ium ethoxide solution during 10 min. The solution turned first orange, then dark red, and upon standing for 48 hr, deposited the orange-yellow crystals of VIII. Recrystallization from butanol gave needles of the same color and mp 272°; the compound sublimed at 230–240° (0.2 mm). Even so, the product was not completely pure, and only chromatography of the benzene solution on alumina gave the pure product in yellow-greenish needles of mp 290° (lit.[6] mp 290–291°); it sublimed at 230–240° (0.2 mm) [(lit.[6] 255–260° (3 mm)]; yield, 0.6 g (12%); fluorescence, 485 mμ (in chloroform).

Anal. Calcd for $C_{38}H_{22}$: C, 95.4; H, 4.6. Found: C, 95.5; H, 4.7.

From the mother liquor, no other defined products could be isolated apart from triphenylphosphine oxide which was identified by melting point and mixture melting point. For comparison, the hydrocarbon VIII was synthesized according to Clapp.[6] Chromatography of the benzene solution on neutral alumina and recrystallization from a benzene–methanol mixture gave yellow-greenish needles of mp 290°. The mixture melting point with VIII showed no depression, and the ultraviolet and infrared spectra (in chloroform and potassium bromide, respectively) were identical.

4,5-Di(*p*-chlorophenyl)acenaphtho[1,2-*j*]fluoranthene.—In a similar reaction, using 5.6 g of 4,4′-dichlorobenzil and completed by refluxing the mixture for 5 hr, yellow needles were obtained by recrystallization from benzene (0.4 g, 7%): mp >305°; fluorescence, 480 mμ (in dioxane).

Anal. Calcd for $C_{38}H_{20}Cl_2$: C, 83.4; H, 3.7; Cl, 13.0. Found: C, 83.4; H, 3.5; Cl, 13.0.

Metallocene Polymers. XIV. Metal–Ring Bond Cleavage by Water-Promoted Zinc Chloride[1]

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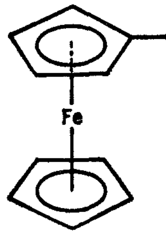
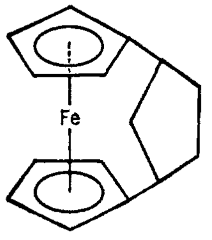
Received November 26, 1965

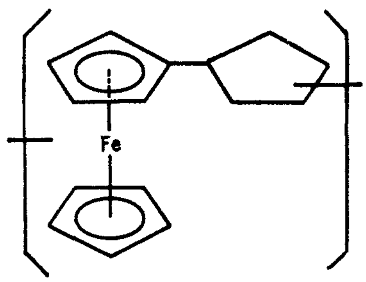
The deleterious effects of strong Lewis acids on the ferrocene system in various solvent media, resulting in cleavage of the metal–ring bond, have been amply documented in the literature. Thus, hydrogen fluoride was reported to cleave ferrocene[2] to give, *via* intermediary cyclopentadiene, cyclopent-1-enylferrocene (I)[3] and a compound independently prepared from ferrocene and aluminum chloride in benzene solution and identified as the heterobridged 1,1′-(1,3-cyclopentylene)-ferrocene[3b] (II). Additional cleavage reactions were described,[3b,c,4,5] some of them giving rise to oligomeric and polymeric cleavage products believed to be composed of such recurring units as exemplified by III. All of these reported reactions proceeded in solution. To this date, however, no mentioning has been made in the literature of analogous cleavage reactions in the melt phase. Such information would be useful in connection with reactions in which molten ferrocene is exposed to the attack of Lewis acids, *e.g.*, in the melt-phase polycondensations of ferrocene with aldehydes.[6] In these Lewis acid catalyzed polycondensation reactions, which for some time have been a major area of interest in this laboratory, the experimental conditions of temperature and heating time occasionally were severe enough to render cleavage of the metallocene system a definite possibility. Such cleavage, with subsequent further involvement of the intermediary cyclopentadiene or its protonated species, the cyclopentenyl cation IV, could conceivably affect the course of polycondensation by causing side-chain and cross-link formation or, under less drastic conditions, merely the incorporation of cyclopentenyl and cyclopentylene groups into the products. Analytical evidence for the presence of cyclopentylene moieties in some of the polymers was indeed obtained in this earlier work.[6d]



