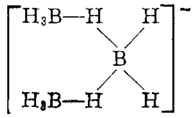
served triborane-9.[14] The borohydride ion reacts readily with strong acids (often with the acid only in the gas phase) to give a sodium salt and additional diborane. It therefore is uniquely non-interfering in the present reaction.

Another mechanism involves formation of diborohydride-7 ion followed by addition of a second borane to form the intermediate



which could lose hydrogen and form triborohydride ion directly.

Still a third possible mechanism which appears less probable involves formation of the diborohydride-7 ion, loss of hydrogen to form a diborohydride-5 ion, and addition of a borane group to give the observed product. Since reaction occurs readily between diborane and lithium borohydride in diethyl ether (a solvent in which diborohydride-7 apparently has low stability since it has not been detected), the third pathway seems less likely. A similar objection applies to the second mechanism. Further studies may well allow one to determine the correct mechanism.

Acknowledgments.—G. L. Brennan, J. A. Dupont, and Beverly Carlson Tollin contributed to the early phases of this investigation and the present results stem in part from their work. This research was supported by the Army Research Office (Durham) under Grant DA-ARO(D)-31-124-699, and by the National Science Foundation under Grant NSF-G-14595.

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[14] R. E. Enrione and R. Schaeffer, *J. Inorg. Nucl. Chem.*, **18**, 103 (1961).

CONTRIBUTION FROM E. I. DU PONT DE NEMOURS AND CO., EXPLOSIVES DEPARTMENT,
EXPERIMENTAL STATION LABORATORY, WILMINGTON, DELAWARE

Organometallic Chemistry of the Transition Metals. III. Reactions between Sodium Cyclopentadienide and Certain Complex Transition Metal Halides[1]

BY R. B. KING[2]

Received October 11, 1962

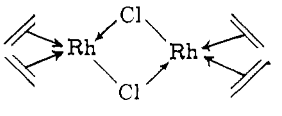
Reaction between $[(C_2H_4)_2RhCl]_2$ and sodium cyclopentadienide in tetrahydrofuran yields the novel ethylene complex $C_5H_5Rh(C_2H_4)_2$ as a yellow, volatile, crystalline solid. On the basis of n.m.r. data a novel structure is proposed for the complex $C_5H_5NiC_{13}H_{17}$ first reported by Criegee and Ludwig.[3] The orange volatile solid $C_{10}H_{12}OCH_3PdC_5H_5$ has been prepared from sodium cyclopentadienide and the palladium complex $[C_{10}H_{12}OCH_3PdCl]_2$ obtained from sodium tetrachloropalladate(II), dicyclopentadiene, and methanol.

Novel cyclopentadienyl derivatives of rhodium have been synthesized by the reaction between sodium cyclopentadienide and certain complex halides of rhodium. Thus sodium cyclopentadienide was found to react with the 1,5-cyclooctadiene complex $[C_8H_{12}RhCl]_2$ to give $C_5H_5RhC_8H_{12}$[4] and with the carbonyl halide $[(CO)_2RhCl]_2$ to give $C_5H_5Rh(CO)_2$.[5]

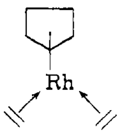
Recently the dimeric ethylene complex of rhodium of formula $[(C_2H_4)_2RhCl]_2$ (I) was described.[6] It seemed possible that this dimeric ethylene complex might react with sodium cyclopentadienide to form the monomeric ethylene complex $C_5H_5Rh(C_2H_4)_2$ analogous to the compounds $C_5H_5RhC_8H_{12}$ and $C_5H_5Rh(CO)_2$ mentioned above.

Reaction between I and sodium cyclopentadienide in tetrahydrofuran at 25 to 65° gave a mixture from which yellow crystals of the expected composition $C_5H_5Rh(C_2H_4)_2$ could be isolated by solvent removal followed by sublimation at 60° (0.1 mm.).

Cyclopentadienyldiethylene-rhodium is a yellow, volatile, air-stable solid soluble in organic solvents to give yellow solutions. The monomeric formulation is consistent with its high volatility and with isopiestic molecular weight determinations in dichloromethane. Indeed, $C_5H_5Rh(C_2H_4)_2$ appears to be the only known complex with two ethylenes bonded to a single metal atom which can be efficiently purified by vacuum sublimation. It is believed to have structure II, which is entirely analogous to the structure proposed for $C_5H_5RhC_8H_{12}$[4] but with two molecules of the monoölefin ethylene replacing one molecule of the chelating diolefin 1,5-cyclooctadiene.



