from each of the acetate and water oxygens) the ground state is given as: $(1a_1)^2(2a_1)^2(1e)^4(1b_1)^2(1b_2)^2(3a_1)^2(2e)^4(2b^*_1)^1$ with a single unpaired electron in a b^*_1 orbital essentially localized on the copper atom (*i.e.*, a $3d_{x^2-y^2}$ orbital). Thus the formation of the binuclear complex *via* Cu–Cu bonding of the two mononuclear species will require the overlap of two $3d_{x^2-y^2}$ orbitals or d_δ–d_δ overlap. In fact this latter approach toward rationalizing the metal–metal bonding in copper acetate dihydrate is probably much more realistic from MO viewpoint than either the F.B. scheme or the present treatment, but is unfortunately considerably more difficult to treat quantitatively.

Lastly, the main aspect of this work is that an approximate MO calculation of the Cu–Cu interaction in binuclear complexes of Cu(II) can lead to results that are not in opposition to either of the previously proposed δ-bond or σ-bond models. The actual theoretical solution apparently lies in a detailed programmed MO treatment of the entire complex.

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Tricarbonyl-(1,1′-bicycloalkenyl)iron(0) Complexes

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Received November 12, 1963

Tricarbonyliron(0) complexes of 1,1′-bicyclopentenyl, 1,1′-bicyclohexenyl, and 1,1′-bicycloheptenyl have been prepared, and their nuclear magnetic resonance spectra have been interpreted to favor structures involving 1,4-addition of the iron atom across the dienic system.

Introduction

The formation of π-complexes between metal carbonyls and unsaturated hydrocarbons continues to be of interest,[1] as do rearrangements in such systems.[2,3] It is of interest to know whether or not isomerization of a once-formed tricarbonyl(diene)iron(0) complex can occur, or whether a conjugated diene can form a complex derived from an isomeric diene in which the double bonds have migrated. To secure information bearing on these questions, we have investigated the reactions of iron carbonyls with 1,1′-bicyclopentenyl, 1,1′-bicyclohexenyl, and 1,1′-bicycloheptenyl.[4,5]

Experimental

General.—Infrared spectra, except as otherwise noted, are of cyclohexane solutions, recorded on a Perkin-Elmer Model 421 instrument, with resolution of one wave number. Nuclear magnetic resonance spectra are of carbon disulfide solutions containing tetramethylsilane as internal standard, recorded on a Varian A-60 instrument. Ultraviolet spectra are of cyclohexane solutions recorded on an Optica CF-4 spectrophotometer. Gas chromatography utilized a 300-ft. capillary column coated with polypropylene glycol, operated at 150° with helium at 35 p.s.i. as carrier gas. Microanalyses and molecular weights (osmometric, in benzene) were obtained from the Analytical Research Division of this company and from Galbraith Laboratories, Inc., Knoxville, Tennessee. The 1,1′-bicycloalkenyls were prepared according to published methods.[4,5]

(1) **Tricarbonyl-(1,1′-bicyclopentenyl)iron(0).** (a).—A mixture of 1.34 g. (10 mmoles) of 1,1′-bicyclopentenyl, 2.0 g. (4 mmoles) of triiron dodecacarbonyl, and 50 ml. of cyclohexane was stirred under nitrogen in an oil bath at 95° for 18 hr. The mixture was cooled to room temperature and chromatographed on alumina. Pentane eluted a yellow band, evaporating to an orange oil; from this was distilled (25° (0.05 mm.) to a surface cooled to −78°) 380 mg. of a pale yellow liquid, shown by infrared and v.p.c. analysis to be starting material plus a trace of the iron carbonyl complex. Crystallization (pentane, −78°) of the undistilled portion yielded 400 mg. (15% yield) of golden crystals, m.p. 33°.

(b).—A mixture of 2.0 g. (15 mmoles) of 1,1′-bicyclopentenyl, 14.6 g. (75 mmoles) of iron pentacarbonyl, and 40 ml. of ethylcyclohexane was stirred under nitrogen in an oil bath at 130° for 66 hr. The mixture was cooled and chromatographed on alumina. Pentane eluted a yellow band, evaporating to an orange oil. After removal by distillation of 240 mg. of oil, shown by infrared and v.p.c. analysis to be unchanged starting material with a trace of complex, crystallization (pentane, −78°) yielded 2.9 g. (71% yield) of golden needles, m.p. 34–35° (I, $n = 1$).

