

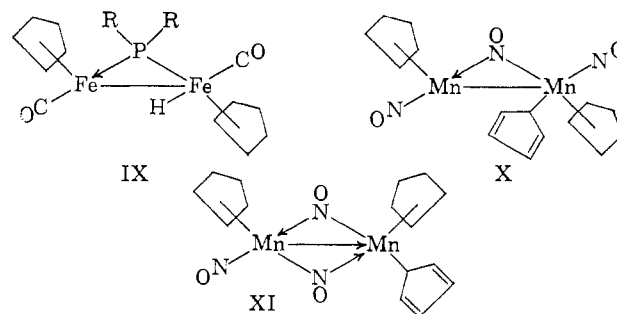
nitrosyl group would be expected to be similar to the nitrogen-oxygen bond in an amine oxide, R_3NO . It is of interest that Bellamy¹⁹ reports amine oxides to absorb at 1200–1300 cm^{-1} in the infrared spectrum, in reasonable agreement with the band at 1313 cm^{-1} in $(C_5H_5)_6Mn_6(NO)_3$ assigned to the three-way bridging nitrosyl groups.

It is thus apparent that the chemical and spectroscopic properties of $(C_5H_5)_6Mn_6(NO)_3$ are in accord with structure VIII. However, X-ray studies currently in progress in another laboratory should provide more definite information regarding the structure of $(C_5H_5)_6Mn_6(NO)_3$.

(D) $(C_5H_5)_3Mn_2(NO)_3$.—The synthesis of several new nitrosyl derivatives with bridging nitrosyl groups in this work made of interest a further study of the compound $(C_5H_5)_3Mn_2(NO)_3$ prepared several years ago by Piper and Wilkinson³ from manganese(II) cyclopentadienide and nitric oxide. We have confirmed the preparation of $(C_5H_5)_3Mn_2(NO)_3$ and our analyses on chromatographed material for all elements, including a direct oxygen analysis, confirm the composition suggested by Piper and Wilkinson. A proton n.m.r. spectrum of $(C_5H_5)_3Mn_2(NO)_3$ exhibits two broad cyclopentadienyl resonances at $\tau \sim 4.7$ and ~ 5.6 of relative intensity $\sim 2:1$, supporting the postula-

(19) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co. Ltd., London, 1958, pp. 307–308.

tion of Piper and Wilkinson of two different types of cyclopentadienyl rings in $(C_5H_5)_3Mn_2(NO)_3$. Recent syntheses of compounds such as IX by Hayter²⁰ make the related structure X for $(C_5H_5)_3Mn_2(NO)_3$ with only one bridging nitrosyl group and two terminal nitrosyl groups as probable as the structure XI²¹ suggested by Piper and Wilkinson³ with two bridging nitrosyl groups and one terminal nitrosyl group. At this stage we are unable to provide definite evidence for either structure, but hope that X-ray studies currently in progress in another laboratory will provide a solution to this problem.



(20) R. G. Hayter, *J. Am. Chem. Soc.*, **85**, 3120 (1963).

(21) A manganese-manganese bond has been added to the structure of $(C_5H_5)_3Mn_2(NO)_3$ proposed by Piper and Wilkinson (ref. 3) in accord with more recent views on the structure of polynuclear transition metal derivatives.

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Organometallic Chemistry of the Transition Metals. VIII.

π -Cyclopentadienyl- π -pyrrolyliron and π -Cyclopentadienyl- π -indenyliron^{1,2}

BY R. B. KING AND M. B. BISNETTE

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Ferrous chloride reacts with a mixture of sodium cyclopentadienide and sodium pyrrolide in tetrahydrofuran to give red, very volatile, crystalline $C_5H_5FeC_4H_7N$ in very low yield. Ferrous chloride reacts with a mixture of sodium cyclopentadienide and sodium indenide to give red-violet crystalline $C_9H_7FeC_9H_7$. Hydrogenation of $C_9H_7FeC_9H_7$ gives orange volatile $C_9H_9FeC_9H_{11}$.