I



II

The proton n.m.r. spectrum of $C_5H_5Rh(C_2H_4)_2$ shows a sharp peak at 5.08 p.p.m. due to the five cyclopentadienyl protons and two broad resonances at 2.75 and 1.00 p.p.m. due to the eight protons of the two ethylene

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[1] For Part II see R. B. King, *Z. Naturforsch.*, **18b**, 157 (1963).
[2] Mellon Institute, Pittsburgh 13, Pennsylvania.
[3] R. Criegee and P. Ludwig, *Ber.*, **94**, 2038 (1961).
[4] J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 4735 (1957).
[5] E. O. Fischer and K. Bittler, *Z. Naturforsch.*, **16b**, 225 (1961).
[6] R. D. Cramer, *Inorg. Chem.*, **1**, 722 (1962).

groups. The presence of two resonances rather than only one resonance due to the eight protons of the two complexed ethylene molecules is somewhat surprising. Since several explanations for this behavior are at least conceivable, it seems premature to speculate on the cause of these two resonances due to the complexed ethylene molecules until additional data are available.

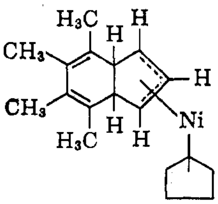
Another compound of interest to react with sodium cyclopentadienide is tetramethylcyclobutadiene-nickel dichloride.[7] Because of the tendency for a nickel atom to attain the inert gas configuration by having groups around it which donate a total of eight electrons, it seemed reasonable that sodium cyclopentadienide besides forming a cyclopentadienyl derivative also would attack the tetramethylcyclobutadiene residue in such a manner so as to finally produce a nickel complex with an inert gas configuration. Five of the necessary eight electrons would be obtained from a π-bonded cyclopentadienyl ring and the remaining three electrons from an organic system formed from the action of sodium cyclopentadienide on the tetramethylcyclobutadiene system.

It was found that reaction between excess sodium cyclopentadienide and tetramethylcyclobutadiene-nickel dichloride gave a red volatile solid of composition $C_5H_5NiC_{13}H_{17}$. Before this compound was examined in detail, however, it was reported by Criegee and Ludwig,[3] who assigned it structure III for the following reasons:

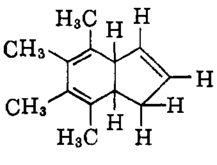
(1) Degradation by *p*-toluenesulfonic acid in benzene to cyclopentadiene and a hydrocarbon identified as IV.

(2) Absorption of two moles of hydrogen on hydrogenation giving a hydrogenated complex, $C_5H_5NiC_{13}H_{21}$, of similar physical properties.

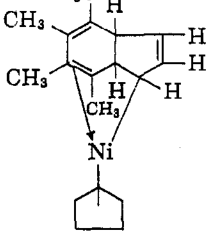
In order to obtain a better idea as to the nature of this interesting nickel complex, it seemed of interest to investigate its proton n.m.r. spectrum. If the nickel complex actually had the structure III suggested by Criegee and Ludwig, its n.m.r. would be expected to exhibit no more than two resonances for the four methyl groups because of the symmetrical manner in which the 4,5,6,7-tetramethyl-8,9-dihydroindenyl residue is bonded to the nickel atom. However, four methyl resonances were observed at 2.34, 1.54, 0.95, and 0.91 p.p.m., indicating that all four methyl groups are different. On this basis structure V is proposed for this nickel complex. Like III, V is a 4,5,6,7-tetramethyl-8,9-dihydroindenyl derivative and would be degraded by *p*-toluenesulfonic acid to cyclopentadiene and 4,5,6,7-tetramethyl-8,9-dihydroindene (IV). Also V, like III, has two double bonds which are not involved in the bonding to the nickel atom and therefore would be expected to absorb two moles of hydrogen to give a nickel complex with physical properties similar to those of the unhydrogenated material. However, structures III and V differ in one important aspect. In structure III the 4,5,6,7-tetramethyl-8,9-dihydroindenyl system donates three electrons to the nickel atom *via* a π-allyl-type bond involving three adjacent carbon atoms in the five-membered ring, the bonding being similar to the cyclopentenyl-nickel bonding in $C_5H_5NiC_5H_7$.[8] In structure V, on the other hand, the 4,5,6,7-tetramethyl-8,9-dihydroindenyl system donates two electrons to the nickel atom by means of a π-type bond between one of the two double bonds of the *six*-membered ring and the nickel atom and the third electron by means of a σ-type bond between one of the carbon atoms of the five-membered ring and the nickel atom. Because of this difference in bonding V is much less symmetrical than III and as a consequence of this all four methyl groups are non-equivalent and therefore would be expected to give four separate methyl peaks in the proton n.m.r. spectrum.[8a]



