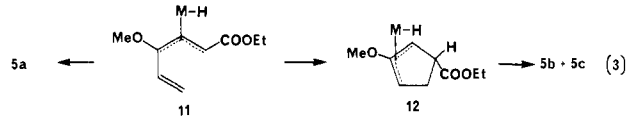
dichotomy and the production of both **5b** and **5c**, rather than only the vinylcyclopropane–cyclopentene[18] rearrangement product **5c**, is consistent with the generation of **12** from the initially formed[4] η^3-allyl metal hydride complex **11** (eq 3). The formation of **12**



and subsequent production of **5b** and **5c** are presumed to be competitive with the generation of **5a** from **11** in the copper catalyzed reactions. Further extensions of these and related transformations are currently being investigated in our laboratory.

Acknowledgment. The support of this research by the National Science Foundation is gratefully acknowledged.

Supplementary Material Available: Experimental details for the preparation of vinyl ethers from oxocyclopropanes as well as pertinent physical properties and NMR data for **1a–5a** (3 pages). Ordering information is given on any current masthead page.

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syn- and *anti*-Norcaradieneiron Tricarbonyl

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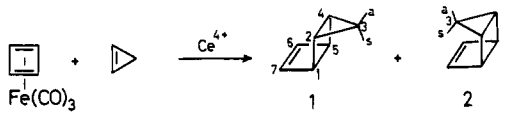
Received March 30, 1981

The bicyclo[4.1.0]hepta-2,4-diene structure, commonly known as norcaradiene, does not possess a particularly high strain or electronic energy but still lacks molecular reality. Its illusiveness is attributed to the easy valence isomerization to cycloheptatriene, which is well documented for some of its derivatives.[1] Although the energy difference between the two valence isomers seems to have been overestimated,[2] there is no clear evidence for an equilibrium concentration of norcaradiene in cycloheptatriene.

Several unstable structures have been isolated as ligands in transition-metal complexes, and in the case of norcaradiene the iron tricarbonyl group seems an especially fitting partner. From a number of cycloocta-1,3,5-triene–bicyclo[4.2.0]octa-2,4-diene equilibria the less stable bicyclic component is complexed by this group either selectively[3] or via isomerization of the monocyclic ligand.[4] Cycloheptatriene, however, only yields the monocyclic iron tricarbonyl complex[5] and so does a 7,7-disubstituted derivative[6] with a high equilibrium concentration of the norcaradiene isomer. It has been postulated[6] that *anti*-norcaradieneiron tricarbonyl is less stable than the cycloheptatriene complex and is an intermediate in the rapid 1,3-metal shift of the latter.

Cyclooctatetraene, whose equilibrium concentration of bicyclo[4.2.0]octa-2,4,7-triene is well established,[7] also gives only the monocyclic iron tricarbonyl complex,[8] but the syn and anti complex of its bicyclic valence isomer have been obtained via ring opening of *anti*- and *syn*-tricyclo[4.2.0.$0^{2,5}$]octa-3,7-dieneiron tetracarbonyl.[9] The bicyclooctatriene complexes do not rearrange to the more stable cyclooctatetraene complex even at 60 °C; evidently the iron tricarbonyl group effectively blocks the ring opening of the ligand that in the free form occurs at −20 °C.[10]

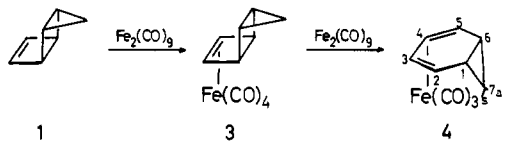
We patterned our synthesis of the norcaradieneiron tricarbonyls upon these results. The required valence isomer of norcaradiene with a contracted cyclohexadiene ring, i.e., tricyclo[3.2.0.$0^{2,4}$]-hept-6-ene, was built up as mixture of the anti and syn stereoisomer **1** and **2** in a straightforward way by Diels–Alder reaction of cyclopropene with cyclobutadiene: Cyclobutadieneiron tri-



