Metal–Allyl Bonding Studied by $J(^{13}C,^{13}C)$

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The $J(^{13}C,^{13}C)$ coupling constants of simple allyl compounds of lithium, potassium, magnesium bromide, tin, zirconium, chromium, molybdenum, tungsten, nickel, and platinum as well as of several alkyl-substituted (η^3-allyl)(η^5-cyclopentadienyl)nickel isomers and five- to eight-membered cyclic (η^3-allyl)(η^5-cyclo-pentadienyl)nickel complexes have been determined on natural abundant samples. In the delocalized allyl residues of Li and K $^1J(^{13}C,^{13}C)$ lies at about 59 Hz whereas in the transition-metal complexes $^1J(^{13}C,^{13}C)$ is found between 50 and 40 Hz, depending on the bonding situation. The variations of $^1J(^{13}C,^{13}C)$ can be rationalized by the relative weighting of donor and acceptor bonding in contrast to $J(^{13}C,H)$ and $J(H,H)$ that, in addition to the metal–allyl bonding, are markedly influenced by deviations of the protons from the coplanarity of the allyl skeleton. Alkyl substituents in the syn position at C_x produce an increase in $^1J(^{13}C_x,^{13}C)$ of the allyl skeleton. In the cyclic η^3-allyl compounds $^1J(^{13}C,^{13}C)$ is not affected by the central allyl bond angle.

Introduction

Transition-metal allyl complexes occupy a central position in both the catalytic transformations of olefins[1] and the understanding of the metal π bonding.[2] Although nearly the complete series of the transition-metal complexes of the type $M_n(\text{allyl})_m$ was prepared in the early sixties,[3] the solution and solid-state structure of some of them is still unknown and a systematic discussion of their NMR data with respect to the role of the metal is overdue.[4] Several reasons may account for this. First, only for some of the allyl compounds, a X-ray structure could be obtained.[5–7] On the other hand, in solution several isomers may exist,[8,9] and various fluxional processes may preclude the deduction of their structure by NMR techniques. Recently, the gap between X-ray and high-resolution NMR information has been shortened by the development of low-temperature solid-state NMR facilities,[10] and solid-state NMR spectra of some pure allyl compounds,[11] using the CPMAS technique[12] seem rather promising. Second, even if all the standard solution NMR parameters of the different metal allyl isomers in the absence of any dynamic process are available, they are still difficult to quantify. For example, the coordination shift $\Delta\delta(^{13}C \text{ NMR})$[13] cannot be estimated in the usual way, since the shifts of the allyl ligand itself are unknown. Information about the allyl bonding in principle also can be expected from the $J(^{13}C,H)$[14] and $J(H,H)$ coupling constants.[9,15] However, in η^3-delocalized allyl systems we have found $^2J(H,H)$ and

$^4J(H,H)$ to be relatively small. This also holds for the variations of $^3J(H,H)$ with the metal. Marked changes, however, are found for $^1J(^{13}C,H)$. As well as the proton–

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† Dedicated to Professor Dr. Mult. G. Wilke, on the occasion of his 60th birthday.

Table I. Optimal Cyclization of the Transmitter and Receiver Phases in the INADEQUATE[26b] Experiment without Refocusing[a]

no.	90	180	90	90	FID
1–8	x	±x	x	x	x
9–16	x	±x	x	y	−y
17–24	x	±x	x	−x	−x
25–32	x	±x	x	−y	y
33–40	x	±x	−x	x	−x
41–48	x	±x	−x	y	y
49–56	x	±x	−x	−x	x
57–64	x	±x	−x	−y	−y
65–72	x	±y	x	x	−x
73–80	x	±y	x	y	y
81–88	x	±y	x	−x	x
89–96	x	±y	x	−y	−y
97–104	x	±y	−x	x	x
105–112	x	±y	−x	y	−y
113–120	x	±y	−x	−x	−x
121–128	x	±y	−x	−y	y

[a] Each row of this table is cycled in four steps and therefore yields eight scans in total.

proton spin coupling constants, this parameter can also be expected to be affected by deviations of the protons from the coplanarity of the allyl skeleton.[16] $J(^{13}C,^{13}C)$[17,18] provides the most direct information on the allyl bonding of the allyl moiety. We have therefore employed the IN-ADEQUATE[19] technique for the systematically investigation of $J(^{13}C,^{13}C)$ in a variety of metal allyl compounds using samples containing ^{13}C in natural abundance.