Although cyclopentadienyl derivatives of transition metals have been known for over 12 years and hundreds of such compounds have been prepared, little is known of the corresponding pyrrolyl transition metal derivatives despite the analogy between the relationship of the pyrrolide anion (I)³ to the cyclopentadienide anion and the relationship of pyridine to benzene. Occasionally during the past several years R. B. K. as well as other workers in the field⁴ attempted to prepare

π -pyrrolylmetal complexes by a variety of methods but always without success. In view of these negative results it appeared for a long time that π -pyrrolyl derivatives would not be stable. However, finally in late 1962 Joshi and Pauson⁵ reported the synthesis of π -pyrrolylmanganese tricarbonyl (II) by heating dimanganese decacarbonyl with pyrrole. These positive results indicating that π -pyrrolyl derivatives had appreciable stability led us to investigate more thoroughly the synthesis of other π -pyrrolyl derivatives in order to permit comparison of these π -

(1) For part VII of this series see R. B. King and M. B. Bisnette, *Inorg. Chem.*, **3**, 791 (1964).

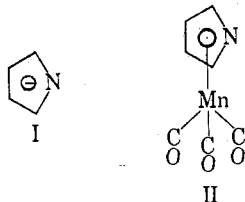
(2) For a preliminary communication on some of this work see R. B. King and M. B. Bisnette, *Angew. Chem.*, **75**, 642 (1963).

(3) By analogy with "cyclopentadienyl" we prefer the term "pyrrolyl" rather than "pyrryl" for the C_4H_4N derivatives discussed in this paper.

(4) (a) Work in the research group of G. Wilkinson, Harvard University, 1952–1956 (L. T. Reynolds, private communication, June, 1959); (b) E. O. Fischer and K. Öfele, *Ber.*, **91**, 2395 (1958).

(5) K. K. Joshi and P. L. Pauson, *Proc. Chem. Soc.*, 326 (1962).

pyrrolyl derivatives with the corresponding π -cyclopentadienyl derivatives. More specifically, it appeared that sodium pyrrolide would be a useful reagent for the preparation of π -pyrrolyl derivatives similar to the use of sodium cyclopentadienide for the preparation of π -cyclopentadienyl derivatives. The numerous early negative results, however, clearly indicated that the number of π -pyrrolyl compounds would be severely limited in comparison with the numerous π -cyclopentadienyl compounds.



In general our attempts to synthesize π -pyrrolyl derivatives from sodium pyrrolide and various complex transition metal halides which form stable π -cyclopentadienyl derivatives with sodium cyclopentadienide were not successful. However, the new iron complex π -cyclopentadienyl- π -pyrrolyliron ("azaferrocene") was synthesized in low yield by the action of a mixture of sodium cyclopentadienide and sodium pyrrolide on ferrous chloride. After the work described in this paper was completed, we were informed of the independent and different synthesis of $C_5H_5FeC_4H_4N$ by Joshi and Pauson from potassium pyrrolide and $C_5H_5Fe(CO)_2I$.⁶

This paper describes our work on π -cyclopentadienyl- π -pyrrolyliron as well as details of our work on the related π -cyclopentadienyl- π -indenyliron previously outlined in a brief communication.²

Experimental

Infrared spectra were taken in potassium bromide pellets and recorded on a Perkin-Elmer Model 21 spectrometer. Proton n.m.r. spectra were taken in carbon disulfide solution with hexamethyldisiloxane as an internal standard and recorded on a Varian A-60 spectrometer. Ultraviolet spectra were taken in cyclohexane solution and recorded on a Cary Model 14 spectrometer. Microanalyses and molecular weight determinations (Mechrolab osmometer in benzene solution) were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany, and by Schwarzkopf Microanalytical Laboratory, Woodside, New York.

Materials.—Tetrahydrofuran was always distilled from lithium aluminum hydride immediately before use. Pyrrole was purchased from the Aldrich Chemical Company, Milwaukee, Wisconsin, and redistilled under vacuum. It was converted to sodium pyrrolide as needed by refluxing with a stoichiometric amount of 50% sodium dispersion in mineral oil in tetrahydrofuran under nitrogen. A yellow solution sometimes containing white crystals thus was obtained which was used without isolation of the sodium pyrrolide. Imidazole and pyrazole, both white crystalline solids, were purchased from Aldrich and used without further purification. They were converted to the sodium salts similarly by treatment with a stoichiometric amount of 50% sodium dispersion in mineral oil suspended in tetrahydrofuran. Sodium imidazolide precipitated from the tetrahydrofuran solution as a white crystalline solid. Sodium pyrazolide, on the other hand, remained dissolved in the tetrahydrofuran forming a nearly colorless solution.

Indene, purchased from various commercial sources, unless excessively dark in color, was used without redistillation. Refluxing it with a stoichiometric amount of 50% sodium dispersion in mineral oil suspended in tetrahydrofuran until all of the sodium dissolved converted it to a clear yellow solution of sodium indenide which rapidly darkened on exposure to air.

