solvent was stripped off. The yellow residue was chromatographed on 10 g of neutral alumina. Nothing eluted with hexane, indicating the disappearance of the starting VII. Benzene eluted an air-sensitive yellow liquid (45 mg): ir (CH_2Cl_2) 3496 (w), 2953 (w), 2869 (m), 2790 (w), 2040 (s), 1973 (s), 1029 (m) cm^{-1}; nmr ($CDCl_3$) broad absorptions at τ 2.8, 4.0, 4.5, 6.6, 7.5, and 8.6 (br s). This product may be dimeric in nature, as evidenced by the intricate nmr spectrum.

Method B. With DMAD Present. VII (0.20 g, 0.6 mmol) and DMAD (0.20 g 1.4 mmol) in 50 ml of xylene were stirred in an oil bath at 150° for 8 hr. The mixture was cooled to room temperature, the solvent stripped off, and the residue chromatographed on 25 g of neutral alumina. Benzene eluted a yellow compound (70 mg) with an ir spectrum similar to that described above. A brown band eluted in methanol; the solvent was evaporated from this product, 25 ml of benzene and *ca.* 100 mg of 10% Pd/C were added, and air was bubbled through the mixture for 2 days. The residue after stripping the benzene was placed on 20 g of neutral alumina. Ethyl ether eluted a slow-moving purple band (0.031 g, 16%). Purification by tlc on a 2 mm × 20 cm × 20 cm silica gel plate gave a blue band. Extraction of the center portion of this band with 95% ethanol gave a uv-visible spectrum with the following maxima: 555 nm (rel absorbance 0.16), 344 (0.16), 298 (1.6), 290 (0.95), 236 (0.45); *cf.* 1,2-dicarbomethoxyazulene.[4]

Method C. With TCNE Present. The complex VII (0.20 g, 0.6 mmol) and TCNE (0.10 g, 0.25 mmol) were refluxed for 10 hr in 40 ml of *n*-butyl ether. A black-brown solid (0.2 g) was then filtered off, and the brown solution was evaporated under reduced pressure. The residue was chromatographed on 20 g of neutral alumina to yield the following fractions.

Fraction 1. Hexane eluted a yellow-orange liquid (*ca.* 0.03 g): ir (film) 2976 (m), 2890 (m), 2833 (m), 2045 (s), 1972 (vs), 1499 (s), 1456 (m), 1445 (m), 1435 (m), 868 (w), 742 (w), 706 (w) cm^{-1}.

Fraction 2. Ethyl acetate eluted an orange, waxy oil (*ca.* 0.05 g): ir (film) 3367 (w), 2890 (m), 2882 (s), 2817 (m), 2024 (w), 1957 (w), 1835 (w), 1730 (s) (CO?), 1701 (m), 1664 (m), 1621 (m), 1484 (m), 1435 (m), 1366 (m), 1236 (m), 1174 (w), 1109 (w), 1072 (w), 1034 (w), 912 (w), 872 (w), 759 (m), 701 (m), 682 (w) cm^{-1}.

Fraction 3. Methanol eluted a red-brown viscous liquid (*ca.* 0.03 g): ir (film) 3425 (s), 2941 (m), 2066 (m), 1992 (m), 1742 (s) (CO?), 1724 (w), 1456 (m), 1385 (m), 1263 (m), 703 (m) cm^{-1}.

The black-brown precipitate which had been filtered from the reaction mixture was insoluble in organic solvents: ir (KBr) 3300 (m), 2941 (m), 2865 (m), 2217 (m), 2114 (w), 2062 (m), 1988 (m), 1592 (s), 1453 (m), 1387 (w), 1280, 1107 (w) cm^{-1}.

Heptafulvenediiron Hexacarbonyl (XIII). The heptafulveneiron tricarbonyl complex VII (0.20 g, 0.8 mmol) was dissolved in 50 ml of hexane and stirred overnight with 15 g (41 mmol) of $Fe_2(CO)_9$. The solution was then heated to reflux for 1 hr to decompose the small amount of $Fe_2(CO)_9$ still remaining. After cooling, the reaction mixture was filtered through infusorial earth, the hexane was evaporated, and the green residue was chromatographed on 15 g of neutral alumina. Benzene eluted an orange band which, upon solvent removal, yielded 0.24 g (77%) of orange-red crystals, mp 177–180° dec (recrystallized from a CH_2Cl_2–hexane mixture at −78°). The crystals were very insoluble in organic solvents. Attempted purification by sublimation (80°, 0.1 mm) led to mixtures of VII and XIII. The mass spectrum of XIII is recorded in Table III: ir (CH_2Cl_2) 2967 (w), 2890 (m), 2817 (w), 2040 (s) (CO), 1980 (s) (CO), 1580 (w), 1464 (w), 1443 (w), 1361 (w), 1099 (m), 1015 (m), 873 (m), 810 (m) cm^{-1}; nmr (acetone-d_6) τ 4.0 (m, 2 H), 6.0 (m, 2 H), 8.4 (m, 2 H), 8.6 (s, 2 H).

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Preparation of Metallocenes from Hydrocarbon Dianions

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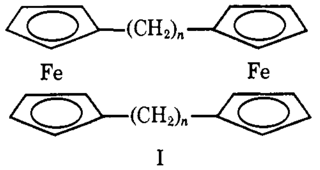
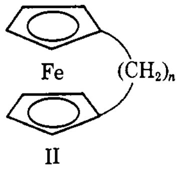
Abstract: Transition metal halides and hydrocarbon dianions composed of two linked cyclopentadienyl residues might yield polymers in which metal atoms and hydrocarbon residues alternate. Procedures are described for preparing a series of cyclic oligomers by treating iron salts with the dianion of bis(cyclopentadienyl)methane. Analogously, dimers are prepared from the dianions of 1,4-bis(cyclopentadienyl)but-2-yne and 1,4-bis(cyclopentadienyl)but-2-ene. The latter also gives a bridged monomer. The dianion of bis(cyclopentadienyl)methane with titanium tetrachloride gives 1,1′-methylenetitanocene dichloride, and this material is used with lithium naphthalenide to fix nitrogen and with diethylaluminum chloride to polymerize ethylene.

The metallocene nucleus has been incorporated into a large number of polymers, the usual procedures beginning with monomeric metallocenes.[1] An alternative, to react a ligand having two cyclopentadienyl moieties with a transition metal halide, a procedure that might generate both the metallocene nucleus and the polymer in one step, has been tried only rarely. The disodium salt of 1,4-bis(cyclopentadienyl)butane with ferrous chloride gives the dimer, I (n = 4), [4.4]-ferrocenophane, and possibly related higher polymers that were not characterized, as well as the bridged monomeric ferrocene, II (n = 4), [4]ferrocenophane,[2,3] while analogous experiments wherein n = 2,[4] 3,[2] and 5[2] give II, but neither I nor higher polymers. The dilithium salt of the *as*-indacenyl anion with ferrous



I



II

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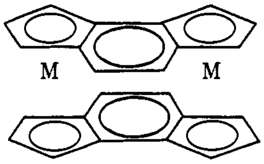
(1) (a) H.-J. Lorkowski, *Fortschr. Chem. Forsch.*, **9**, 207 (1967); (b) E. Neuse and H. Rosenberg, *J. Macromol. Sci., Rev. Macromol. Chem.*, **4**, 1 (1970).

