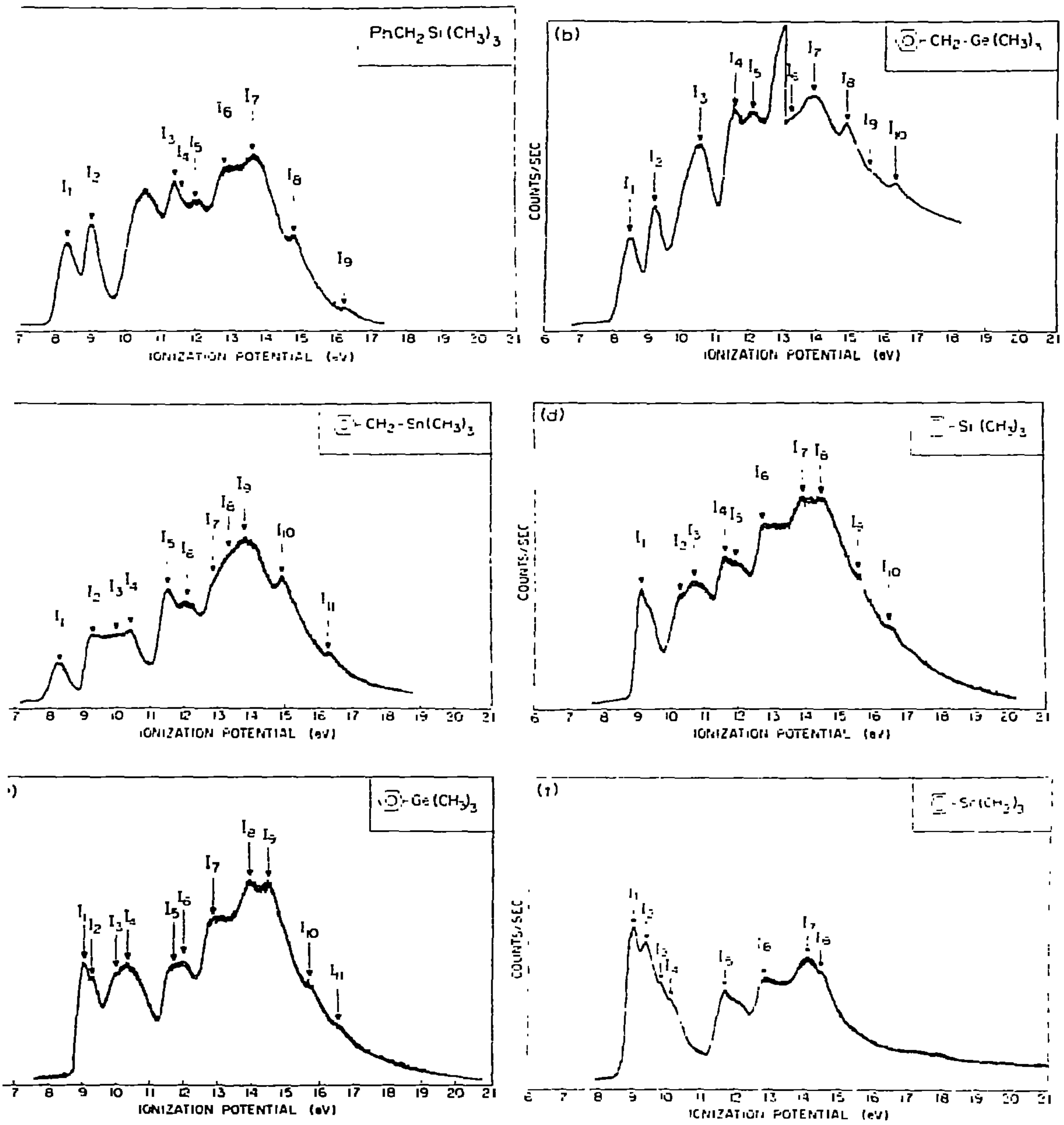


Fig. 1. Photoelectron spectra of (a) benzyltrimethylsilane; (b) benzyltrimethylgermane; (c) benzyltrimethylstannane; (d) phenyltrimethylsilane; (e) phenyltrimethylgermane; (f) phenyltrimethylstannane.

