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(25) A stronger limitation has also been derived,[15] on the assumptions that the reactions are uncoupled and reversible. However, the observed quantum yields[2] are in excess of this limitation.
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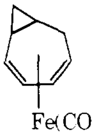
Received January 6, 1975

Addition of Methylene to Uncoordinated Double Bonds in Polyolefin Transition Metal π Complexes

Sir:

Research in the area of polycyclic metal π-olefin complexes has been stimulated by both interest in compounds of this type[1] and studies on how metals influence the thermal rearrangements of olefins.[2] This second aspect of the chemistry can also be a synthetic problem; that is, many reactions between polycyclic olefins and low valent transition metals produce products in low yields that frequently do not contain the 1:1 metal to olefin adduct.[3] This report describes preliminary results on a new synthetic approach to polycyclic metal complexes, the reaction of methylene with uncoordinated double bonds present in polyolefin metal π complexes. Other workers have demonstrated that the free double bonds in compounds like η^4-1,2,3,4-cycloheptatrieneiron tricarbonyl (**1**) are essentially unperturbed by the metal and will undergo electrophilic reactions[4] and catalytic hydrogenation.[5] On the other hand, olefinic character of coordinated double bonds is significantly reduced as shown from both X-ray studies[6] and the resistance of these bonds to catalytic hydrogenation.[7] Thus, it seemed reasonable that methylene would react exclusively with uncoordinated double bonds while the metal would prevent addition to coordinated double bonds. Successful reactions of this type could be developed into procedures in which the metal would direct the location of methylene addition.

One attempted methylene addition reaction on an organometallic molecule containing a free double bond has been reported by Johnson et al.[4] They treated **1** with the Simmons-Smith reagent,[8] but the product of the reaction was hexacarbonyl[bi(cyclohepta-2,4,6-trienyl)]diiron formed by hydrogen abstraction and not the CH_2 addition product. Precise experimental details were not given although the reaction was carried out in ether. Because the addition of CH_2 to **1** would yield a known compound,[9] our investigation began with attempts to add CH_2 to this complex. Accordingly, **1** (11.6 mmol) was dissolved in ether (20 ml) and added dropwise to a refluxing ethereal solution (20 ml) of CH_2I_2 (58 mmol) over Zn/Cu couple (3.8 g) with a catalytic amount of iodine present. The resulting solution was refluxed for 2 days and then chromatographed on alumina to yield after solvent evaporation a yellow oil. This oil was shown to be bicyclo[5.1.0]octa-2,4-dieneiron tricarbonyl (**2**) (0.49 g, 23%) by comparing the ^{1}H and ^{13}C NMR and infrared spectra with those of an authenic sample.[9] None of the product obtained by Johnson et al.[4] was observed. From either preparation, of the two possible isomers of **2,** the isomer that has been isolated has the cyclopropyl ring trans to the metal.[10] Thus, the methylene addition occurs anti to the metal in this case.



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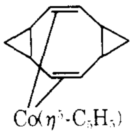

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It was decided to demonstrate the generality of this synthetic approach by allowing two complexes to react that contain the same carbocyclic ring coordinated differently to two different metal systems. Thus, η^4-1,2,5,6-cyclooctatetraenecobalt (η^5-cyclopentadienyl) (**3**) (8.8 mmol) was dissolved in ether (20 ml) and added dropwise to a refluxing solution of CH_2I_2 (7.1 ml, 87.7 mmol) in ether (20 ml) over Zn/Cu couple (5.6 g) with a catalytic amount of I_2 present. After refluxing gently for 2 days, the ether was evaporated, the residue dissolved in hexane (20 ml), and this solution filtered and chromatographed on alumina (3 × 30 cm). Elution with hexane yielded after solvent evaporation a yellow solid that was shown from the high resolution mass spectrum to have the formula $C_{15}H_{17}Co$ (0.43 g, 19%) (calcd, 256.0660; found, 256.0632). The proton decoupled ^{13}C NMR spectrum has signals[11] at 83.9 assigned to the η^5-C_5H_5 carbons, at 65.6 assigned to four equivalent metal π-coordinated olefinic carbons, at 21.3 assigned to the four methine carbons of the cyclopropyl rings, and at 12.6 assigned to the methylene carbons.[12] This compound is thus formulated as η^4-2,3,7,8-tricyclo[7.1.0.0^{4,6}]deca-2,7-dienecobalt (η^5-cyclopentadienyl) (**4**), the addition product of 2 equiv of CH_2 to nonadjacent double bonds of the cyclooctatetraene ring in **3.** Both of the cyclopropane rings are most likely cis to the metal although the above data do not rigorously establish this fact. No monoadduct was isolated or observed.

A reaction of η^4-1,2,3,4-cyclooctatetraeneiron tricarbonyl (**5**) (8.2 mmol) and the Simmons-Smith reagent (82 mmol) was carried out exactly as described above for the cobalt complex **3.** Chromatography yielded a yellow fraction followed by a red fraction. The red fraction was starting material (ca. 0.4 g, 20%), while evaporation of solvent from the yellow fraction yielded a yellow solid that was shown from the high resolution mass spectrum to have the formula $C_{14}H_{14}FeO_3$ (0.59 g, 25%) (calcd, 286.0291; found, 286.0300), the product of addition of 3 equiv of methylene to **5.** The following data show that this compound is best formulated as η^4-6,7,8,9-tricyclo[8.1.0.0^{3,5}]undeca-6,8-dieneiron tricarbonyl (**6**), pictured in Figure 1. The infrared spectrum in hexane solution showed carbonyl stretching bands (cm^{-1}) at 2035 1970, and 1960, similar but not identical with those of the starting material. The proton decoupled ^{13}C NMR spectrum is shown in Figure 1A. Figure 1B is the ^{13}C NMR spectrum of the d^6 analog