III



IV



V

A compound with ligand–metal bonding similar to the nickel complex V is the palladium compound $[C_{10}H_{12}OCH_3PdCl]_3$ obtained from dicyclopentadiene, methanol, and sodium tetrachloropalladate(II).[9] This compound is believed to have either structure

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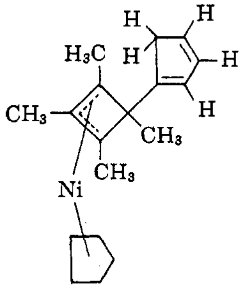
(7) R. Criegee and G. Schröder, *Ann.*, **623**, 1 (1959).

(8) B. L. Shaw and N. Sheppard, *Chem. Ind.* (London), 517 (1961); M. Dubeck and A. H. Filbey, *J. Am. Chem. Soc.*, **83**, 1257 (1961); E. O. Fischer and H. Werner, *Tetrahedron Letters*, 17 (1961).

(8a) NOTE ADDED IN PROOF.—A very recent X-ray determination (L. F. Dahl, private communication) has yielded the surprising structure Va for the nickel complex $C_5H_5NiC_{13}H_{17}$.

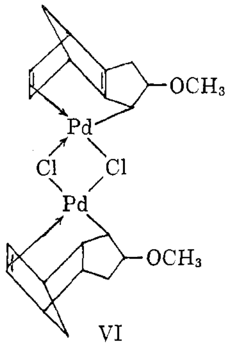


Va

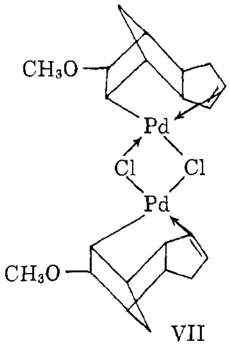
It thus appears that the degradation studies presented originally by Criegee and Ludwig[3] as evidence for their structure III and assumed to be correct in the discussion in this paper are actually incorrect. The author has been informed by Criegee (private communication) that the degradation of $C_5H_5NiC_{13}H_{17}$ with *p*-toluenesulfonic acid and the chemistry of the resulting $C_{13}H_{18}$ hydrocarbon are being reinvestigated in his laboratory. It will be noted that the observed proton n.m.r. spectrum of $C_5H_5NiC_{13}H_{17}$ is consistent with structure Va as well as with structure V.

(9) J. Chatt, L. M. Vallarino, and L. M. Venanzi, *J. Chem. Soc.*, 3413 (1957).

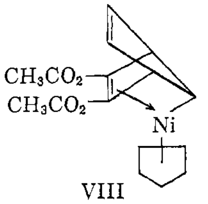
VI or VII, insufficient data being available to permit one to decide between these two structures. In either of these structures a methoxy derivative of the dicyclopentadiene system donates two electrons to the palladium atom by means of π-type bonding involving a double bond and a third electron by means of a σ-type bond involving a carbon next to the methoxy group. Because of this it seemed quite likely that a compound $C_{10}H_{12}OCH_3PdC_5H_5$ could be prepared by reaction between $[C_{10}H_{12}OCH_3PdCl]_2$ and sodium cyclopentadienide. This was found to be the case, orange air-stable crystals of this composition being isolated from the reaction mixture in 40% yield. Like the nickel compound V and unlike the starting chloride VI or VII, this new palladium compound would be expected to be monomeric and volatile. Indeed this compound could be readily sublimed at 80° (0.1 mm.). Conspicuous features of its proton n.m.r. spectrum are the presence of a sharp peak at 5.33 p.p.m. due to the five protons of the π-bonded cyclopentadienyl group and the presence of a sharp peak at 3.14 p.p.m. due to the three methyl protons of the methoxy group; interpretation of the remainder of the spectrum is uncertain until other related compounds are synthesized.