(2) A. Lüttringhaus and W. Kullick, *Makromol. Chem.*, **44–46**, 669 (1961).

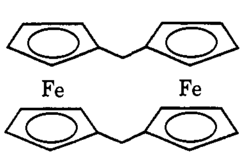
(3) Ferrocenophanes were reviewed by W. E. Watts, *Organometal. Chem. Rev.*, **2**, 231 (1967).

(4) H. L. Lentzner and W. E. Watts, *Tetrahedron*, **27**, 4343 (1971).

chloride[5] and nickel bromide[6] gives the dimers III



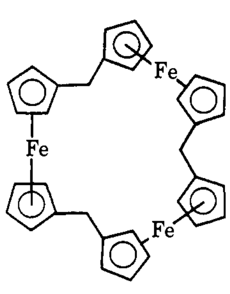
III



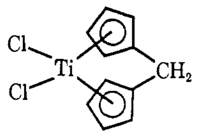
IV

(M = Fe, Ni), but again no higher polymer could be characterized. However, the dilithium salt of bis(cyclopentadienyl)methane with ferrous chloride does give polymers larger than dimers, and a series of oligomers, a dimer, trimer, tetramer, and pentamer, the so-called [1^n]ferrocenophanes, of which the first two are pictured as structures IV and V, could be separated and characterized.[7–9]

The preparation of the [1^n]ferrocenophanes was reported in a brief communication,[7] and we give below the details of the synthesis. We also give details of the chemistry of VI, 1,1′-methylenetitanocene dichloride, that were not given in the communication initially reporting its preparation and its use in polymerizing ethylene and fixing nitrogen.[10]

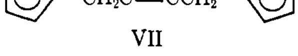


V

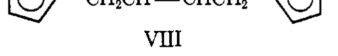


VI

Two further attempts to make ferrocene polymers are also reported using salts VII and VIII, which were chosen because they should be easy to prepare and because it was hoped that polymers derived from VII could be isomerized to butadienes,[11] providing a conjugated system that would allow electron delocalization across the whole molecule.



VII

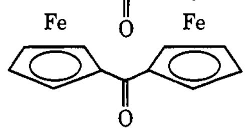


VIII

Results

Treatment of bis(cyclopentadienyl)methane[12] in tetrahydrofuran (THF) with n-butyllithium in hexane and then with either ferrous chloride or ferrous hexaammine thiocyanate gives the first four [1^n]ferrocenophanes, $n = 2$, 3, 4, and 5, in comparable amounts and fair yield. The total yield after purification was 14% when the iron reagent used was ferrous chloride and 30% when ferrous hexaammine thiocyanate. The ferrocenophanes can be separated by dry column chromatography on silica gel and purified by simple crystallization ($n = 2$, 3, and 4) or by rechromatography and crystallization ($n = 5$). Attempts to use other iron reagents for the preparation were unsuccessful. Fe(py)$_4$(SCN)$_2$[13] (py = pyridine) gave, after chromatography, only black intractable materials. Mixtures of [(CH$_3$)$_3$Si]$_2$NNa[14] and FeCl$_2$, which with cyclopentadiene gave a 37% yield, based on [(CH$_3$)$_3$Si]$_2$NNa, of ferrocene itself,[15] with bis(cyclopentadienyl)methane gave only recovered hydrocarbon.

The dimer, [1^2]ferrocenophane, was previously prepared by reducing the diketone IX with LiAlH$_4$ and AlCl$_3$,[16] but the diketone was not readily available.[17] Spectroscopic data for the diketone have not been reported previously and are given in the Experimental Section for a sample prepared by oxidizing [1^2]ferrocenophane with MnO$_2$.[16b]



IX

Bis(cyclopentadienyl)methane in THF reacts with n-butyllithium and then TiCl$_4$ to give VI in 30% yield.[18] No oligomers could be found. That mixtures of the titanocene dichloride VI with lithium naphthalenide fix nitrogen approximately as efficiently as do mixtures of titanocene dichloride itself with lithium naphthalenide[19] is shown by experiments described in the Experimental Section in which the two sets of reagents were simultaneously reacted under identical conditions with nitrogen. The amount of ammonia formed was determined by the Kjeldahl procedure after the reactions were quenched with dilute sulfuric acid. Similarly, mixtures of VI with diethylaluminum chloride polymerize ethylene approximately as efficiently as do mixtures of bis(cyclopentadienyl)titanium dichloride itself with diethylaluminum chloride.[19]

1,4-Bis(cyclopentadienyl)but-2-yne[20] was prepared from sodium cyclopentadienide and 1,4-dichlorobut-2-yne. After aqueous work-up, the product was purified by chromatography on silica gel using hexane as the eluent. Attempted distillation produces large amounts

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(5) (a) T. J. Katz, V. Balogh, and J. Schulman, *J. Amer. Chem. Soc,*, **90**, 734 (1968); (b) T. J. Katz and J. Schulman, *ibid.*, **86**, 3169 (1964); (c) R. Gitany, I. C. Paul, N. Acton, and T. J. Katz, *Tetrahedron Lett.*, 2723 (1970).

(6) Unpublishd experiments of Dr. Nancy Acton.

(7) T. J. Katz, N. Acton, and G. Martin, *J. Amer. Chem. Soc.*, **91**, 2804 (1969).

(8) For an explanation of the nomenclature, see footnote 7 of ref 7. In this paper the notation [1^2] is used for the [1.1] form of ferrocenophane; [1^3] for [1.1.1], etc.

(9) The three-dimensional structure of [1^3]ferrocenophane has been determined by X-ray diffraction: S. J. Lippard and G. Martin, *J. Amer. Chem. Soc.*, **92**, 7291 (1970).

(10) T. J. Katz and N. Acton, *Tetrahedron Lett.*, 2497 (1970).

(11) (a) R. J. Bushby, *Quart. Rev., Chem. Soc.*, **24**, 585 (1970); (b) F. Sondheimer, D. A. Ben-Effraim, and R. Wolovsky, *J. Amer. Chem. Soc.*, **83**, 1675 (1961); (c) F. Sondheimer and R. Wolovsky, *ibid.*, **84**, 260 (1962); (d) K. Schlögl and A. Mohar, *Monatsh. Chem.*, **93**, 861 (1962).

(12) H. Schaltegger, M. Neuenschwander, and D. Meuche, *Helv. Chim. Acta*, **48**, 955 (1965).

(13) H. Grossmann and F. Hünsler, *Z. Anorg. Allg. Chem.*, **46**, 361 (1905).

(14) U. Wannagat and H. Niederprüm, *Chem. Ber.*, **94**, 1540 (1961).

(15) Bis(cyclopentadienyl)zinc, -cadmium, and -mercury have been made in this way: J. Lorberth, *J. Organometal. Chem.*, **19**, 189 (1969).