Sodium cyclopentadienide was prepared by the usual procedure of adding excess freshly distilled cyclopentadiene under nitrogen to a 50% sodium dispersion in mineral oil suspended in tetrahydrofuran.

Suspensions of ferrous chloride in tetrahydrofuran were obtained by refluxing stoichiometric quantities of iron powder and anhydrous ferric chloride in tetrahydrofuran.⁷

π -Cyclopentadienyl- π -pyrrolyliron.—A solution of 300 mmoles of sodium pyrrolide in 300 ml. of redistilled tetrahydrofuran was added to a suspension of 250 mmoles of ferrous chloride in 300 ml. of tetrahydrofuran. This mixture was then treated dropwise with a solution of 250 mmoles of sodium cyclopentadienide in 250 ml. of tetrahydrofuran. The resulting black reaction mixture was refluxed at the boiling point under nitrogen for 15 hr. After cooling to room temperature tetrahydrofuran was removed at ~ 30 mm. leaving a black residue.

After admitting nitrogen this residue was extracted with benzene in several 50–100 ml. portions until the extracts were no longer colored. These extracts were filtered by suction and the filtrate then chromatographed on a 5×50 cm. alumina column. A large orange band of ferrocene appeared and moved down the column on development with benzene. A second much smaller orange band of $C_5H_5FeC_4H_4N$ appeared which remained very near the top of the column despite prolonged development with benzene. The large orange band of ferrocene was eluted with benzene. Evaporation of the orange eluate left behind ~ 7.5 g. (16% yield) of orange crystals of ferrocene.

After removing the ferrocene the chromatography column was washed with ~ 1 l. of dichloromethane, causing the weak orange band of $C_5H_5FeC_4H_4N$ to move about 25 cm. down the column. The orange band of $C_5H_5FeC_4H_4N$ was then eluted with acetone. The red-orange eluate was filtered, and the solvent then was removed from the filtrate at ~ 30 mm. leaving red-orange crystals of crude $C_5H_5FeC_4H_4N$. If the residue of $C_5H_5FeC_4H_4N$ failed to crystallize at this stage (as in one experiment where the dichloromethane washing of the column was omitted), the chromatography was repeated a second time on a 2×50 cm. column.

The crystals of crude $C_5H_5FeC_4H_4N$ were dissolved in 50 ml. of pentane, and the solution was filtered by gravity. The filtrate was cooled to -78° causing orange crystals to separate. After removal of these crystals by filtration, final purification was accomplished by sublimation at 35° (0.3 mm.) to give 0.39 g. (0.85% yield) of red crystalline $C_5H_5FeC_4H_4N$, m.p. 114 – 115° .

Anal. Calcd. for C_5H_5NFe : C, 57.8; H, 4.8; N, 7.5; Fe, 29.9; mol. wt., 187. Found: C, 57.9, 57.9; H, 4.9, 4.9; N, 7.6, 7.4; Fe, 29.6, 29.5; mol. wt., 198.

Infrared Spectrum.—C-H band at 3090 (w) cm^{-1} ; other bands at 1405 (m), 1385 (m), 1345 (w), 1265 (w), 1184 (m), 1109 (s), 1060 (w), 1003 (s), 853 (w), 816 (s), and 770 (w, br) cm^{-1} .

Ultraviolet Spectrum.—Maximum at 330 $m\mu$ (ϵ 178). Strong "end absorption" (at 210 $m\mu$, ϵ 15,400).

Visible Spectrum.—Maximum at 442 $m\mu$ (ϵ 107).

Proton N.m.r. Spectrum.—Resonances at τ 4.74, 5.55, and 5.85 of relative intensities 2:2:5.

π -Cyclopentadienyl- π -indenyliron.—Solutions of 300 mmoles of sodium indenide in 300 ml. of redistilled tetrahydrofuran and of 250 mmoles of sodium cyclopentadienide in 150 ml. of tetrahydrofuran were added simultaneously at 40 – 50° to a suspension of 250 mmoles of ferrous chloride in 250 ml. of tetrahydrofuran. The reaction mixture was then boiled under reflux for ~ 15 hr. After cooling to room temperature tetrahydrofuran was removed at ~ 30 mm. After admitting nitrogen the resulting dark-colored residue was extracted with 500 ml. of pentane in four

(6) K. K. Joshi, private communication.