The corresponding higher ionization energies ($I_n > 1$) are shown in Table 2. First ionization potentials and those calculated by MINDO/3 are shown in Table 1. Figure 2 shows orbital correlation diagrams for the two series of compounds I and II.

TABLE 2

HIGHER IONIZATIONS

Molecule	PES I_n ($n > 1$)
Benzene	11.44, 12.23, 13.77, 14.61, 15.54, 16.63
Toluene	9.07, 11.55, 12.08, 13.43, 14.01, 15.11, 16.47
Ia	9.13, 10.73, 11.41, 12.10, 12.49, 13.81, 14.56
Ib	9.08, 10.53, 11.40, 11.98, 12.78, 13.55, 14.79, 16.28
Ic	9.12, 10.41, 11.43, 12.01, 12.92, 13.67, 14.74, 15.58, 16.32
Id	9.21, 9.90, 10.32, 11.42, 11.99, 12.83, 13.25, 13.76, 14.88, 16.28
IIa	9.31, 10.92, 11.39, 12.11, 12.72, 12.93 14.93, 16.53
IIb	9.27, 10.21, 10.60, 11.56, 11.91, 12.70, 13.88, 14.45, 15.53, 16.49
IIc	9.25, 9.98, 10.30, 11.63, 11.97, 12.80, 13.91, 14.47, 15.71, 16.51
IId	9.29, 9.71, 10.02, 11.58, 12.02, 12.72, 13.87, 14.35

First let us consider the monosubstituted benzenes (I) derived from toluene by replacing one of the methyl hydrogen atoms by the bulky group $M(CH_3)_3$. Steric effects will force the molecule to adopt the conformation where the benzylic C—M bond is parallel to the $2p$ AO of the adjacent carbon atom in the ring.

From perturbation theory [17] the change in the orbital energy (E_μ) of a π MO ψ_μ due to a substituent at position i can be divided into inductive and conjugative (or hyperconjugative) contributions $\delta E_\mu^{\mathrm{I}}$ and $\delta E_\mu^{\mathrm{H}}$, given by:

$$\delta E_\mu^{\mathrm{I}} = q_{\mu i}\delta W_i \tag{1}$$

$$\delta E_\mu^{\mathrm{H}} = \beta^2 q_{\mu i}\Delta E^{-1} \tag{2}$$

where $q_{\mu i}$ is the orbital density of ψ_μ at position i, δW_i is the change in effective valence state ionization potential of carbon atom I due to the inductive effect of the substituent, β is the effective resonance integral between the $2p$ AO of carbon atom i and the substituent, and ΔE is the difference in energy between ψ_μ and the orbital of the substituent concerned in conjugation (or hyperconjugation).