(16) (a) W. E. Watts, *ibid.*, **10**, 191 (1967); (b) T. H. Barr, H. L. Lentzner, and W. E. Watts, *Tetrahedron*, **25**, 6001 (1969).

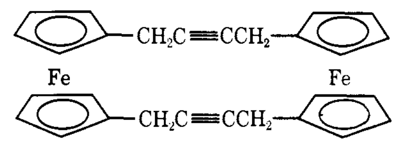
(17) The best yield reported is 3–7%, obtained as a product of the reaction of 1,1′-ferrocenecarbonyl chloride with ferrocene.[16] In the one attempt we made to repeat this preparation, however, we obtained none.

(18) Dicyclopentadienyltitanium dichloride is made similarly: G. Wilkinson and J. M. Birmingham, *J. Amer. Chem. Soc.*, **76**, 4281 (1954); L. Summers, R. H. Uloth, and A. Holmes, *ibid.*, **77**, 3604 (1955).

(19) For references see ref 10.

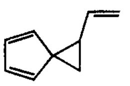
(20) Belgian Patent 625,804 (1963); *Chem. Abstr.*, **60**, 14697e (1964).

of polymer, and even dilute hexane solutions polymerize in air. Nevertheless, the material remaining after the hexane is removed rapidly at reduced pressure behaves as, and undoubtedly largely is, 1,4-bis(cyclopentadienyl)but-2-yne. Attempts to form the dianion VII by reacting this material with *n*-butyllithium in THF produces black intractable tars. However, the dianion can be prepared successfully if diethyl ether is used in place of THF. Addition of ferrous chloride and THF then gives the ferrocene X. If no THF is added, no ferrocene is obtained. Purification may be effected by extraction into CS_2, chromatography on silica gel, and crystallization from CS_2. The yield is 3%.

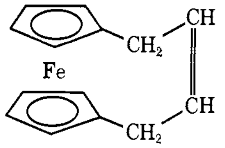


X

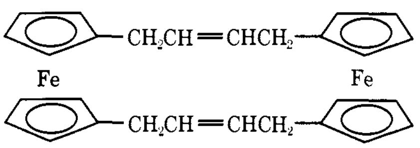
1,4-Bis(cyclopentadienyl)but-2-ene[20,21] was prepared by treating sodium cyclopentadienide in THF with 1,4-dichloro-*trans*-but-2-ene.[22] The reaction yields XI, which is isolated by distillation in 36–51% yield,[23] and 1,4-bis(cyclopentadienyl)but-2-ene, which is isolated in 24% yield after chromatography of the distillation residue. This latter hydrocarbon polymerizes upon attempted distillation or upon standing in air, and it was therefore used without extensive purification. Attempts to form the dianion VIII by reaction with *n*-butyllithium in THF, like the corresponding attempts to make VII, gave black tars, but again substituting diethyl ether for THF was effective. In diethyl ether a white slurry was produced that reacted with ferrous chloride and THF to give a mixture of ferrocenes from which, after purification, XII was obtained in 13% yield and XIII in 6% yield. The THF was required for the reaction to work. The ferrocenes were separated by chromatography on silica gel. The monomer XII, after sublimation and recrystallization, is a yellow crystalline solid, stable in air, and soluble in organic solvents. The dimer, XIII, can also be crystallized, is orange in color, and is at most only sparingly soluble in organic solvents.



XI



XII



XIII

The monomer XII seems to have the interesting property of allowing rotation to occur a number of times per second at room temperature about the single bonds connecting the olefinic and methylenic carbon atoms. That the rotation is rapid is indicated by the compound's proton nmr spectrum being matched by a spectrum calculated assuming a coupling pattern of the form $A_2XX'A_2'$;[26] if the rotation were not rapid the two protons attached to each methylene carbon atom would be magnetically inequivalent. Molecular models show that the rotation should be hindered by forces attempting to keep the cyclopentadienyl rings parallel, and these forces must therefore not be great. The rotation should be slowed at reduced temperature, but at −75° the 60-MHz spectrum is unchanged from that at 37°, implying that the free energy barrier to the rotation is less than 10 kcal/mol.

The parameters required to make a calculated proton nmr spectrum match the spectrum observed for XII are given in the Experimental Section, and they include the requirement that the coupling between the olefinic protons be 10.4 Hz, implying that the stereochemistry about the double bond is cis.[27,29] Molecular models show that the cis isomer should be more stable than the trans, but we do not know why it is isolated from the reaction of a sample of 1,4-dichloro-2-butene that is largely trans. However, the same isomer, XII, is also obtained when 1,4-dichloro-*cis*-but-2-ene[31] is used for the synthesis or when the 1,4-bis(cyclopentadienyl)but-2-ene used is prepared by hydrogenating 1,4-bis(cyclopentadienyl)but-2-yne over palladium on barium sulfate.[32]

Attempts to rearrange the diacetylene X to the butadiene were unsuccessful. Potassium *tert*-butoxide in either benzene–*tert*-butyl alcohol,[33] hexamethylphosphoric triamide, or dimethyl sulfoxide gave after aqueous work-up and chromatography only small amounts (<10%) of red material, which showed the proton nmr absorptions characteristic of ferrocene (τ 5.8) and not characteristic of the original methylene group (τ 6.65), but its olefin absorptions were either small or absent.

Experimental Section

All reactions were carried out under argon unless otherwise indicated. Proton nmr spectra were determined with either Varian A-60A or HA 100 instruments, infrared spectra with a Perkin-Elmer 621, unless otherwise indicated, uv and visible spectra with a Cary 14, and mass spectra with a Perkin-Elmer Hitachi RMU-6D, except that the mass spectra of [1^4]- and [1^5]ferrocenophane were determined using a CEC 21-110B. Only those mass spectrometric peaks whose relative intensity is 10% or greater are listed.

Fe(py)$_4$(SCN)$_2$.[13] Ferrous thiocyanate [28 g, 95% (Alfa Inorganics)] and 160 ml of dry pyridine were stirred at room temperature for 25 min. The thick yellow precipitate was collected, washed with pyridine, and recrystallized from 350 ml of boiling pyridine giving 35 g (44%), mp (with prior decomposition) 255–260°.

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(21) A. Renner, F. Widmer, and A. von Schultess, *Kunststoffe*, **53**, 509 (1963); *Chem. Abstr.*, **59**, 15437f (1963).

(22) "Approximately 90% trans, 10% cis" from Matheson Coleman and Bell division of the Matheson Co., Inc., East Rutherford, N. J.

(23) This material had previously been prepared by photolyzing diazocyclopentadiene in butene,[24,25] and by reacting potassium cyclopentadienide with *cis*-1,4-dichlorobut-2-ene.[24]

(24) D. Schönleber, *Chem. Ber.*, 102, 1789 (1969).

(25) M. Jones, Jr., R. N. Hochman, and J. D. Walton, *Tetrahedron Lett.*, 2617 (1970).

(26) The calculations were performed by Jeffrey Johnson using the program LAOCN3, available as program 111 from the Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind. 47401.