I



II



III

IV

We have, therefore, undertaken to study the effect of the same catalyst system used in these ferrocene–aldehyde polycondensations, *viz.* water-promoted[7] zinc chloride, on ferrocene in the molten state and in the absence of any additional reactants. When fused for 0.5–2.0 hr at 180° with zinc chloride and water in molar ratios comparable with those generally employed in the ferrocene–aldehyde condensations (*e.g.*, ferrocene–$ZnCl_2$–H_2O, 1.0:0.3:0.1), ferrocene was indeed found to undergo cleavage as expected. Work-up by selective extraction, chromatography, and reprecipitation furnished, aside from 70–90% unreacted ferrocene, the cyclopentylene derivatives II, V, and VI in 1–3% combined yield. The heterobridged II was identified by direct comparison with an authentic product.[8]

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[1] Parts I–XIII of this series appeared under the general title: "Ferrocene-containing Polymers." (Part XIII: E. W. Neuse, and K. Koda, *J. Polymer Sci.*, in press.)

[2] V. Weinmayr, *J. Am. Chem. Soc.*, **77**, 3009 (1955).

[3] Structure independently ascertained by (a) K. L. Rinehart, Jr., *et al.*, *ibid.*, **82**, 4111 (1960); (b) S. G. Cottis and H. Rosenberg, *Chem. Ind.* (London), 860 (1963); (c) A. N. Nesmeyanov, N. S. Kochetkova, P. V. Petrovsky, and E. I. Fedin, *Dokl. Akad. Nauk SSSR*, **152**, 875 (1963).

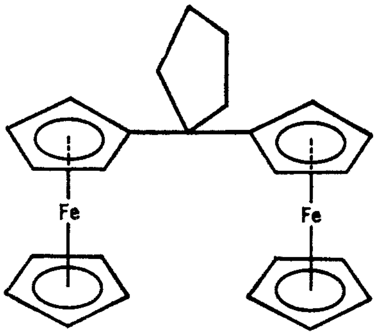
[4] (a) A. N. Nesmeyanov and N. S. Kochetkova, *ibid.*, **126**, 307 (1959); (b) A. N. Nesmeyanov, N. S. Kochetkova, and R. B. Materikova, *ibid.*, **136**, 1096 (1960); (c) S. J. Goldberg, *J. Am. Chem. Soc.*, **84**, 3022 (1962); (d) S. G. Cottis and H. Rosenberg, *J. Polymer Sci.*, **B2**, 295 (1964).

[5] A. N. Nesmeyanov, N. S. Kochetkova, and R. B. Materikova, *Dokl. Akad. Nauk SSSR*, **147**, 113 (1962).

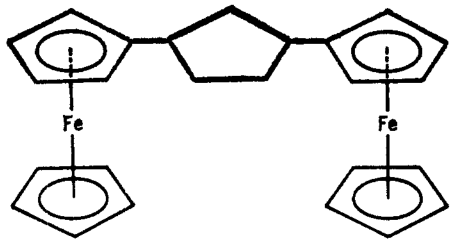
[6] (a) E. W. Neuse and D. S. Trifan, Abstracts, 148th National Meeting of the American Chemical Society, Sept 1964, p 5S; (b) E. W. Neuse, *Nature*, **204**, 179 (1964); (c) E. W. Neuse, K. Koda, and E. Carter, *Makromol. Chem.*, **84**, 213 (1965); (d) E. W. Neuse and E. Quo, *Bull. Chem. Soc. Japan*, in press.

[7] Water formed according to the equation (R = alkyl, aryl, etc.; see ref 6b): $(n + 1)\ C_{10}H_{10}Fe + nRCHO \rightarrow H{+}C_{10}H_8Fe{-}CH(R){+}_nC_{10}H_9Fe + nH_2O$.

[8] The CH out-of-plane deformation region in the infrared spectrum of II was characterized by two distinctly separated band groups, a triplet centered near 11.6 μ and a singlet at 12.50 μ, replacing the broad absorption usually exhibited by ferrocene derivatives at 12.2–12.3 μ. We have observed a similar pattern in this region with a large number of heterobridged ferrocene compounds.