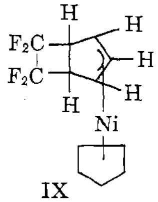
VI



VII



VIII



IX

A nickel compound VIII with a structure similar to the nickel and palladium compounds described in this paper has been reported as being formed from bis-cyclopentadienylnickel and dimethyl acetylenedicarboxylate.[10] Attempts to prepare nickel compounds with metal–ligand bonding similar to V and VIII by treatment of bis-cyclopentadienylnickel either with bicyclo-[2,2,1]heptene derivatives to displace one of the cyclopentadienyl groups to form an analog of VIII or with polyolefinic derivatives such as cycloöctatetraene or butadiene to form a novel three-electron donor system have been unsuccessful although many unexplored possibilities remain. Evidence for the formation of a red-purple liquid product in the reaction between bis-cyclopentadienylnickel and butadiene was obtained. Unfortunately this material was too air-sensitive for proper purification and characterization. After the work described in this paper was completed, a communication[11] appeared on the reaction between bis-cyclopentadienylnickel and the fluoroölefin tetrafluoroethylene to give the nickel complex IX.

Experimental

Infrared spectra were taken in potassium bromide pellets and recorded on a Perkin-Elmer Infracord machine. Proton n.m.r. spectra were taken in carbon disulfide solution and recorded on a Varian A-60 machine. Chemical shifts are given in p.p.m. downfield from tetramethylsilane and were reproducible to ±0.02 p.p.m. Melting points were determined in sealed capillaries and are uncorrected.

Diethylene-rhodium(I) chloride dimer (I) was prepared from commercial hydrated rhodium(III) chloride (Engelhard Industries) and ethylene in aqueous methanol.[6] Tetramethylcyclobutadiene-nickel dichloride was prepared from nickel tetracarbonyl and tetramethyldichlorocyclobutene[12] according to the procedure of Criegee and Schröder.[7] The 30% sodium dispersion in xylene was purchased from Anderson Chemical Company, Weston, Mich. Cyclopentadiene was freshly prepared by thermal dedimerization of dicyclopentadiene. Tetrahydrofuran was purified by distillation over lithium aluminum hydride.

Cyclopentadienyldiethylene-rhodium.—A solution of sodium cyclopentadienide was prepared under nitrogen from 17 ml. of 30% sodium dispersion in xylene (~200 mmoles of sodium) and 20 ml. (16 g., 240 mmoles) of cyclopentadiene in 200 ml. of redistilled tetrahydrofuran by dropwise addition of the cyclopentadiene to a stirred slurry of the sodium dispersion in the tetrahydrofuran. After all of the sodium had dissolved, the resulting sodium cyclopentadienide solution was treated with 16.7 g. (43 mmoles) of diethylene-rhodium(I) chloride dimer.[6] The action mixture was refluxed for 30 min. under nitrogen and then stirred for 16 hr. at room temperature. Solvent then was removed at ~30 mm., leaving a brown residue. After admitting nitrogen this residue was transferred under nitrogen to a sublimation apparatus. The product was isolated by sublimation at 50–100° (~1 mm.) for 4 hr. to a probe cooled by running water to give 9.0 g. (47% yield) of yellow crystalline cyclopentadienyldiethylene-rhodium, m.p. 72–73°.

Anal. Calcd. for $C_9H_{13}Rh$: C, 48.2; H, 5.8; Rh, 46.0; mol. wt., 224. Found (two independent preparations): C, 47.9, 47.8; H, 5.7, 5.9; Rh, 45.6 (by ignition to Rh_2O_3); mol. wt., 245 (isopiestic in dichloromethane).

Infrared Spectrum.—C–H bands at 3090 (w), 3010 (w), and 2950 (w) cm.$^{-1}$; other bands at 1490 (vw), 1435 (m), 1400 (m), 1200 (s, sh), 1189 (s), 1107 (w), 1018 (m), 991 (vw), 969 (m), 856 (w), 825 (vw), 794 (s), and 725 (m) cm.$^{-1}$.