(27) The parameters are similar to those required by the spectrum of 1,4-dichloro-*cis*-but-2-ene.[28]

(28) H. G. Hecht and B. L. Victor, *J. Amer. Chem. Soc.*, **89**, 2532 (1967).

(29) Trans olefin coupling constants are much larger than 10 Hz,[30] and in 1,4-dichloro-*trans*-but-2-ene the constant is 17.0 Hz.[28]

(30) A. A. Bothner-By, *Advan. Magn. Resonance*, **1**, 195 (1965).

(31) J. M. Bobbitt, L. H. Amundsen, and R. I. Steiner, *J. Org. Chem.*, **25**, 2230 (1960).

(32) D. J. Bram and N. L. Allinger, *J. Amer. Chem. Soc.*, **78**, 2518 (1956).

(33) I. C. Calder, Y. Gaoni, and F. Sondheimer, *ibid.*, 90, 4946 (1968).

$Fe(NH_3)_6(SCN)_2$.[34] Dry ammonia was passed for several hours through a hot tube (120°, 2 × 30 cm) containing 8.1 g of $Fe(py)_4(SCN)_2$ giving 3.85 g (80%, off-white powder).

$[1^n]$Ferrocenophanes. Bis(cyclopentadienyl)methane was prepared after slight modification of a published procedure.[12] Cyclopentadiene (100 g, 1.5 mol) was added to 36 g of NaH in 1 l. of THF at 0°. After methylene chloride (74 ml) was added during 30 min, the mixture was warmed slowly during 2 hr and refluxed without external heating (30 min). After cooling, addition of water (50 ml) coagulates NaCl. The THF solution was decanted, washed (saturated NH_4Cl, then brine), dried (Na_2SO_4), and stripped. The product, divided in three lots, was distilled through a very short path (0.1 mm, pot temperature = 75°), giving 13 g (12%).

(a) **Using $Fe(NH_3)_6(SCN)_2$.** The hydrocarbon was added to a solution of *n*-butyllithium (20 ml, 1.6 *N*, in hexane) in THF (20 ml) at −78°. The mixture was stirred at 0° for 20 min and then poured in portions onto $Fe(NH_3)_6(SCN)_2$ (7.4 g, 27 mmol) and THF (30 ml), 20 ml of additional THF being being used to complete the transfer. The black mixture was stirred at room temperature for 1 hr, and the solvents were stripped. The residue was taken up in 1.5 l. of CS_2 and filtered through Na_2SO_4 and Celite, and the solvent was stripped, leaving 3.75 g of yellow solid. This was dissolved in CS_2, the mixture was filtered, and 15 g of silica gel (previously deactivated by adding 25% water) was added. The solvent was removed by rotary evaporation. The powder was added to the top of a column of silica gel (deactivated by the addition of 18% water) contained in a thin nylon tube (81 × 4.7 cm).[35] The column was developed with CS_2 and cut into four fractions, and each section was extracted under N_2 with CH_2Cl_2 in a Soxhlet apparatus. Removal of solvent from the first section left 517 mg of yellow crystalline material, which on recrystallization from acetone afforded 214 mg (5.6%) of pure $[1^2]$ferrocenophane, mp (vacuum) 245–248°, lit.[16] 254–256°. The second section afforded 618 mg of crystalline material, which on recrystallization from CS_2 gave 467 mg (12.1%) of pure $[1^3]$ferrocenophane, mp (vacuum) 278.5–280.5°. The third section afforded 692 mg of yellow solid, which on recrystallization from toluene gave 354 mg (9.2%) of $[1^4]$ferrocenophane, which darkens at 265°, but does not melt up to 300°. The fourth section contained 269 mg (7%) of a yellow-brown oil ($[1^5]$ferrocenophane). Crude material (196 mg) was chromatographed on silica gel (35 × 1 cm) eluting with CS_2 and then mixtures of CS_2 and CH_2Cl_2 (gradient elution). Removal of solvent left a yellow viscous material, which was taken up in 6 ml of warm toluene, and after standing at room temperature overnight, deposited 15 mg of a light yellow precipitate, mp (vacuum) 114–122°.

(b) **Using $FeCl_2$.** The dilithium salt of bis(cyclopentadienyl)methane prepared from 2.8 g of bis(cyclopentadienyl)methane, as above, was added in portions to 3.2 g (25 mmol) of $FeCl_2$. After the mixture was stirred for 20 min at room temperature, the solvents were removed, and the crude product was taken up in CS_2, filtered, and stripped. The residue (2.3 g) was chromatographed on a dry column. After crystallization there was obtained 135 mg (3.5%) of $[1^2]$ferrocenophane, 179 mg (4.6%) of $[1^3]$ferrocenophane, and 150 mg (3.9%) of $[1^4]$ferrocenophane. The $[1^5]$ferrocenophane (64 mg, 1.6%) was a yellow-brown powder after it was washed with pentane, but it was not crystallized.

(c) **Attempt Using $Fe(py)_4(SCN)_2$.** The dianion slurry from 2.8 g (20 mmol) of hydrocarbon and 32 mmol of *n*-butyllithium in 100 ml of THF was poured in portions onto 12.2 g (25 mmol) of $Fe(py)_4(SCN)$. After 1 hr at room temperature, the solvent was stripped and volatile materials were pumped away at *ca.* 0.1 mm for 2 hr. The black residue was extracted by repeatedly grinding it under CS_2 in a mortar, and then filtering (*ca.* 750 ml of CS_2 total) and refiltering through Na_2SO_4 and Celite. Removal of solvent under reduced pressure left 1.7 g of black, sticky material that smelled strongly of pyridine. This was chromatographed on a dry column of deactivated silica gel as in method a above. Most of the material moved with the solvent (CH_2Cl_2 R_f 0.95, 0.99 g, 86% of eluted material) and was a brown-black sticky material that even after pumping at 0.1 mm smelled of pyridine. The proton nmr showed a broad singlet at τ 6.15, and other peaks were minor. Because of its intractability, it was not further investigated.

(d) **Attempt Using $NaN[Si(CH_3)_3]_2$ and $FeCl_2$.** Sublimed $NaN[Si(CH_3)_3]_2$ (11.3 g, 0.061 mol)[14] and 3.8 g of $FeCl_2$ (0.03 mol) in 75 ml of dry THF were refluxed for 1 hr. After cooling, the mixture was filtered from NaCl under argon, and THF stripped. The residue was taken up in 125 ml of anhydrous ether, and 1.9 g (13.2 mmol) of hydrocarbon was added. The dark green solution was stirred overnight under argon at room temperature. Water was added and the mixture was filtered from slime. The orange filtrate was washed with water, dried ($MgSO_4$), filtered, and stripped. The proton nmr of the residue showed mainly recovered hydrocarbon, no ferrocene resonances (τ 6), and at most small amounts of other products.

