Preliminary communication

$J(^{13}C—^{13}C)$ IN ALLYLMETAL COMPLEXES

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Summary

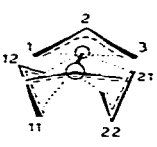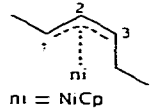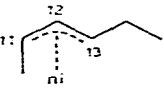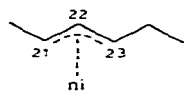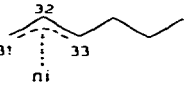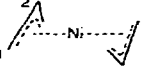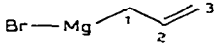The $J(^{13}C—^{13}C)$ coupling constants of simple allyl compounds of nickel, chromium, magnesium and lithium have been determined on natural abundance samples. In transition metal complexes $^1J(^{13}C—^{13}C)$ is reduced to 41 Hz (Ni) whilst in allyllithium it is 58.7 Hz.

The structure and fluxional behaviour of the simple allylmetal complexes has been well studied by X-ray analysis or NMR spectroscopy [1,2]. In spite of considerable volume of NMR data [3] the chemical shifts and spin—spin coupling constants are difficult to interpret and in particularly difficult to quantify, since the NMR parameters of the allyl ligand itself cannot be obtained. Moreover, there is discussion [2c,4] about the interpretation of the relatively small $^1J(C(2)—H)$ coupling constants in allyl-alkali metal compounds. In order to get more insight into the nature of the allyl-metal bonding we have determined the NMR parameter $^1J(^{13}C—^{13}C)$ by using the double quantum coherence technique [5] for measuring $^1J(^{13}C—^{13}C)$ in natural abundance in a variety of simple allyl-metal complexes.

In Table 1 are listed selected $^1J(^{13}C—^{13}C)$ coupling constants together with the corresponding $^1J(C—H)$ couplings and some bond lengths of (tetraallyl)dichromium (I) [1b], η^5-cyclopentadienyl-η^3-*syn*-1-methyl-*anti*-3-ethylallylnickel (II), η^5-cyclopentadienyl-η^3-*anti*-1-methyl-*syn*-3-ethylallylnickel (III), η^5-cyclopentadienyl-η^3-*svn*-1-methyl-*syn*-3-ethylallylnickel (IV), η^5-cyclopentadienyl-η^3-*syn*-3-propylallylnickel (V) [6], diallylnickel (VI) [1,7], allyllithium (VII) [1a,2] and allylmagnesium bromide (VIII) [1a,2a]. In I $^1J(^{13}C—^{13}C)$ is significantly larger in the non-bridging η^3-allyl groups than in the bridging η^3-allyl groups, indicating that there is more σ-character in the bond of C(11)—C(12) than in C(1)—C(2) or C(2)—C(3). Of special interest is the fact that all the differences in the bond lengths [8] are also reflected in the $^1J(^{13}C—^{13}C)$ couplings, at least qualitatively.

TABLE 1

SELECTED $^1J(^{13}C-^{13}C)$, $^1J(C-H)$ COUPLING CONSTANTS AND BOND DISTANCES IN I—VIII. I measurement in THF-d_8 at $-20°C$, VI in toluene-d_8 at $-30°C$, VII in THF-d_8 at $-70°C$, II, III, IV, V and VIII in THF-d_8 at $+37°C$. For I, II, III, IV, V and VII the double quantum technique with recofussing was employed; for VI and VIII the spectra were recorded in the normal mode. Long range couplings in VI (*trans* isomer): $^2J(C(1)-H_{meso})$ 3.7, $^3J(C(2)-H_{syn})$ 10.5 and $^3J(C(1)-H_{anti})$ 3.7.

		$^1J(^{13}C-^{13}C)$ (Hz)		$^1J(C-H)$ (Hz)				$d(C-C)$ (Å)	
	(I)	(±0.5)		1-*syn*	= 161.7;	1-*anti* = 149.0			
				2-*meso*	= 151.4				
				3-*syn*	= 164.8;	3-*anti* = 150.4	[8]		
		1,2	= 46.4	11-*syn*	= 152.2;	11-*anti* = 152.2		1,2	= 1.39
		2,3	= 47.9	12-*meso*	= 151.4			2,3	= 1.38
		11,12	= 43.6	21-*syn*	= 159.5;	21-*anti* = 148.3		11,12	= 1.42
		21,22	= 44.2	22-*meso*	= 151.4			21,22	= 1.42
	(II)	(±0.3)							
		1,2	= 44.1	1-*anti*	= 154.9				
		2,3	= 41.6	2-*meso*	= 161.1				
		1,CH_3	= 41.3	3-*syn*	= 150.9				
		3,CH_2	= 41.0						
	(III)	(±0.3)							
		11,12	= 42.4	11-*syn*	= 153.2				
		12,13	= 44.0	12-*meso*	= 160.9				
		11,CH_3	= 41.6	13-*anti*	= 153.4				
		13,CH_2	= 41.3						
	(IV)	(±0.3)							
		21,22	= 43.5	21-*anti*	= 154.4				
		22,23	= 44.1	22-*meso*	= 160.2				
		21,CH_3	= 41.4	23-*anti*	= 152.6				
		23,CH_2	= 41.3						
	(V)	(±0.3)							
		31,32	= 42.7	31-*syn*	= 157.3,	31-*anti* = 157.3			
		32,33	= 43.5	32-*meso*	= 161.2				
		33,CH_2	= 41.3	33-*anti*	= 152.9				
	(VI)	(±0.8)							
		1,2	= 43.5	1-*syn*	= 161.2;	1-*anti* = 150.8	[7]		
				2-*meso*	= 154.0		1,2 = 1.41		
	(VII)	(±0.8)							
		1,2	= 58.7	1-*syn*	= 149.8;	1-*anti* = 140.8			
				2-*meso*	= 132.4				
	(VIII)	(±1)		½(1-H+3-H) = 136.0					
		½(1,2+2,3)	= 53.5	2-H	= 138.7				

