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Preliminary communication

$^{13}C-^{13}C$ coupling constants in a series of η^2-alkene complexes of rhodium(I)

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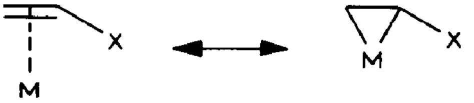
Abstract

^1J(C–C) has been determined in a series of closely related η^2-alkenerhodium(I) complexes and found to decrease by about 22 Hz on coordination. It is also observed to be linearly related to the electronegativity of the substituent in coordinated CH_2=CHX (X = C, O or Si).

We have recently measured ^1J(C–H) and ^1J(C–C) coupling constants in a series of closely related rhodium(I) complexes [1 *] and report our preliminary results at this time. The ^1J(C–C) values were observed at 125.8 MHz in samples containing carbon-13 in natural abundance using the double quantum coherence technique (INADEQUATE) [2]. The results are shown in Table 1.

Values for ^1J(C–H) of the alkenyl carbons in the rhodium complexes are essentially unchanged from those in the free alkenes. This effect is well documented in alkene complexes [4,5], and Tolman et al. [4] have noted that ^1J(C–H) changes by only 4 Hz in going from cyclopropane (^1J(C–H) 161 Hz) to ethene (^1J(C–H) 157 Hz). Using arguments based on earlier $^{13}C-^{13}C$ coupling data [6] they concluded that angle strain in three membered rings leads to a concentration of carbon *p*-orbital character in the C–C bonds of the ring and a corresponding concentration of *s*-orbital character in the C–H bonds. Consequently it is not possible to assess the relative importance of π-complex and metallocyclopropane contributing forms (I and II below) through measurement of ^1J(C–H).



(I) (II)

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* Reference number with asterisk indicates a note in the list of references.

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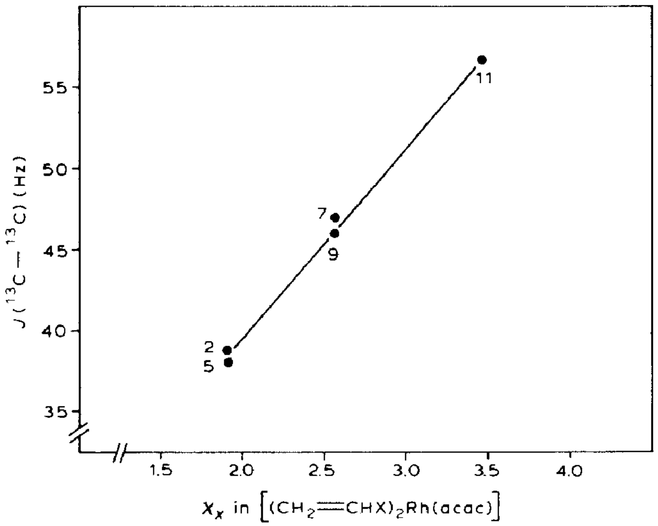

Fig. 1. Plot of $J(^{13}C-^{13}C)$ vs. the Pauling electronegativity [14] of X in $[(CH_2{=}CHX)_2Rh(acac)]$ [15*].

In striking contrast to the behavior of ${}^1J$(C–H), all known values of ${}^1J$(C–C) in alkene π-complexes are smaller than those observed in the uncoordinated alkenes. In a series of η^5-Cp-η,η^2-alkenylnickel(II) complexes, ${}^1J$(C–C) averages about 45 Hz [7], and for the tetracarbonyliron(0) and tetracarbonylruthenium(0) complexes of acrolein ${}^1J$(C–C) has the values of 45.2 and 44.0 Hz respectively [8]. This decrease in coupling upon complexation has been analyzed using the familiar model of Dewar [9] and Chatt and Duncanson [10] in terms of the relative importance of a metallo-cyclopropane contributing form (II above) in the structure of alkene-metal π-complexes [7]. Carbon–carbon coupling data are also known for a considerable number of η^4-butadiene [8,11] and η^3-allyl [12] complexes. They are consistent with known structural parameters and can be interpreted in terms of carbon hybridization changes, from sp^2 toward sp^3, in the complexed ligand.

We have also observed reduced carbon–carbon coupling in alkene-rhodium complexes. The value of ${}^1J$(C–C) in the vinylsilane complexes, **2** and **3**, is 38 and 38.6 Hz (see Table 1) respectively and is apparently insensitive to the minor perturbations in electron density at rhodium caused by substitution of Cp for acac. It also appears to be insensitive to substitution of OC_2H_5 for Me at silicon as seen in **5** (${}^1J$(C–C) 38 Hz). However, ${}^1J$(C–C) increases significantly to 46.8 Hz in **7** and 45.9 Hz in **9** when carbon replaces silicon as a substituent on the alkene. It increases even more to 56.6 Hz in **11** where oxygen is attached to the coordinated alkene. Interestingly, the shift in J(C–C) upon coordination, ΔJ(C–C), is remarkably constant in the series at about -22 ± 2 Hz.