Our main interest was to evaluate whether $J(^{13}C,^{13}C)$ may be regarded as a reliable parameter to study the role of the metal in bonding to the allyl carbon atoms. In addition, besides variation of the metal, we have also studied the influence of substituents in the allyl moiety and the dependence of $J(^{13}C,^{13}C)$ on ring strain and the bond angle in the allyl residue by taking into account also cyclic allyl compounds. Furthermore it was hoped that a correlation could be found between $J(^{13}C,^{13}C)$ and the bond length where available from X-ray data. Finally, an understanding of $J(^{13}C,^{13}C)$ in relation to bonding in the metal allyls should permit a better interpretation of $J(C,H)$ and $J(H,H)$.

Experimental Section

Materials. The allyl compounds 1–10 were prepared by using standard procedures.[20] The synthesis of the various alkyl-substituted $(\eta^3$-allyl$)(\eta^5$-cyclopentadienyl)nickel isomers 12–17[21] as well as the cyclic $(\eta^3$-allyl$)(\eta^5$-cyclopentadienyl)nickel complexes 18–22[22] has been reported previously together with some NMR spectral parameters.[23-25]

The NMR measurements were carried out using highly concentrated or saturated solutions in tetrahydrofuran-d_8 and a sample volume of ca. 3 mL in a sealed 10-mm sample tube at

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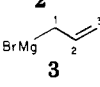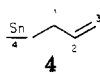
Scheme I. $J(C,C)$ in Allyl Metal Complexes
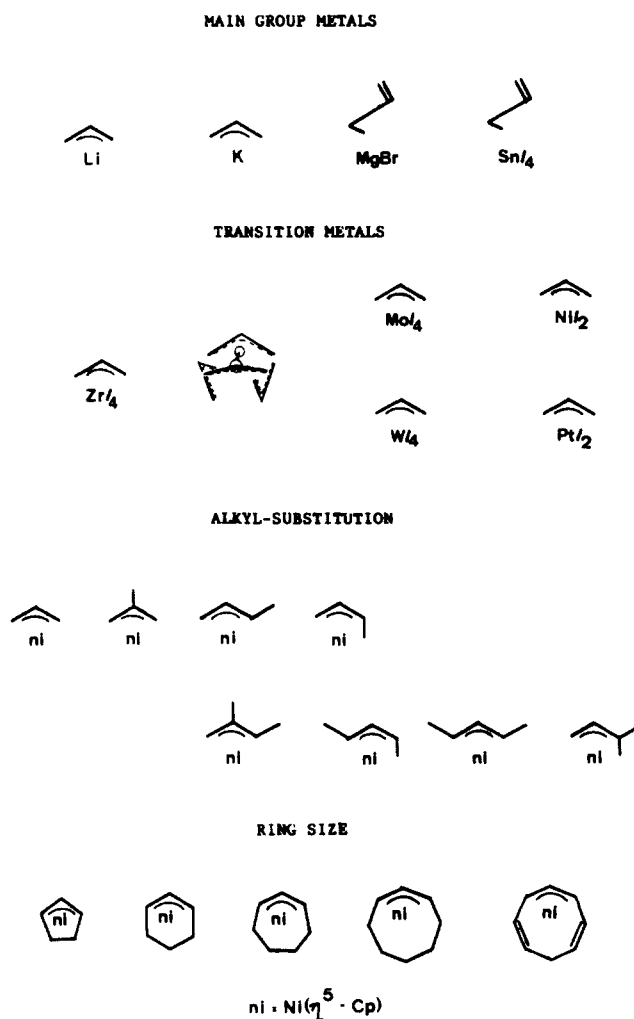
ambient temperatures (cf. Tables II–IV).