(7) G. Wilkinson, *Org. Syn.*, **36**, 31 (1956).

portions, and the extracts were filtered by suction. After concentration of the filtrate to ~150 ml. it was chromatographed on a 5 × 60 cm. alumina column. Upon development with pentane, a yellow band of ferrocene appeared followed by an incompletely separated red-violet band of $C_5H_5FeC_9H_7$. These bands were eluted with pentane or hexane. The ferrocene obtained from the orange band was contaminated with indene. It was separated from the indene by recrystallization from pentane. The $C_5H_5FeC_9H_7$ obtained from the red-violet band was severely contaminated with ferrocene. The ferrocene was removed by fractional sublimation at 50° (0.1 mm.). The $C_5H_5FeC_9H_7$ was isolated from this residue by further sublimation at 70–80° (0.1 mm.) and purified finally by a second sublimation under the same conditions.

From this experiment 6.8 g. (14.7% yield) of orange crystalline ferrocene and 5.2 g. (8.8%) of red-violet crystalline $C_5H_5FeC_9H_7$ were obtained. When pure, $C_5H_5FeC_9H_7$ melted at 74–76°.

In an alternate preparation of $C_5H_5FeC_9H_7$, a mixture of 110 mmoles of ferric chloride, 110 mmoles of cyclopentadiene, 150 mmoles of indene, and 200 ml. of diethyl ether was reduced with 500 mmoles of ethereal isopropylmagnesium bromide at –78°. After warming to room temperature and careful decomposition with methanol, the product was isolated from the evaporated reaction mixture by pentane extraction and purified by chromatography on alumina, recrystallization from pentane, and finally sublimation. The yield of $C_5H_5FeC_9H_7$ by this method was only 0.4%.

Anal. Calcd. for $C_{14}H_{12}Fe$: C, 71.2; H, 5.1; Fe, 23.7; mol. wt., 236. Found: C, 71.1; H, 5.1; Fe, 23.5; mol. wt., 244.

Infrared Spectrum.—C–H bands at 3070 (vw) and 3050 (vw) cm^{-1} ; other bands at 1405 (vw), 1370 (vw), 1334 (m), 1195 (vw), 1179 (vw), 1100 (m), 1025 (m), 1003 (w), 999 (w), 982 (vw), 888 (vw), 870 (vw), 836 (w), 828 (w), 816 (m), 810 (m), 804 (m), 800 (m), 775 (vw), 744 (m), 738 (s), and 726 (s) cm^{-1} .

Ultraviolet Spectrum.—Maximum at 228 $m\mu$ (ϵ 29,700).

Visible Spectrum.—Maximum at 519 $m\mu$ (ϵ 264).

Proton N.m.r. Spectrum.—Resonances at τ 2.59 (double doublet, $J_1 = 3$ c.p.s., $J_2 = 7$ c.p.s.), τ 3.22 (double doublet, $J_1 = 3$ c.p.s., $J_2 = 7$ c.p.s.), τ 5.25 (doublet, $J = 2.5$ c.p.s.), τ 6.11 (triplet, $J = 2.5$ c.p.s.), and τ 6.38 (singlet) of relative intensities 2:2:2:1:5.

π -Cyclopentadienyl- π -1,2,3,4-tetrahydroindenyliron.—A solution of 0.9072 g. (3.84 mmoles) of $C_5H_5FeC_9H_7$ in ~50 ml. of absolute ethanol was hydrogenated at atmospheric pressure in the presence of 0.2257 g. of 10% palladium on charcoal in an apparatus permitting measurement of the hydrogen absorbed. After 21 hr. 200 ml. (26°, 740 mm.) of hydrogen was absorbed, corresponding to 7.3 mmoles, or 1.9 moles of hydrogen for each mole of $C_5H_5FeC_9H_7$.

The ethanol solution of the hydrogenated product was filtered from the catalyst. Solvent was removed from the orange filtrate at ~30 mm. leaving an orange liquid residue. This was dissolved in 30 ml. of pentane and the filtered solution cooled in a –78° bath, orange crystals separating. These were filtered and dried in the air to give 0.32 g. (35% yield) of orange, air-stable crystalline $C_5H_5FeC_9H_{11}$, m.p. 38–40°. From the filtrate an additional 0.13 g. of product was isolated by evaporation and sublimation of the resulting oil at ~80° (0.1 mm.) onto a probe cooled to –78° to give a total yield of 0.45 g. (49%) of $C_5H_5FeC_9H_{11}$. The losses are probably due to codistillation of some of the rather volatile product with the ethanol during the solvent removal.

