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The Reaction of Iron Carbonyls with Bis-5,8-trimethylsilyl-1,3,6-cyclooctatriene

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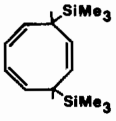
Bis-5,8-trimethylsilyl-1,3,6-cyclooctatriene reacts with $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ to produce two major products (a bicyclic diene irontricarbonyl, $C_8H_8[Si(CH_3)_3]_2\cdot Fe(CO)_3$, and a monocyclic triene diironhexacarbonyl, $C_8H_8[Si(CH_3)_3]_2\cdot Fe_2(CO)_6$) and several minor products. It is postulated that fluxional behavior is not observed in these bis-silyl substituted cyclooctatriene iron carbonyls because in the "instantaneous" structures the silyl substituents occur in different positions in the allylic portion of the cyclooctatriene. Therefore, the equal energy "instantaneous" structures required for stereochemical nonrigidity do not exist and the substitution of silyl substituents prevents the fluxional character observed in the unsubstituted analogues.

Introduction

Cyclooctatetraene and cyclooctatrienes have frequently been utilized as ligands in metal carbonyl systems; some of these complexes have shown the interesting feature of fluxional behavior (stereochemical nonrigidity). Recently we have reported the synthesis and characterization of bis-5,8-trimethylsilyl-1,3,6-cyclooctatriene (I),[1] and bis-5,8- and bis-7,8-dimethylsilylcyclooctatrienes.[2]

Compound (I) was reacted with $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ in order that we might determine the properties of bis-silyl substituted cyclooctatrienes as ligands in metal carbonyl systems and compare the products to the more widely studied unsubstituted cyclooctatriene iron carbonyls.



(I)

Experimental

The Reaction of $C_8H_8[Si(CH_3)_3]_2$ with $Fe_2(CO)_9$

The ligand (2.0 g, 8.0 mmol) and $Fe_2(CO)_9$ (2.5 g, 6.9 mmol) were refluxed under nitrogen in methylcyclohexane solvent for 19 hours. A solid residue was filtered and the methylcyclohexane was removed on a rotary evaporator. The dark orange oil which remained was chromatographed on alumina (Brockman, activity II, 2 × 85 cm). Elution using 40/60 petroleum ether gave a broad yellow band (1), followed by an orange band (2), while a brown band (3) remained at the top of the column. Bands (1) and (2) were eluted with petroleum ether, and band (3) was removed using ethyl ether.

$C_8H_8[Si(CH_3)_3]_2\cdot Fe(CO)_3$

Band (1) in petroleum ether had an IR spectrum indicative of a compound containing a $-Fe(CO)_3$ group. When the solvent was evaporated, about 2 ml of an orange oil remained. This oil was dissolved in 5 ml of 40/60 petroleum ether and cooled to −78° C. The pale yellow crystals which formed were collected by filtration, recrystallized from petroleum ether and from acetone at −78° C, and ultimately purified (mp = 54.5–55.5° C) by sublimation. The compound (250 mg, 0.64 mmol; yield = 8%) isolated from band (1) was identified as $C_8H_8[Si(CH_3)_3]_2\cdot Fe(CO)_3$ primarily on the basis of its mass spectrum and its PMR spectrum (found: C, 52.39; H, 6.78. $C_8H_8[Si(CH_3)_3]_2\cdot Fe(CO)_3$ calcd: C, 52.30; H, 6.71%). The infrared spectrum of this compound (dissolved in hexane) displayed CO stretching frequencies at 1969, 1979, and 2044 cm^{-1}. The mass spectrum showed a parent ion at m/e = 390, peaks at 362, 334, and 306 (loss of 1–3 CO groups), and a large peak at m/e = 73 corresponding to Me_3Si^+. The PMR spectrum exhibits a doublet at 5.22 δ [1H], a multiplet at 3.65 δ [1H], a doublet at 3.41 δ [1H], a broad multiplet at 2.37 δ [2H], a broad multiplet at 1.22 δ [3H], and two large singlets at 0.23 δ [9H] and −0.08 δ [9H] (all values are relative to an internal $CHCl_3$ standard at 7.25 δ).

$C_8H_8[Si(CH_3)_3]_2\cdot Fe_2(CO)_6$

Band (2) appeared to be a $Fe_2(CO)_6$-containing compound, since the infrared spectrum displayed five strong bands in the carbonyl region. Red-orange crystals which remained after the petroleum ether had been evaporated were vacuum sublimed to a probe at

$-78°$ C. The crystals appear to decompose at the melting point of 116–118° C. The compound (20 mg; 0.5% yield) which was isolated from band (2) was identified as $C_8H_8[Si(CH_3)_3]_2 \cdot Fe_2(CO)_6$ on the basis of its mass spectrum and PMR spectrum (found: C, 45.01; H, 4.93. $C_8H_8[Si(CH_3)_3]_2 \cdot Fe_2(CO)_6$ calcd: C, 45.30; H, 4.94%). The infrared CO stretching frequencies of this compound dissolved in hexane are 1963, 1977, 1992, 2014, and 2059 cm^{-1}. The mass spectrum shows a parent ion at $m/e = 530$, peaks corresponding to the loss of 1–6 CO groups, and a large peak at $m/e = 73$ corresponding to Me_3Si^+. The PMR spectrum shows a broad multiplet centered at 3.98 δ [4H], a broad multiplet at 1.30 δ [4H], and two sharp singlets at 0.37 δ [9H] and 0.14 δ [9H].