One bond couplings between sp^2 hybridized carbons are generally larger [9] : the reduction of $^1J(C-C)$ in I may therefore be attributed to back-donation of electrons from the metal orbitals into the ψ_2 and ψ_3 allyl orbitals, which also affects the vicinal H,H couplings [1b] and the bond lengths [8]. Compared with the early transition metal complexes η^3-allyl complexes of nickel can be assumed to involve stronger back-bonding, and this is in line with smaller $^1J(^{13}C-^{13}C)$ values in II—VI compared to those of the non-bridging allyl groups of I. In II—V some long range couplings could be observed. In II $^3J(CH_3-C(3))$ is 4.8, $^3J(C(1)-CH_2)$ is 2 and $^3J(C(2)-CH_3)$ is 3.6 Hz, an average of the former two values. Just like the $^3J(C-H)$ couplings (cf. Table 1), the $^3J(C-C)$ couplings show a Karplus-type
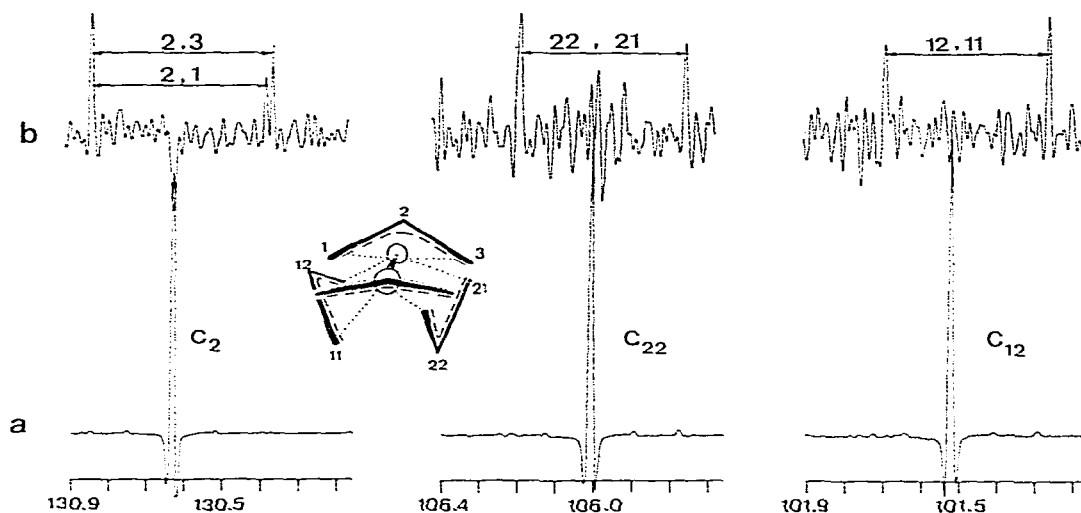
Fig. 1. 100.6 MHz spectrum of $(\eta^3\text{-allyl})_4Cr_2$ in THF-d_8 at $-20°$C. (a) carbon signals 2, 22 and 12 of the broadband decoupled spectrum; (b) ^{13}C—^{13}C coupling constants from INADEQUATE spectra with refocussing. All lines are resolution enhanced by Lorentz-to-Gauss transformation.

bond angle dependence [10] on the allyl skeleton: $^3J(C$—$C)$ for dihedral angles of $\phi = 180°$ is greater than found for $\phi = 0°$.

In the main group allylmetal complexes VII and VIII, $^1J(C$—$C)$ is significantly larger than in the transition metal complexes. The average for $^1J(^{13}C$—$^{13}C)$ in the fluxional η^1-allylmagnesium bromide (VIII) is 53.5 Hz, close to the average value for propene (56 Hz) [9]; the 2.5 Hz reduction may be due to the electropositivity of magnesium. In contrast to VIII, the allyl group in VII forms a delocalized symmetrical trihapto-allyl system, as evidenced by the low temperature NMR spectra [1a]. Some low temperature ^{13}C NMR data are given in Table 1; as in the other η^3-allyl complexes, $^1J(C$—$C_{syn})$ is significantly larger than $^1J(C$—$C_{anti})$ indicating that the *anti*-protons are bent out of the allyl plane and point away from the metal. This interpretation is in agreement with the results of the X-ray analysis of VI [7a] and theoretical calculations for VI [7b] and VII [11]. In VII $^1J(C$—$C)$ is 58.7 Hz [12], and so in the range of values found for sp^2 carbon atoms with π-bond order less than unity [9]. In VII the small $^1J(C$—$H)$ couplings, especially $^1J(C(2)$—$H)$ and the relatively large $^1J(C$—$C)$ coupling, can be rationalized if a dominant anionic type of bonding with $C(1)$—$C(2)$—$C(3)$ angle widening is assumed, but a minor degree of overlap of the HOMO of the anion and the vacant Li^+ p-type orbital cannot be ruled out.

These results show that in allyl metal complexes the values of $^1J(^{13}C$—$^{13}C)$ provide a sensitive parameter for investigation of the nature of the allyl bond.

References

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12 In ref. 2c for VII ^1J(C—C) 55.9 Hz is reported. The value in Table 1 refers to a 25% solution of VII in THF-d_8 measured at −70°C (under these conditions the frozen structure of VII is observed at 100.6 MH: using a natural abundance sample and the double quantum coherence technique. 58.7 Hz fit well to a π-bond order of 0.707 in the allyl anion (HMO modell, for comparison: in benzene ^1J(C—C) is 57.0 and the π-bond order is 0.67).