

Preliminary communication

DIRECT MEASUREMENT OF $^1J(^{13}\text{C}-^{13}\text{C})$ IN COORDINATED DOUBLE BONDS

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Summary

$^1J(^{13}\text{C}-^{13}\text{C})$ has been determined in naturally abundant samples of η^1, η^2 -alkenyl- η^5 -cyclopentadienylnickel complexes; for the coordinated double bonds $^1J(\text{C}-\text{C})$ lies between the value for free ethylene and cyclopropane, and therefore gives direct insight into the relevant bonding situation.

Complexation of olefins to transition metals is generally described by the Chatt—Dewar—Duncanson model [1] due to which the resonance hybrids (A) and (B) may be regarded as extreme descriptions of the bonding possibilities. (A)



characterises the donor bonding from the olefin π -orbitals to the metal orbitals, whereas (B) describes the backbonding from the filled metal orbitals into the π^* -ethylene orbitals. The variations of the ^1H [2] and ^{13}C [3] chemical shifts upon complexation of the olefin are often rationalised in terms of the relative weighting of (A) and (B), although the basis for this approach has been criticised. In contrast to the chemical shifts the $^1J(\text{C}-\text{H})$ coupling constants alter little upon complexation, and this may be due to a similar $^1J(\text{C}-\text{H})$ coupling constant in free ethylene (156.3 Hz) and cyclopropane (160.5 Hz) [4]. The vicinal H,H couplings are more sensitive to complexation but the changes are relatively small and difficult to interpret (typical values are 9 Hz for *cis* and 12 Hz for *trans* couplings in coordinated ethylene [2]). The most marked changes can, however, be expected for $^1J(^{13}\text{C}-^{13}\text{C})$ in coordinated

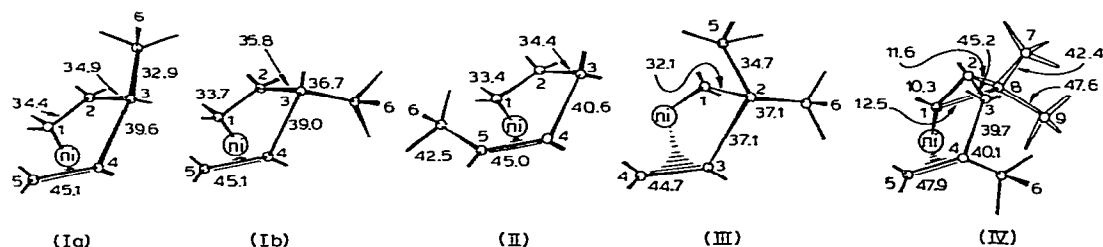
double bonds, since this coupling is 67.2 Hz in free ethylene and about 13 Hz in cyclopropane [5]. We have therefore measured the ^{13}C – ^{13}C coupling constants in a series of η^1, η^2 -alkenyl- η^5 -Cp-transition metal complexes in naturally abundant samples using the double quantum coherence technique [6].

The $J(\text{C}–\text{C})$ coupling constants of η^5 -Cp- η^1, η^2 -3-methyl-4-pentenylnickel (I), η^5 -Cp- η^1, η^2 -(*Z*)-4-hexenylnickel (II), η^5 -Cp- η^1, η^2 -2,2-dimethyl-3-butenylnickel (III) [7] and η^5 -Cp- η^1, η^2 -[2,2-dimethyl-3(*Z*)-(2'-methyl-2'-propenyl)]-cyclopropylnickel (IV) [8] are listed in Table 1.

TABLE 1

CHEMICAL SHIFTS AND COUPLING CONSTANTS OF I–IV

(The shifts were measured at 310 K and are referenced to the solvent THF- d_8 ($\delta \equiv 25.3$). The coupling constants stem from one-dimensional double quantum measurements at 100.62 MHz. Error limits for $J(\text{C}–\text{C})$: in I ± 0.3 , in II ± 0.5 , in III ± 0.2 and in IV ± 0.7 Hz)



ni = NiCp

	δ	δ	δ	δ	δ
1	2.14	5.13	8.79	-7.64	21.97
2	33.51	33.64	39.49	35.48	28.68
3	41.73	38.53	28.11	58.43	37.89
4	85.46	87.82	83.01	48.95	103.11
5	43.14	45.80	63.33	32.26	53.75
6	21.63	21.98	16.26	29.98	29.49
7	—	—	—	—	28.11
8	—	—	—	—	21.53
9	—	—	—	—	23.60