Proton N.m.r. Spectrum.—Sharp peaks at 5.08 p.p.m. due to the five cyclopentadienyl protons, broad resonances at 2.75 and 1.00 p.p.m. with relative intensities ~1:1 due to the eight protons of the two ethylene groups.

The Reaction between Tetramethylcyclobutadiene-nickel Dichloride and Sodium Cyclopentadienide.—The preparation of the compound $C_5H_5NiC_{13}H_{17}$ was carried out by essentially the same procedure as that described by Criegee and Ludwig.[3] Red crystals, m.p. 73–74° (lit.[3] 74.5–75°), were obtained which were purified by crystallization and sublimation.

Anal. Calcd. for $C_{15}H_{22}Ni$: C, 72.8; H, 7.4; Ni, 19.8; mol. wt., 297. Found (two independent preparations): C, 72.2, 73.0; H, 7.1, 7.8; Ni, 19.8 (by EDTA titration after sample decomposition); mol. wt., 270 (isopiestic in chloroform).

Proton N.m.r. Spectrum.—Sharp peak due to five cyclopentadienyl protons at 5.06 p.p.m.; peaks due to the four methyl

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(10) M. Dubeck, *J. Am. Chem. Soc.*, **82**, 6193 (1960).

(11) D. W. McBride, R. L. Pruett, E. Pitcher, and F. G. A. Stone, *ibid.*, **84**, 497 (1962).

(12) R. Criegee and A. Moschel, *Ber.*, **92**, 2181 (1959).

groups at 2.34, 1.54, 0.95, and 0.91 p.p.m.; other resonances centered at 6.21 (singlet), 6.17 (doublet, $J = 10$ cycles), 5.75 (doublet, $J = 10$ cycles), 2.75 (singlet), and 2.55 (singlet) p.p.m., each of which may be attributed to a single proton.

The Palladium Compound $C_{10}H_{12}OCH_3PdC_5H_5$.—The $[C_{10}H_{12}OCH_3PdCl]_2$[9] required for this preparation was prepared in quantitative yield from commercially available sodium palladium(II) chloride (Englehard Industries) by treatment with excess dicyclopentadiene in methanol solution. The resulting pale yellow crystalline precipitate was filtered after several hours; washed with water, methanol, and pentane; and dried overnight in a vacuum desiccator.

Sodium cyclopentadienide was prepared under nitrogen from 0.8 ml. of 30% sodium dispersion in xylene (~10 mmoles of sodium) and 2.0 ml. (1.6 g., 24 mmoles) of cyclopentadiene in 150 ml. of tetrahydrofuran. After all of the sodium had dissolved, 2.0 g. (6.5 mmoles) of $[C_{10}H_{12}OCH_3PdCl]_2$ was added. The reaction mixture was stirred 2 hr. at room temperature and then refluxed for 3 hr., becoming dark red. After the reaction period was over, solvent was removed at ~50 mm., leaving a rather sticky residue. Nitrogen was admitted and this residue was extracted with three 50-ml. portions of dichloromethane. The extract was filtered. Solvent was removed from the deep orange filtrate at ~50 mm., leaving a dark yellow liquid. This liquid was extracted with two 15-ml. portions of pentane and the extracts filtered. Cooling the orange filtrate in a $-78°$ bath for 1.5 hr. precipitated orange crystals of the product. These were filtered and dried giving 980 mg. (45% yield) of crude $C_{10}H_{12}OCH_3PdC_5H_5$. Sublimation of this material at 80–110° (0.1 mm.) for 2 hr. through glass wool to a water-cooled probe gave 800 mg. (37% yield) of pure $C_{10}H_{12}OCH_3PdC_5H_5$, m.p. 74–75.5°.

Anal. Calcd. for $C_{16}H_{20}OPd$: C, 57.3; H, 6.0; Pd, 31.9; OCH_3, 9.0; mol. wt., 334. Found (two independent preparations): C, 56.8, 56.4; H, 6.1, 6.2; Pd, 31.4, 31.1; OCH_3, 7.8, 7.4; mol. wt., 352 (Mechrolab osmometer in benzene solution).