The analytical sample, m.p. 39–41°, was obtained by sublimation of some of the recrystallized material at 70–80° (0.1 mm.) onto a –78° probe. Except for mechanical losses this sublimation was quantitative.

Anal. Calcd. for $C_{14}H_{16}Fe$: C, 70.0; H, 6.7; Fe, 23.3; mol. wt., 240. Found: C, 70.1; H, 6.6; Fe, 23.4; mol. wt., 239.

Infrared Spectrum.—C–H bands at 3070 (vw), 2910 (m), and 2850 (w) cm^{-1} ; other bands at 1465 (vw), 1445 (w), 1436

(sh), 1405 (vw), 1345 (w), 1234 (w), 1100 (m), 1021 (w), 998 (m), 944 (vw), 908 (w), 845 (w), 838 (w), 827 (w), 822 (m), and 801 (m) cm^{-1} .

Ultraviolet Spectrum.—Maximum at 326 $m\mu$ (ϵ 74). Strong "end absorption" (at 207 $m\mu$, ϵ 44,700).

Visible Spectrum.—Maximum at 439 $m\mu$ (ϵ 111).

Proton N.m.r. Spectrum.—Resonances at τ 6.16 (singlet), τ 7.56 (complex not clearly resolved multiplet), and τ 8.25 (complex not clearly resolved multiplet) of relative intensities 8:4:4.

Bis- π -indenyliron.—The preparation of unsubstituted $(C_9H_7)_2Fe$ has apparently not been described in the literature since the two original reports^{8,9} nearly 10 years ago using indenylmagnesium bromide and ferric chloride. Inspired by more recent developments in this area of preparative chemistry, we have developed an improved preparation of $(C_9H_7)_2Fe$ from sodium indenide and ferrous chloride.

A suspension of 100 mmoles of ferrous chloride in 300 ml. of tetrahydrofuran was treated under nitrogen with a solution of 270 mmoles of sodium indenide in 300 ml. of tetrahydrofuran. The resulting black reaction mixture was boiled under reflux for 16 hr. After cooling to room temperature tetrahydrofuran was removed at ~30 mm. After admitting nitrogen to the residue, it was transferred to the thimble of a Soxhlet extraction apparatus and extracted continuously with boiling pentane until the originally black-violet extracts became colorless (~40 hr.). The pentane was heated with an oil bath at the minimum temperature necessary for steady reflux of the pentane in order to minimize overheating. The use of a nitrogen atmosphere during this extraction step is unnecessary since the pentane vapors protect the $(C_9H_7)_2Fe$ sufficiently from atmospheric oxidation.

The black pentane extract of $(C_9H_7)_2Fe$ thus obtained was cooled to –78° to precipitate the product. After filtration and drying in a vacuum desiccator the crude black $(C_9H_7)_2Fe$ weighed 7.5 g. (26.5% yield). On sublimation of 3.0 g. of the crude product at 130° (0.25 mm.), 2.4 g. (80% recovery) of pure $(C_9H_7)_2Fe$, m.p. 178–182° (lit. 179–181°^{8a}, 184–185°^{8b}), was obtained.

Anal. Calcd. for $C_{18}H_{14}Fe$: C, 75.5; H, 4.9; Fe, 19.6. Found: C, 74.3; H, 4.9; Fe, 19.7.

Infrared Spectrum.—C–H band at 3000 (vw) cm^{-1} ; other bands at 1475 (vw), 1445 (vw), 1330 (w), 1196 (vw), 1175 (vw), 1023 (w), 1018 (w), 804 (w), 740 (m), and 723 (m) cm^{-1} .

Proton N.m.r. Spectrum.—Resonances at τ 3.20 (singlet), τ 5.54 (doublet, $J = 2.5$ c.p.s.), and τ 6.08 (triplet, $J = 2.5$ c.p.s.) of relative intensities 4:2:1.

An attempt to prepare bis- π -pyrrolyliron, $(C_4H_4N)_2Fe$, by an exactly analogous procedure but using sodium pyrrolide rather than sodium indenide was completely unsuccessful, the pentane extracts, even initially, being colorless.

