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Preliminary communication

Carbon magnetic resonance spectra of representative organometallic π-propene complexes

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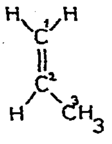
SUMMARY

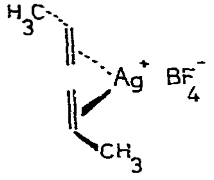
The ^{13}C magnetic resonance spectra of silver, rhodium and iron complexes of propene are reported and discussed.

Recent advances, and in particular pulsed Fourier transform techniques, allow ^{13}C NMR spectra to be obtained routinely for compounds of moderately high molecular weight[1], and have led to a number of recent communications regarding application to transition metal organometallic systems[2]. Since the local magnetic anisotropies and shieldings which complicate interpretation of proton chemical shifts are very much less important in CMR valuable information on the nature of metal–ligand bonding may become available through systematic study of carbon chemical shifts. We have therefore begun an examination of π-propene complexes derived from various transition metals, and offer some preliminary observations which suggest certain general conclusions. The spectra of propene (I), dipropene silver tetrafluoroborate (II)[3], cyclopentadienyl(propene)irondicarbonyl trifluoroacetate (III)[4] and dipropenerhodium acetylacetonate (IV)[5] were recorded as 20–50% solutions in $CDCl_3$ by pulsed Fourier transform (typical conditions; $T_W = 8$ μsec, $T_R = 0.99$ sec, 2000 scans) at 25.41 MHz and results are recorded in Table 1.

It is fruitful to consider the data with regard to the extreme canonical structures corresponding to pure donor bonding (V) and acceptor bonding (VI). The effect of (V) upon carbon chemical shifts is uncertain, since one has the deshielding due to positive charge density in opposition to a shielding induced by reduction of π-bond-order. It is likely, however, that the chemical shift difference between the olefinic carbon atoms of propene will be increased since positive charge will be more readily accommodated at the methyl-bearing carbon. Conversely, contribution of (VI) to the bonding scheme will



(I)



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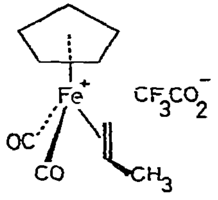

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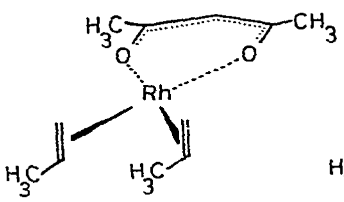
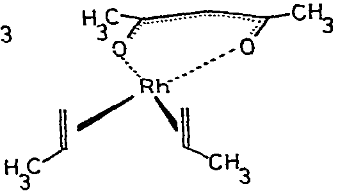


(IVa)

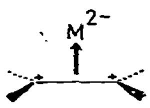


(IVb)

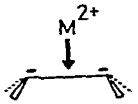
TABLE 1[a]

	C_1	C_2	C_3	$\delta(C_2-C_1)$	Other		
(I)	118.6	136.8	22.4	18.2			
(II)	109.4	138.5	23.0	29.1			
(III)	58.0	88.8	24.4	30.8	Cp 91.3		
(IV)	65.0[b]	75.8[c]	23.3	11.4	Acac	CH_3	30.14
	63.8[b]					CH	101.8
						C–O	125.3

[a] Spectra were referenced to internal $CDCl_3$ and are recorded in ppm. (δ $(CH_3)_4Si$ 0).
[b] J(Rh–C) 13.7 Hz. [c] J(Rh–C) 15.5 Hz.



(V)



(VI)

cause shielding through rehybridisation, and is likely to decrease the chemical shift difference between the carbon atoms of propene, since it is well-recognised that methyl substitution affects the chemical shift of unsaturated carbon more than that of saturated carbon★.

On this basis it is apparent, in line with the observations of Roberts and co-workers[6]

★ Closely related models for the effect of rehybridisation, e.g., (I) vis-a-vis propylene oxide or sulphide, are apparently not available.

on cyclopentene complexes of silver nitrate, that π-donation is the major contributor to silver–olefin bonding. There is an appreciable shielding of C_1, and back-donation from silver cannot be entirely ruled out[7]★ although it is at best feeble. The iron complex (III) shows a similar $\delta(C_1-C_2)$, but both resonances are shifted much further upfield, clearly indicating a much greater contribution from back-donation. Dissipation of positive charge to the cyclopentadienyl ring is indicated by deshielding relative to cyclopentadienyliron dicarbonyl chloride (δ 85.6 ppm) and ferrocene (δ 68.4 ppm). In the rhodium complex (IV) the average chemical shift of C_1 and C_2 is similar to the values found for (III), but the splitting $\delta(C_1-C_2)$ is very considerably smaller; we interpret this as implying an increased contribution of (VI) relative to (V) in the neutral complex. The close similarity of the methyl resonances in (I)–(IV) is notable, and accords with the similarity between the methylene chemical shift of cycloheptatriene and its Group VI tricarbonyl metal complexes[8].

There are two further features of interest in (IV). The ^{13}C NMR spectrum of the corresponding ethylene complex has been recorded[9], and shows an ethylene resonance at 35.9 ppm, which is 28.5 ppm upfield of the C_1 resonance in (IV) notwithstanding the fact that the corresponding chemical shifts in ethylene and propene are within 3 ppm. This implies that ethylene is a considerably better acceptor than propene. Furthermore, the C_2 resonance in (IV) is split into two doublets. The minor splitting is due to rhodium–carbon coupling, but it seems necessary to postulate the existence of two geometrical isomers ((IVa) and (IVb) or related rotamers) in order to explain the second splitting. The ^1H NMR spectrum of (IV) at 60 and 220 MHz may also be interpreted on this basis, but the carbon spectrum shows the effect very much more clearly.

ACKNOWLEDGEMENT

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★The π-acceptor component of silver–olefin bonding is predicted to be weak by extended Hückel calculations. Additionally the C=C bond length in silver–olefin complexes is similar to that of the olefins themselves.