The first three ionization potentials of benzene correspond to a degenerate

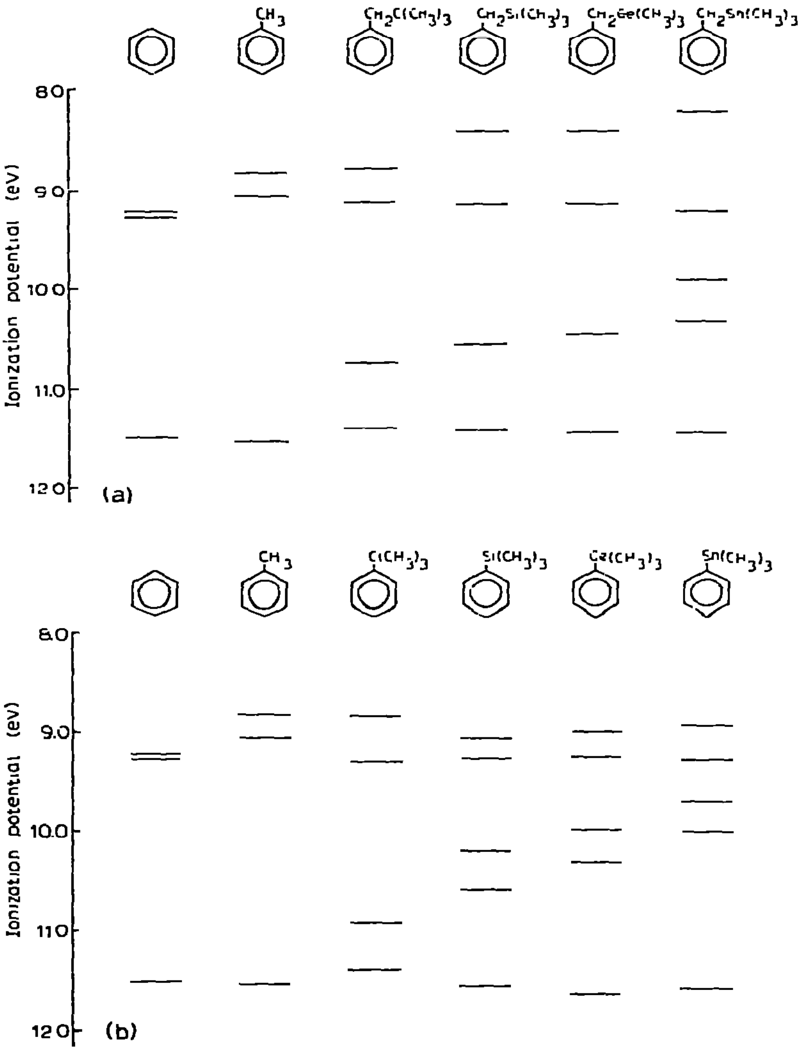


Fig. 2. Correlation diagram of the ionization potentials of (a) Benzyl—Group IVb Compounds; (b) phenyl—Group IVb compounds.

e_{1g} π level (π_1, π_2) (9.25 eV), a σ level (σ_B) (11.44 eV) and the third π level (π_3) (12.23 eV). Figure 3 shows the orbital densities in the three π MOs.

The first four levels of toluene correlate with those of benzene (Fig. 2), implying that the additional CH MOs lie below 12.2 eV. From symmetry, the methyl will occupy position A in Fig. 3; from eqns. 1 and 2, one (π_2) of the e_{1g} π MOs should remain unchanged in energy, having a node at the point of attachment of methyl, and the same should be true of σ_B. The remaining MOs should be raised in energy by both the inductive and hyperconjugative effect (eqns. 1 and 2) since the methyl CH orbitals lie below both in energy. Figure 2a shows that the ionization energies follow this pattern.

The inductive effect should raise the energy of π_1 twice as much as that of π_2 (Fig. 3) while hyperconjugation should have at least as great an effect on π_3

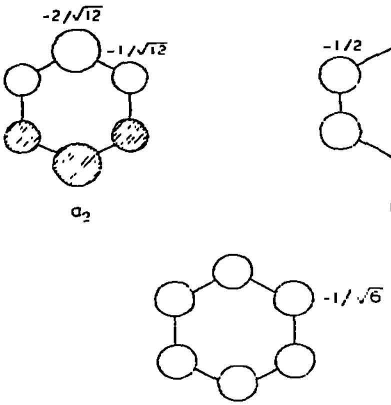


Fig. 3.

as π_1 since the CH MOs must lie very much closer to π_3 than to π_1 in energy (see eqn. 2). The fact that the decrease in the ionization energy corresponding to π_2 (0.42 eV) is more than double that for π_3 (0.17 eV) suggests that the inductive effect predominates.

Consider now the effect of replacing a methyl hydrogen in toluene by $M(CH_3)_3$ to form one of the compounds Ia-d. The MOs π_2 and σ_B should again remain almost unaffected but π_1 and π_3 should be altered in energy both by the inductive effect of the $M(CH_3)_3$ group and by hyperconjugation with the benzylic C—M bond.

In $M(CH_3)_4$, the MC bond orbitals interact, as do the CH bond orbitals in methane, to give a low-energy *s*-type MO and three degenerate *p*-type MOs. In I, one of the *p*-type MOs lies along the benzyl—M bond and can hyperconjugate with the benzene ring while the other two will remain degenerate. Ionization from the degenerate level will give an orbitally degenerate ion in which the degeneracy will be removed by a Jahn-Teller distortion. The CM ionizations in I should therefore appear as a single peak and a Jahn-Teller broadened doublet.