Reaction between $(C_9H_7)_2Fe$ and Sodium Cyclopentadienide.—

A solution of ~6 mmoles of sodium cyclopentadienide in 60 ml. of tetrahydrofuran was refluxed with 0.86 g. (3 mmoles) of $(C_9H_7)_2Fe$ for 16 hr. with magnetic stirring to give a dark red solution. Volatile materials were removed from this solution at ~1 mm. leaving a black residue. This residue was dissolved in 100 ml. of pentane, and the filtered red solution after concentration to ~50 ml. was chromatographed on a 2 × 50 cm. alumina column. Development of the chromatogram with pentane gave a yellow-orange band followed by a red-violet band. The yellow-orange band gave 0.19 g. (34% yield) of ferrocene on elution with pentane, evaporation of the eluate, and recrystallization of the residue from pentane. In a similar manner 0.03 g. (4% yield) of $C_5H_5FeC_9H_7$ was isolated from the red-violet band. These products were identified by comparison of melting points and infrared and n.m.r. spectra with those of authentic samples.

(8) (a) E. O. Fischer and D. Seus, *Z. Naturforsch.*, **8b**, 694 (1953); (b) P. L. Pauson and G. Wilkinson, *J. Am. Chem. Soc.*, **76**, 2024 (1954).

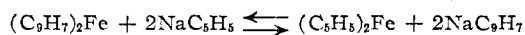
(9) Recently prepared of several similar bis(alkylindenyl)iron derivatives from the corresponding lithium alkylindenides and ferrous chloride have been described [E. B. Sokolova, M. P. Shebenova, and H.-C. Chou, *Zh. Obshch. Khim.*, **33**, 217 (1963), *Chem. Abstr.*, **59**, 658f (1963)].

Discussion

The experiments described in this paper suggest that the synthesis of π -pyrrolyl derivatives is more difficult than the synthesis of the corresponding π -indenyl derivatives. Thus, the yield of $C_8H_5FeC_9H_7$ (~9%) was consistently about ten times that of $C_8H_5FeC_4H_4N$ (~0.9%). Moreover, bis- π -pyrrolyliron could not be prepared by a method completely analogous to a satisfactory preparation of bis- π -indenyliron.

In view of the fact that substitution of even one nitrogen atom for a CH group in the cyclopentadienyl ring decreases drastically the ease of preparation of π -bonded transition metal derivatives, it is scarcely surprising that attempts to prepare either π -cyclopentadienyl- π -pyrazolyliiron or the isomeric π -cyclopentadienyl- π -imidazolyliiron containing a heterocyclic ring with two nitrogen atoms π -bonded to an iron atom by preparative techniques used for $C_8H_5FeC_4H_4N$ were unsuccessful. Thus treatment of ferrous chloride with a mixture of sodium cyclopentadienide and sodium pyrazolide or sodium imidazolide in tetrahydrofuran gave only ferrocene. It must be pointed out, however, that a limitation in the synthetic techniques described in this paper is the necessity for an anion such as pyrrolide with only a very weak tendency to bond to a transition metal atom to compete with the cyclopentadienyl anion with an extremely strong tendency to bond to a transition metal atom. If the competition between the two anions is too unequal, the much stronger π -complexing cyclopentadienyl anion will form only ferrocene. Since the synthesis of $C_4H_4NMn(CO)_3$ of Joshi and Pauson⁵ does not involve such competition with cyclopentadienide ion, it should be more suitable for preparing derivatives of anions such as pyrazolyl and imidazolyl with only a very weak tendency to bond to transition metals. Joshi and Pauson have indeed indicated briefly that their synthesis can be extended to the preparation of certain related imidazolyl and pyrazolyl derivatives although further details have not yet appeared.

In view of the fact that $(C_9H_7)_2Fe$ is a moderately stable compound, it is interesting that none was detected in the reaction mixture from the preparation of $C_8H_5FeC_9H_7$ from ferrous chloride, sodium cyclopentadienide, and sodium indenide in boiling tetrahydrofuran. However, in a separate experiment $(C_9H_7)_2Fe$ was converted to ferrocene by treatment with sodium cyclopentadienide in boiling tetrahydrofuran. This indicates that a mixture of sodium indenide and ferrocene in tetrahydrofuran is more stable thermodynamically than a mixture of sodium cyclopentadienide and $(C_9H_7)_2Fe$ as represented by the equation



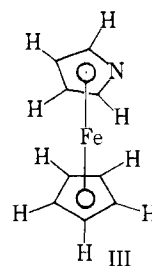
Moreover, the rate of attainment of equilibrium in this system is appreciable in boiling tetrahydrofuran. A small amount of $C_8H_5FeC_9H_7$ was also detected in the reaction mixture obtained from $(C_9H_7)_2Fe$ and sodium cyclopentadienide. These observations indicate that

any $(C_9H_7)_2Fe$ initially formed in the synthesis of $C_8H_5FeC_9H_7$ from ferrous chloride, sodium cyclopentadienide, and sodium indenide is destroyed by the sodium cyclopentadienide during the heating period, thereby accounting for its absence in the final reaction product.