NMR Spectra. All ^{13}C NMR spectra were obtained at 100.6 MHz under temperature control by using a 10-mm broad-band multinuclear probe of high sensitivity. The length of the 90° carbon pulse was 19 μs. In addition to the INADEQUATE spectra proton broad-band decoupled and gated decoupled spectra were recorded under similar conditions for all the samples. Generally, the whole spectra range up to the 15 000 Hz spectral width was covered, but in some cases subspectra were also recorded. The corresponding digital resolution of the FIDs varied from 0.2 to 0.9 Hz. The INADEQUATE spectra were recorded both with and without refocusing, but due to the relatively long T_1 values of the samples (between 2 and 30 s at 310 K) marked differences in signal sensitivity were not detected. In nearly all cases a preparation time on the order of T_1 of a carbon bearing only one proton was chosen.[26] For the INADEQUATE spectra a 128-phase cycling (Table I) was employed. For the more dilute samples polarization transfer techniques[26,27] were applied prior to the INADEQUATE sequence, while for some mixtures of alkyl-substituted $(\eta^3$-allyl$)(\eta^5$-cyclopentadienyl)nickel isomers INADEQUATE was combined with SEFT[28] for better satellite separation. The FIDs were subjected to apodization with Gauss functions[29] in those cases where the signal to noise ratio was high, or otherwise exponential multiplication was performed. Before Fourier transformation zero filling was carried out yielding a

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Table II. ^{13}C Chemical Shifts ^1J(C,H), and ^1J(^{13}C,^{13}C) of Simple Metal Allyl Compounds[a]

Compound	^1J(C,C), Hz		$\delta\ ^{13}$C			^1J(C,H), Hz					b
	1,2	2,3	1	2	3	1s	1a	2	3s	3a	
1 (Li)	(0.8) 58.7	58.7	50.3	145.9	50.3	149.8	140.8	132.2			
2 (K)	(1.0) 59.9	59.9	52.8	144.3	52.8	154.9	142.8	131.8			
3 (BrMg)	(1.0) 54.2	54.2	57.3	137.3	57.3	$^1/_2$(1,H + 3,H) = 136.0		138.7			
4 (Sn)	(1.0) 41.5	69.6	16.4	136.7	111.4	131.8		150.9	157.7	152.6	
6a (Cr)	(0.5) 46.4	47.9	70.9	130.6	76.5	161.7	149.0	151.4	164.8	150.4	1-3
	43.6	43.6	58.6	101.5	58.6	152.2	152.2	151.4	152.2	152.2	11, 12
	44.2	44.2	55.8	106.0	55.8	159.5	148.3	151.4	159.5	148.3	21, 22
6b (Cr)	(0.8) c	c	72.9	131.0	75.6	161.8	148.4	150.2	164.5	150.9	31-33
	46.6	48.3	69.8	135.7	76.1	161.8	148.1	148.9	165.1	148.4	41-43
	44.5	44.5	57.6	102.6	54.2	151.8	151.8	150.2	151.8	151.8	51-53
	44.4	44.4	54.8	104.4	53.5	c	c	152.6	157.6	147.5	61-63
5 (Zr)	(0.8) 48.2	48.2	66.1	138.4	66.1	153.2		148.5	153.2		
7 (Mo)	(0.3) 45.5	45.5	66.4	102.9	48.8	158.6	149.4	156.7	63.5	155.8	
8[d] (W)	(0.3) 42.4	43.2	61.4	99.3	43.2	157.5	147.3	158.2	164.6	155.2	
9 trans (Ni)	(0.8) 43.5	43.5	52.6	112.0	52.5	161.2	150.9	154.0	161.2	150.9	
10a[e] trans (Pt)	(0.4) 40.0	40.0	46.7	102.8	46.7						
10b[e] cis (Pt)	(0.4) 40.4	40.4	48.5	104.8	48.5	161.0	155.5	157.9	161.0	155.5	

[a] a = anti; s = syn. [b] Numbering of the allyl carbons in 6a and 6b. [c] Not assigned. [d] J(W,C$_1$) = 13.8 Hz and J(W,C$_3$) = 7.5 Hz. [e] 10a, J(Pt,C$_1$) = 224.6 Hz and J(Pt,C$_2$) = 61.2 Hz. 10b, J(Pt,C$_1$) = 225.8 Hz and J(Pt,C$_2$) = 54.8 Hz.

maximal transformation size of 256 K. The measurement times for the satellite spectra varied between 1 h and overnight.

Results and Discussion

All the J(^{13}C,^{13}C) coupling constants have been obtained from samples containing ^{13}C in natural abundance. Due to the relatively low solubility (2, 3, 9, 10) and to the thermal sensitivity (5, 6, 9, 10), high demands were placed upon the stability and sensitivity of the spectrometer. The satellite spectra of bis(η^3-allyl)platinum 10 (cf. Figure 1) may serve as an example for the precision achieved in such measurements.

