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^{13}C—^{13}C COUPLING CONSTANTS IN μ_2- AND μ_4-(η^2-ACETYLENE) COMPLEXES OF COBALT

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Summary

A drastic decrease in ^1J(CC) is observed on going from free acetylene to complexes in which the acetylene is bonded to two and four cobalt atoms, respectively. The relationship between ^1J(CC) and the hybridization state of the carbon atoms is discussed by working out CNDO calculations in connection with the method developed by Maciel et al. to evaluate the Fermi contact term for directly bonded atoms.

The bonding scheme adopted by a coordinated alkyne in transition metal complexes is a topic of relevant interest since its better understanding will also provide new light on the chemisorption mechanism of an alkyne on a metallic surface [1].

A number of complexes containing an η^2-acetylene ligand coordinated to one or more (up to four) metal atoms has been reported and several spectroscopic parameters have been used to assess the actual bonding system of the coordinated alkyne [2].

Among them, the coordination shift observed in the NMR spectra (both ^{1}H and ^{13}C) does not provide unambiguous information owing to the well known difficulties found in the estimation of the various contributions which determine the observed chemical shift.

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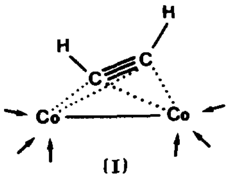
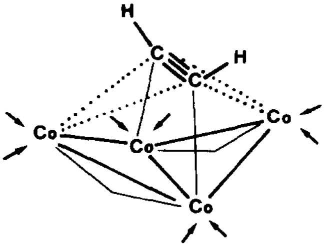
On the other hand coupling constants are usually better suited for describing the bonding picture.

Unfortunately, the low natural abundance of C-13 nuclei (1.1%) strongly limits the detection of coupling constants involving ^{13}C-nuclei; the few ^{1}J(CC) values reported for organometallic systems were obtained via the observation of the satellites subspectra in the case of highly soluble samples [3]. Recently, Benn and Rufińska showed that the use of a double quantum coherence technique allows an easy determination of several carbon—carbon coupling constants in allyl- and olefin-metal complexes [4,5].

We report herein some preliminary results concerning the observation of the ^{1}H NMR spectra of C-13-enriched acetylene complexes. Two types of complexes have been considered, namely $Co_2(CO)_6(HC{\equiv}CH)$ (I) and $Co_4(CO)_{10}(HC{\equiv}CH)$ (II), in which the acetylene is μ_2—η^2 and μ_4—η^2 bonded, respectively [6].



(I)



(II)

The ^{1}H NMR spectrum of I, recorded at −50°C (to limit the broadening due to the quadrupolar relaxation of the ^{59}Co-nuclei [7]), is reported in Fig. 1.

This spectrum can be easily analyzed since it is the X part of an AA'XX' spectrum (the A part is obviously the C-13 spectrum): the number of lines is lower than expected since ^{3}J(HH) (i.e. ^{3}J(XX')) is negligible in this system [8]., As is shown in Fig. 1, the presence of ~10% of the single ^{13}C-labelled acetylene, $H^{13}C{\equiv}CH$, provides a further aid to obtaining ^{1}J(CH) and ^{2}J(CH), whose sum corresponds to the separation between the two principal peaks, ^{1}J(CC) is given by the separation between the peaks 6,9 and 5,10 (or between 7,12 and 11,8).

In the case of II, the quality of the spectrum is slightly lower since some lines overlap and also because an effective "thermal" decoupling of the quadrupolar cobalt nuclei was not achieved; as a consequence, less accuracy is obtained in the determination of the ^{1}J(CC) value.

The values reported in Table 1 for ^{1}J(CC), ^{1}J(CH) and ^{2}J(CH) are not easily understood in terms of the simple rules successfully empoyed for coupling constants involving carbon nuclei in organic compounds [9]. For instance, if ^{1}J(CC) were simply compared with the values reported for C_2H_4 (67.6 Hz) and for C_2H_2 (171.5 Hz), it would be difficult to rationalize the changes induced in the acetylenic framework by the complexation. In fact, since ^{1}J(CC) in ethane is 34.6 Hz, this would imply that the μ_4-η^2 coordination mode, found in II, has led to the unreasonable situation characterized by a carbon—carbon bond order less than one.