carbonyl[11] (0.66 equiv) is added to an ice cold 0.3 M solution of cyclopropene[12] in 95% aqueous acetone, and 2.5 equiv of ceric ammonium nitrate are added over a period of 10 min. After the usual workup, using butane as extractant, the cycloadducts are obtained in a 47% yield with a syn–anti ratio of 1.3:1 and are isolated by VPC (20% bis(β-cyanoethyl) ether on kieselguhr, 2.5 m × 0.64 cm, 62 °C, 30 mL of He/min). **1**:[13] 6.6 min; ^{1}H NMR (CCl_4) δ 6.40 (narrow m, H-6, -7), 2.87 (narrow m, H-1, -5), 1.80 (m, H-2, -4), 1.13 (q, J = 4.8 Hz, H-3a), 0.88 (narrow m, H-3s); ^{13}C NMR ($CDCl_3$) δ 143.0 (C-6, -7), 48.2 (C-1, -5), 23.7 (C-2, -4), 20.0 (C-3). **2**:[13] 12.8 min; ^{1}H NMR (CCl_4) δ 5.70 (s, H-6, -7), 3.07 (d, J = 5 Hz, H-1, -5), 1.45 (t, J = 5 Hz, H-2, -4), 1.08 (d, J = 5 Hz, H-3s), 0.28 (q, J = 5 Hz, H-3a); ^{13}C (C_6D_6) δ 134.6 (C-6, -7), 38.8 (C-1, -5), 6.8 (C-2, -4), 4.6 (C-3).

The anti configuration of the adduct **1** is derived from the shielding of the allylic protons H-1, -5 as well as from their small coupling constant (<1 Hz) with the tertiary cyclopropane protons H-2, -4.[14] In the syn stereoisomer **2** the allylic protons adsorb at a 0.2 ppm lower field and couple strongly with the tertiary cyclopropane protons. The deshielding of the *syn*-cyclopropane proton is unexpected and may arise from steric compression that overcompensates the shielding by the double bond.

Stirring a 0.1 M pentane solution of **1** at room temperature successively with two 1.5 equiv portions of diiron nonacarbonyl gives after chromatographic workup on alumina with hexane a 14% yield of *anti*-tricyclo[3.2.0.$0^{2,4}$]hept-6-eneiron tetracarbonyl (**3**):[13] ^{1}H NMR (C_6D_6) δ 3.75 (s, H-6, -7), 2.49 (narrow m, H-1,



-5), 1.75 (m, H-2, -4), 0.90 (q, J = 5 Hz, H-3a), 0.69 (m, H-3s) followed by a 50% yield of *syn*-norcaradieneiron tricarbonyl (**4**):[13] mp −5 °C; ^{1}H NMR (C_6D_6) δ 4.48 (AA′ part of AA′XX′ system, J(2,3) = 5.99 Hz, J(2,4) = 1.11 Hz, J(2,5) = 0 Hz, J(3,4) = 3.74 Hz, H-3, -4), 3.15 (XX′ part, H-2, -5), 0.19 (m, H-1, -6, -7a), −0.10 (m, H-7s); ^{13}C NMR (C_6D_6) δ 212.4 (CO), 84.9 (^1J = 173.3

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(14) Cf. the small coupling of the allylic protons in *anti*-tricyclo-[4.3.0.$0^{7,9}$]nona-2,4-diene.[4c]

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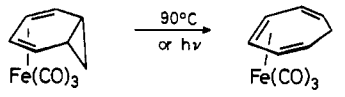
Hz, C-3, -4), 65.9 (^1J = 159.9 Hz, C-2, -5), 15.1 (^1J = 155.0, 156.3 Hz, C-7), 7.8 (^1J = 163.6 Hz, C-1, -6).[15]

The anti configuration of the iron tetracarbonyl group in **3** is deduced from the small shielding of the cyclopropane protons by the metal. The mechanism of the ring opening[9,16] then brings the metal syn to the cyclopropane ring in the norcaradiene complex **4**. This assignment is confirmed by the shielding of the cyclopropane proton H-7s that adsorbs at a 1.0 ppm higher field than the same proton in the trimethylene-bridged norcaradieneiron tricarbonyl[17] with the metal in the anti position.

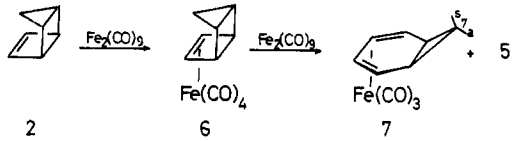
The opening of the bicyclohexene unit in **1** at room temperature with an excess (**5**)[5] diiron nonacarbonyl is unexpected, but it agrees with the proposed mechanism of this process:[9,16] In the rate-determining step a carbonyl group is lost from the tetracarbonyl complex **3** to form the di-η-iron tricarbonyl intermediate which opens readily. The starting dissociation can be activated by heat but also by the "carbonylophile" iron tetracarbonyl that is generated from dissolved $Fe_2(CO)_9$ at room temperature. Accordingly, the isolated tricyclic iron tetracarbonyl complex **3** is transformed into the norcaradiene complex **4** by stirring with diiron nonacarbonyl at room temperature.

