Journal of Organometallic Chemistry, 116 (1976) 99—102

HINDERED ROTATION IN TRIMETHYLENEMETHANE—$Fe(CO)_3$ COMPLEXES

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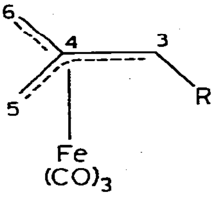
(Received February 13th, 1976)

Summary

^{13}C NMR spectra have been recorded for trimethylenemethane—$Fe(CO)_3$ (I) as well as its acetyl (II), 1-hydroxyethyl (III), 1-acetoxyethyl (IV) and ethyl (V) derivatives respectively. Compounds II—IV exhibit 3 distinct ^{13}CO resonances at room temperature. These signals undergo a reversible broadening and merge into a single sharp signal on warming. $\Delta G^{\ddagger}$ for $Fe(CO)_3$ rotation at the coalescence points is 17—18 kcal mol^{-1}. The rotational barrier is electronic in origin.

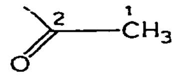
Structures of trimethylenemethane—$Fe(CO)_3$ complexes have been studied by several techniques [1—5]. Almenningen et al. [2] studied the parent compound (I) by electron diffraction. Their data suggested that the molecule is "quite rigid" and that a substantial barrier to rotation of the $Fe(CO)_3$ group relative to the trimethylenemethane ligand exists. Although hindered rotation has been reported for complexes having one or more PF_3 ligands in place of CO ligands [6], no conclusive evidence for the high barrier to rotation for the tricarbonyl complexes has been reported. We have measured the ^{13}C NMR spectra of several trimethylenemethane—$Fe(CO)_3$ complexes and have observed three separate metal carbonyl resonances at room temperature, a clear indication of a relatively high barrier to rotation.



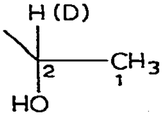
(I — V)

(I) R = H

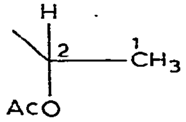
(II) R =



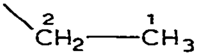
(III) R =



(IV) R =



(V) R =



The spectra of compounds (I—V) were recorded in several solvents. Chemical shifts for these compounds are presented in Table 1. Three separate metal carbonyl resonances are observed at room temperature for compounds II—V in at least one solvent. In methylene chloride two of the peaks are shifted together by a solvent effect and can only be resolved for compound III-D. Owing to a very dilute sample of compound V, the carbonyl peaks could not be located accurately.

The chemical shift assignments in Table 1 are based in part on the coupled spectra. Comparison of the spectra of III-H and III-D permits the unambiguous assignment of C-2 and C-3 in these compounds. Except for C-5 and C-6 the remaining assignments are clear from the coupled spectra. Of the two unassigned triplets, the upfield peak is in all cases assigned to C-5, which experiences a large γ effect from C-2 [8]. For compound V the γ effect is unusually large because C-5 is constrained to be nearly eclipsed with C-2. The γ effect for C-6 (*anti* relationship with C-2) is expected to be smaller and this peak is shifted upfield only slightly compared with compound I [8].

For alcohols III-H and III-D the upfield peak is again assigned to C-5. The smaller shift difference is an example of the *syn*-axial δ effect reported by Grover et al. in which a *syn*-axial hydroxyl group in a δ position produces a considerable downfield shift of the carbon resonance in question [9]. Owing to their method of synthesis and their chemical properties, alcohol III and acetate ester

TABLE 1

^{13}C CHEMICAL SHIFTS IN TRIMETHYLENEMETHANE—Fe(CO)$_3$ COMPLEXES [a]

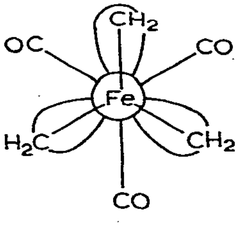
Compound	Solvent	C-1	C-2	C-3	C-4	C-5	C-6	C≡O
I	CH_2Cl_2			54.9	106.1	54.9	54.9	211.9
				53.0 [b]	105.0	53.0	53.0	211.6
II	CCl_4	29.9	200.2	68.8	106.8	53.3	58.4	208.8
		(123) [c]		(157)		(162)	(162)	209.7
								209.8
	CH_2Cl_2	30.4	202.5	69.4	107.3	54.3	58.4	209.8
								210.3
	$C_6H_5CH_3$	29.9	201.0	69.4	107.1	53.7	58.6	209.7
								210.3
								210.4
III-H	CH_2Cl_2	27.5	66.7	85.9	102.6	51.4	52.9	211.0
		(123)	(138)	(147)		(172)	(172)	211.4
	1,4-dioxane	28.0	66.2	87.3	102.9	51.2	53.1	211.3
								212.2
								212.3
III-D	CH_2Cl_2	27.3		85.9	102.8	51.6	53.1	211.2
								211.5
								211.6
IV [d]	CH_2Cl_2	24.5	70.0	79.9	103.6	51.7	[e]	211.3
								212.3
	$C_6H_5CH_3$	24.3	69.4	80.0	103.3	51.2	52.7	213.4
								214.1
								214.3
(V)	CH_2Cl_2	17.0	23.4	82.7	103.2	39.9	50.8	[f]

