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CARBON-13 NMR SPECTRA OF OLEFIN—COPPER(I) COMPLEXES

ROBERT G. SALOMON and JAY K. KOCHI
Chemistry Department, Indiana University, Bloomington, Indiana 47401 (U.S.A.)
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Summary

The carbon-13 NMR spectra of olefin—copper(I) complexes are examined. The change in the chemical shift of the vinyl carbon upon coordination is compared to the change observed in the proton spectrum. The Dewar—Chatt—Duncanson model for olefin—metal bonding is used to compare chemical shift changes observed in polyolefin and monoolefin complexes. The role played by π-back donation in the relatively large upfield shifts observed in monoolefin complexes is described. The use of copper(I) triflate as a CMR shift reagent for olefins is suggested.

Introduction

The proton NMR spectra of various olefin—copper(I) triflates show unusual upfield and downfield shifts of the vinyl protons with mono-dentate and polydentate olefins, respectively [1]. We noted that these shifts, $\Delta\delta^1H$, can be understood in terms of changes in the π-electron density at carbon due to metal—olefin coordination. According to a Dewar—Chatt—Duncanson (DCD) model [2], net shielding results from a preponderance of back donation of metal electron density to the olefin π^* orbital (π-bonding) over donation of olefin π-density to the metal (σ-bonding). Net deshielding results if σ-bonding dominates. The relative contributions of these components may vary greatly from one complex to another as a result of multiple olefin coordination to the copper(I) nucleus.

Powell and coworkers recently demonstrated that $\Delta\delta^{13}C$ for olefin complexes of d^8 Pd^{II} and Pt^{II} are determined primarily by "nonbonding metal d-orbital shielding" effects [3]. However, such effects are not expected for olefin complexes of Cu^I and Ag^I owing to their full d^{10} electron configuration. Our observations on Cu^I olefin complexes (vide infra) as well as recent observations on Ag^I olefin complexes [4] demonstrate that factors other than nonbonding shielding can result in large upfield shifts. It seems likely that variations in chemical shift changes, $\Delta\delta^{13}C$, in these complexes arise from changes in the mode or degree of metal—carbon bonding. In this report we examine the applicability of the DCD model to the interpretation of the carbon-13 magnetic resonance spectra of olefin—copper(I) complexes.

Results and discussion

The carbon-13 NMR spectra of olefin—copper(I) triflate complexes shown in Fig. 1 were examined in CD_3CO_2D solution. The change, $\Delta\delta^{13}C$, in the chemical shift of the vinyl carbons in the complexes shows only upfield shifts relative to the free ligand as indicated in the figure. This behavior is in contrast to the change, $\Delta\delta^{1}H$, in the chemical shift of the corresponding vinyl protons, which are also included for comparison in parenthesis.

There is a general correlation of $\Delta\delta^{13}C$ with the structures of the olefin—Cu^{I} complexes, since these shifts are large for monodentate complexes while small for polydentate complexes. In agreement with variations in $\Delta\delta^{1}H$, this correlation is consistent with a greater π-electron density at carbon for monodentate than for polydentate complexes. However, variations in π-electronic charge alone do not account fully for $\Delta\delta^{13}C$. If both $\Delta\delta^{1}H$ and $\Delta\delta^{13}C$ are linearly and exclusively dependent on the same variable, then a plot of $\Delta\delta^{1}H$ versus $\Delta\delta^{13}C$ should be linear, but Fig. 2 shows that these chemical shift changes are not strictly proportional.

Carbon-13 chemical shifts

Proton chemical shifts are determined primarily by local diamagnetic effects and neighboring group anisotropy. Local paramagnetic effects are unimportant for protons, but for all other nuclei they usually predominate [5]. Unlike local diamagnetic effects, local paramagnetic effects are not necessarily dominated by local electron density. According to the theory developed by Pople and Karplus [6], variations in the chemical shift for a carbon atom are primarily determined by changes in the local paramagnetic contribution σ_p,