A possible way to gain further insight into the actual meaning of these parameters is to consider, at least qualitatively, the approach developed by Maciel et al. of calculating the Fermi contact term for directly bonded atoms [10]. This meth-

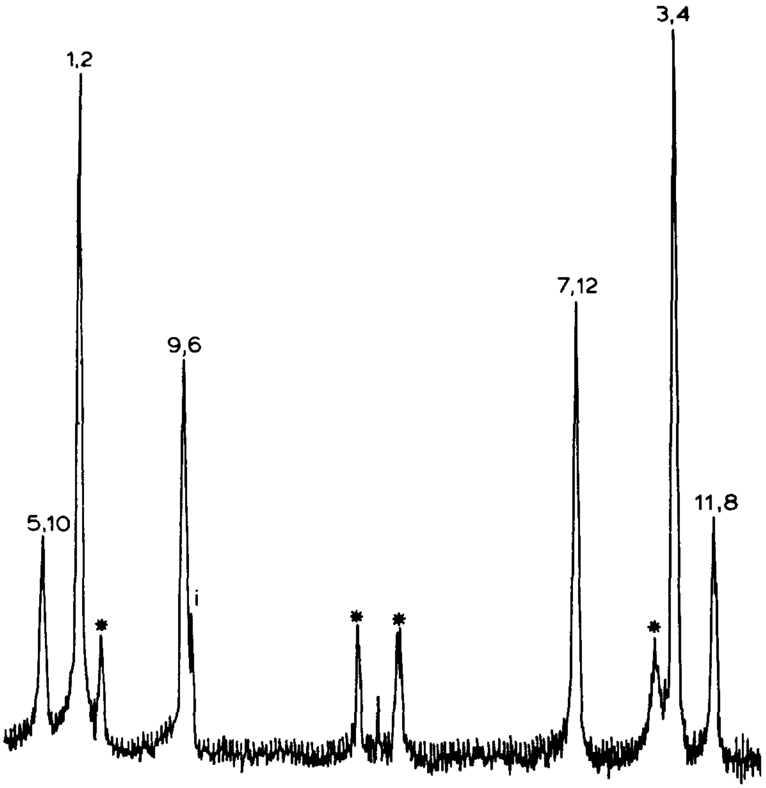


Fig. 1. 60 MHz ^{1}H NMR spectrum of I in $CDCl_3$ at −50° C. The peaks marked with an asterisk are assigned to the isotopomer $Co_2(CO)_6(H^{13}C{\equiv}CH)$; i is the $CHCl_3$ impurity in the $CDCl_3$.

TABLE 1

COUPLING CONSTANTS (Hz) IN THE ACETYLENE LIGAND

Compound	^1J(CC)	^1J(CH)	^2J(CH)
I	55.9	209.8	15.7
II	21	174.7	4.5

od yields a proportionality between the coupling constants ^1J(C(A)C(B)) and the $P s_{C(A)} s_{C(B)}$ term (which represents the elements of the first order density matrix between the valence-shell s-orbitals). This parameter can easily be evaluated through a wide range of quantum mechanical methods and it is highly sensitive to the hybridization of the carbon atoms, as was carefully shown in the original paper [10].

We report here the $P s_{C(A)} s_{C(B)}$ values for a range of free and complexed acetylene obtained on the basis of CNDO calculations, which recently proved rather accurate in discussing the PE spectra of several alkyne cluster derivatives [11,12].

These data show that (i) the coordination induces large variations in the $P s_{C(A)} s_{C(B)}$ terms, and (ii) only a slight effect is obtained when the free acetylene is taken to the excited configuration corresponding to a spatial arrangement adopted by this ligand in a typical η^2-complex.

TABLE 2

OFF-DIAGONAL ELEMENTS OF THE CNDO DENSITY MATRIX FOR A RANGE OF FREE AND COMPLEXED ACETYLENES

Mode	$P_{s_{C(A)}s_{C(B)}}$
free-C_2H_2	0.505
free-C_2H_2 "bent"[a]	0.465
μ_2-η-C_2H_2	0.372
μ_3-$\eta^2(\perp)C_2H_2$ [b]	0.243
μ_4-η^2-C_2H_2	0.268

[a] It represents an excited state of the acetylene in which the two C—H bonds are bent and the C—C bond is elongated to 1.41 Å. [b] According to the notation suggested by Muetterties [2].

The computed trend parallels the experimental values obtained for ^1J(CC), thus providing a direct estimation of the rehybridization at the carbons involved in the bond. However, caution has to be used in relating these parameters to the actual carbon—carbon bond order value. Only in the free acetylene is the $P_{s_{C(A)}s_{C(B)}}$ term directly related to the bond order of the carbon—carbon frame: this is no longer true in the coordinated alkyne owing to the drastic rehybridization effects caused by the interaction with the metal atoms.

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