The correlation diagram (Fig. 2) shows that Ia-d all possess an additional peak intermediate between π_1 and σ_B and the spectra in Fig. 1 show that this appears as a broad structureless band, the overall spread of ionization energies being ca. 0.25 eV for Ib and Ic and ca. 0.4 eV for Id. Attempts to deconvolute the peaks would be pointless in view of the abnormal shapes of the bands corresponding to ionizations when the resulting ions show the Jahn-Teller effect; for it seems evident that these bands indeed correspond to CM ionization.

The changes in energy of π_1 and π_2 on passing from toluene to I can be deduced at once from eqns. 1 and 2 and Fig. 3:

$$\delta\pi_1 = (1/3)\,\delta W' + (1/3)\,\beta^2_{CM}\,(E\pi_1 - E_{CM})^{-1} \tag{3}$$

$$\delta\pi_3 = (1/6)\,\delta W' + (1/6)\,\beta^2_{CM}\,(E\pi_3 - E_{CM})^{-1} \tag{4}$$

Since the energy (E_{CM}) of the CM orbital lies between those of π_1 and π_3, hyperconjugation will raise the energy of π_1 but lower that of π_3.

TABLE 3

INDUCTIVE AND HYPERCONJUGATIVE PARAMETERS FOR $M(CH_3)_3$ IN Ia-d AND CHANGES IN CM ORBITAL ENERGY DUE TO HYPERCONJUGATIVE INTERACTIONS

	C	Si	Ge	Sn
$\delta W'$ $(eV)^{-1}$	0.04	0.91	0.82	1.13
β^2_{CM} $(eV)^{-2}$	0.21	0.50	0.68	1.05
δE_{CM} $(eV)^{-1}$	−0.09	−0.15	−0.17	−0.22

Using the data in Table 2 and eqns. 3 and 4, we arrive at the estimates of $\delta W'$ and β^2_{CM} shown in Table 3. As might be expected, the hyperconjugative contribution rises along the series Ia→d. The inductive contribution, however, is surprisingly constant, apart from a near zero value for Ia and follows the Allred—Rochow [18] ordering.

The change in energy of the CM level, due to hyperconjugative interactions with π_1 and π_2, is given by minus the sum of the corresponding changes in E_{π_1} and E_{π_2}, i.e.:

$$\delta E_{CM} = [1/3\beta^2_{CM}(E_{CM} - E_{\pi_1})^{-1} + 1/6\beta^2_{CM}(E_{CM} - E_{\pi_3})^{-1}] \tag{5}$$

The values calculated in this way are also shown in Table 3; it will be seen that they correlate well with the width of the band corresponding to CM ionizations in the photoelectron spectra (Fig. 2).

Our interpretation of the photoelectron spectra of Ia-d therefore seems reasonable and self-consistent. It leads to the conclusion that the inductive and hyperconjugative effects of the $M(CH_3)_3$ groups are of comparable magnitude.

We now turn to the t-butylbenzene analogs, IIb-d; here the benzene π MOs may be perturbed not only by the inductive effect of the $M(CH_3)_3$ group and hyperconjugation with the CM bonds but also by a direct p_π—d_π conjugative interaction with *d* AOs of M. The photoelectron spectra (Fig. 1) and the corresponding orbital correlation diagram (Fig. 2b) indicate, as expected, that two CM ionizations occur between the e_{1g} and σ_B MOs of benzene. The CM orbitals combine, as do the CM orbitals of the methyl group in toluene, into *p*-type combinations, one parallel to the ring and one orthogonal to the ring. The latter alone can interact hyperconjugatively with the benzene π MOs; the CM ionizations therefore appear as a double peak. Since the CM level is nearer to π_1 than to π_3, and since the orbital density of π_1 at the position adjacent to M is double that of π_3, the net effect of hyperconjugation is to depress the CM ionization (cf. eqn. 5). The lower CM ionization energy therefore corresponds to the unperturbed in-plane MO, the higher to the perturbed MO orthogonal to the ring.

Inserting the values for E_{π_1}, E_{π_2}, the energy of the higher (i.e. unperturbed) CM MO and the splitting of the CM level (E_{CM}) into eqn. 5 we can find β^2.