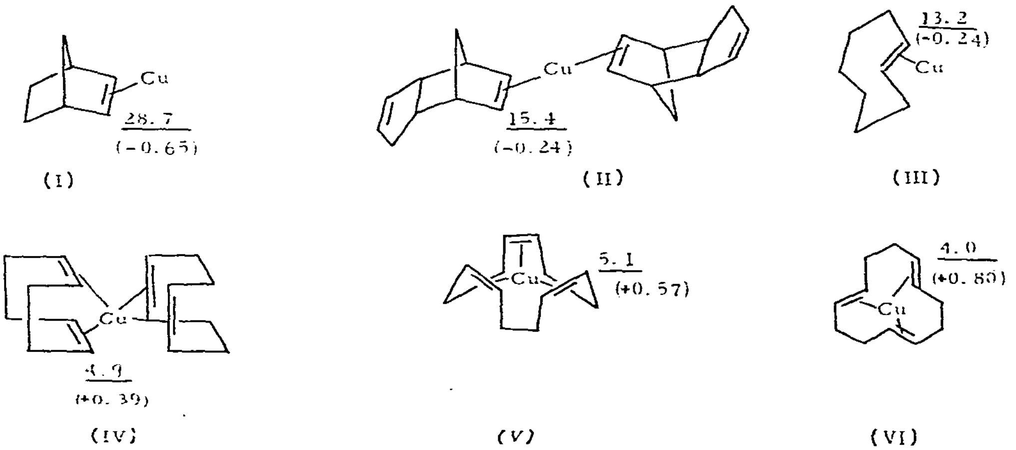

Fig. 1. The changes in chemical shifts $\Delta\delta^{13}C$ of olefin—copper(I) complexes in CD_3CO_2D. Values of $\Delta\delta^{1}H$ in parenthesis.

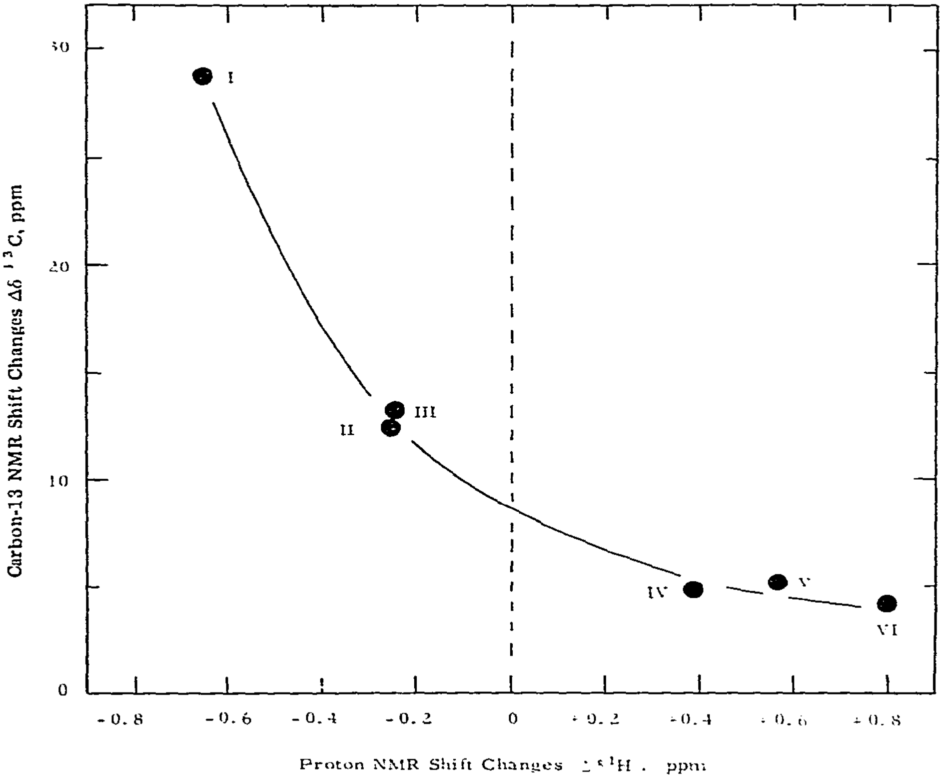

Fig. 2. Relationship between changes in carbon chemical shifts $\Delta\delta\,^{13}C$ and proton shifts $\Delta\delta\,^{1}H$ in olefin—copper(I) complexes.

which is most sensitive to chemical structure. Pople [7] estimates that in hydrocarbons the magnitude of the total variation due to all other contributions to carbon shifts, including diamagnetic terms, is unlikely to exceed 10% of that due to σ_p.

