232. One-Bond $^{13}C,^{13}C$-Spin Coupling in η^4-, η^3- and η^2-Olefin Transition Metal Complexes[1])

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Summary

One-bond $^{13}C,^{13}C$-spin-coupling constants have been measured, with natural isotope abundance, in η^4-diene, η^3-allyl and η^2-ene transition-metal carbonyl complexes. Typical values of $^1J(C,C)$ are given for Fe-, Ru- and Os-complexes with the three types of olefinic ligands. The effects of substituents and the structural significance of the C,C-coupling constants are discussed.

The measurement of C,C-spin-coupling constants with the ^{13}C-isotope in natural abundance has been facilitated by a steady improvement in the sensitivity of commercial spectrometers and by an application of special pulse sequences. Together with the results obtained from labelled substrates, a rapid increase of data for a large variety of organic structures is now being observed [2]. This, in turn, stimulates the interest in the structural interpretation and application of C,C-coupling constants. For simple organic molecules various correlations have been established between $^1J(C,C)$ and structural parameters, such as C,C-bond length [3], *s*-character of the bonding hybrid orbitals [3a] [4] and $^1J(C,H)$ coupling constants [5] [6]. Furthermore, it was shown that $^1J(C,C)$ values can be calculated as the product of two structure-related factors I(C), I(C′) which depend upon C-atom hybridization and substituents effects [6].

To date, only a few organometallic systems, *e.g.* (η^4-diene)$M(CO)_3$ (M = Fe, Ru, Os) [7], methylferrocene [8] and $[LCo(CO)_3]PF_6$ (L = substituted cyclobutadiene) [9] have been analyzed for $^1J(C,C)$ coupling constants. The results indicate a substantial decrease of $^1J(C,C)$ upon complexation of the olefin and a small but significant dependence upon the nature of the transition metal. The values observed for unsubstituted or alkyl substituted sp^2,sp^2- and sp^2,sp^3-systems with metal coordination at the sp^2 C-atoms lie in the range of 37 to 47 Hz as compared with 40 to 75 Hz [2] for the parent hydrocarbons.

We have now extended our studies from η^4-diene to η^3-allyl and η^2-ene systems to explore the dependence of this parameter on the type of olefin coordination. In addition, some substituent effects on $^1J(C,C)$ in these three classes of olefin complexes have been investigated. The one-bond C,C-coupling constants were obtained

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[1]) ^{13}C-NMR. Spectroscopy, Part XXXI; Part XXX: [1].

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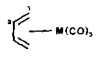
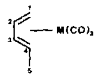
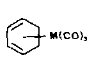
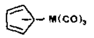
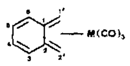
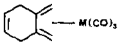
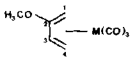
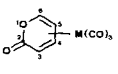
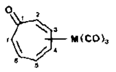
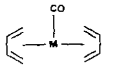
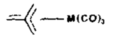
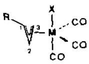
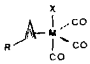
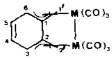
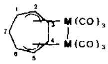
Table 1. *Coupling constants* $^1J(C,C)$ *[Hz]*[a]) *of free and* η^4*-complexed diene ligands*

		M	$J(1,2)$	$J2,3)$	$J(3,4)$	Other	
		-	68.8[b])	53.7[b])			
	1	Fe	43.9				
	2	Ru	42.4				
	3	Os	38.8				
						$J(4,5)$	
		-	69.3	54.0[c])	-	43.7[c])	
	4	Fe	43.3	43.5	46.2	43.0	
	5	Ru	42.1	42.5	44.4	41.5	
	6	Os	38.0	40.2	42.5	40.5	
						$J(1,6)$	
		-	68.0			40.5	
	7	Fe	42.7			38.5	
	8	Ru	40.8			37.5	
						$J(1,5)$	
	9	Fe	43.2			37.1	
			$J(1,1')$			$J(1,6)$	$J(5,6)$
	10	Fe	44.5			54.0	60.0
 **11**		Fe	44.2			41.2	40.6
			$J(1,2)$	$J(2,3)$	$J(3,4)$		
	12	Fe	52.0	53.8	44.8		
			$J(3,4)$	$J(4,5)$	$J(5,6)$	$J(2,3)$	
		-	61.0	50.3	68.7	72.5	
	13	Fe	38.6	43.5	45.5	66.5	
			$J(2,3)$	$J(3,4)$	$J(4,5)$	$J(1,2)$	$J(5,6)$
	14	Fe	38.7	45.2	41.0	50.5	51.2
						$J(6,7)$	$J(1,7)$
						65.7	55.0
			$J(1,2)$				
	15	Fe	46.1				
	**16**	Fe	39.9				

[a]) Error: <0.5 Hz. [b]) From [11]. [c]) Error: ±2 Hz.