Minor Products

Band (3) turned out to be a complex mixture of side products formed in insufficient quantity to allow identification. Recently, Cotton and Troup, for a similar reaction of $Fe_2(CO)_9$ with bicyclo[6.2.0]deca-2,4,6-triene, identified five side products formed in minute amounts in addition to the two major products, a $Fe(CO)_3$ and a $Fe_2(CO)_6$ derivative.[3]

The Reaction of $C_8H_8[Si(CH_3)_3]_2$ with $Fe_3(CO)_{12}$

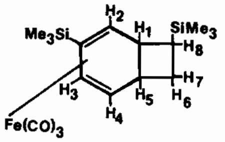
The ligand (I) (1.60 g, 6.40 mmol) and $Fe_3(CO)_{12}$ (2.50 g, 4.96 mmol) were refluxed under nitrogen in methylcyclohexane solvent for 27 hours. A solid residue was filtered, and the methylcyclohexane was removed on a rotary evaporator. The orange oil was chromatographed on alumina (Brockman, activity II, 2 × 85 cm). Elution using 40/60 petroleum ether gave two bands, yellow (1) and orange (2). These bands were shown by IR and NMR to be the same $Fe(CO)_3$ and $Fe(CO)_6$ compounds prepared in the reaction with $Fe_2(CO)_9$.

Physical Measurements

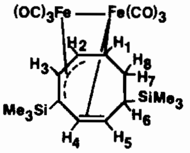
The mass spectra were obtained on an Associated Electrical Industries MS-9 spectrometer using an ionizing voltage of 70 eV and an ionizing current of 50 microamps. The PMR spectra were recorded on a Varian HA-100. Unless otherwise stated the samples were run as solutions in CS_2 solvent using $CHCl_3$ as internal standard. Positive values on the δ scale refer to ppm downfield from TMS. The IR spectra were run on a Perkin–Elmer Model 257 Spectrometer.

Results and Discussion

Two major products are formed from the reaction of either $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ with bis-5,8-trimethylsilyl-1,3,6-cyclooctatriene. Elemental analysis, infrared, and mass spectral evidence indicate that these two products may be formulated as $C_8H_8[Si(CH_3)_3]_2 \cdot Fe(CO)_3$ and $C_8H_8[Si(CH_3)_3]_2 \cdot Fe_2(CO)_6$. These complexes are most likely the bicyclic tricarbonyl (II) and the monocyclic hexacarbonyl (III).



(II)



(III)

The PMR spectrum of (II) supports the suggestion that (II) is a bicyclic tricarbonyl. The two large singlets at 0.23 δ and -0.08 δ can be assigned to the two $(CH_3)_3Si–$ groups. The aliphatic protons (H_6, H_7, and H_8) produce the broad multiplet at 1.22 δ. Protons on bridgehead carbons generally appear at lower field than aliphatic protons; thus the broad multiplet at 2.37 δ [2H] is assigned to H_1 and H_5. The doublet at 3.41 δ is assigned to H_2 since that proton should undergo extensive coupling with H_1 and thus produce a doublet. Coupling to H_3 and H_5 causes H_4 to present the complex multiplet at 3.65 δ. The doublet at 5.22 δ is assigned to H_3. Thus, the PMR spectrum of (II) is consistent with a bicyclic structure.

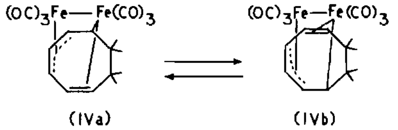
It might be noted that bicyclic derivatives have been previously observed as products of reactions between cyclopolyenes and metal carbonyls. A bicyclic diene complex may be formed from ring closure of a monocyclic triene complex, and it has been shown that an equilibrium exists between a monocyclic triene irontricarbonyl and a bicyclo diene irontricarbonyl[3], both of which are isomers of $C_8H_{10} \cdot Fe(CO)_3$. Although the uncomplexed cyclooctatriene prefers a tub structure, bonding with a $Fe(CO)_3$ group forces the bound diene moiety into a nearly planar configuration, thereby inducing considerable strain in the C_8H_{10} ring. Therefore, the bicyclo diene structure, which has less strain, is more stable than the monocyclic triene complex.

The PMR spectrum of (III) has a broad multiplet in the olefinic region centered about 3.98 δ [4H] assigned to protons H_2, H_3, H_4, and H_5. In the aliphatic region there is also a very broad multiplet centered around 1.30 δ [4H] due to protons H_1, H_6, H_7, and H_8. There are also two sharp singlets at 0.37 δ [9H] and 0.14 δ [9H] which are assigned to the two nonequivalent trimethylsilyl groups. Thus, the four olefinic and four aliphatic protons suggest that (III) has the structure indicated.