$[1^2]$Ferrocenophane: nmr (60 MHz, CS_2) τ 5.77 (distorted t, 2.0 H), 5.96 (distorted t, 2.0 H), 6.53 (s, 1.0 H); ir (KBr disk, cm^{-1}) 3085 w, 3069 w, 2845 w, 1476 w, 1437 m, 1429 m, 1397 w, 1037 m, 1225 w, 1199 m, 1154 w, 1072 s, 1046 s, 1036 s, 933 m, 916 w, 846 m, 813 s; visible and uv [λ_{max} (ϵ)] in cyclohexane, 439 nm (177.5), 247 (9040); mass spectrum [75 eV, *m/e* (rel intensity)] 56 (82), 82 (12), 89 (11), 94 (17), 112 (12), 115 (59), 116 (13), 120 (11), 121 (56), 134 (25), 139 (51), 140 (25), 141 (46), 142 (17), 170 (15), 171 (12), 172 (10), 184 (10), 195 (10), 196 (25), 197 (21), 198 (61), 199 (10), 202 (10), 260 (12), 262 (21), 318 (36), 394 (17), 396 (100), 397 (30).

Anal. Calcd for $C_{11}H_{10}Fe$: C, 66.71; H, 5.09; Fe, 28.20. Found: C, 66.85; H, 5.05; Fe, 28.57.

$[1^3]$Ferrocenophane: nmr (60 MHz, CS_2) τ 5.99 and 6.06 (distorted triplets, 3.94 H), 6.42 (s, 1.07 H); ir (KBr disk, cm^{-1}) 3060 w, 2901 w, 1512 w, 1463 w, 1423 w, 1385 w, 1289 w, 1214 m, 1043 m, 1030 s, 928 m, 866 w, 835 m, 804 s; visible and uv [λ_{max} (ϵ)] in methylcyclohexane, 441 nm (312), 323 sh (232), 250 sh (11,480); mass spectrum [75 eV, *m/e* (rel intensity)] 76 (14), 121 (12), 198 (25), 297 (14), 316 (10), 318 (24), 395 (15), 396 (24), 450 (12), 592 (21), 594 (100), 595 (43), 596 (10).

Anal. Calcd for $C_{11}H_{10}Fe$: C, 66.71; H, 5.09; Fe, 28.20. Found: C, 66.60; H, 5.35; Fe, 28.34.

$[1^4]$Ferrocenophane: nmr (60 MHz, toluene-d_8, 100°) τ 5.97 (s, 3.99 H), 6.30 (s, 1.01 H); ir (KBr, cm^{-1}) 3080 w, 2905 w, 2831 w, 1470 m, 1463 m, 1427 m, 1391 w, 1357 w, 1292 m, 1226 m, 1194 w, 1147 w, 1135 w, 1055 w, 1047 w, 1037 s, 1024 s, 930 m, 918 m, 852 m, 826 s, 808 s, 799 s, 750 w, 728 w, 480 s; visible and uv in methylcyclohexane, 430 nm (646), 320 sh (1009), 246 sh (18,450); mass spectrum [75 eV, PFK calibration, *m/e* (rel intensity)] 50 (10), 51, (19), 52 (12), 53 (13), 55 (19), 56 (23), 57 (19), 63 (13), 65 (29), 66 (41), 67 (16), 69 (10), 77 (26), 78 (16), 79 (38), 81 (11), 91 (29), 95 (12), 109 (15), 110 (18), 115 (38), 116 (14), 121 (71), 124 (10), 128 (24), 129 (25), 139 (16), 141 (34), 142 (18), 143 (14), 144 (27), 196 (14), 197 (15), 198 (32), 199 (28), 241 (10), 262 (19), 270 (17), 275 (10), 276 (12), 277 (14), 316 (10), 317 (17), 318 (28), 319 (32), 331 (10), 342 (27), 395 (11), 396 (14), 446 (100), 447 (41), 538 (13), 540 (50), 541 (24), 736 (14), 738 (53), 739 (28), 740 (17), 792 (24, parent ion), 793 (11).

Anal. Calcd for $C_{11}H_{10}Fe$: C, 66.71; H, 5.08; Fe, 28.20. Found: C, 66.58, 66.71; H, 5.40, 5.14; Fe, 28.20, 27.84.

$[1^5]$Ferrocenophane: nmr (60 MHz, CS_2) τ 6.12 (s, 4.05 H), 6.76 (s, 0.95 H); ir (KBr, cm^{-1}) 3078 w, 2918 w, 1720 w, 1460 w, 1425 m, 1389 w, 1352 w, 1289 m, 1220 m, 1122 w, 1034 s, 1020 s, 925 m, 852 w, 818 s, 802 s, 745 w, 476 s; visible and uv in methylcyclohexane, 450 nm sh (*ca.* 647), 316 sh (*ca.* 2005); mass spectrum [75 eV, PFK calibration, *m/e* (rel intensity)] 115 (12), 121 (21), 129 (15), 141 (12), 144 (10), 146 (10), 149 (20), 167 (10), 186 (12), 198 (27), 199 (26), 200 (13), 260 (10), 262 (21), 263 (10), 264 (13), 275 (11), 276 (15), 277 (24), 278 (10), 296 (16), 315 (10), 316 (14), 317 (19), 318 (49, 319 (35), 331 (10), 340 (20), 342 (85), 343 (25), 344 (46), 345 (10), 369 (12), 394 (16), 395 (25), 396 (71), 397 (24), 410 (19), 462 (13), 474 (11), 538 (18), 540 (100), 541 (38), 542 (50), 543 (16), 594 (17), 660 (10), 672 (15), 736 (20), 737 (11), 738 (93), 739 (47), 740 (39), 741 (18), 742 (11), 792 (15), 990 (3.5).

Anal. Calcd for $C_{11}H_{10}Fe$: C, 66.71; H, 5.08; Ge, 28.20. Found: C, 67.67; H, 5.41; Fe, 27.17.

$[1^2]$Ferrocenophanedione.[16] A mixture of $[1^2]$ferrocenophane (49 mg, 0.12 mmol) and MnO_2 (1 g, Winthrop Labs) in $CHCl_3$ (15 ml) was stirred at reflux for 19 hr. Filtering and stripping left 33 mg of red solid. Crystallization from $CHCl_3$ gave 28 mg (55%) of red hair-like crystals: nmr (60 MHz, $PhNO_2$-d_5, 130°) τ 4.58 (t, *J* = 2 Hz, 8.26 H), 5.39 (t, *J* = 2 Hz, 7.74 H); ir (KBr, cm^{-1}) 3138 w, 3113 vw, 3090 vw, 1613 vs, 1600 sh, 1470 s, 1467 s, 1435 w, 1399 w, 1383 m, 1362 vw, 1337 w, 1300 s, 1196 m, 1078 m, 1066 m, 1059 sh, 1053 sh, 1028 w, 903 w, 850 w, 823 m, 812 s, 777 sh, 774 w, 695 w, 614 w, 590 w, 521 w, 502 s, 478 s; mass spectrum [75 eV, *m/e* (rel intensity)] 330 (12), 422 (12), 424 (100), 425 (29).

1,1′-Methylenetitanocene Dichloride. Bis(cyclopentadienyl)methane (1.9 g, 13.2 mmol) in 5 ml of THF was added to a solution of THF (7 ml) and *n*-butyllithium (26.4 mmol, 16.5 ml, 1.6 *N*, in

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[34] G. Spacu, *Ann. Sci. Univ. Jassy*, **8**, 162 (1914); *Chem. Zentr.*, II, 608 (1914).