The paramagnetic contribution is attributed to the opposing currents on carbon atom A resulting from the mixing of ground and excited electronic states by the magnetic field, and is given by:

$$(\sigma_p^{AA})_{zz} = -\left(\frac{e^2\cdot\hbar^2}{2m^2\cdot c^2}\right)\frac{\langle r^{-3}\rangle_{2p}\cdot[(Q_{AA})_{zz} + \Sigma_{B\neq A}(Q_{AB})_{zz}]}{\Delta E}, \qquad (1)$$

in which ΔE is an average electronic excitation energy [7]. Both the factor $\langle r^{-3}\rangle_{2p}$ and the term $(Q_{AA})_{zz}$ depend primarily on the local electron density on the carbon atom. As the total electronic charge on carbon A increases, the orbitals expand and $\langle r^{-3}\rangle_{2p}$ decreases. The terms involving Q_{AB} arise because the external magnetic field acting on atom B mixes in excited electronic states of the molecule and thereby induces a current flow on atom A. Q_{AB} is significant only if there is both σ- and π-bonding between A and B. It has been called a "multiple bond effect" and depends directly on the multiple bond order between these atoms. Eqn. (1) predicts the following changes in chemical shift due to perturbations on the electronic environment of a particular carbon nucleus:

Perturbation	*Chemical shift change*
decrease electron density	deshielding
decrease multiple bond order	shielding
decrease av. excitation energy	deshielding

Metal coordination to an olefin can be pictured as such a perturbation of the electronic environment of the vinyl carbon atoms [8]. An analysis of this perturbation in terms of the Dewar—Chatt—Duncanson model of the olefin—metal interaction gives rise to the changes in vinyl carbon chemical shifts upon coordination listed in Table 1.

The (π—π^*) transition which has the lowest excitation energy in olefins, does not contribute to ΔE[*]. Transitions from an occupied σ-orbital to the vacant π^*-orbital and from the occupied π-orbital to a vacant σ^*-orbital contribute heavily to ΔE of olefins, resulting in substantial deshielding of the vinyl carbons compared to their saturated counterparts. A decrease in π-orbital energy of the olefinic ligand due to σ-bonding with Cu^I produces an upfield change of $\Delta\delta^{13}C$ by increasing the energy of the (π—σ^*) transition as illustrated schematically in Fig. 3[**]. Shielding effects due to σ-bonding and resultant changes in ΔE were noted previously for olefin coordination with Ag^I [3,10].

A similar effect which is associated with back bonding has not been discussed[***]. Thus, interaction of a vacant olefin π^*-orbital with an occupied metal d-orbital can raise the energy of the π^*-orbital as shown in Fig. 3. The latter also results in an increase in ΔE and causes shielding of the vinyl carbons of the complexed olefin compared to those of the free olefin. In addition, both olefin—metal σ-bonding and back donation result in a decrease of the olefin π-bond order (as indicated by a decrease in the infrared stretching frequency in Table 2), which also contributes to shielding of the vinyl carbons.

TABLE 1

CHANGES IN CHEMICAL SHIFT ACCORDING TO THE DCD MODEL FOR OLEFIN-COPPER(I) COMPLEXES

Perturbation due to σ-bonding	*Change in chemical shift*
Decrease electron density	Deshielding
Decrease multiple bond order	Shielding
Increase ΔE	Shielding
Perturbation due to π-backbonding	
Increase electron density	Shielding
Decrease multiple bond order	Shielding
Increase ΔE	Shielding

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[*] The excited state must be such that it can be mixed with the ground state by the rotational operator $\Sigma\delta/\delta\phi_k$ [9]. A (π—π^*) transition does not meet the symmetry requirements of this operator.

[**] For energies of donor and acceptor orbitals in organometallic π-complexes see ref. [8].

[***] The (π—σ^*) and (σ—π^*) excited states are both of B_{2g} symmetry in the D_{2h} point group. Both transitions have about the same energies, and thus both should make similar contributions to ΔE.

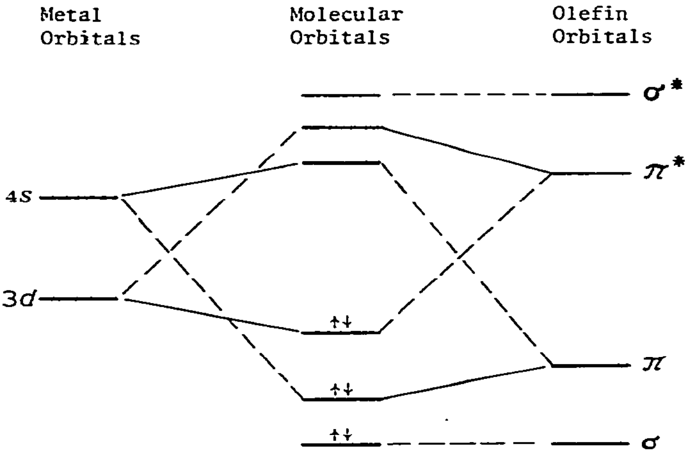

Fig. 3. Schematic energy level diagram for olefin—copper(I) coordination.