In (η^3-allyl)transition-metal complexes ^1J(^{13}C,^{13}C) lies between 40 and 50 Hz (cf. Tables II–IV). For their discussion with respect to the bonding in metal allyls the dichromium tetraallyl complex 6a will be taken as a representative example and the donor–acceptor bonding scheme due to the Chatt, Dewar, and Duncanson model[2] will be used for interpretation. In the major isomer 6a[9]

there are two allyl groups that bridge the two chromium atoms and two nonbridging η^3-allyl groups. These different bonding situations are also reflected by ^1J(^{13}C,^{13}C), which is smaller for the bridging allyl groups.

We interpret this as being due to significant participation of the ψ_2 allyl orbital in this bonding. On the other hand, the larger value of J(^{13}C,^{13}C) in the nonbridging allyl group indicates a dominant donor bonding by overlap of the low-lying metal orbitals with ψ_1. The interpretation given above is also in line with the geminal proton–proton spin–spin coupling constants[9] that indicate more rehybridization toward sp^3 at the terminal carbons of the bridging allyl groups (smaller J(^{13}C,^{13}C)) rather than at the nonbridging ones (larger J(^{13}C,^{13}C)). This picture can be extended to all the simple transition-metal allyl compounds listed in Table II. Consequently, the largest ^1J(^{13}C,^{13}C) values are found in the group 4B metal complexes, indicating a relatively strong involvement of donor bonding with ψ_1 and that back-bonding plays only a minor part.

Table III. ^{13}C Chemical Shifts, ^1J(C,H), and ^1J(^{13}C,^{13}C) of Substituted (η^3-Allyl)(η^5-cyclopentadienyl)nickel Compounds[a]

allyl group	^1J(C,C), Hz	$\delta\ ^{13}$C 1	2	3	4	5	J(C,H), Hz 1	2	3	4	5
12	1,2 = 42.1 (0.5) 2,3 = 42.1	40.24	91.54	40.24			157.4	164.6	157.4		
13	1,2 = 41.2 (0.6) 2,3 = 41.2 2,4 = 42.5	42.51	107.05	42.51	24.24		156.4		156.4	127.0	
14a	1,2 = 42.5 2,3 = 43.5 3,4 = 41.4	36.33	92.32	58.37	21.37		157.0	162.2	154.9	126.1	
14b	1,2 = 42.8 (0.5) 2,3 = 42.3 3,4 = 41.4	38.60	91.29	56.49	16.88		157.0	161.7	153.4	126.7	
15a	1,2 = 42.3 2,3 = 43.3 3,4 = 41.5 4,5 = 33.8	36.25	90.43	66.72	28.46	15.33	157.3	163.1	153.1	126.3	125.6
16a	1,2 = 42.4 (0.5) 2,3 = 43.7 5,6 = 34.3	36.24	91.16	64.41	37.84	24.54 13.73	157.3	163.7	153.0	127.1	126.0 126.2
15d	1,2 = 41.2 (0.5) 2,3 = 42.3 3,4 = 41.0	38.66	89.72	65.19	24.14	16.78	157.0	163.7	153.0	127.1	126.8
17a	1,2 = 42.7 2,3 = 43.0 2,CH$_3$ = 42.1 3,CH$_3$ = 41.7	40.97	104.27	56.97	18.43	26.26	156.7		151.9	126.5	126.8
17b	1,2 = 42.6 2,3 = 43.8 3,4 = 41.5 3,5 = 41.5	35.86	91.66	72.15	30.92	23.17	156.7	163.5		125.8	126.4
15b	1,2 = 43.7 2,3 = 43.7 3,4 = 41.5	54.06	94.40	54.06	20.81		154.5	160.3	154.5	126.0	
15c	1,2 = 44.6 2,3 = 42.6 1,CH$_3$ = 41.5 3,4 = 41.4	55.93	93.12	51.95	17.53 21.41 (CH$_3$)		154.8	161.5	153.1	126.3 126.5 (CH$_3$)	
16b	1,2 = 43.5 2,3 = 44.1 1,CH$_3$ = 41 3,4 = 41.2 4,5 = 34.2	54.32	92.46	62.57	28.11 20.84 (CH$_3$)	15.85	154.5	159.9	154.0	125.7 126.2 (CH$_3$)	126.2
16c	1,2 = 44.3 2,3 = 41.5 1,CH$_3$ = 41.4 3,4 = 40.5 4,5 = 35.1	56.24	91.57	60.95	24.92 21.45 (CH$_3$)	16.71	154.8	161.2	151.0	126.2 126.2 (CH$_3$)	126.8
16d	1,2 = 42.6 2,3 = 44.1 1,CH$_3$ = 41.0 3,4 = 41.3 4,5 = 34.1	52.08	91.24	64.33	28.66 17.53 (CH$_3$)	15.46	153.2	162.0	153.4	126.2 126.5 (CH$_3$)	127.0

[a] T = 310 K; solvent is THF-d_8. Error limit for ^1J(^{13}C,^{13}C) = 0.3 Hz, unless in parentheses.