Since the 3*d* AOs of M are very much closer in energy to π_1 than to π_3, and since the orbital density of π_1 at the point of attachment of M to the ring is double that for π_3, it is likely that any effect of p_π—d_π conjugation on π_3 will be small. As a first approximation we may neglect it.

The change in energy of π_3, due to the group $M(CH_3)_3$, will then be given by eqn. 4. Using the value found above for β^2, we can then estimate $\delta W'$. Knowing β^2 and $\delta W'$ we can then use eqn. 3 to estimate the change in energy of π_1 due to the inductive and hyperconjugative effects of $M(CH_3)_3$. The difference between this and that obtained will then be a measure of the effect of p_π—d_π bonding.

The values found in this way are admittedly rather rough because the spectra are poorly resolved and it is therefore difficult to estimate the various ionization energies accurately. The calculation can be illustrated by taking IIb as an example. Here the higher CM ionization is at 10.21 eV and $\delta E_{CM} = 0.39$ eV. The ionization potentials of π_1 and π_3 are 9.24 eV and 12.23 eV respectivel
Hence from eqn. 3:

$$\frac{\beta^2/6}{10.21-9.24} - \frac{\beta^2/6}{12.23-10.21} = 0.39 \text{ eV} \quad (6)$$

whence:

$$\beta^2 = 1.48 \text{ (eV)}^2 \quad (7)$$

From eqn. 4, using the data from Table 2,

$$\delta E_{\pi_3} = 0.27 = (1/6)\,\delta W' + (1/6)\,\beta^2(12.23-10.21)^{-1} \quad (8)$$

whence:

$$\delta W' = 2.35 \text{ eV} \quad (9)$$

From eqn. 3,

$$\delta E_{\pi_1} = \frac{\beta^2/3}{10.21-9.24} + (1/3)\,\delta W' = 1.29 \text{ eV} \quad (10)$$

The observed change in the energy of π_1 (Table 1) is only 0.19 eV. Thus the change in energy of π_1, due to p_π—d_π conjugation, is —1.10 eV.

The values found in this way for the contributions of p_π—d_π conjugation are:

$PhSi(CH_3)_3$, —1.09 eV; $PhGe(CH_3)_3$, —0.86 eV; and $PhSn(CH_3)_3$, —0.51 eV.

Thus the effect of p_π—d_π conjugation is large and, as expected, it decreases along the series IIb > IIc > IId.

Table 4 summarizes the result of these calculations, showing the contributic of the various factors to the overall changes in energy of π_1 and π_3. While no great reliance can be placed on the quantitative accuracy of our estimates, we feel that they probably give a good general indication of the relative importance of the various effects. There seems in any case no doubt that p_π—d_π conjugation must be important in IIb and IIc; for one cannot otherwise account for the fact that the decrease in the π_3 ionization energy from that of benzene is greater than that for π_1.

TABLE 4

CONTRIBUTIONS TO THE CHANGES OF ENERGY OF THE π MOs OF BENZENE DUE TO VARIOUS EFFECTS OF A $M(CH_3)_3$ SUBSTITUENT

	Contributions to δE_{π_1} (eV)				Contributions to δE_{π_3} (eV)		
	Inductive	Hyper-conjugative	$p_\pi - d_\pi$	Total	Inductive	Hyper-conjugative	Total
Ib	0.30	0.10		0.40	0.15	−0.05	0.10
Ic	0.28	0.14		0.42	0.14	−0.07	0.07
Id	0.38	0.23		0.61	0.19	−0.10	0.09
IIb	0.78	0.51	−1.09	0.20	0.39	−0.12	0.27
IIc	0.64	0.38	−0.82	0.20	0.32	−0.06	0.26
IId	0.48	0.34	−0.51	0.31	0.24	−0.03	0.21

Acknowledgements

This work was supported by the Air Force Office of Scientific Research through Contract F44620-71-C-0119 and by the Robert A. Welch Foundation through Grant F-126. We wish to thank Dr. W. Adcock of The Flinders University of South Australia for supplying us with some of the samples used in this investigation. The calculations were carried out using the CDC 6400/6600 computer at the University of Texas Computation Center.