Of the complexes studied, (IV), (V) and (VI) exhibit the slightest shieldings of the vinyl carbons (Fig. 1). In these complexes the σ-bonding component predominates over π-bonding (as indicated by the deshielding of the vinyl protons). Thus, the deshielding effect caused by a decreased electron density on the vinyl carbon as a result of σ-bonding is apparently balanced by shielding effects due to an increase in ΔE and a decrease in π-bond order. (See Table 1). The shieldings in complexes (IV), (V) and (VI) are essentially constant, showing little dependence on the degree to which σ-bonding predominates.

The transition from complexes (IV), (V), (VI) exhibiting net deshielding to complexes (I), (II) and (III) showing net shielding of the vinyl protons is accompanied by a rapid increase in shielding of the vinyl carbons (Fig. 2). The contributions to shielding resulting from an increase in ΔE and a decrease in the π-bond order both augment the effect of increased electron density at the vinyl carbons associated with back donation.

The foregoing analysis shows that chemical shift changes of vinyl protons and vinyl carbons in olefins coordinated to copper(I) are qualitatively understandable in terms of the Dewar—Chatt—Duncanson model of the olefin—metal bond. Qualitative differences in the magnitude of $\Delta\delta^{13}$C for various olefins can be related to variations in the relative contributions of the two synergistic components comprising the metal—olefin bond. No doubt other explanations of the observed relationship of the structures of metal—olefin complexes with vinyl carbon chemical shift changes of the olefinic ligands may

TABLE 2

INFRARED C=C STRETCHING FREQUENCIES (CM^{-1}) OF FREE AND Cu^{I}-COORDINATED OLEFINS

Complex	Free olefin	Coordinated olefin
(I)	1565	1480
(II)	(1615) 1570	(1620) 1540
(III)	1650	1570
(IV)	1650	1595
(V)	1640, 1655	1585
(VI)	1670	1600

also be possible. We do not intend to exclude other interpretations since it is conceivable, e.g., that such a relationship may be explicable in terms of the inherent anisotropy of the metal—olefin bond*.

Copper(I) as a "shift" reagent

Copper(I) triflate may be useful as a "shift reagent" for analysis of olefin CMR spectra [11]. The effect of CuOTf on the spectrum of *endo*-dicyclopentadiene is an example of such an application, since the vinyl carbon resonances of this olefin are not all resolved. In the presence of 0.5 equivalent of CuOTf all four resonances are resolved as shown in Fig. 4. It is known from the PMR and IR spectra that CuOTf coordinates with the 8,9-C=C of (II)[12]. Differentiation of the C8 and C9 vinyl carbon resonances from those due to C3 and C4 can be made on the basis of $\Delta\delta^{13}C$. Thus two vinyl carbon resonances are shifted only slightly by CuOTf while two are strongly shifted. The latter must be C8 and C9 while the former are C3 and C4.

Experimental

Elemental microanalysis was performed by Spang Microanalytical Laboratory, Ann Arbor, Michigan. Analysis for copper(I) was performed by oxidation of a solution of ferric chloride and back titration with standard ceric solution.

Proton magnetic resonance spectra were obtained on a Varian A-60 spectrometer. Carbon magnetic resonance spectra were obtained on a Varian DP-60 Fourier Transform spectrometer with proton decoupling. In addition, off resonance decoupled spectra were recorded for the free ligands to aid in assignment of pertinent carbon resonances. All magnetic resonance measurements were made on solutions of the olefin complexes at the same concentrations (1 - 2*M*) or solutions of the respective free ligands in d_4-acetic acid. Infrared spectra were recorded on a Perkin—Elmer 137G spectrometer. The spectra of the complexes were examined as Fluorolube mulls and the free ligands were examined neat.

Preparation of olefin complexcs

All reactions were conducted under a blanket of dry nitrogen. Benzene was freshly distilled from sodium benzophenone ketyl. Pentane was purified by stirring for 12 h with concentrated sulfuric acid, then with 0.5 *M* potassium permanganate in 3 *M* sulfuric acid for 12 h. It was washed successively with water and aqueous sodium bicarbonate and dried over anhydrous magnesium sulfate and finally with phosphorus pentoxide. It was fractionally distilled under nitrogen. All other solvents were reagent grade materials used without further purification.

