^{13}C NMR SPECTRA OF η^3-ALLYLMANGANESE TETRACARBONYL COMPOUNDS; STRUCTURAL IMPLICATIONS *

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Summary

The ^{13}C NMR spectra of η^3-allylmanganese tetracarbonyl complexes are consistent with an overall C_s symmetry and involving a σ_v plane in the Mn(CO)$_4$ fragment. A dynamic carbonyl interchange process was looked for but the results are inconclusive, however the barrier for this process is certainly greater than 42 kJ/mol. This observation suggests an octahedral type geometry rather than a square pyramid type configuration.

Introduction

The bonding and rotational barriers in transition metal M(CO)$_3$ compounds have recently been studied theoretically by Hoffmann et al. [1] (fragment analysis). In connection with other synthetic interests, we have had occasion to further investigate the geometric structure of some η^3-allylmanganese tetracarbonyl compounds, a much less investigated class. The parent allyl compound has been studied by Davidson and Andrews [2] using IR and Raman spectroscopy. These authors considered two possible structures, both having C$_s$ symmetry and both having a square pyramidal base for the Mn(CO)$_4$ group, i.e. structures I and II. These structures have, respectively, a σ_v and σ_d symmetry plane, involving the M(CO)$_4$ fragment. The "σ_v" structure I was tentatively favored.

Recently, ^{13}C NMR spectroscopy has become widely used for metal carbonyl structure determinations and is ideally suited to both distinguish between these possibilities and to potentially measure the rotational barrier between I and II. In addition, the ^{13}C chemical shifts for the allyl carbons in the η^3-allyl part and in the corresponding σ-allylmanganese pentacarbonyl complex were measured.

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* Dedicated to Professor H.C. Brown in recognition of his contributions to chemistry.

Top view

(I)

σ_v

(II)

σ_d
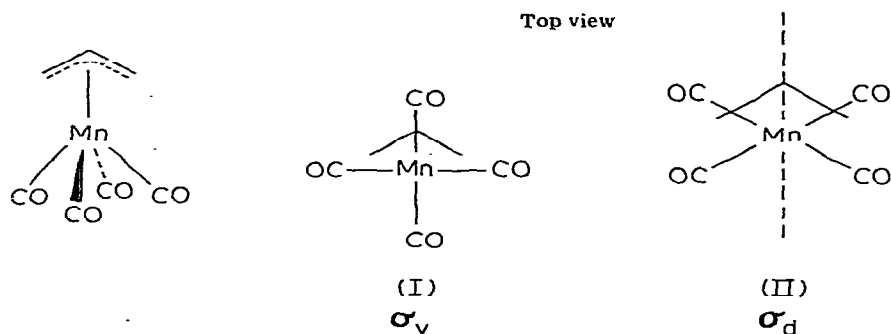
Results

Three η^3-allyl compounds were studied, the parent (III, R = H), and the ethyl and isopropyl-substituted analogs III (R = ethyl and isopropyl respectively). The ^{13}C.NMR data are collected together in Table 1. At $-95°$C, the carbonyl

(III)
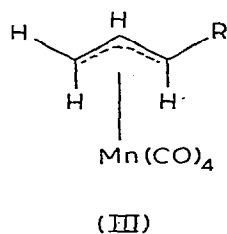
region of the parent compound shows three peaks, in a 2/1/1 intensity ratio,

TABLE 1

^{13}C NMR CHEMICAL SHIFTS AND COUPLING CONSTANTS[a] OF ALLYLMANGANESE CARBONYLS

Compound	C(1)	C(2)	C(3)	CO	Others
III (R = H)	43.2	93.8	43.2	222.6(x2)	
	(161)	(157)	(161)	216.4	
				215.6	
III (R = Et)	37.0	92.7	71.0	221.5	28.7 (C(4))
	(162)	(157)	(150)	220.8	17.2 (C(5))
				217.0	
				215.6	
III (R = i-Pr)	36.9	91.2	80.1	222.1	33.7 (C(4))
	(160—165)	(155)	(157)	221.4	23.6 (C(5))
				217.4	23.9 C(5'))
				215.9	
IV	9.0	147.7	106.2	213.9(x4)	
	(141)	(148)	(153)	211.8	

[a] Measured at $-95°$C relative to internal TMS, coupling constants are in brackets in Hz.
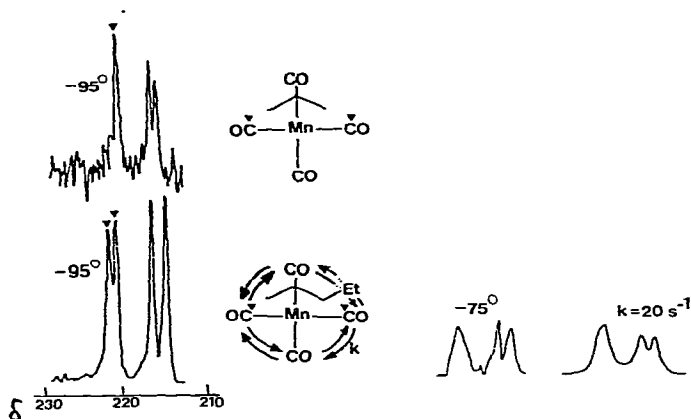
Fig. 1. Carbonyl region of the ^{13}C NMR spectrum of the manganese tetracarbonyl complexes shown. Matching curves are for the line-broadening expected from a possible turnstile rotation.