Carbon–carbon coupling constants in free alkenes are known to be linearly dependent on the electronegativity of X in $CH_2{=}CHX$ [13]. The constant value of ΔJ(C–C) indicates that this linear dependence is retained in the rhodium complexes (see Fig. 1). Because of this, routine linking of observed carbon–carbon coupling data to arguments involving carbon hybridization in rhodium(I) complexes of substituted alkenes could lead to erroneous conclusions unless electronegativity effects are also carefully considered.

Table 1

Carbon-13 NMR chemical shifts, $J(^{13}C-^{1}H)$ and $J(^{13}C-^{13}C)$ for free alkenes and metal complexes [a] [3*]

No.	Compound	Chemical shifts [b]		Coupling constants [b]			ΔJ(C–C) (Hz)
		δ(C(1)) (ppm)	δ(C(2)) (ppm)	^1J(C(1) –H)	^1J(C(2) –H)	^1J(C(1) –C(2))	
1	$CH{=}CHSiMe_3$	140.2	131.1	131.5	153.4	58.8±1.3	–
2	$[(acac)Rh(CH_2{=}CHSiMe_3)_2$	64.1	69.0	134.4	157.2	38.6±0.9	–20.2
3	$[(C_5H_5)Rh(CH_2{=}CHSiMe_3)_2]$	53.4	39.5	131.6	156.2	38.0±1.2	–20.8
4	$CH_2{=}CHSi(OEt)_3$	130.6	136.0	143.1	159.4	58.2±11.2	–
5	$[(acac)Rh(CH_2{=}CHSi(OEt)_2)_2]$	54.8	70.0	138.7	160.4	38.0±3.0 [c]	–20
6	$(CH_2{=}CHCH_2)_2SiMe_2$	134.6	113.4	150.8	155.1	69.7±1.3	–
7	$[(acac)Rh(CH_2{=}CHCH_2)_2SiMe_2]$	77.0	61.0	157.0	157.0	46.8±1.7	–22.9
8	$CH_2{=}CHCMe_3$	149.6	109.3	149.6	155.3	70.0±1.2	–
9	$[(acac)Rh(CH_2{=}CHCMe_3)_2]$	90.4	57.2	149.0	156.9	45.9±1.5	–24.1
10	$CH_2{=}CHOEt$	152.2	85.9	179.8	158.7	78.4±1.3	–
11	$[(acac)Rh(CH_2{=}CHOEt)_2]$	113.5	38.7	176.7	154.8	56.6±1.6	–21.8
12	*trans*-$[PtCl_2(py)(CH_2{=}CHOEt)]$	139.5	42.9	186.2	163.4	51.0±1.3	–27.4

[a] $\underset{2}{C}{=}\underset{1}{C}$–X. [b] ^1J(C–H) (±3.6 Hz) and Chemical Shifts (±2.2 Hz) were assigned from the gated decoupled spectra and were observed at 90.8 MHz. ^1J(C–C) was observed at 125.8 MHz. [c] Broad resonance.

Although we have examined only a very limited number of complexes at this time we suggest that ΔJ(C–C) rather than ^1J(C–C) itself may be the important parameter to be used in discussing bonding and hybridization changes in coordinated alkenes. In this regard we note that ΔJ(C–C) in **12**, a platinum(II) complex, is –27.4 Hz, which is significantly larger than that found for the rhodium complexes. Additional studies are in progress.

References and Notes

1 (a) Complexes **2**, **5**, **7**, **9** and **11** were prepared as described in J.W. Fitch and W.T. Osterloh, J. Organomet. Chem., 213 (1981) 493; (b) Complex **3** was prepared from $[ClRh(CH_2{=}CHSiMe_3)_2]_2$ as described in S.M. Nelson, M. Sloan and M.G.B. Drew, J. Chem. Soc., Dalton Trans. (1973) 2195; (c) complex **12** was prepared as described in M.A.M. Meester, H. Van Dam, D.J. Stufkens and A. Oskam, Inorg. Chim. Acta, 20 (1976) 155. Samples were characterized spectrally and analytically and gave satisfactory results.

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3 Complexes were run in C_6D_6 (~ 0.5 g sample/ml). Typical INADEQUATE spectral parameters are: (a) For the free ligands τ 3.6 to 4.2 msec (corresponding to ^1J(C–C) ≈ 60 to 69 Hz) and; (b) For the metal complexes τ 6.25 msec, (corresponding to ^1J(C–C) ≈ 40 Hz). 16000 to 90000 pulses (in case of compound **5**).

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15 $R = 0.99844$ with a std. error of ± 0.04078. *F*-test shows this coefficient significant at the 0.0001 level.