The π -pyrrolyl derivative $C_8H_5FeC_4H_4N$ (III) is a very volatile red crystalline solid moderately soluble in organic solvents. Its volatility and solubility resemble very much those of ferrocene, making impossible the separation of $C_8H_5FeC_4H_4N$ and ferrocene by fractional crystallization or sublimation. Its stability to thermal and oxidative decomposition, although still appreciable, is much lower than that of the very stable ferrocene. It thus turns brown slowly over a period of several days in air and darkens on heating above its melting point.

The π -pyrrolyl derivative, $C_8H_5FeC_4H_4N$, is much more strongly retained on an alumina column than ferrocene, permitting easy separation of the two compounds by chromatography. While ferrocene can be eluted from an alumina column with benzene, $C_8H_5FeC_4H_4N$ clings tenaciously to the top of the column as an orange band even on prolonged treatment with benzene. The much more powerful eluent acetone is necessary to remove $C_8H_5FeC_4H_4N$ from the column.

The proton n.m.r. spectrum of $C_8H_5FeC_4H_4N$ may be clearly understood on the basis of the obvious structure III. The singlet resonances at τ 4.74 and 5.55 each of relative intensity 2 may be assigned to the two pairs of



equivalent protons (bonded to the α and β carbon atoms relative to the nitrogen) of the π -pyrrolyl ring and the singlet resonance at τ 5.85 of relative intensity 5 to the five equivalent protons of the π -cyclopentadienyl ring. The portion of this spectrum due to the π -pyrrolyl ring is very similar to the n.m.r. spectrum of $C_4H_4NMn(CO)_3$ reported by Joshi and Pauson⁵ except that the π -pyrrolyl resonances in $C_8H_5FeC_4H_4N$ occur at an appreciably higher field than the corresponding resonances in $C_4H_4NMn(CO)_3$. This upward shift of resonances of protons bonded to carbon atoms involved in π -bonding to a transition metal when three carbonyl groups are replaced by a π -cyclopentadienyl ring with the necessary change in the central metal atom appears to be a general phenomenon. Other examples have been noted in this laboratory. For example, the π -cyclopentadienyl protons of $C_8H_5Mn(CO)_3$ occur at τ 5.35 whereas the π -cyclopentadienyl protons of ferrocene occur at τ 5.87. Also of interest in the n.m.r. spectra of $C_8H_5FeC_4H_4N$ and C_4H_4NMn-

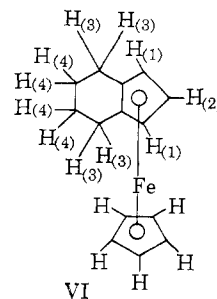
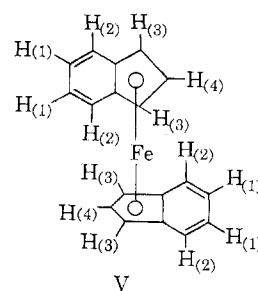
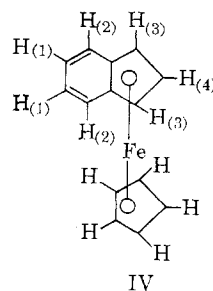
(CO)₅ is the lack of evidence of splitting between the two different types of protons of the π -pyrrolyl ring.

The meager quantities of C₅H₅FeC₄H₄N available because of the <1% yield in its preparation prevented a study of its reactions.

The complex C₅H₅FeC₉H₇ (II) forms red-purple air-stable crystals of volatility intermediate between ferrocene and (C₉H₇)₂Fe. Attempts to prepare a benzoyl derivative by treatment with benzoyl chloride in the presence of aluminum chloride in carbon disulfide solution led instead to decomposition. Treatment with butyllithium at room temperature did not appear to metalate C₅H₅FeC₉H₇, as indicated by a lack of change in appearance of the reaction mixture and isolation of only undeuterated C₅H₅FeC₉H₇ on decomposition of the reaction mixture with deuterium oxide. Since ferrocene undergoes both electrophilic and nucleophilic substitution reactions, it thus appears that the presence of the π -indenyl ring interferes with both of these types of substitution reactions. It is, of course, very possible that sufficient modification of reaction conditions might permit such substitution reactions on C₅H₅FeC₉H₇; this possibility, being beyond the general aims of the organometallic research in this laboratory, was not explored in detail.