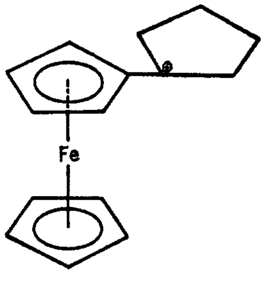
V



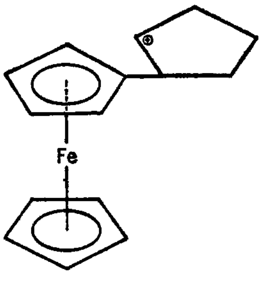
VI

The assignment of V (1,1-diferrocenylcyclopentane) was based on elemental analyses, molecular weight determinations, and spectroscopic evidence. The infrared spectrum (KBr pellet) was closely related to that of ferrocenylcyclopentane,[2] showing moderately strong aliphatic CH stretching absorption at 3.39 and 3.48 μ, the corresponding bending absorption near 6.9 μ, and the well-known bands typical of homoannularly substituted ferrocene. The nmr spectrum (at 60 Mc/sec in CDCl$_3$), while lacking methinyl proton absorption, gave ferrocene (τ 5.85–6.12) and complex alicyclic methylene (τ 7.6–8.3) signals in the approximate 18:8 area ratio. VI was found by elemental composition, molecular weight, and infrared spectrum to be isomeric with V. Independent synthesis by hydrogenation of 1,4-diferrocenylcyclopenta-1,3-diene[9] identified the product as a 1,3-diferrocenylcyclopentane. The fact that only a single saturated product could be isolated in this hydrogenation suggests the *cis* configuration for VI because of greater probability of formation under these conditions, taking both 1,2 and 1,4 addition into account. The position of the methinyl proton nmr signal (two protons) at τ 6.9–7.4, practically coinciding with that of ferrocenylcyclopentane, also supports the *cis* structure,[10] as does the broad, complex methylene resonance (six protons) in the τ region 7.7–8.5, lacking the superimposing triplet signal expected in the *trans* case for the equivalent C-2 methylene protons coupling with the two likewise equivalent methinyl protons. For an unambiguous steric assignment, however, a direct comparison of the nmr spectra of both 1,3 isomers would be required. It is unfortunate that the second 1,3 species, undoubtedly present (along with 1,2 isomers) in one of the several multicomponent, chromatographic fractions left unidentified, could not be isolated in this work.

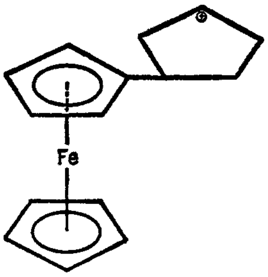
In addition to the mono- and dinuclear ferrocenylcyclopentanes described in the foregoing, polymers were separated in 5–15% yield, which had number-average molecular weights, $\bar{M}_n$, of 2000–2500 and roughly corresponded in elemental composition to the unit III much as did the polymers formed in AlCl$_3$-catalyzed solution reactions.[3c,4d] These polymers probably arose from Friedel–Crafts type polyalkylation of intermediary cyclopentenylferrocenes *via* the same equilibrating cations VII believed to be the precursors of II and the various diferrocenylcyclopentanes. (In other experiments, an increase above unity of the cyclopentyl–ferrocenyl ratio was observed, indicating additional immediate attack of cyclopentenyl cations IV on ferrocene groups of the original recurring units III.) The relatively high yields in which, despite the low instantaneous concentrations of their precursor cations VII, these polymers were obtained in successful competition with the rapid first-order reactions of these cations by cyclialkylation (to give II) or attack on ferrocene (to give diferrocenylcyclopentanes) are not surprising in view of the enhanced nucleophilicity expected for cyclopentyl substituted, as compared to unsubstituted, ferrocenyl rings. Oligomers with $\bar{M}_n$ in the 700–1000 range and compositions similar to those of the polymers were also separated (by column chromatography) in these experiments. The methylene–methinyl proton area ratio, on the average in the vicinity of 4, suggests *ca.* 20% of the units in these oligomers to possess the *gem*-diferrocenyl substituent disposition. Since only hexane-soluble material was originally placed on the column used for the separation (whereas the oligomers isolated showed very limited solubility in hexane), one may



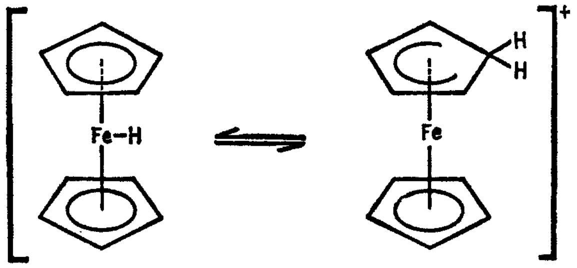
VIIa



VIIb



VIIc



VIIIa VIIIb

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[9] E. W. Neuse and R. K. Crossland, paper in preparation.