from the ^{13}C-satellites of the proton-noise-decoupled ^{13}C-NMR. spectra with the isotope in natural abundance. At 25.2 and 50.3 MHz the ^{13}C-satellites are usually of the *AX* type since the coordination shifts for the two neighbouring olefinic C-atoms are sufficiently different. In the parent hydrocarbons these chemical shift differences may become small and are in the order of magnitude of the C,C-coupling constants. As an example, the resonances of C(1) and C(2) in 1,3-cyclohexadiene form an *AB* system which is partly hidden between the strong signals of the ^{13}C,^{12}C-isotopomers. In such cases an application of the pulse sequence DQBAX [10] allows to suppress the strong signals and thus an analysis of the *AB*-system. In the proton-noise-

Table 2. *Coupling constants* $^1J(C,C)$ *[Hz]*[a]) *of* η^3*-complexed allyl systems*

		R	M	X	$J(1,2)$	$J(2,3)$	$J(1,R)$
 A	**17A**	CH_3	Fe	Cl	45.8	44.0	40.6
	18A	H	Fe	Br	43.7		
	20A	H	Ru	Br	42.5		
 **B**	**18B**	H	Fe	Br	44.2		
	19A	H	Fe	J	44.2		
	19B	H	Fe	J	44.7		
					$J(1,1')$	$J(2,3)$	$J(3,4)$
	**21**		Fe		46.5	44.0	51.2
					$J(1,2)$	$J(2,3)$	$J(1,7)$
	**22**		Fe		43.8	44.5	40.0

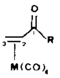
[a]) Error: <0.5 Hz.

decoupled spectra of η^4-complexed symmetric dienes the two central C-atoms are magnetically equivalent which does not allow the $^1J(C,C)$ coupling constant to be obtained.

The $^1J(C,C)$ data obtained from η^4-diene, η^3-allyl and η^2-ene complexes are collected in *Tables 1, 2* and *3*, respectively. The influence of the transition metal on the C,C-coupling constant in a complexed olefin can best be illustrated in the η^4-complexes. It has been shown that $J(1,2)$ exhibits a steady decrease in the sequence Fe,Ru,Os [7]. On the other hand, shielding of the terminal C-atom C(1) increases from 40.5 ppm in **1** to 32.7 ppm in **2** and 24.2 ppm in **3**, whereas C(2) is only very little affected. This indicates a considerable change in bonding of C(1) to the transition metal, which has also been described in terms of the ratio of coordination shifts $p = \Delta\delta C(1)/\Delta\delta C(2)$, which was found to increase from Fe to Os [12]. This effect can be described as arising from rehybridization of the terminal C-atom towards sp^3 and is also manifest in a relatively large negative $^2J(H,H)$ value (-3.48 Hz) in **3**. Since $^1J(C,C)$ is known to decrease with decreasing *s*-character of the σ-bond carbon orbitals, the observed behaviour of the C,C-coupling constants is thus in line with other experimental evidence [13] [14].

A comparison of $^1J(C,C)$ values in η^4-, η^3- and η^2-coordinated olefins shows a small but significant increase in this series, both for Fe and Ru complexes. The typical values given in *Table 4*, however, do not include data of substituted ligands. Furthermore, the coupling constants in η^4-diene complexes are not significantly influenced by the nature of the diene system, *e.g.*, very similar values are observed for complexes **1, 7, 9, 10** and **11**. Methyl substitution at C(1) of the butadiene ligand leads to a significant increase in the coupling constant at the substituted C-atom ($+2.4$ to $+4$ Hz). This effect is also observable in the substituted allyl complex **17**. Much larger substituent effects can be observed for heteroatoms as found in the 2-methoxybutadiene complex **12**. The trend is the same as in uncomplexed olefins [15]. The rather large OCH_3 substituent effect ($+8$ to 10 Hz) is confined to the coupling constants of C(2) with C(1) and C(3) and does not extend to the C(3), C(4)-bond indicating the inductive nature of the effect. For a discussion of the C,C-coupling constants in (α-pyrone)$Fe(CO)_3$ (**13**) and (tropone)$Fe(CO)_3$ (**14**), it is

Table 3. *Coupling constants* $^1J(C,C)$ *[Hz]*[a]) *of free and* η^2*-complexed ene ligands*

Complex		R	M	$J(2,3)$	$J(1,2)$
		H	–	68[b])	51.5
	23	H	Fe	45.2	50.6
	24	H	Ru	44.0	49.2
		OCH_3	–	68.5[b])	70.0
	25	OCH_3	Fe	47.2	73.3
	26	OCH_3	Ru	45.5	66.2