References

1 M.J.S. Dewar and D.W. Goodman, J. Chem. Soc. Faraday Trans. II, 68 (1972) 1784;
2 (a) G.E. Coates, M.L.H. Green and K. Wade, Organometallic Compounds, Vol. 1, Methuen, London, 1967.
(b) C. Eaborn, Organosilicon Compounds, Butterworths, London, 1960
3 A.R. Bassindale, C. Eaborn, D.R.M. Walton and D.J. Young, J. Organometal. Chem., 20 (1969) 49 and references therein.
4 (a) W. Hanstein, H.J. Berwin and T.G. Traylor, J. Amer. Chem. Soc., 92 (1970) 7476 and references therein.
(b) J.M. Jerkunica and T.G. Traylor, ibid., 93 (1971) 6278.
5 (a) W. Adcock, S.Q.A. Rizir and W. Kitching, ibid., 94 (1972) 3657.
(b) A.J. Smith, W. Adcock and W. Kitching, ibid., 92 (1970) 6140 and references therein.
6 (a) C.G. Pitt, J. Organometal. Chem., 23 (1970) C35.
(b) H. Bock and H Alt, J. Amer. Chem. Soc., 92 (1970) 1569 and references therein.
7 H. Bock, H. Siedl and M. Fochler, Chem. Ber., 101 (1968) 2815.
8 (a) P. Mollere, H. Bock, G. Becker and G. Fritz, J. Organometal. Chem., 46 (1972) 89.
(b) U. Weidner and A. Schweig, ibid., 39 (1972) 261.
(c) R.A.N. McLean, Can. J. Chem., 51 (1973) 2089.
9 For reviews containing principles and assumptions in the method see:
(a) D.W. Turner, C. Baker, A.D. Baker and C.R. Brundle, Molecular Photoelectron Spectroscopy, Wiley, New York, 1970.
(b) C.R. Brundle and M.B. Robin, Determination of Organic Structures by Physical Methods, Vol. 3, Academic Press, New York, 1971.
(c) S.D. Worley, Chem. Rev., 71 (1971) 295.
(d) H. Bock and B.G. Ramsey, Angew. Chem. Int. Ed. Engl., 12 (1973) 734.
10 C.G. Pitt, J. Organometal. Chem., 61 (1973) 49.
11 (a) C.J. Attridge, Organometal. Chem. Rev. Sect. A, 5 (1970) 323.
(b) T.B. Brill, J. Chem. Educ., 50 (1973) 392.
(c) B.G. Ramsey, Electronic Transitions in Organometalloids, Academic Press, New York, 1969.

12 (a) N.C. Baird and M.J.S. Dewar, J. Phys. Chem., 50 (1969) 1262.
(b) N.C. Baird, M.J.S. Dewar and R. Sustmann, ibid., 50 (1969) 1275.
13 R.C. Bingham, M.J.S. Dewar and D.H. Lo, to be published.
14 (a) W.C. Davidon, Angonne Nat. Lab. Report ANL-5990 (Rev. TlD 4500), 1959.
(b) R. Fletcher and M.J.D. Powell, Comp. J., 6 (1963) 163.
15 For a detailed description and drawings, see D.W. Goodman, Dissertation, The University of Texas at Austin, 1973.
16 D.W. Turner, Proc. Roy. Soc. A, 307 (1968) 15.
17 M.J.S. Dewar, Molecular Orbital Theory of Organic Chemistry, McGraw-Hill, New York, 1969, p. 190.
18 A.L. Allred and E.G. Rochow, J. Inorg Nucl. Chem., 5 (1958) 264.
19 H. Gilman and F.J. Marshall, J. Org. Chem., 71 (1949) 2066.
20 R.J. Cross and F. Glocking, J. Chem. Soc., (1964) 4125.
21 H.H. Huang and K.M. Hui, J. Organometal. Chem , 2 (1964) 288.
22 F.B. Deans and C. Eaborn, J. Chem. Soc., (1959) 2299.
23 D. Seyferth and D.L. Alleston, J. Inorg. Nucl. Chem., 2 (1963) 417.
24 T. Koopmans, Physica, 1 (1933) 104.