[35] B. Loev and M. M. Goodman, *Chem. Ind.* (*London*), 2026 (1967).

hexane) at −78°. After stirring for 30 min at −78° and 30 min at ambient temperature, the dianion slurry was poured cautiously with stirring onto an ice-cooled mixture of 2 ml of $TiCl_4$ and 5 ml of pentane. After the mixture was stirred for 4–5 hr at room temperature, solvents were removed under reduced pressure, and the residue was taken up in 250 ml of $CHCl_3$. Filtration, stripping, and sublimation (215–230° (10^{-8} mm)) gave first a colorless sticky liquid, which was cleaned off the cold finger, and then the product, a dark red solid. Crystallization from hot $CHCl_3$ continuously saturated with HCl[36] gave 1.03 g (30%), unmelted to 360°: nmr (60 MHz, DMSO-d_6) τ 3.16 (t, J = 2.7 Hz, 4.02 H), 4.08 (t, J = 2.7 Hz, 4.06 H), 5.84 (s, 1.91 H); ir (KBr, cm^{-1}) 3120 w, 3113 m, 3100 w, 3095 w, 3080 m, 3075 m, 2950 m, 1478 m, 1468 m, 1435 w, 1416 w, 1379 w, 1268 w, 1258 m, 1254 m, 1237 w, 1213 w, 1087 w, 1078 w, 1054 w, 1044 w, 1040 m, 1038 m, 943 w, 938 w, 931 w, 927 w, 894 w, 882 w, 860 w, 843 w, 836 m, 821 s, 816 s, 760 s, 658 s, 466 m, 422 m, 386 w, 379 w, 357 m, 348 m; mass spectrum [75 eV, *m/e* (rel intensity)] 39 (33), 51 (21), 52 (11), 63 (21), 83 (38), 85 (19), 115 (37), 118 (15), 120 (12), 139 (11), 141 (13), 161 (10), 185 (11), 186 (20), 187 (76), 188 (75), 189 (19), 198 (11), 222 (27), 223 (40), 224 (100), 225 (59), 226 (43), 227 (19), 260 (80), 261 (21), 262 (56), 263 (11), 264 (11).

Anal. Calcd for $C_{11}H_{10}TiCl_2$: C, 50.62; H, 3.86; Ti, 18.35; Cl, 27.17. Found: C, 50.84; H, 3.84; Ti, 18.30; Cl, 27.20.

Nitrogen Fixation by $(C_5H_5)_2TiCl_2$ and by 1,1′-Methylenetitanocene Dichloride. The extent of nitrogen fixation by the two titanium derivatives was determined simultaneously and under identical conditions.[37] Lithium naphthalenide was prepared under argon by stirring 3.2 g (25 mmol) of naphthalene and 200 mg of lithium wire in 400 ml of THF at room temperature for 1 hr; 150-ml portions (*ca.* 9.4 mmol of lithium naphthalenide) were transferred to two 500-ml flasks each equipped with a magnetic stirrer, serum cap inlet, gas inlet, and gas outlet. In early experiments the gas outlet was connected to a trap containing dilute H_2SO_4. However, a Kjeldahl analysis showed that no ammonia was reaching the trap. $(C_5H_5)_2TiCl_2$ (374 mg, 1.5 mmol) was added to one flask, and 392 mg (1.5 mmol) of 1,1′-methylenetitanocene dichloride to the other. Nitrogen was bubbled through the rapidly stirred solutions. At intervals aliquots (20 ml = 0.2 mmol of Ti) were withdrawn by syringe and quenched in 5 ml of 20% H_2SO_4. Most of the THF was removed from the aliquots under reduced pressure, and the aqueous solutions were made basic with 10 ml of 40% KOH. The aqueous solutions were distilled almost to dryness into a receiver containing 30 ml of 0.01 N HCl, and the excess acid was back titrated with 0.018 N NaOH (methyl red end point). The results are collected in Table I.

Table I. Comparison of $(C_5H_5)_2TiCl_2$ and 1,1′-Methylenetitanocene Dichloride as Nitrogen-Fixing Reagents

$(C_5H_5)_2TiCl_2$			1,1′-Methylenetitanocene dichloride		
Time, hr	NH_3, mmol	NH_3/Ti	Time, hr	NH_3, mmol	NH_3/Ti
0.40	0.23	1.15	0.42	0.17	0.85
0.84	0.22	1.10	0.85	0.196	0.98
1.67	0.23	1.15	1.68	0.19	0.95
4.05	0.26	1.30	4.06	0.22	1.10
6.50	0.23	1.15	6.51	0.22	1.10

Polymerization of Ethylene.[38] (a) **$(C_5H_5)_2TiCl_2$ as Cocatalyst.** A 500-ml three-necked flask was fitted with a magnetic stirrer, a gas inlet and exit, and a serum cap. After flame-drying and flushing with nitrogen, 208 mg (0.835 mmol) of $(C_5H_5)_2TlCi_2$ was introduced, followed by 200 ml of purified toluene.[39] The orange solution was purged for a few minutes with ethylene, and then 2 ml of a toluene solution of $(C_2H_5)_2AlCl$ (0.92 M by EDTA titration[40]) syringed in. The mixture immediately became dark and warm, and polyethylene precipitated. After a few minutes the mixture became light green, and after about 40 min again orange. The reaction was quenched 45 min after the addition of $(C_2H_5)_2AlCl$ by adding 10 ml of methanol. The polyethylene, which was collected, washed with hexane, and dried at 0.2 mm, was a white granular material, 4.3 g, mp 126–134°.

(b) **1,1′-Methylenetitanocene Dichloride as Cocatalyst.** The reaction was repeated exactly as in method a, but using 218 mg (0.835 mmol) of 1,1′-methylenetitanocene dichloride. There was obtained 4.0 g of polyethylene, mp 127–129°.

1,4-Bis(cyclopentadienyl)but-2-yne. Sodium cyclopentadienide was prepared at 0° by adding 26 g of cyclopentadiene (0.39 mol) during 45 min to a stirred suspension of 9.7 g (0.4 mol) of sodium hydride (17 g of 57% dispersion in mineral oil, washed four times with pentane) in 250 ml of dry THF. The anion solution was stirred for 30 min at 0°, and then 24 g (0.2 mol) of 1,4-dichlorobut-2-yne was added during 30 min. The dark blue solution was stirred for 1.5 hr at 0°, and quenched by adding 20 ml of water, which discharged the blue color. The THF solution was decanted from coagulated sodium chloride, washed with saturated NH_4Cl (2 × 100 ml), and diluted with 300 ml of hexane. The diluted solution was washed several times with water, dried (Na_2SO_4), concentrated under reduced pressure, and passed through a silica gel column (35 × 5 cm, hexane) giving 10–15 g of product (27–41%). The compound was stored in dilute hexane solution over hydroquinone at −10°. Attempted short-path distillation led to extensive polymerization, so the product was not purified further. The residue, left after the solvent was rapidly removed at reduced pressure, was characterized: nmr (60 MHz, $CDCl_3$) multiplets centered at τ 3.72 (5.6 H), 6.71 (broad singlet, 4.4 H), 7.10 (m, 4.0 H); ir (neat, Perkin-Elmer Model 137) weak acetylene stretch at 2240 cm^{-1}; mass spectrum [75 eV, *m/e* (rel intensity)] 39 (33), 41 (16), 42 (13), 51 (22), 56 (13), 63 (16), 65 (23), 66 (100), 67 (11), 77 (24), 78 (13), 91 (47), 103 (18), 115 (79), 116 (28), 117 (72), 132 (13), 139 (13), 152 (23), 154 (20), 165 (12), 167 (13), 182 (27).