Complexes were prepared in vessels sealed with an air tight rubber septum cap, and separated from the mother liquor by filtration through a sintered glass disk with the aid of a positive pressure of nitrogen. After washing, the complexes were dried under a stream of dry nitrogen in the same apparatus.

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* Other factors which may be important include the role of the counterion, the solvent and strain in the olefin. A rigorous theoretical treatment will hopefully shed more light on this problem.

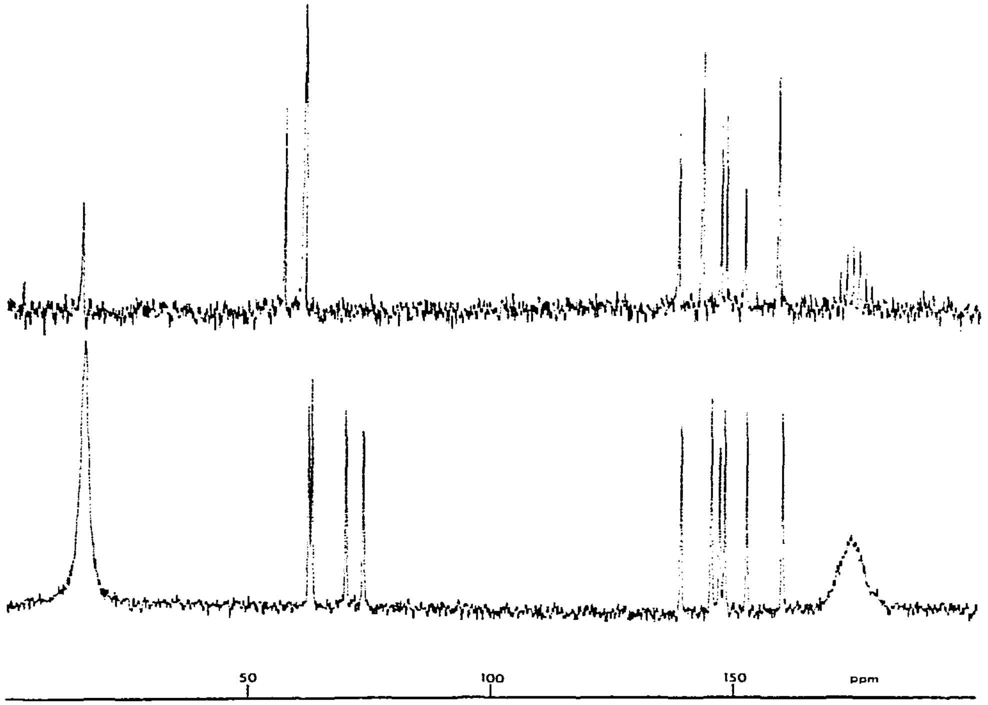

Fig. 4. Carbon-13 NMR spectrum of *endo*-dicyclopentadiene - copper(I) triflate in CD_3CO_2D (lower spectrum), free olefinic ligand (upper spectrum).

Solutions of the olefin complexes in 2-butanone [complexes (*I*), (*II*), (*III*) and (*IV*)] or benzene [complexes (*V*) and (*VI*)] were prepared by combining the cuprous triflate—benzene complex, $(CuOTf)_2 \cdot C_6H_6$ [12], with an excess of the appropriate olefinic ligand in these solvents. The complexes precipitated as crystalline stoichiometric white solids upon addition of pentane. The stoichiometries and elemental analytical data for these complexes are given in Table 3.

In general, $\Delta\delta^{13}C$, for aliphatic carbons of the olefinic ligands examined,

TABLE 3

ANALYSIS OF OLEFIN—COPPER(I) TRIFLATE COMPLEXES

Complex	Olefin	Stoichiom. Cu/Olefin	Composition	Elemental analysis found (calcd.) (%)		
				Cu	C	H
(I)	Norbornylene	1/1	$C_7H_{10}CuF_3O_3S$	19.8 (20.7)	31.16(31.32)	3.38(3.29)
(II)	*endo*-Dicyclopentadiene	1/2	$C_{21}H_{24}CuF_3O_3S$	14.0 (13.3)		
(III)	*trans*-Cyclooctene	1/3[a]	$C_{25}H_{42}CuF_3O_3S$	11.8 (11.7)	55.16(55.28)	7.83(7.79)
(IV)	1,5-Cyclooctadiene	1/2	$C_{18}H_{24}CuF_3O_3S$	14.5 (14.8)	47.69(47.59)	5.75(5.64)
(V)	(*Z,Z,Z*)-1,5,9-cyclododecatriene	1/1	$C_{13}H_{18}CuF_3O_3S$		41.78(41.65)	4.88(4.84)
(VI)	(*E,E,E*)-1,5,9-cyclododecatriene	1/1	$C_{13}H_{18}CuF_3O_3S$	16.8 (16.9)	41.75(41.65)	4.92(4.84)

[a] Dissociates to give 1/2 complex plus free olefin in solution.