At 90.5 °C in benzene solution *syn*-norcaradieneiron tricarbonyl (**4**) cleanly rearranges to cycloheptatrieneiron tricarbonyl (**5**)[5] in a first-order reaction with $k_{90.5} = (2.51 \pm 0.03) \times 10^{-5}$ s^{-1}.



4 5

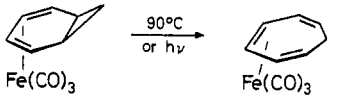
Treatment of *syn*-tricyclo[3.2.0.0^{2,4}]hept-6-ene (**2**) with diiron nonacarbonyl in the same way as above gives after chromatography with hexane on alumina a 5% yield of the iron tetracarbonyl complex **6**:[13] ^{1}H NMR (C_6D_6) δ 3.32 (s, H-6, -7), 2.57 (d, J =



2 6 7

5 Hz, H-1, -5), 1.65 (d, J = 6 Hz, H-3s), 1.49 (m, H-2, -4), 0.34 (q, J = 6 Hz, H-3a) followed by a mixture (17%) of *anti*-norcaradieneiron tricarbonyl (**7**) and cycloheptatrieneiron tricarbonyl (**5**). After protonation of the latter with 1 equiv of trifluoroacetic acid in benzene solution, filtration over alumina and evaporation of solvent furnishes a 10% yield of pure **7**:[13] ^{1}H NMR (C_6D_6) δ 4.82 (AA′ part of AA′XX′ system, H-3, -4), 3.24 (XX′ part, H-2, -5), 1.0 (m, H-1, -6, -7a), 0.79 (m, H-7s). The proton chemical shifts of **7** are close to those of the *anti*-norcaradieneiron tricarbonyl with a trimethylene bridge[17] and corroborate its structure.

anti-Norcaradieneiron tricarbonyl (**7**) is of similar thermal stability as its syn stereoisomer and opens to cycloheptatrieneiron tricarbonyl (**5**) at 90.5 °C with the first-order rate constant $k_{90.5} = (3.16 \times 0.1)10^{-5}$ s^{-1}.



7 5

The isomerizations of **4** and **7** prove that indeed norcaradiene is less stable than cycloheptatriene also when bonded to the iron tricarbonyl group, but their slow rates rule out either of them as reaction path for the ca. 10^8 times faster 1,3-metal shift in cycloheptatrieneiron tricarbonyl.[6] Irradiation of **4** or **7** in degassed THF solution with a high-pressure mercury lamp through Pyrex also effects their clean rearrangement into **5**.

In short, we have shown that norcaradiene can be frozen out as ligand in a stereoisomeric pair of iron tricarbonyl complexes which may prove a convenient storing form, since methods for its liberation at low temperatures are envisionable.

Acknowledgment. We thank the Fonds der Chemischen Industrie and the Verein der Freunde and Förderer der Universität Köln for unspecified financial support.

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High-Field ^{17}O NMR Spectroscopy: Solution Structures and Dynamics of ^{17}O Enriched $Co_4(CO)_{12}$ and $HFeCo_3(CO)_{12}$

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Received April 22, 1981

We have combined the advantages of ^{17}O NMR studies of metal carbonyl clusters[1] with the benefits of work at high magnetic field (9.4 T) on ^{17}O enriched samples.[2] This has enabled us to resolve the longstanding problem of the solution structure and dynamics of $Co_4(CO)_{12}$. The solid-state structure determined by X-ray analysis[3] has C_{3v} symmetry (see Figure 1) in which there are four equally populated CO environments (apical, two types of basal terminal, and one type of basal bridging) and two Co environments (apical and basal) in the ratio of 1:3. The structure in solution has presented problems since, although a complete analysis of the infrared spectrum[4] and observation of the ^{59}Co spectrum (two resonances, 1:3)[5,6] are in agreement with the C_{3v} structure, the ^{13}C NMR spectrum[5,7] is anomalous, giving three equally intense signals consistent with a D_{2d} structure.[7,8] This uncertainty has been partially removed by comparison of the exact ^{13}C shift of the single peak produced in the high temperature limiting spectrum,[9] which is consistent with C_{3v} symmetry. Studies based on

(1) The advantages are that metal carbonyls have narrow ^{17}O lines compared with most organic samples, line widths can be more favorable even than for ^{13}C if a quadrupolar metal is involved, and the temperature range for the study of fluxional dynamics therefore can be extended. Aime, S.; Milone, L.; Osella, D.; Hawkes, G. E.; Randall, E. W. *J. Organomet. Chem.* **1979**, *178*, 171-175.

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