X. A 500-ml three-necked flask was fitted with mechanical stirrer, solid addition funnel, argon inlet, and serum cap. The dilithium salt of 1,4-bis(cyclopentadienyl)but-2-yne was prepared at −78° by adding 21.2 ml of *n*-butyllithium in hexane (34 mmol) to a solution of 3.1 g of the hydrocarbon (17 mmol) in 200 ml of dry ether. After the mixture was stirred at −78° for 20 min and at ambient temperature for 30 min, anhydrous $FeCl_2$ (2.4 g, 19 mmol) was added, followed by 60 ml of dry THF. The mixture was stirred overnight at room temperature, and the solvents were stripped. The residue was extracted with 600 ml of CS_2 and filtered, and the solvent evaporated, leaving 1.1 g of residue, which was chromatographed on silica gel (40 × 2 cm) using 1:1 CS_2–hexane and then CS_2 as eluents. The major fraction was evaporated and the brown solid residue washed with CS_2 and crystallized from CS_2, giving 131 mg (3.2%) of orange-brown crystals. Recrystallization from toluene produced large golden-brown prisms, mp (vac) 246–249°, at most sparingly soluble in organic solvents: nmr (100 MHz, toluene-d_8, 100°) τ 5.78 (t, J = 1.6 Hz, 7.92 H), 6.03 (t, J = 1.6 Hz, 7.92 H), 6.65 (s, 8.17 H); ir (KBr, cm^{-1}) 3101 w, 3093 w, 3078 w, 2914 vw, 2888 vw, 2879 vw, 1463 vw, 1435 w, 1424 m, 1394 m, 1301 w, 1288 m, 1222 m, 1205 w, 1063 vw, 1037 m, 1027 s, 920 m, 856 m, 815 s, 695 vw, 530 m, 492 s, 450 vw, 427 m; mass spectrum [75 eV, *m/e* (rel intensity)] 236 (12), 470 (15), 472 (100), 473 (35).

Anal. Calcd for $C_{28}H_{24}Fe_2$: C, 71.22; H, 5.12; Fe, 23.66. Found: C, 71.36; H, 4.93; Fe, 23.89.

XII and XIII. (a) **From 1,4-Dichloro-*trans*-but-2-ene.** Sodium cyclopentadienide was prepared as above. 1,4-Dichloro-2-butene (25 g, 0.2 mol)[22] was then added in drops. Heat evolved and sodium chloride precipitated. After 30 min 25 ml of water was added, and the THF solution was decanted, washed two times with saturated NH_4Cl, and then diluted with 300 ml of hexane. The diluted solution was washed five times with water, dried (Na_2SO_4), and stripped. Distillation at ambient temperature (1 mm) gave 8.5–14 g (36–54%) of XI, which on redistillation boiled at 78° (40 mm), lit.[24] 43–44° (9 mm). The distillation residue was chromatographed on silica gel (35 × 5 cm, hexane) giving 8.8 g (24%) of 1,4-bis(cyclopentadienyl)but-2-ene. Attempted short-path distillation polymerized it, so it was not further purified. The residue left

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(36) G. Wilkinson and J. M. Birmingham, reference cited in ref 18.

(37) The procedure is modeled on that of G. Henrici-Olivé and S. Olivé, *Angew. Chem., Int. Ed. Engl.*, **8**, 650 (1969).

(38) D. S. Breslow and N. R. Newburg, *J. Amer. Chem. Soc.*, **81**, 81 (1959).

(39) Toluene was purified by repeatedly shaking with concentrated H_2SO_4, washing with water, drying (KOH), distilling under nitrogen from sodium onto 4A molecular sieves, and passing through a 40 × 2 cm column of silica gel directly into the reaction flask.

(40) "Aluminum Alkyls...specifications, properties and procedures," Texas Alkyls, Inc., specialty chemical division of Stauffer Chemical Co., New York, N. Y., undated technical brochure.

after rapidly removing the solvent at reduced pressure was characterized: nmr (60 MHz, CCl_4) multiplets from τ 3.5 to 4.7 (8.07 H), 6.92 (broad singlet, 3.84 H), two multiplets centered at 7.15 (4.08 H); mass spectrum [75 eV, *m/e* (rel intensity)] 39 (34), 41 (24), 51 (16), 52 (10), 53 (12), 63 (12), 65 (22), 66 (10), 67 (10), 77 (53), 78 (22), 79 (42), 91 (71), 92 (33), 103 (15), 104 (30), 105 (100), 106 (11), 115 (19), 116 (10), 117 (50), 118 (20), 119 (12), 128 (12), 141 (10), 184 (47).

The dilithium salt of 1,4-bis(cyclopentadienyl)but-2-ene was prepared at −78° by adding 60 ml of *n*-butyllithium in hexane (96 mmol) in drops to a stirred solution of 8.9 g (48 mmol) of the above hydrocarbon in 250 ml of ether. The white slurry was stirred for 15 min at −78°, then at ambient temperature for 40 min. Dry $FeCl_2$ (6.1 g, 48 mmol) was added, followed by 120 ml of dry THF. The dark mixture was stirred overnight at room temperature, diluted with 1 l. of CS_2 and filtered, and the solvent evaporated. XII and XIII were partially separated by chromatography on silica gel (70 × 2.5 cm) using 1:1 hexane–CS_2. The monomer, which eluted first, was extracted into pentane to remove a small amount of dimer, which is insoluble. It was then rechromatographed on silica gel (80 × 2.5 cm, hexane) and finally sublimed at 100° (0.1 mm) giving 1.5 g (13.5%) of material. Recrystallizing a sample three times from cold pentane gave bright yellow crystals, mp (vacuum) 86–88°. Recrystallization of the dimer from toluene gave 683 mg (3%) of orange plates, mp (vacuum) 219–223°.

XII: nmr (100 MHz, CS_2) τ 4.05 (sym mutiplet, 1.95 H), 6.15 (m, 7.96 H), 7.12 (sym m 4.08 H); ir (KBr, cm^{-1}) 3080 w, 3012 w, 2897 w, 2883 w, 2840 w, 1458 w, 1442 m, 1386 w, 1360 w, 1287 s, 1244 w, 1230 w, 1214 w, 1170 vw, 1144 vw, 1044 m, 1035 m, 1020 s, 940 m, 920 vw, 907 vw, 888 vw, 869 vw, 847 m, 840 m, 801 s, 793 s, 780 s, 619 w, 600 s, 511 s, 495 s, 484 s, 440 vw, 403 w, 390 w; mass spectrum [75 eV, *m/e* (rel intensity)] 56 (60), 81 (11), 115 (10), 121 (13), 134 (14), 236 (12), 238 (100), 239 (18).