Anal. Calcd. for $C_{13}H_{14}O_3Fe$: C, 56.96; H, 5.14; mol wt., 274. Found: C, 56.59, 56.97; H, 5.36, 5.22; mol. wt., 280.

A 2:1 pentane–dichloromethane mixture eluted a red band, evaporating to a red-violet solid, recrystallized (pentane, −78°) to 60 mg. of violet solid, m.p. 109–110° (IV).

Anal. Calcd. for $C_{24}H_{26}O_4Fe_2$: C, 58.80; H, 5.34; mol. wt., 490. Found: C, 58.35; H, 5.33; mol. wt., 400.

(c).—A solution of 0.78 g. of tricarbonyl-(1,1′-bicyclopentenyl)iron(0) in 22 ml. of ethylcyclohexane was heated under nitrogen in an oil bath at 130° for 66 hr. Only the carbonyl bands of the starting material were seen in the infrared spectrum of the product after cooling and removal of solvent. The recovered complex was mixed with 3 ml. of iron pentacarbonyl and 25 ml. of ethylcyclohexane; after an additional 67 hr. in an oil bath at 130°, no sign of IV was seen in the infrared spectrum.

(2) **Tricarbonyl-(1,1′-bicyclohexenyl)iron(0).** (a).—A mixture of 2.5 g. (15 mmoles) of 1,1′-bicyclohexenyl and 4.0 g. (8 mmoles) of triiron dodecacarbonyl in 50 ml. of cyclohexane was heated under nitrogen in an oil bath at 95° for 20 hr. The cooled mixture was chromatographed on alumina. Pentane eluted a yellow band, evaporating to an oil, from which crystallization (pentane, −78°) yielded 500 mg. (11% yield) of orange crystals, m.p. 33° (I, $n = 2$).

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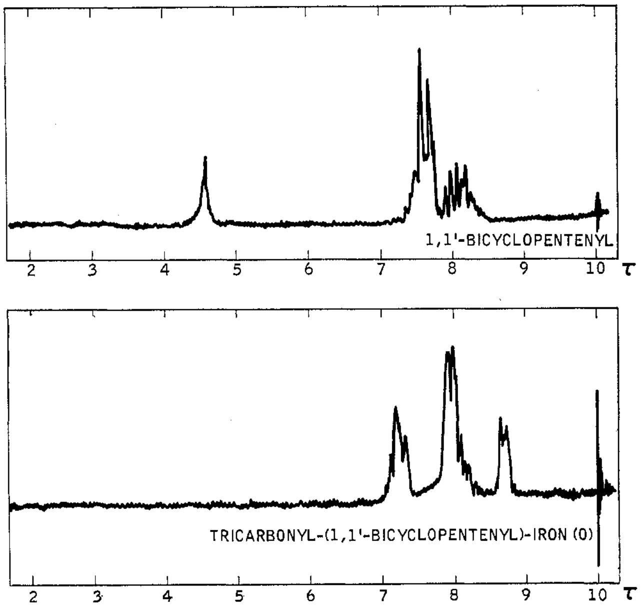


Fig. 1.—Nuclear magnetic resonance spectra.

Anal. Calcd. for $C_{15}H_{18}O_3Fe$: C, 59.62; H, 6.00. Found: C, 59.73, 59.82; H, 6.27, 6.22.

Examination by infrared and v.p.c. analysis of hydrocarbons recovered from the crude products of other runs by distillation (60° (0.05 mm.) to a surface at −78°) showed that no isomerization had occurred.

(**b**).—A mixture of 2.5 g. (15 mmoles) of 1,1′-bicyclohexenyl and 14.6 g. (75 mmoles) of iron pentacarbonyl in 50 ml. of ethylcyclohexane was stirred under nitrogen in an oil bath at 130° for 66 hr. The cooled mixture was chromatographed on alumina. Pentane eluted a yellow band, evaporating to a yellow oil from which crystallization (pentane, −78°) yielded 400 mg. (9% yield) of orange crystals, m.p. 33°.