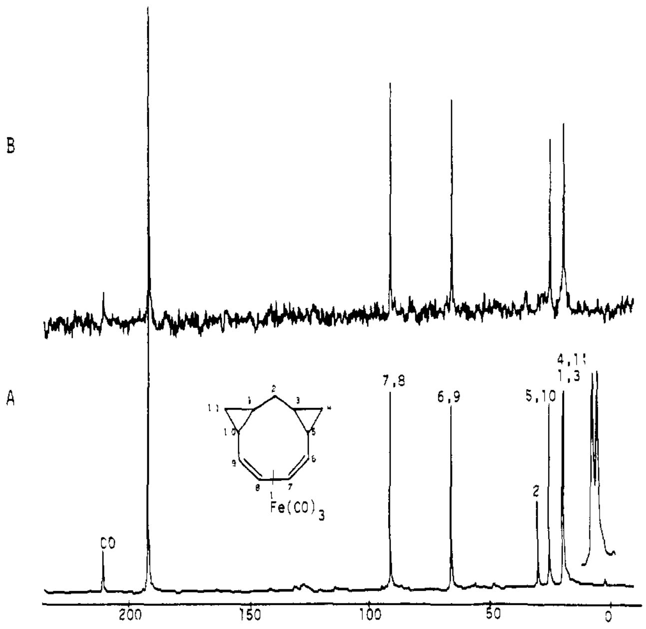

Figure 1. Proton decoupled ^{13}C NMR spectra: (A) compound **6** with peak assignments and proposed structure (Insert at right is an expansion of the resonances assigned to carbons 1, 3, 4, and 11.); (B) the d^6 analog of **6**, deuterated at positions 2, 4, and 11. The resonance at 193 in both is from the CS$_2$ solvent.

of **6** prepared by using CD_2I_2 in a Simmons-Smith reaction with **5** as described above. Due to carbon to deuterium coupling, the resonances for the CD_2 carbons are not observed. Assignments of resonances can be made as shown in Figure 1 for our proposed structure. The chemical shift of the peak assigned to the cyclopropyl methylene resonance is the same as that of the analogous cyclopropyl methyl resonance in compound **2**, assigned by preparing 8,8′-dideuterio-**2**. Further conformation of the structure comes from the ^{1}H NMR of the d^6 analog of **6**. In CS_2 solution, it shows complex resonances at δ 5.16 and 3.76 assigned to a symmetrically metal coordinated diene and an AB pattern centered at δ 1.18 assigned to the equivalent set of resonances from positions 3,5 and 1,10. The ^{2}H NMR[13] of the d^6 derivative of **6** and the ^{1}H NMR of **6** also are consistent with this structure. We are at present attempting to determine the mechanism for the formation of **6**. No mono- or diadducts have been isolated or observed.

The reactions described above show that polycyclic metal complexes can be prepared by the addition of methylene to uncoordinated double bonds present in metal olefin π complexes. The conditions of the reaction are mild enough to prevent thermal rearrangement of the products unless a vinylcyclopropane is formed as in the reaction with **5**. Thus, potentially, methylene addition can be directed to desired locations in polyolefins by proper choice of coordinating metal. We are now attempting to cleave from the metal and isolate the tricyclic rings in compounds **4** and **6** (both unknown organic compounds) to show that this approach can be useful in the synthesis of new organic compounds.

Acknowledgment. Support of this research by the Research Corporation is gratefully acknowledged.

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Received November 6, 1974

Perturbed Pericyclic Reactions. Electrocyclic Ring Closure of Heteroacycles Isoelectronic with the Allyl Anion

Sir:

The orbital symmetry conservation principle has proven enormously popular and effective for rationalizing the stereochemistry and relative energies of a host of reactions involving cyclic transition states. Its application, particularly in the form of the Woodward–Hoffmann (W-H) rules,[1,2] usually depends on a knowledge of the behavior of a few critical high-lying molecular orbitals[3] derived from symmetrical hydrocarbons. Nonetheless the rules have been routinely applied to unsymmetrical substances including both highly substituted hydrocarbons as well as hetero derivatives. The justification for this procedure, suggested explicitly by Woodward and Hoffmann,[4] lies partly in the assumption that a small deviation from molecular symmetry is expected to produce an equally small change from the symmetry of the derived molecular orbitals. Consequently the slightly perturbed system is anticipated to lead to the same overall result as for the symmetric analog.[5,6] The question which naturally arises concerns the magnitude of the deviation from symmetry a molecule can withstand before the W-H rules no longer apply in a straightforward fashion.

The present work concerns itself with the heteroacyclic unit **1**, isoelectronic with the allyl anion, and its CNDO-computed[8] ring closure to the corresponding three-membered ring **2**. For the nine cases **3–11** all possible acyclic stereoisomers were transformed stepwise through both conrotatory and disrotatory transition states[9a] to all possible cyclic conformations.[9b] An orbital correlation diagram was constructed for each reaction investigated.

As a test for the predictive ability of this procedure, three cases (**3**, **7**, and **11**) were repeated with an energy-geometry optimization at each of the points along the reaction coordinate. The qualitative result was retained in every essential respect:[10] (i) the relative magnitude of the energy difference between the disrotatory and conrotatory modes; thus (ii) the favored stereochemistry for ring closure, and (iii) the details of the orbital correlation diagrams.

The results of the calculations reveal that heteroatom substitution of **1** leads to three types of ring closures. The first is represented by the least perturbed series **3**, **4**, and **5**. The symmetrical aziridine system **4** has been shown experimentally to conform to the W-H rules.[11] The computed