The reverse is true in the group 8B metal complexes, and consequently in diallylplatinum J(^{13}C,^{13}C) is lowered to 40 Hz.

In the main-group metal allyl compounds 1–4 J(^{13}C,^{13}C) is relatively large (cf. Table II). In the η^1 complexes 3 and 4 the average value for J(^{13}C,^{13}C) is 55 Hz, just like for propene.[30] The delocalized allyl system in the Li and K complexes yields larger values in good agreement with ionic bonding. Significant overlap from the ψ_2 orbital of the allyl anion into the Li orbitals of p-type can be ruled out, since this should produce smaller J(^{13}C,^{13}C) values.

The influence of substituents at the allyl carbon atoms on ^1J(^{13}C,^{13}C) has been investigated by using different alkyl-substituted (η^3-allyl)(η^5-cyclopentadienyl)nickel isomers. Generally, ^1J(^{13}C,^{13}C) is only affected a little by such substituents (cf. Table III). The increase in ^1J(^{13}C,^{13}C) of about 1–2 Hz when the substituents are in the syn position seems significant. Similar effects are observed when ethylene is substituted with alkyl groups,[30] and this is

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Table IV. ^{13}C Chemical Shifts, ^1J(C,H), and ^1J(^{13}C,^{13}C) of Cyclic (η^3-Allyl)(η^5-cyclopentadienyl)nickel Complexes[a]

allyl group	^1J(C,C), Hz	δ ^{13}C					^1J(C,H), Hz				
		1 = 3	2	4	5	6	1	2	4	5	6
18	1,2 = 40.6 (0.2) 3,4 = 37.5	62.4	88.6	37.5			165.4	175.2	131.8		
19	1,2 = 40.2 3,4 = 38.8 (0.2) 4,5 = 34.0	59.2	86.3	27.5	23.9		156.4	167.1	125.7	127.6	
20	1,2 = 40.5 (0.3) 3,4 = 39.8 4,5 = 34.1	63.8	87.9	34.2	27.0		149.6	160.9	125.0	125.0	
21	1,2 = 41.5 3,4 = 39.7 (0.8) 4,5 = 31.4 5,6 = 34.7	59.0	94.2	33.8	27.3	24.4	152.0	161.7	126.3	125.1	126.9
22	1,2 = 43.4 3,4 = 53.0 (0.8) 4,5 = 70.2 5,6 = 39.7	59.7	79.3	131.0	122.7	28.4	151.7	163.7	160	151	130

[a] All samples in THF-d_8; T = 310 K. Error limits for ^1J(^{13}C,^{13}C) in parentheses.
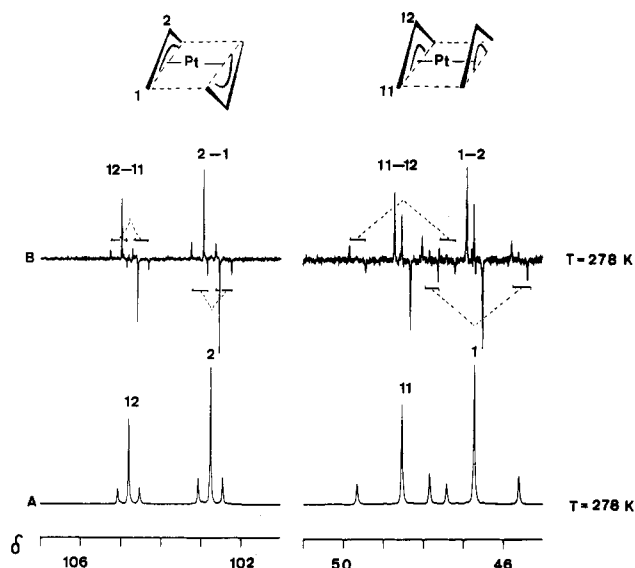