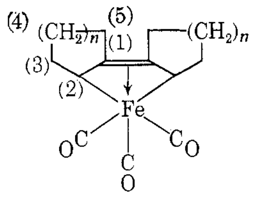
(**3**) **Tricarbonyl-(1,1′-bicycloheptenyl)iron(0).** (**a**).—A mixture of 1.0 g. (5.3 mmoles) of 1,1′-bicycloheptenyl and 2.5 g. (5 mmoles) of triiron dodecacarbonyl in 50 ml. of cyclohexane was stirred under nitrogen in an oil bath at 95° for 21 hr. The cooled mixture was chromatographed on alumina. Pentane eluted a yellow band, from which evaporation and crystallization (pentane) yielded 1.0 g. (57% yield) of yellow crystals, m.p. 92.5–94°.

Anal. Calcd. for $C_{17}H_{22}O_3Fe$: C, 61.81; H, 6.71. Found: C, 62.00; H, 6.85.

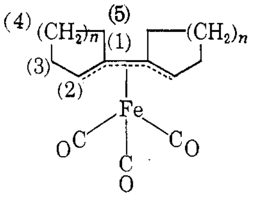
(**b**).—A mixture of 1.0 g. (5.3 mmoles) of 1,1′-bicycloheptenyl and 14.6 g. (75 mmoles) of iron pentacarbonyl in 40 ml. of ethylcyclohexane was stirred under nitrogen in an oil bath at 135° for 65 hr. The cooled mixture was chromatographed on alumina. Pentane eluted a yellow band from which evaporation and recrystallization (pentane) yielded 0.95 g. (54% yield) of yellow crystalline complex, m.p. 93–94°.

Discussion

The 1,1′-bicycloalkenyls each form tricarbonyl-(diene)iron(0) complexes when heated with iron pentacarbonyl or triiron dodecacarbonyl.



I (n=1, 2, 3)



II (n=1, 2, 3,)

Fig. 2.—Carbonyl stretching bands of tricarbonyl-(1,1′-bicycloheptenyl)iron(0).

Whether I or II is the best representation of such compounds is unsettled. Certain nuclear magnetic resonance spectra[6–8] and X-ray structure determinations[9,10] support structures of type I; the older representation of type II is supported by infrared[6–8] and X-ray structural[11] data. The tricarbonyl-(1,1′-bicycloalkenyl)iron(0) complexes appear to be typical members of the class. Their ready preparation and stability indicate that the cyclic structures of the ligands, in which one of the terminal substituents on the diene system is pinned back, are not unfavorable for complex formation. Complexes such as tricarbonyl-(1,3-cyclohexadiene)iron(0)[7,12] (III) have been made hitherto from cyclic systems, in which one of the terminal substituents on the diene system is pinned back

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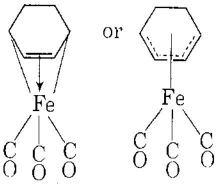
TABLE I