Attempts to prepare an iron tricarbonyl derivative of C₅H₅FeC₉H₇ by treatment with Fe(CO)₅ or Fe₂(CO)₉ under various reaction conditions were unsuccessful, only unchanged C₅H₅FeC₉H₇ being recovered. The uncomplexed conjugated double bonds in C₅H₅FeC₉H₇ are thus not particularly reactive. Treatment of C₅H₅FeC₉H₇ with tetracyanoethylene caused immediate reaction, but the reaction mixture was relatively complex and a pure product was not isolated. As in (C₉H₇)₂Fe,¹⁰ the uncomplexed double bonds of the π -indenyl residue in C₅H₅FeC₉H₇ were readily hydrogenated in ethanol solution at atmospheric pressure in the presence of palladium on charcoal. The resulting π -tetrahydroindenyl derivative C₅H₅FeC₉H₁₁ is a low-melting air-stable orange crystalline solid resembling ferrocene in appearance.

Some interesting observations were made concerning the proton n.m.r. spectra of the indenyl and tetrahydroindenyl derivatives IV, V, and VI. The n.m.r. spectrum of C₅H₅FeC₉H₇ exhibits a sharp singlet at τ 6.38 due to the five equivalent π -cyclopentadienyl protons. This is one of the highest known π -cyclopentadienyl resonances. In addition, four resonances due to the π -indenyl ring are observed. The two double doublets at τ 2.59 and 3.22, each of relative intensity 2, may be attributed to the two types of uncomplexed olefinic protons H₍₁₎ and H₍₂₎. On the basis of the available data it is not clear which of these two resonances is due to H₍₁₎ and which of these resonances is due to H₍₂₎. The observed coupling constants of 7 and 3 c.p.s. are due to coupling between H₍₁₎ and H₍₂₎



in the *ortho* and *meta* positions, respectively. In addition, a doublet at τ 5.25 due to the two H₍₃₎ protons and a triplet at τ 6.11 due to the single H₍₄₎ proton are observed. The coupling constant between H₍₃₎ and H₍₄₎ is 2.5 c.p.s.

The n.m.r. spectrum of the π -indenyl residues in (C₉H₇)₂Fe resembles that in C₅H₅FeC₉H₇ in that a doublet at τ 5.54 and a triplet at τ 6.08 due to H₍₃₎ and H₍₄₎, respectively, are observed and that the coupling constant between H₍₃₎ and H₍₄₎ is also 2.5 c.p.s. However, the protons H₍₁₎ and H₍₂₎ in (C₉H₇)₂Fe, unlike the corresponding protons in C₅H₅FeC₉H₇, have identical chemical shifts exhibiting in the n.m.r. spectrum a singlet at τ 3.20 instead of two double doublets. This effect is not yet understood but should be clarified by the examination of n.m.r. spectra of additional π -indenyl derivatives.

It is also of interest to compare the n.m.r. spectrum of C₅H₅FeC₉H₁₁ (VI) with that of C₅H₅FeC₉H₇ (IV). The chemical shifts of the five π -cyclopentadienyl protons and the three protons of two different types bonded to carbon atoms of the π -indenyl residue directly involved in the bonding to the iron atom (H₍₁₎ and H₍₂₎ in VI) are identical in C₅H₅FeC₉H₁₁, exhibiting a single sharp resonance of relative intensity corresponding to eight protons. This contrasts with the n.m.r. spectrum of C₅H₅FeC₉H₇ already discussed above where the chemical shift differences between the corresponding protons (H₍₃₎, H₍₄₎, and the cyclopentadienyl protons in IV) are appreciable. This indicates that fusion of a benzene ring to a π -bonded cyclopentadienyl ring affects the chemical shifts of its protons whereas the corresponding fusion of a saturated cyclohexane ring to a π -bonded cyclopentadienyl ring does not significantly affect the chemical shifts of its protons. This is not surprising since fusion of a benzene ring would be expected to disturb electronically the cyclopentadienyl ring due to overlap between the π -orbitals of the two rings, whereas a cyclohexane ring cannot cause such an effect,

(10) E. O. Fischer and D. Seus, *Z. Naturforsch.*, **9b**, 386 (1954).