Figure 1. 100.6-MHz spectra of bis(η^3-allyl)platinum 10. (a) Normal proton broad-band decoupled spectrum at 278 K. In both isomers the platinum satellites are broadened due to the chemical shift anisotropy relaxation. (b) INADEQUATE spectrum without refocusing using the 128-phase cycles. Even the platinum satellites of the ^{13}C–^{13}C satellites can be detected, but an isotope effect for J(^{13}C–^{13}C,^{195}Pt) was not observed.

interpreted as due to changes in the electronegativity. Similar arguments should hold for the allyl system, and in line with this interpretation a shortening of the C1–C2 bond length is observed when alkyl substituents are introduced in the syn position to C_1.[31a] Alkyl substituents in the antiposition do not alter ^1J(C_1–C_2). Apparently, the effects due to the changes in electronegativity are compensated by changes in geometry of the allyl skeleton.

Before discussing the role of the metal in allyl bonding, it is essential to prove that ^1J(^{13}C,^{13}C) is not governed by other factors like steric effects or strain in the allyl residue. We have therefore investigated J(^{13}C,^{13}C) in cyclic (η^3-allyl)(η^5-cyclopentadienyl)nickel complexes (cf. Table IV).

Scheme II

$ni = (\eta^5\text{-Cp})Ni$
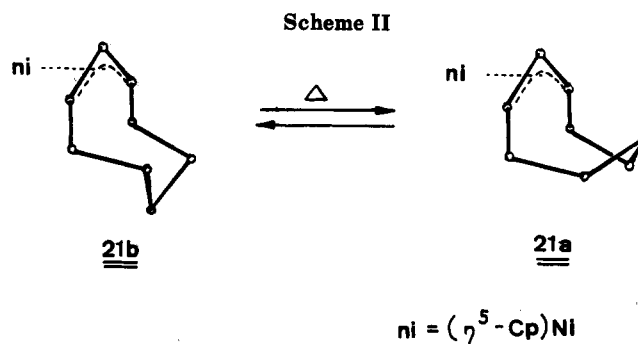
In contrast to the H,H and C,H spin–spin coupling constants the carbon–carbon constants remain nearly unchanged for the allyl carbon atoms and are close to those observed for the corresponding noncyclic η^3-allyl compound 12. (Note that substituents in the anti position do not alter ^1J(^{13}C,^{13}C) as has been discussed in the previous section.) On the other hand, J($^{13}C_3$,$^{13}C_4$) seems to depend on the ring size, as was also observed in cyclic alkenes.[30] The relatively small value for ^1J($^{13}C_4$,$^{13}C_5$) in the eight-membered ring 21 is remarkable. Moreover, the spectra of 21 are temperature dependent: resonances 1, 2, 3, 5, and in particular 6 broaden between 283 and 193 K and additionally resonance 1 is shifted continuously by 1.5 ppm and resonance 6 by 2.1 ppm to lower δ values when the temperature is lowered to 173 K. In contrast the δ value and half-width of 4 remain unaffected between 300 and 173 K. Even at 173 K, when all lines were sharp again, no second set of signals could be observed. We interpret this as due to a temperature-dependent equilibrium between conformations 21a and 21b (cf. Scheme II). At lower temperatures in 21 the quasi-boat conformation is dominantly populated (γ-gauche interaction between C-6 and C-1 or C-3), whereas at higher temperatures the chair conformation becomes more populated.

A reasonable correlation has been noted between ^1J(^{13}C,^{13}C) and the force constant (K) for the C—C and C=C bonds.[32] We have looked for a relation between J(^{13}C,^{13}C) and the bond distances in the allyl skeleton. Although

(31) (a) Jolly, P. W.; Wilke, G. "The Organic Chemistry of Nickel"; Academic Press: New York, 1976, Vol. 1, p 359. (b) *Ibid.* p 370.

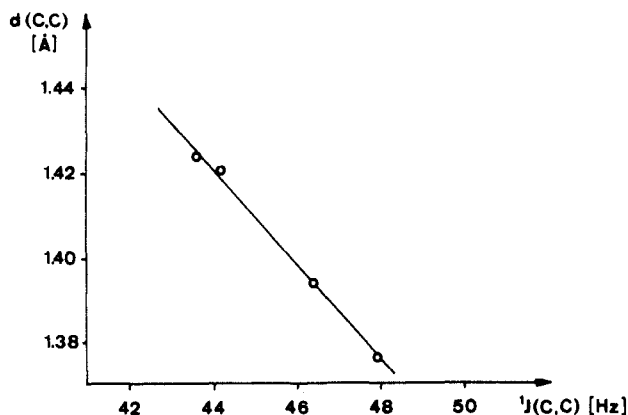(32) Kamienska-Trela, K. *Spectrochim. Acta, Part A* 1980, *36A*, 239.