[a]) Error: <0.5 Hz [b]) Error: ±2 Hz

important to note that the substituent effect of a carbonyl group is small (+1 to 2 Hz), as reported for substituted olefinic and aromatic compounds [15] [16]. The parent compounds of both complexes are stabilized by cyclic π-electron delocalization leading to planar ring systems with aromatic character. The η^4-complexation of the diene system, however, is expected to destroy the planar structure of the ligands. As shown by X-ray analysis of the tropone complex [17] the plane of the four complexed C-atoms forms an angle of 43° with the plane of the three other ring C-atoms. Similarly, a non-planar ring structure was found for a bis($Fe(CO)_3$)-complexed styrene derivative [18]. Therefore, a non-planar structure can also be expected for the pyrone complex **13**. Owing to a rehybridization at the terminal C-atoms of the diene systems rather small C,C-coupling constants have to be expected for the terminal C,C-bonds in **13** and **14**. Whereas this is actually observed for $J(3,4)$ in **13** (38.6 Hz) and $J(2,3)$ in **14** (38.7 Hz) the values for the other terminal C,C-bond are larger as a result of specific substituent effects. Thus $J(5,6)$ in **13** (45.5 Hz) shows the characteristic positive effect of an O-bearing substituent (+7 Hz). A smaller but significant effect in the same direction is observed for the enone substituent at C(5) in **14**. The difference between $J(2,3)$ (38.7 Hz) and $J(3,4)$ (45.2 Hz) is in agreement with the C,C-bond lengths obtained from the crystal structure of **14** ($r(2,3) = (144.2 \pm 1.3)$ pm; $r(3,4) = (139.6 \pm 1.3)$ pm) [17]. The $^1J(C,C)$ data of the two compounds **15** and **16** which formally belong to this class of η^4-olefin complexes have been included in *Table 1*. Bis(butadiene)monocarbonyliron (**15**) gives $J(1,2) = 46.1$ Hz, a higher value than (butadiene)tricarbonyliron (**1**), whereas (trimethylenemethane)tricarbonyliron (**16**) yields the significantly lower value of 39.9 Hz. These deviations indicate a sensitivity of the C,C-coupling constant to a change in olefin-metal interaction, which in the present cases is also reflected in two very different ^{57}Fe shielding constants as compared with **1** [19].

The $J(C,C)$ values of η^3-allyl complexes *(Table 2)* do not exhibit a significant dependence upon the halogen ligand, *endo/exo* configuration of the C_3 unit or the presence of a metal-metal bond in the binuclear complexes. Methyl substitution, on the other hand, increases $J(1,2)$ and the corresponding value for **17** has not been included in *Table 4*.

The slight increase in $J(C,C)$ from η^4- to η^3-coordinated olefins extends towards η^2-ene complexes, for which a typical value of 46.0 ± 1.0 Hz can be extracted from the data given in *Table 3* for (ene)tetracarbonyliron complexes if the small substituent effect is taken into account [13].

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Table 4. *Typical ^1J (C,C) values [Hz] in complexed olefins*[a])

Coordination	Metal		
	Fe	Ru	Os
η^4	43.5 ± 0.5	42.3 ± 0.5	39.0 ± 1.0
η^3	44.2 ± 0.5	43.0 ± 0.5	
η^2	46.0 ± 1.0	44.5 ± 1.0	

[a]) sp^2,sp^2-Bonds without substituents.

Experimental Part

The ^{13}C-NMR. spectra were measured in the FT mode on *Varian* XL-100 (25.2 MHz) and XL-200 (50.3 MHz) spectrometers using 10 mm sample tubes equipped with a spherical microcell (0.4 ml) and stopcock joints. The sample solutions (50–80% *v/v*) were carefully prepared under N_2 with CD_2Cl_2 or C_6D_6. Proton-noise-decoupled spectra were obtained with 4 to 8 s acquisition time using double-precision accumulation (31 bit word length and 65 K words) on the XL-100 or floating point FT on the XL-200. For some spectra the pulse sequence DQBAX was used [10]. Under these conditions the C,C-coupling constants are accurate to better than ± 0.5 Hz.

The following compounds are commercially available and were purified before use: **1**, **4**, **7** *(Strem Chemicals Inc.)*, **15** *(Emser Werke)*, 1,3-pentadiene, 1,3-cyclohexadiene, acrolein, methyl acrylate, *α*-pyrone *(Fluka)*. Compounds **11** and **21** were kindly supplied by Prof. *S. Sarel* (Jerusalem). All other complexes were prepared according to literature: **2** [20], **3**, **5**, **6** [7], **8** [21], **9** [22], **13** [23], **16** [24], **17** [25], **18**, **19** [26], **20** [27], **23**, **25** [28]. The syntheses of the following complexes have been modified and details are described in two dissertations: **10**, **14**, **22** [14], **12**, **24**, **26** [13].

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