For I diastereoisomers are obtained with the methyl group in the *endo* (Ia) and *exo* (Ib) positions relative to the ring defined by Ni and C(1)–C(5). Since most of the respective C–C coupling constants of Ia and Ib are identical within the error limits the assignments of the individual carbons was confirmed by a two-dimensional carbon–proton shift correlation map [9] from the known proton shifts [7]. The assignment of the carbons in III [7] and IV [8] is based on the proton shifts using the selective decoupling technique [10]. The relative assignment of C(2) and C(3) in II is unambiguous from $^1J(\text{C}–\text{C})$. For III two “long range” carbon–carbon couplings could be obtained (cf. Fig. 1(c)) by choosing the delay for the creation of the double quantum coherence 0.08 s which corresponds to $J(\text{C}–\text{C}) = (2n + 1)/(4 \times 0.08)$ ($n = 0, 1, 2, \dots$) [6]. In III $^2J(\text{C}(1)–\text{C}(3))$ is 8.5 and $^3J(\text{C}(4)–\text{C}(6))$ is 3.2 Hz.

$^1J(\text{C}–\text{C})$ for the complexed double bonds lies between 44 and 48 Hz (cf. Table 1) and is in the middle of the values for free propylene and cyclopropane

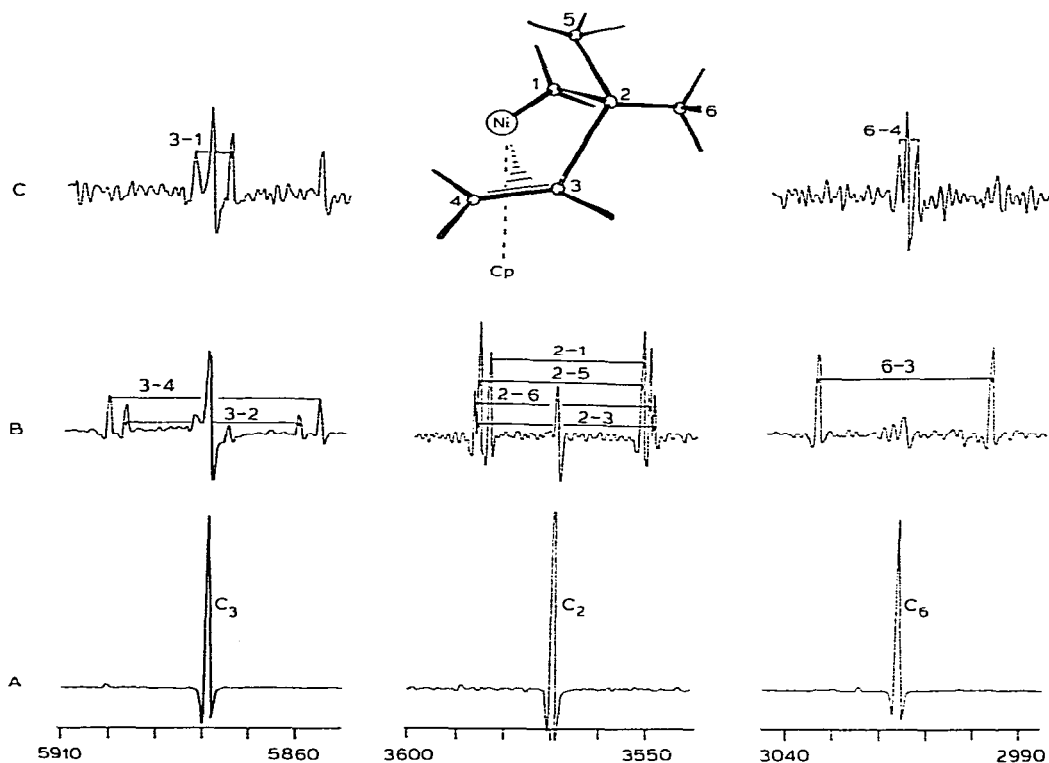


Fig. 1. 100.6 MHz ^{13}C -spectrum of III in $\text{THF-}d_8$. (A) normal spectrum of C(2), C(3) and C(6); (B) and (C) double quantum spectra with refocussing; spectral width 5000 Hz, the 90° ^{13}C pulse was $21 \mu\text{s}$, the delay for creation of the double quantum coherence was 0.0062 s in (b) and 0.08 s in (c). The spectra were recorded with 32 phase cycling and a total of 1600 scans. The lines are resolution enhanced using the Lorentz-to-Gauss line shape transformation.