NUCLEAR MAGNETIC RESONANCE SPECTRA OF 1,1′-BICYCLOALKENYLS AND THEIR TRICARBONYLIRON(0) COMPLEXES

Compound	Peak center (or base), τ	Structure	Relative intensity	Assignment (formula I)
$C_{10}H_{14}$	4.53 (4.42–4.60)	Unresolved triplet	2	Olefinic protons 2
	(7.42–7.75)	Doublet superimposed on complex peak	8	Allylic protons 3 and 5
	(7.88–8.33)	Complex quintet	4	Methylenic protons 4
$C_{12}H_{18}$	4.33 (4.22–4.45)	Unresolved	2	Olefinic protons 2
	7.90 (7.75–8.08)	Unresolved	8	Allylic protons 3 and 5
	(8.25–8.58)	Complex, unresolved	8	Methylenic protons 4
$C_{14}H_{22}$	4.27	Triplet, J = 7 c.p.s.	2	Olefinic protons 2
	(7.60–8.05)	Complex	8	Allylic protons 3 and 5
	(8.05–8.75)	Complex	12	Methylenic protons 4
$C_{10}H_{14}Fe(CO)_3$	7.23	Triplet, J = 6 c.p.s.	4	Allylic protons 5
	(7.60–8.35)	Doublet superimposed on complex peak	8	Allylic protons 3 and methylenic protons 4
	(8.60–8.80)	Unequal doublet	2	Olefinic protons 2
$C_{12}H_{18}Fe(CO)_3$	7.30	Triplet, J = 6 c.p.s.	4	Allylic protons 5
	(7.70–8.50)	Doublet superimposed on complex peak	12	Allylic protons 3 and methylenic protons 4
	(8.72–8.97)	Unequal triplet	2	Olefinic protons 2
$C_{14}H_{22}Fe(CO)_3$	(6.71–7.23)	Complex, two unequal doublets J = 6 c.p.s. for each	2	Part of allylic protons 5
	(7.38–8.90)	Complex, two main groups of approximately equal intensity	18	Part of allylic protons 5, allylic protons 3, methylenic protons 4
	(9.00–9.40)	Unequal triplet	2	Olefinic protons 2

in the opposite sense to that in I. In such cases as III the iron atom must be more nearly under the rest of the hydrocarbon ring than in I.


III

The nuclear magnetic resonance spectra of the 1,1′-bicycloalkenyls and their complexes are quite similar, their complexity increasing with ring size. Figure 1 reproduces the simplest of these spectra, of 1,1′-bicyclopentenyl and its tricarbonyliron(0) complex. Certain inferences may be drawn from a qualitative comparison of the spectra of the ligands and the complexes (Table I).

Three groups of peaks are discernible, and the absence of absorption in the region of 4–5 τ (expected for the central protons of a complexed diene system)[6] clearly shows that the carbon atoms involved in the complex formation are those originally unsaturated. The relative intensities and consistency with other data[6–8] assure that the peaks at highest field are due to the protons at position 2. This resonance is found at higher fields than is the resonance of the terminal protons in complexes like III.[6] A shift of this proton to higher fields, as well as broadening, occurs as the ring size increases in I. The peaks assigned to the methylenic protons at position 4 are not much affected by complex formation. The two equal-intensity groups of allylic protons (position 3 and 5) are shifted in opposite directions in I. One group, assigned in agreement with previous data[6] to position 3, which is allylic to a 1,2 double bond, is shifted upfield to the region of the methylenic protons. The last group, which is shifted downfield, we assign to position 5, which is allylic to a 1,2 or 1,1′ double bond. These shifts, we believe, support the assignment of the structures as I rather than II. In structure I, position 5 would be allylic and position 3 methylenic, as we have observed. Despite the complexity of much of the spectrum, a triplet structure of the peak assigned to position 5 is clearly seen; this is consistent with splitting by the two protons on position 4.

The high-resolution infrared spectra of the complexes I show three very strong bands in the carbonyl stretching region (Table II), as well as a consistent pattern of very much weaker bands and shoulders (Fig. 2), showing that the local C_{3v} symmetry of the iron tricarbonyl group has been destroyed. This effect, too, is consistent with structures of type I.

TABLE II

CARBONYL STRETCHING FREQUENCIES

Compound	Carbonyl stretching frequencies, cm.$^{-1}$		
$C_{10}H_{14}Fe(CO)_3$	2035	1970	1956
$C_{12}H_{18}Fe(CO)_3$	2034	1967	1952
$C_{14}H_{22}Fe(CO)_3$	2038	1971	1960

The expected similarity of the bonding in the bicycloalkenyl complexes is also shown by their ultraviolet spectra (Table III).