Infrared Spectrum.—C–H bands at 2980 (sh), 2950 (m), and 2900 (m) cm.$^{-1}$; other bands at 1455 (w), 1450 (sh), 1440 (w), 1365 (w), 1333 (w), 1291 (w), 1279 (sh), 1272 (w), 1259 (w), 1240 (vw), 1230 (vw), 1202 (w), 1179 (w), 1162 (sh), 1157 (m), 1120 (m), 1083 (s), 1057 (w), 1039 (m), 1019 (sh), 1011 (w), 988 (m), 969 (sh), 961 (m), 940 (m), 928 (m), 920 (sh), 885 (w), 854 (w), 849 (sh), 836 (m), 817 (w), 798 (w), 763 (sh), 757 (s), 747 (m), 710 (w), and 673 (w) cm.$^{-1}$.

Proton N.m.r. Spectrum.—Sharp peak at 5.53 p.p.m. due to the five cyclopentadienyl protons; sharp peak at 3.14 p.p.m. due to the three methyl protons of the methoxy group; other resonances centered at 5.03 (doublet, $J \sim 6$ cycles), 3.43 (singlet), 3.35 (doublet, $J \sim 6$ cycles), 2.53 (very broad), 2.21 (broad and asymmetric), 1.53 (doublet, $J = 10$ cycles), and 0.92 (doublet, $J = 10$ cycles) p.p.m.

Acknowledgment.—The author acknowledges the helpful advice of Dr. R. D. Cramer in the preparation of $[(C_2H_4)_2RhCl]_2$.

CONTRIBUTION FROM E. I. DU PONT DE NEMOURS AND CO.,
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Reactions of Alkali Metal Derivatives of Metal Carbonyls. I. Reactions between $C_5H_5Fe(CO)_2Na$ and Certain Organic Polyhalogen Compounds

BY R. B. KING[1]

Received December 10, 1962

Reactions between the sodium derivative $C_5H_5Fe(CO)_2Na$ and the α,ω-dibromides, $Br(CH_2)_nBr$ (n = 3, 4, 5, and 6) have been found to yield the stable orange crystalline solids $(CH_2)_n[C_5H_5Fe(CO)_2]_2$. Reaction between 1,4-dichlorobutyne-2 and $C_5H_5Fe(CO)_2Na$ yields the acetylenic derivative $C_5H_5Fe(CO)_2CH_2C{\equiv}CCH_2Fe(CO)_2C_5H_5$ as well as significant quantities of $[C_5H_5Fe(CO)_2]_2$. Reaction between $C_5H_5Fe(CO)_2Na$ and cyanuric chloride has been found to yield orange crystalline $C_3N_3Cl[C_5H_5Fe(CO)_2]_2$.

Recently several organometallic derivatives of transition metals with metal–carbon σ-bonds have been synthesized by the reaction of alkali metal salts of carbonyl hydride derivatives with various alkyl and aryl halides. These include such compounds as the methyl derivatives $Mn(CO)_5CH_3$[2] and $C_5H_5Fe(CO)_2CH_3$[3] prepared by reaction between the appropriate sodium derivatives and methyl iodide. It seemed of interest to investigate reactions between various sodium derivatives and various organic polyhalogen derivatives in attempts to synthesize organometallic derivatives containing more than one transition metal atom bonded to a single organic residue. This paper reports reactions between the readily available sodium derivative, $C_5H_5Fe(CO)_2Na$,[3] and various organic polyhalogen derivatives which have resulted in the syntheses of a variety of new compounds containing two $-Fe(CO)_2C_5H_5$ residues bonded to a single organic molecule.

Experimental

Infrared spectra were taken in potassium bromide pellets and recorded on a Perkin-Elmer Infracord machine unless otherwise indicated. Proton n.m.r. spectra were taken in carbon disulfide solution and recorded on a Varian A-60 machine. Chemical shifts are given in p.p.m. downfield from tetramethylsilane and were reproducible to ±0.02 p.p.m. Molecular weight determinations were carried out in benzene solution in a Mechrolab vapor pressure osmometer. Melting and decomposition points were determined in sealed capillaries and are uncorrected.

Preparation of the Compounds $(CH_2)_n[C_5H_5Fe(CO)_2]_2$ (n = 3, 4, 5, and 6).—The reaction was conducted under nitrogen in a

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[1] Mellon Institute, Pittsburgh 13, Pennsylvania.

[2] R. D. Closson, J. Kozikowski, and T. H. Coffield, *J. Org. Chem.*, **22**, 598 (1957).

[3] G. Wilkinson and T. S. Piper, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956).