Unsubstituted cyclooctatetraene reacts with iron carbonyls to form at least two products which show fluxional characteristics. The PMR spectrum of $C_8H_8 \cdot Fe(CO)_3$, which consists of a single line, was explained when the limiting spectrum of the ruthenium analogue at −128° C demonstrated 1,3-diene metal character.[4–7] Also, one of the two isomeric $C_8H_8 \cdot Fe_2(CO)_6$ products[8] shows fluxional character. Other cyclopolyene substituted iron carbonyls which are fluxional include $C_8H_{10} \cdot Fe_2(CO)_6$[9–11] and $C_{10}H_{12} \cdot Fe_2(CO)_6$[12]. Cyclooctatetraene and cyclooctatriene form similar complexes with ruthenium carbonyls, some of which also are fluxional.[13]

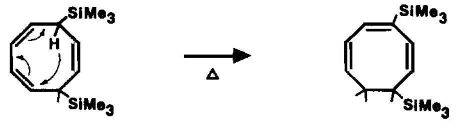
It appears, however, that $C_8H_8[Si(CH_3)_3]_2 \cdot Fe_2(CO)_6$ (III) is not fluxional at room temperature, since if it were, protons H_1 and H_5 should produce a signal midway between the olefinic and aliphatic protons. Such a signal is not observed. In order to determine if (III) is fluxional at higher temperature, the PMR of (III) was recorded in chlorobenzene solvent at 30°, 60°, and 90° C. Changes in the PMR spectrum were minor, and the analogous ruthenium compound also displayed a temperature-invariant PMR spectrum up to 100° C.[14] Thus, although a number of cyclopolyene substituted $M_2(CO)_6$ compounds are fluxional, it appears that the substitution of two trimethylsilyl groups onto the cyclooctatriene ring inhibits or prevents the ring from functioning as a fluxional ligand.

Since the definition of a fluxional molecule requires more than one thermally accessible structure in which the configuration of the nuclei are equivalent and hence of *equal free energy,* it can be understood why (III) is not fluxional. As mentioned above, the compound $C_8H_{10} \cdot Fe_2(CO)_6$ is known to be fluxional and the two forms shown below are of equivalent free energy.

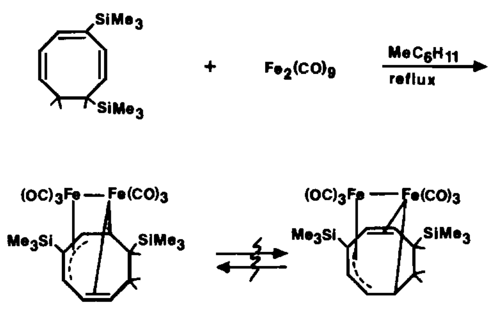


(IVa) (IVb)

For the bis-silyl substituted $C_8H_{10}[Si(CH_3)_3]_2 \cdot Fe_2(CO)_6$, however, the two forms are not of equivalent free energy. Although the starting ligand, $C_8H_8[Si(CH_3)_3]_2$, is a 1,3,6-cyclooctatriene, it could easily convert to a 1,3,5-cyclooctatriene by a 1,5 hydrogen shift, a type of thermal equilibrium which has been well studied by



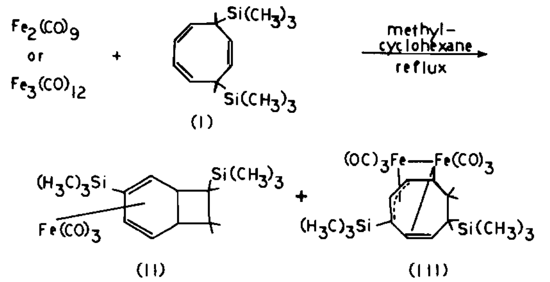
Roth.[15] It is quite probable that a 1,5-hydrogen shift could occur with bis-5,8-trimethylsilyl-1,3,6-cyclooctatriene at the temperature of refluxing methyl cyclohexane (101° C). The rearranged ligand could then react with $Fe_2(CO)_9$ to give (III).



(IIIa) (IIIb)

It can be seen, however, that forms (IIIa) and (IIIb) are *not* of equal free energy since in structure (IIIa) the $(H_3C)_3Si$ group is in the middle of the allyl group and in (IIIb) it is in the terminal position. Thus, a molecule with the structure of (III) cannot be fluxional.

The reaction of bis-5,8-trimethylsilyl-1,3,6-cyclooctatriene with $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ may be summarized as



producing two major products which appear to be $Fe(CO)_3$ and $Fe_2(CO)_6$ containing species, the structures of which appear to be analogous to those found in the reaction of unsubstituted cyclooctatrienes; however, the products are not fluxional.

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