while the substituted analogs show all four carbonyls as distinct peaks. The ^{13}C NMR spectra of the carbonyl region for the parent and ethyl-substituted compounds are shown in Fig. 1. As one raises the temperature of the solution, the carbonyl peaks broaden and also appear to decrease in area. A spectrum of the ethyl compound (III, R = ethyl), at —75°C, is shown in Fig. 1 and a computer calculated matching curve for the line-broadening expected for a turnstile mechanism is also shown (an alternative ligand "flip-over" process would broaden only two of the carbonyl peaks). The rate constant shown is that based on a single step, which can statistically be either clockwise or anticlockwise. At temperatures higher than —55°C, the C≡O peaks become weak and broad and no useful matching could be attempted. However, the temperature response of the line-broadening seems rather flat and it is very probable that the quadrupolar ^{55}Mn nucleus is also instrumental in causing line-broadening. At 25°C, for example, a sharp averaged peak would be expected from dynamic averaging, whereas only a very weak and broad peak was observed, albeit in approximately the position for an averaged chemical shift. In any case, we can certainly put an upper limit of $k = 20$ sec^{-1} at —75°C for a possible turnstile mechanism, $\Delta G^{\neq} \geqslant$ 42 kJ/mol, the implication being however that the origin of the observed broadening is not conclusively proven. It should be noted that similar, temperature dependent, quadrupolar broadening has been observed in the ^{13}C spectra of η^1-pentacarbonylmanganese complexes [3], although at —75°C, the signals appear fairly sharp. Relaxation agents are not particularly useful for Mn—CO complexes [4].

The number of carbonyl peaks observed is consistent only with a "σ_v" symmetry for the $M(CO)_4$ fragment and one can confidently assign the two carbonyl ^{13}C regions as shown in Fig. 1. However, the relatively large rotational barriers which would have to exist between I and II lead us to question the square pyramid assumption. Using the treatment of Elian and Hoffmann [5], one can qualitatively compare the energy levels for the $M(CO)_4$ fragment in the square pyramid configuration and in the alternative C_{2v} "partial octahedral" configuration (Fig. 2). In either case, the main correlation is between a singly filled (mainly d_{yz} in character) e or b_2 orbital and the π_2 level of the allyl fragment.
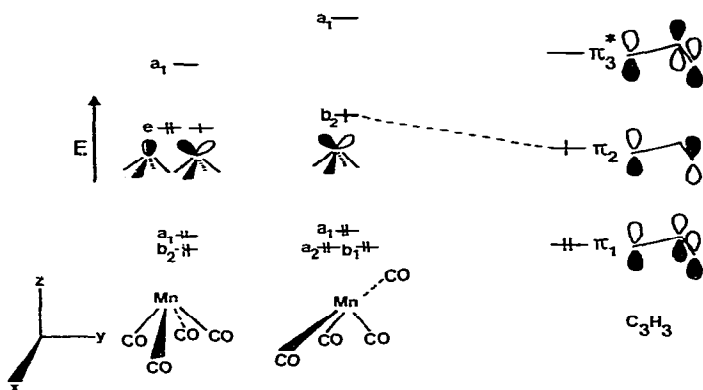
Fig. 2. Fragment interaction diagram for the Mn(CO)$_4$ fragment and an allyl fragment (no MO's are shown). On the left, the energy levels are given for both the square pyramid and "partial octahedral" geometries.

In the square pyramid structure, this orbital is degenerate with a mainly d_{xz} orbital and hence neither are directional in the M(CO)$_4$ fragment. This degeneracy is only broken by the allyl fragment itself and this would suggest rather low rotational barriers for a turnstile rotation of the M(CO)$_4$ group. However, one can distort the M(CO)$_4$ fragment to remove the degeneracy present in the square pyramid structure and this would logically involve increasing the CO—M—CO angle for the CO ligands in the xz plane. With a corresponding decrease in the other CO—M—CO angle, this leads eventually to the "partial octahedral" levels shown in Fig. 2. In this latter case, the bonding to the allyl fragment is expected to be strongly directional and the compound should have the high rotational barriers typical of octahedral complexes. This arrangement retains the overall C_s symmetry and the σ_v plane and thus agrees with the vibrational spectra results. For steric reasons, one might actually have a compromise situation between the extremes shown in Fig. 2.

The ^{13}C chemical shifts and coupling constants for the allyl portion of these complexes are listed in Table 1. One notes that the central C(2) carbon is found at lowest field, consistent with the donation of electron density from the metal to the π_2 orbital of the allyl fragment, in which C(2) contains a nodal plane. The ^{13}C—H coupling constants are typical of sp^2-hybridized carbons, as expected for a π-bonded allyl framework.