[a] Chemical shifts (±0.1) in ppm downfield from internal TMS. [b] ±1.0 Hz, data from ref. 5. [c] ^1J(C—H) (±5 Hz) measured from coupled spectra are given in parentheses. [d] Acetate methyl, δ 21.1 ppm (CH_2Cl_2), hidden by solvent peak in $C_6H_5CH_3$; acetate carbonyl, δ 169.9 (CH_2Cl_2), 171.5 ppm ($C_6H_5CH_3$). [e] Peak hidden by solvent peak. [f] Carbonyl signals too weak to locate accurately.

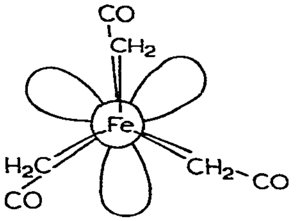
IV are believed to possess the relative configurations and (approximately) the conformations shown. The spectrum of the acetate, IV, follows from that of the alcohol. For the ketone, II, a smaller γ effect than for V would be expected, as is observed.

Variable temperature spectra were measured for compounds II and III-H. For the alcohol, spectra were run in dioxane at 27°, 47°, 57°, 77°, and again at 27°C. As the temperature was raised the three carbonyl resonances broadened to give a single broad peak at 57°C ($\Delta G_c^{\ddagger} = 17 \pm 2$ kcal/mol^{-1}). This peak sharpened considerably on increasing the temperature to 77°C; upon return to 27°C three sharp peaks reappeared exactly as before. Spectra of compound II were taken at approximately five degree intervals from 32° to 88°C with a two degree interval at the first coalescence point. The two downfield metal carbonyl peaks coalesce at 59°C ($\Delta G_c^{\ddagger} = 18 \pm 1$ kcal/mol^{-1}) and this peak coalesces with the upfield resonance at 71°C ($\Delta G_c^{\ddagger} = 18 \pm 1$ kcal/mol^{-1}). Cooling to 32°C produced the original 3-line spectrum.

The origin of rotational barriers in the PF_3 substituted complexes may arise from steric or electronic effects [6], but those in the tricarbonyl complexes II—IV clearly are electronic barriers. Such a barrier is expected on the basis of the bonding capabilities of a d^8 $Fe(CO)_3$ fragment of C_{3v} symmetry, presented by Elian and Hoffmann [10]. The e and a_1 orbitals or optimum energy for bond formation can be resolved into 3 hybrid orbitals which are directed in space so that the $Fe(CO)_3$ fragment possesses pseudooctahedral symmetry. Direction of these hybrids at the 3 methylene groups of a tetramethylenemethane ligand gives the staggered geometry (VI) found for all trimethylenemethane—$Fe(CO)_3$ complexes to date [1—4,11].



(VI)



(VII)

A 60° rotation of the $Fe(CO)_3$ group reduces overlap between the iron bonding hybrids and the carbon $2p$ orbitals at the methylenes (VII). Prof. Roald Hoffmann has informed us that a preliminary estimate of the rotational barrier in I using the extended Hückel method gave a value of 0.7 ev. We wish to thank Prof. Hoffmann for communication of this result.

Experimental section

Compounds I and II were prepared using modified literature procedures [12]. Compounds III-H and III-D were prepared by reduction of II with $NaBH_4$ and $NaBD_4$ respectively while IV was produced by acetylation of III using acetic anhydride in pyridine. V was prepared by $LiAlH_4/AlCl_3$ reduction of II. Details of these syntheses will be reported elsewhere.

^{13}C NMR spectra were measured on a Bruker HX-90 spectrometer at 22.63 MHz with broad-band ^1H decoupling and using a short pulse width and a long delay time (4—5 sec). The spectra were accumulated and transformed using a Nicolet Series 1080 computer system. Temperature was regulated by the Bruker B-ST 100/700 variable temperature unit and was calibrated using a Cu/constantan thermocouple and potentiometer.

Acknowledgment

We wish to thank the National Science Foundation for a grant in partial support of this work.

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