[10] In the *trans* compound, an upfield displacement would be expected for this signal as a consequence of the ever so limited residence time of each methinyl proton in the positive shielding cone of the corresponding *cis*-ferrocenyl substituent. *Cf.* in this connection D. Y. Curtin, H. Gruen, and B. A. Shoulders, *Chem. Ind.* (London), 1205 (1958).

conclude that these oligomers were generated on the alumina in the column from cyclopentenylferrocenes unstable under these conditions. Failure to isolate I or any of its isomers, which were doubtlessly formed as cleavage products, is consistent with this inference.

It is of interest to note that, while the cleavage reactions discussed above proceeded readily in the presence of the zinc chloride–water system, no such reactions were observed with zinc chloride under anhydrous conditions. This suggests initiation by a protonation step, possibly one involving Fe–H bond formation, with subsequent cleavage *via* the protonated species VIIIa[11] and the tautomeric σ-complex VIIIb leading to the cyclopentenyl cation IV. The latter will immediately attack surrounding ferrocene to give cyclopentenylferrocenes[3b] or their respective cations VII, with further reaction then occurring as proposed.

The demonstrated ease with which the ferrocene system is cleaved by the zinc chloride–water catalyst[12] confirms the earlier suggestion that the presence of cyclopentylene groups should quite generally be expected in ferrocene polymers prepared under comparable experimental conditions. To what extent this competing side reaction will become significant is, then, merely a question of relative reactivities.

Experimental Section

The experiment described below, while not necessarily representing optimal cleavage conditions, may exemplify the general procedure.

The mixture of ferrocene (0.3 mole), zinc chloride (fused, anhydrous, 0.1 mole), and water (0.03 mole), contained in a round-bottom flask, was quickly heated to 180°, and the resulting melt was stirred for 1 hr at this temperature under N_2. The reaction product was washed with water, dried, and extracted with hexane. Extraction of the hexane-insoluble residue with benzene, followed by precipitation with isopropanol from the concentrated extract, gave a tan polymer in 5.9% yield (up to 15% under more rigorous conditions), which was soluble in dioxane, benzene, and chlorohydrocarbons: melting range, 125–135°; M_n, 2030 (determined by vapor pressure osmometry in benzene).

Anal. Calcd for $(C_{15}H_{16}Fe)_n$ (III): C, 71.45; H, 6.40; Fe, 22.15. Found: C, 71.88; H, 6.61; Fe, 21.30.

The hexane extract from the foregoing operations was chromatographed on Alcoa Grade F-20 activated alumina, using hexane as eluent. The first, fast-moving zone eluted gave ferrocene (87.6% recovery). The second band furnished 0.9% yield of crude II, which, after vacuum sublimation, had mp 139° (undepressed by admixture of authentic sample,[2,3b] identical X-ray diffractograms). The third band was rechromatographed on alumina slightly deactivated by a 4-hr exposure to air of 50% relative humidity. In addition to small amounts of unidentified orange oils and a few milligrams of two compounds melting at 74–76° (25.19% Fe, infrared spectrum indicates isomer of V, VI) and 167° (trinuclear; mol wt, 620), the two diferrocenylcyclopentanes V (mp 168–169°) and VI (mp 104–105°, both compounds recrystallized from ethanol) were eluted successively in yields of 0.4 and 0.2%, respectively.

Anal. Calcd for $C_{25}H_{26}Fe_2$ (V and VI: mol wt, 438): C, 68.53; H, 5.98; Fe, 25.49. Found for V: C, 68.54; H, 6.01; Fe, 25.55; mol wt, 445. Found for VI: C, 68.43; H, 5.99; Fe, 25.27; mol wt, 450.

The fourth, multilayer band was extracted with ether–benzene. Reprecipitation of the resinous evaporation residue from dioxane by aqueous isopropyl alcohol (1:1) provided yellow, powdery oligomer (3.9%) which dissolved readily in benzene, dioxane, and halohydrocarbons, but only with difficulty in hexane: melting range, 95–105°; M_n, 790.