Anal. Calcd for $C_{14}H_{14}Fe$: C, 70.62; H, 5.93; Fe, 23.46. Found: C, 70.46; H, 5.87; Fe, 23.32.

XIII: nmr (100 MHz, toluene-d_8, 80°) τ 4.22 (m, 4.00 H), 6.00 (s, $W_{1/2}$ = 3 Hz, 16.14 H), 6.91 (m, 7.86 H); ir (KBr, cm^{-1}) 3096 w, 3080 w, 3021 vw, 2969 w, 2915 w, 2880 w, 2820 vw, 1514 w, 1459 w, 1426 m, 1380 w, 1365 w, 1331 w, 1278 m, 1261 w, 1220 w, 1187 w, 1163 vw, 1064 w, 1059 w, 1035 s, 1025 s, 978 s, 920 m, 904 m, 848 w, 810 s, 520 m, 500 w, 480 s, 420 m; mass spectrum [75 eV, *m/e* (rel intensity)] 56 (100), 81 (10), 102 (10), 103 (18), 115 (27), 121 (57), 134 (32), 135 (14), 158 (18), 159 (10), 171 (13), 172 (10), 236 (19), 237 (13), 238 (31), 474 (10), 476 (74), 477 (27).

Anal. Calcd for $C_{28}H_{28}Fe_2$: C, 70.62; H, 5.93; Fe, 23.46. Found: C, 70.45; H, 5.82; Fe, 23.32.

(b) From 1,4-Dichloro-*cis*-but-2-ene. Sodium cyclopentadienide (0.8 mol) and 1,4-dichloro-*cis*-2-butene[31] (50 g, 0.4 mol) were combined as above. Distillation to 36° (0.1 Torr) gave 20 g of material, redistillation of which at 60–69° (25 Torr) gave 12 g (25%) of XI, contaminated with small amounts of spiro[4.4]nona-1,3,7-triene[41] and 4,7-dihydroindene,[42] and unidentified material (dimer of spiro-[4.4]nonatriene?, 8 g), bp 106–110° (0.1 Torr). Chromatography of the residue of the original distillation (45 × 5 cm silica gel, hexane eluent) gave 17 g (23%) of 1,4-bis(cyclopentadienyl)but-2-ene.

This hydrocarbon (10 g, 54 mmol) was converted as above into XII by sequential treatment with *n*-butyllithium (108 mmol) in pentane–ether, $FeCl_2$ (54 mmol), and dry THF (100 ml). Extraction with hexane, concentration, and elution through a silica gel column (35 × 2 cm, hexane) gave 4 g of crude product, whose pmr spectrum, although showing some extraneous resonances, had one ferrocene resonance that was 3.94 times as intense as that of the characteristic olefin pattern at τ 4.05, indicating that no ferrocene other than XII was present. XII crystallized in a few days and, after washing with hexane and recrystallization from hexane, was obtained in 2.5% yield (329 mg). Its pmr and ir spectra were superimposable on those of XII prepared from *trans*-dichloride. No attempt was made to isolate XIII in this experiment.

(c) From 1,4-Bis(cyclopentadienyl)but-2-yne. Quinoline (10 ml) and 5% $Pd/BaSO_4$ (1 g) were added to a solution of 1,4-bis(cyclopentadienyl)but-2-yne (*ca.* 4.4 g, 24 mmol) in 100 ml of ethyl acetate.[32] Hydrogen was consumed at atmospheric pressure, and the reaction was stopped when 555 ml had been absorbed (*ca.* 1 hr). The solution was filtered, concentrated, and passed through a silica gel column (35 × 2 cm, hexane). The hexane solution was washed (3 *N* HCl, 5% $NaHCO_3$, water) and dried (Na_2SO_4). The hydrocarbon (*ca.* 3.3 g) was used without further purification.

It was converted into XII using the same procedure described above. Thus *ca.* 3.3 g (18 mmol) of hydrocarbon with 37 mmol of *n*-BuLi in ether–pentane gave a white dianion slurry. To this was added 2.5 g (19.7 mmol) of $FeCl_2$ and 40 ml of THF. Work-up followed by silica gel chromatography afforded 200 mg (4.7%) of pure (pmr analysis) XII. No attempt was made to isolate XIII in this experiment.

Proton Nmr Spectrum of XII. The 100-MHz spectrum was determined in CS_2 solution and analyzed using the computer program LAOCN3.[26] The spectrum was matched with a calculated $A_2XX'A_2'$ pattern ($\tau_A = 7.14$, $\tau_X = 4.07$); $J_{XX'} = 10.40 \pm 0.04$ Hz and $J_{AX} = 8.1$, $J_{AX'} = -0.95$, $J_{AA'} = -0.04$ Hz. (The spectrum calculated was independent of $J_{AA'}$.) The coupling constants are similar to those required by the spectrum of 1,4-dichloro-*cis*-but-2-ene.[28] Calculated spectra could not be matched to the experimental one if $J_{XX'}$ was assumed to be much larger than 10 Hz. The outermost lines in both the A and X part of the calculated spectra were then separated too much, and there were other discrepancies. The spectrum was unchanged between 37 and −75°.

Attempts to Rearrange X to a Diene. The material balance in all these experiments was poor.

(a) Refluxing 19 mg of X in 40 ml of benzene and 1 ml of saturated *tert*-C_4H_9OK in *tert*-C_4H_9OH overnight, followed by aqueous work-up, gave material showing broad proton nmr absorptions centered at τ 5.8 and possibly traces of olefinic absorption at 3.8. X's methylene resonance at 6.65 was gone. The ratio of olefin: ferrocene peaks was not increased after chromatography on silica gel (1:1, CS_2–hexane).

(b) X (37 mg) mixed with 50 ml of dry HMPA and a saturated solution of *tert*-C_4H_9OK in HMPA (2 ml) was refluxed for 2 hr, giving a red-brown solution. After aqueous work-up, silica gel chromatography (1:1, CS_2–hexane) yielded a singlet peak, whose proton nmr showed broad ferrocene absorptions, traces of olefinic absorption at τ 3.9, and no methylene peak.

(c) X (171 mg) in 25 ml of DMSO and 1 ml of saturated *tert*-C_4H_9OK in DMSO were stirred at 100° for 4 hr. Aqueous work-up followed by chromatography afforded 28 mg of orange product, which was sublimed at 200° (10^{-6} mm), and then recrystallized from toluene, giving 13 mg of material whose nmr (toluene-d_8, 95°) showed only broad absorptions centered at τ 5.9 and a small peak at τ 6.8, residual, X. No olefinic nmr absorptions could be detected.

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(41) Singlet at τ 7.57; *cf.* ref 24: τ 7.67.

(42) Broad singlets at τ 7.08 and 7.2; *cf.* ref 25: τ 7.03 and 7.2.