Figure 2. Correlation between $^1J(^{13}C,^{13}C)$ and the corresponding bond distances in **6a**. The bond lengths are taken from an X-ray analysis.[6c] Although there is no element of crystallographic symmetry for **6a** in the solid state, the distances to those carbons that become equivalent in solution are identical within the limits of error: $d(C_1,C_2)$ = 1.394 ± 0.003 Å, $d(C_2,C_3)$ = 1.376 ± 0.002 Å, $d(C_{11},C_{12})$ = 1.424 ± 0.002 Å, and $d(C_{21},C_{22})$ = 1.421 ± 0.008 Å.

Scheme III
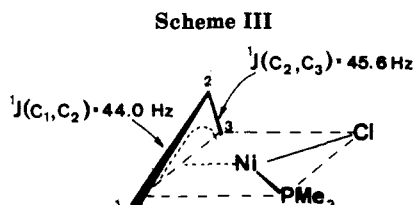
more X-ray data have to be collected for a more quantitative analysis (e.g., for **5**, **10**, and in particular **1** more refined data would be of interest), the linear correlation in **6** seems promising (cf. Figure 2).

Furthermore the X-ray data for **9**[7] and bis(η^3-cyclooctatrienyl)nickel[8] are very similar, in line with the nearly identical $J(^{13}C,^{13}C)$ values for **9** and **22**. Although there are no X-ray data of **18–21** available to us, we should note that for a corresponding four-membered cyclic η^3-allyl compound, $(\eta^3\text{-}(CH_3)_4C_4C_5H_5)Ni(\eta^5\text{-}C_5H_5)$, the allyl bond length is relatively large (1.44 (2) Å),[31b] consistent with a relatively small $^1J(^{13}C,^{13}C)$ value in **18–21**. The trans effect in metal complexes with a square-planar geometry can also be monitored by $J(^{13}C,^{13}C)$. In (η^3-allyl)(trimethylphosphane)nickel chloride besides the chemical shifts the

$^1J(^{13}C,^{13}C)$ values of the allyl carbons reflect the difference in the bond lengths directly (cf. Scheme III).

Comparing the metal allyl compounds **1–10** it is striking that $J(^{13}C,^{13}C)$ decreases when descending the relevant groups of the periodic table and when going from the early to the late transition metals (e.g., compare $J(^{13}C,^{13}C)$ in **7, 8, 9**, and **10a**). This can be rationalized by the increasing involvement of the ψ_2 and ψ_3 orbitals in the transition metal-allyl bonding. It should be noted that these trends cannot be monitored as easily by $\delta(^{13}C)$ and $^1J(C,H)$, which are usually used for the discussion of the bonding situation.[33] This interpretation is also in line with the fluxional behavior of the homoleptic allyl complexes. Generally syn–anti exchange processes, for which σ-allyl forms are assumed as intermediates, proceed at higher rates in **10a** rather than in **9** and in **8** rather than in **7**, respectively. According to the changed role of donor and acceptor orbitals in the ionic metal-allyl bonding $J(^{13}C,^{13}C)$ appears to be larger in **1** rather than in **2**. Again, this is in line with the configurational stability of the allyl anions that increases with the electropositivity of the metal atom.[34]

To summarize, the carbon–carbon coupling constants in metal allyl complexes are dominantly affected by the type of metal and its orbitals involved in the allyl bonding. They correlate with the bond lengths within the allyl skeleton, while the C–C bond angle leaves $^1J(^{13}C,^{13}C)$ unaffected.

(33) Apparently the different $^1J(C,H_{syn})$ and $^1J(C,H_{anti})$ coupling constants in **9** indicate the different degrees of deviation of the respective protons from the allyl plane (for the detailed proton positions cf. ref 7c). This interpretation probably can be extended to all the corresponding $^1J(C,H)$ couplings in **1–10**.

(34) Vrieze, K. In "Dynamic Nuclear Magnetic Resonance Spectroscopy"; Jackman, L. M., Cotton, F. A., Eds.; Academic Press: New York, 1975; p 448.