Anal. Calcd for $(C_{15}H_{16}Fe)_n$ (III): C, 71.45; H, 6.40; Fe, 22.15. Found: C, 71.01; H, 6.71; Fe, 22.50.

Acknowledgment.—The authors are grateful to Mr. G. P. Kazokas and his staff for obtaining the infrared spectra and molecular weights. Dr. V. Weinmayr, E. I. du Pont de Nemours and Company, kindly provided a sample of ferrocenylcyclopentane for spectroscopic comparison.

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[11] M. Rosenblum and J. O. Santer, *J. Am. Chem. Soc.*, **81**, 5517 (1959). One is tempted to propose similar intermediary involvement of protonated species analogous to VIII in the facile aluminum chloride catalyzed ring exchange recently observed with ferrocene compounds [A. N. Nesmeyanov, N. A. Volkenau, and I. N. Bolesova, *Tetrahedron Letters*, **No. 25**, 1725 (1963); *Dokl. Akad. Nauk SSSR*, **149**, 615 (1963); D. E. Bublitz, *Can. J. Chem.*, **42**, 2381 (1964)]. Probably related herewith are the displacement reactions discussed by I. G. Morrison and P. L. Pauson [*Proc. Chem. Soc.*, 177 (1962)], in which the intermediacy of cations of the type VIIIa was postulated by the authors. It would not appear unreasonable to assume that in the last-named reactions, metal–ring bond cleavage, rather than simple substituent displacement, occurred much as in Nesmeyanov's and Bublitz's work, this cleavage being followed by π-cyclopentadienyl ring exchange.

[12] It should be of interest to study analogous reactions involving the more powerfully protonating ZnCl–HCl system, for which enhanced cleavage of the iron-ring bond and, hence, increased abundance of cyclopentylene groups in the products, can be predicted.

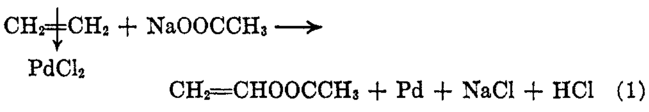
Metal–Olefin Complexes. A Convenient Synthesis of *syn*-7-Norbornenol[1a]

William C. Baird, Jr.[1b]

Central Basic Research Laboratory, Esso Research and Engineering Company, Linden, New Jersey

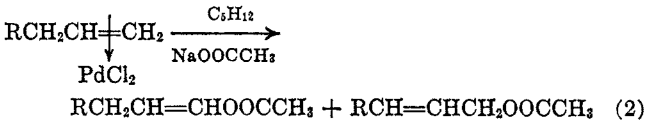
Received November 18, 1965

The preparation of vinyl esters, most notably vinyl acetate, by the reaction of the palladium chloride–ethylene π complex has been reported[2] (eq 1). Re-



$$\underset{\downarrow\ PdCl_2}{CH_2{=}CH_2} + NaOOCCH_3 \longrightarrow CH_2{=}CHOOCCH_3 + Pd + NaCl + HCl \quad (1)$$

cent experiments in these laboratories[3] have revealed that the reaction of palladium chloride complexes of olefins higher than ethylene are sensitive to both olefin structure and reaction medium. The influence of these factors is reflected in some instances by the formation of mixtures of isomeric unsaturated acetates[4] (eq 2)



$$\underset{\downarrow\ PdCl_2}{RCH_2CH{=}CH_2} \xrightarrow[NaOOCCH_3]{C_5H_{12}} RCH_2CH{=}CHOOCCH_3 + RCH{=}CHCH_2OOCCH_3 \quad (2)$$

and in others by the formation of saturated bifunctional compounds such as di- and haloacetates (eq 3). Subjecting norbornene to the general reaction illustrated by eq 3 leads to the formation of *exo*-2-chloro-*syn*-7-acetoxynorbornane (I), a convenient precursor

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(1) (a) Presented in part at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966; (b) Enjay Chemical Laboratories, Linden, N. J.

(2) (a) I. I. Moiseev, M. N. Vargaftik, and Y. K. Sirkin, *Dokl. Akad. Nauk SSSR*, **133**, 377 (1960); (b) E. W. Stern and M. L. Spector, *Proc. Chem. Soc.*, 370 (1961).

(3) W. C. Baird, Jr., unpublished results. A manuscript entitled, "Metal–Olefin Complexes. The Synthesis of Acetate Esters," is in preparation.

(4) The formation of isomeric acetates had also been previously noted. See ref 2b.