[5]. These values also agree well with those found for $^1J(\text{C}(1)\text{—C}(2))$ in η^4 -butadienetricarbonyliron [11]. The reduction of this coupling can be interpreted with significant participation of resonance hybrids of the type (B). Apparently in I–IV there is no simple correlation between $^1J(\text{C—C})$ of the complexed double bond and the coordination shift [12]. In III the situation is complex: $^1J(\text{C}(1)\text{—C}(2))$ and $^1J(\text{C}(2)\text{—C}(3))$ are relatively small and $^2J(\text{C}(1)\text{—C}(3))$ becomes remarkable large (possibly due to the existence of several coupling pathways or due to considerable strain in the chain). Normally the two bond couplings are less than 5 Hz [5,10] and often not resolvable. Since I–IV have rigid conformations the differences for $^1J(\text{C—CH}_3)$ are of special interest. The $^1J(\text{C—CH}_3)$ couplings are enhanced up to 37.1 Hz when the methyl group lie in, or nearly in the plane of the double bond as C(6) in Ib and III.

These results show that $^1J(\text{C—CH}_3)$ are structure dependent parameters and $^1J(\text{C—C})$ of coordinated double bonds throws light on the bonding situation and may indicate the complexation strength.

References

- 1 M.J.S. Dewar, *Bull. Soc. Chim. France*, (1951) C71; J. Chatt and L.A. Duncanson, *J. Chem. Soc.*, (1953) 2939.
- 2 M.L. Maddox, S.L. Stafford and H.D. Kaesz, *Adv. Organomet. Chem.*, 3 (1965) 1.
- 3 O.A. Gansow and W.D. Vernon, *Top. Carbon-13 NMR Spectrosc.*, 2 (1976) 269.
- 4 J.B. Stothers, *Carbon-13 NMR Spectroscopy*, Academic Press, New York, 1972.
- 5 V. Wray, *Progr. Nuc. Magn. Res. Spectros.*, 13 (1979) 177.
- 6 A. Bax, R. Freeman and S.P. Kempell, *J. Am. Chem. Soc.*, 102 (1980) 4849.
- 7 The preparation of Ia, Ib, II and III and some ^{13}C assignments are reported by H. Lehmkuhl, A. Ruffńska, R. Benn, G. Schroth and R. Mynott, *Liebigs Ann. Chem.*, (1981) 317.
- 8 H. Lehmkuhl, Ch. Naydowski, R. Benn and A. Ruffńska, *J. Organometal. Chem.*, 216 (1981) C41; R. Benn, J. Klein, A. Ruffńska and G. Schroth, *Z. Naturf. B*, 36 (1981) 1595.
- 9 A. Bax and G.A. Morris, *J. Magn. Res.*, 42 (1981) 501.
- 10 F.W. Wehrli and T. Wirthlin, *Interpretation of Carbon-13 NMR Spectra*, Heyden, New York, 1978.
- 11 K. Bachmann and W. von Philipsborn, *Org. Magn. Reson.*, 8 (1976) 648.
- 12 The coordination shifts $\Delta\delta$ are defined as $\Delta\delta = \delta(\text{complex}) - \delta(\text{ligand})$; $\Delta\delta$ values can be obtained by comparison of the shifts of the complexed double bonds (cf. Table 1) with those of the corresponding alkenes [4]; arithmetic averages $\overline{\Delta\delta}$ for the two double bond carbons in I-IV are $\overline{\Delta\delta}$ (Ia) = -64.3; $\overline{\Delta\delta}$ (Ib) = -61.8; $\overline{\Delta\delta}$ (II) = -54.3; $\overline{\Delta\delta}$ (III) = -75.3; $\overline{\Delta\delta}$ (IV) = -49.6. In $\eta^5\text{-Cp-}\eta^1, \eta^2\text{-[2,2-dimethyl-3(Z)-(1',1'-dimethyl-2'-propenyl)]cyclopropyltriphenylphosphinoruthenium } ^1J(\text{C}(4)\text{-C}(5))$ is 43.9 Hz and $\overline{\Delta\delta}$ is -75.4.