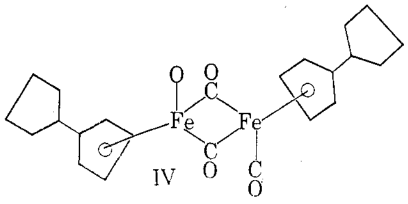
No isomerization was detected in the uncomplexed hydrocarbons recovered from the reaction mixtures. However, from the reaction of iron pentacarbonyl with 1,1′-bicyclopentenyl we obtained a small amount of a violet compound believed on the basis of its infrared

TABLE III

ULTRAVIOLET SPECTRA

Compound	ϵ_{220}	$\lambda_{\text{shoulder}}$, mμ	$\epsilon_{\text{shoulder}}$	λ_{max}, mμ	ϵ_{max}
$C_{10}H_{14}Fe(CO)_3$	2.3×10^4	228	2.2×10^4	313	2.3×10^3
$C_{12}H_{18}Fe(CO)_3$	6.7×10^4	233	4.7×10^4	308	2.3×10^3
$C_{14}H_{22}Fe(CO)_3$	6.7×10^4	230	6.0×10^4	297	2.6×10^3

spectrum (carbonyl stretching bands (CS_2 solution, NaCl optics) at 2041, 1996, 1957, and 1783 cm.$^{-1}$) to be di-π-(cyclopentylcyclopentadienyl)tetracarbonyldiiron (IV) analogous to the well-known di-π-cyclopentadienyltetracarbonyldiiron[13] (carbonyl stretching bands (CS_2 solution, NaCl optics) at 2041, 2000, 1957, and 1786 cm.$^{-1}$). We found no evidence that tricarbonyl-(1,1′-bicyclopentenyl)iron(0) could be converted to IV. Thus, the essential rearrangement must have occurred before I was formed.



IV

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Metal–Oxygen Bonds in Complexes: Raman Spectra of Trisacetylacetonato and Trisoxalato Complexes of Aluminum, Gallium, and Indium[1]

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Received October 14, 1963

The Raman spectra of the complex oxalates and acetylacetonates of aluminum, gallium, and indium have been studied, principally for information on the nature and strength of their metal–oxygen bonds. Highly polarized, low frequency Raman lines have been found which are attributable to the metal–oxygen symmetric stretching modes, and an interesting correlation with the C—O and C=O stretching frequencies is found in the oxalate series. $\partial\bar{\alpha}/\partial Q$ values have been calculated for these M–O bonds from the Raman line intensities and found to be unusually large (Al = 1.33, Ga = 1.37, In = 1.47 Å.^{2} (a.w.)$^{-1/2}$) in the acetylacetonate series, indicating metal–oxygen π-bonding in these very stable complexes.

Metal–oxygen bonds have recently been the subject of much interest in complex coordination compound chemistry, but little application of the powerful technique of Raman spectroscopy has been made to date. A considerable amount of infrared work has been reported dealing with the symmetries and vibrational frequency assignments of coordination compounds of metals with the chelating ligands oxalate, $C_2O_4^{2-}$, and acetylacetonate, $C_5H_7O_2^-$. Assignment of the abundance of spectral lines in such complexes to the normal modes of vibration has been a difficult task, especially in the interesting low frequency region below ~800 cm.$^{-1}$ where metal–oxygen stretching fundamentals occur. This difficulty has led to contradictions[2-9] in the recent literature over the location of metal–oxygen stretching modes. Correct assignments must precede any calculation of force constants, and hence of metal–oxygen bond strengths. The unique selection rules for Raman spectra and the information on depolarization ratios obtainable with the Raman method are of considerable importance for solving this problem of frequency assignments.

The Raman intensity of the pth normal mode of vibration of a molecule, Q_p, is given by the expression

$$I_p = \frac{KM(\nu_0 - \nu)^4}{\nu[1 - \exp(-h\nu/kT)]} 45\left(\frac{\partial\bar{\alpha}}{\partial Q_p}\right)^2\left(\frac{6}{6 - 7\rho}\right) \quad (1)$$

where M is the molar concentration of the species, ν_0 is the Rayleigh frequency, ν is the Raman frequency shift, ρ is the degree of depolarization, $\bar{\alpha}$ is the mean molecular polarizability, and K is a constant. The quantity $\partial\bar{\alpha}/\partial Q_p$ (written $\bar{\alpha}'$ henceforth) is zero for all vibrational modes other than totally symmetric ones, but for these totally symmetric modes $\bar{\alpha}'$ has been shown to be related to the strength and degree of covalency of the bonds being stretched in this pth normal mode.[10,11] Evaluation of the quantity $\bar{\alpha}'$ for

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