^{13}C NMR spectra of an η^1-allylpentacarbonyl derivative

Table 1 also lists the ^{13}C chemical shifts and C—H coupling constants for the monohapto-allyl complex IV. The CO region consists of two peaks in a 4/1 area ratio, as expected for octahedral geometry [3] and rapid rotation about the Mn—CH$_2$ bond. The allyl shifts are quite normal except that the C(1)—H coupling constant is rather large for an sp^3-hybridized carbon.

$$\begin{array}{c}
\text{H} \\
| \\
\text{CH}_2\text{—C}\text{=\!=}\text{CH}_2
\end{array}$$

OC — CO

Mn

OC — CO

CO

(IV)
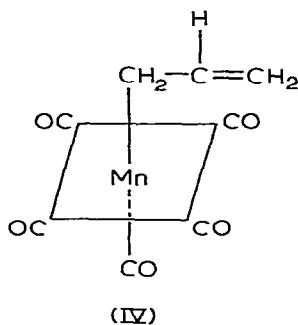
Experimental

The ^{13}C NMR spectra of the complexes were determined (ca. 10% solutions) in acetone-d_6 or CFCl$_3$ solutions using a Bruker WH-90 NMR spectrometer and are referenced to internal tetramethylsilane. No relaxation agents were added [4]. The temperature calibration of the instrument was checked using a thermocouple. Infrared spectra were determined for all of the complexes and are available on request (Perkin—Elmer model 467). Proton NMR spectra were determined using a Varian HA-100 (the data in brackets are multiplicity, d = doublet, t = triplet, dt = two sets of triplets etc., number of protons and assignment). NMR line-broadening was simulated using a computer-derived solution of the exchange modified Bloch equations.

Compounds

η^3-Allylmanganese tetracarbonyl (III, R = H) was prepared via the η^1-allyl precurser using described procedures [6,7]. The ethyl analog, tetracarbonyl [(1,2,3-η)-2-pentenyl]manganese (III, R = ethyl) was prepared in a similar manner using a 1-bromo-2-pentene/3-bromo-1-pentene (7/3) mixture [8,9], b.p. 69—71°C/3 mmHg. The ^{1}H NMR had (CDCl$_3$): δ 1.42 (d, 1, anti-H(1)), 2.44 (d, 1, syn-H(1)), 4.54 (dt, 1, H(2)), 2.74 (quintet, 1, H(3)), 1.96 (quintet), 2, H(4)), 1.12 (t, 3, H(5)); $J_{anti\text{-}1\text{-}2}$ 12 Hz, $J_{syn\text{-}1\text{-}2}$ 6 Hz, J_{23} 12 Hz, J_{34} 6 Hz, J_{45} 7 Hz. IR: ν(CO) at 2072, 2020, 1992, 1974, 1956 cm^{-1}. Anal.: Found: C, 45.61; H, 3.80. C$_9$H$_8$O$_4$Mn calcd.: C, 45.78; H, 3.84%. The isopropyl analog, tetracarbonyl-[(1,2,3-η)-4-methyl-2-pentenyl]manganese (III, R = isopropyl) was prepared from 1-bromo-4-methyl-2-pentene (mixture) [8,10]. The η^1-complex was distilled at 45°C/0.01 mmHg and had ^{1}H NMR (CDCl$_3$): δ 1.80, (d, 2, 1-CH$_2$), 5.76 (dt, 1, H(2)), 5.30 (dd, 1, H(3)), 2.11 (octet, 1, H(4)), 0.95 ppm (d, 6, CH$_3$); J_{12} 14.2 Hz, J_{34} 6.2 Hz, J_{13} 0.8 Hz, J_{45} 6.5 Hz. IR: ν(CO) 2005, 1950, 1940 cm^{-1}. The η^3-complex was formed on heating the pentacarbonyl to 85—95°C and had ^{1}H NMR (CDCl$_3$): δ 1.39 (d, 1, anti-H(1)), 2.43 (dd, 1, syn-H(1)), 4.54 (dt, 1, H(2)), 2.72 (dd, 1, H(3)), 2.15 (octet, 1, H(4)), 1.12 and 1.14 ppm (d, 3, 3, 5 and 5' CH$_3$). $J_{anti\text{-}1\text{-}2}$ 11.1.Hz, $J_{syn\text{-}1\text{-}2}$ 7.0 Hz, $J_{anti\text{-}1\text{-}syn\text{-}2}$ 2.0 Hz, J_{23} 11.2 Hz, J_{45} 6.0 Hz. IR: ν(CO) 2063, 2009, 1988, 1970, 1952 cm^{-1}. Anal.: Found: C, 47.81; H, 4.36. C$_{10}$H$_{11}$O$_4$Mn calcd.: C, 48.02; H, 4.43%.

Acknowledgements

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