TABLE 4

PROTON MAGNETIC RESONANCE SPECTRA OF OLEFIN—COPPER TRIFLATE COMPLEXES

Complex	Olefin	Chemical Shifts (δ)[a]	
		Vinyl	Allylic
(I)	Norbornylene	5.37 (6.02)	3.08 (2.84)
(II)	*endo*-Dicyclopentadiene	5.74 (5.98) 5.48 (5.53)	
(III)	*trans*-Cyclooctene	5.30 (5.54)	
(IV)	1,5-Cyclooctadiene	5.96 (5.57)	2.52 (2.36)
(V)	(*Z*,*Z*,*Z*,)-1,5,9-cyclododecatriene	6.20 (5.63)	2.65 (2.15)
(VI)	(*E*,*E*,*E*)-1,5,9-cyclododecatriene	5.82 (5.02)	2.38 (2.06)

[a] Chemical shift of free olefin in parenthesis.

TABLE 5

CARBON-13 MAGNETIC RESONANCE SPECTRA OF OLEFIN—COPPER(I) TRIFLATE COMPLEXES[a]

Complex	Olefin	Chemical Shifts[b]		
		Vinyl	Allylic	Other
(I)	Norbornylene	85.2 (56.5)	149.8 (151.6)	148.0 (145.0) -C7 168.8 (167.4) -C5,6
(II)	*endo*-Dicyclopentadiene	69.8 (57.4) 73.4 (61.2) 62.2 (61.4) 62.8 (61.4)		
(III)	*trans*-Cyclooctene	72.8 (59.6)		
(IV)	1,5-Cyclooctadiene	69.7 (64.8)	165.1 (165.3)	
(V)	(*Z*,*Z*,*Z*)-1,5,9-cyclododecatriene	67.9 (62.8)	165.7 (165.2)	
(VI)	(*E*,*E*,*E*)-1,5,9-cyclododecatriene	65.8 (61.8)	158.1 (160.9)	

[a] All chemical shifts are expressed in ppm upfield from CS_2. [b] Chemical shifts of free olefin in parenthesis.

are small, ± at most 3 ppm, compared with the shifts observed for vinyl carbons. The shifts of several specific carbons in Table 5 have been assigned by single frequency off-resonance proton decoupling experiments or analysis of proton coupled spectra.

Acknowledgement

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References

1 R.G. Salomon and J.K. Kochi, J. Organometal. Chem., 43 (1973) C7.
2 (a) M.J.S. Dewar, Bull. Soc. Chim. Fr., 18 (1951) C79.
(b) J. Chatt and L.A. Duncanson, J. Chem. Soc., (1953) 2939.
3 D.G. Cooper, R.P. Hughes, J. Powell, J. Amer. Chem. Soc., 94 (1972) 9244.
4 C.D.M. Beverwijk and J.P.C.M. van Dongen, Tetrahedron Lett., (1972) 4291.
5 J.M. Sichel and M.A. Whitehead, Theor. Chim. Acta (Berl.), 5 (1966) 35.
6 M. Karplus and J.A. Pople, J. Chem. Phys., 38 (1963) 2803.
7 J.A. Pople, Mol. Phys., 7 (1963) 301.
8 R. Mason, Chem. Soc. Revs., 1 (1972) 441; R. McWeeny, R. Mason and A.D. Towl, Discuss. Faraday Soc., 47 (1969) 21.

9 J.A. Pople, W.G. Schneider, and H.J. Bernstein, "High-Resolution Nuclear Magnetic Resonance", McGraw Hill, New York 1959, p. 172.
10 R.G. Parker, J.D. Roberts, J. Amer. CHem. Soc., 92 (1970) 742.
11 Cf. also ref. [4].
12 R.G. Salomon and J.K. Kochi, J. Amer. Chem. Soc., 95 (1973) 1889.