THESIS

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PART I. SYNTHESIS OF AND CATALYSIS BY USING 1-DIMETHYLAMINOMETHYLFERROCENE-2-THIOETHERS. PART II. BIS(η^6-4-CHLOROANISOLE)CHROMIUM

presented by

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Major professor

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PART I. SYNTHESIS OF AND CATALYSIS BY USING 1-DIMETHYL-AMINOMETHYLFERROCENE-2-THIOETHERS

PART II. BIS(η^6-4-CHLOROANISOLE)CHROMIUM

By

Robert V. Honeychuck

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ABSTRACT

PART I. SYNTHESIS OF AND CATALYSIS BY USING 1-DIMETHYL-AMINOMETHYLFERROCENE-2-THIOETHERS

PART II. BIS(η^6-4-CHLOROANISOLE)CHROMIUM

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PART I

A number of previously unknown ferrocenyl thioethers (η^5-C_5H_5)Fe(η^5-C_5H_3-1-CH_2NMe_2-2-SR), R = Me, Et, i-Pr, i-Bu, i-pentyl, and Ph, have been made from dimethylaminomethyl ferrocene via lithiation at the number 2 position and subsequent reaction with RSSR. These compounds are air-stable yellow solids which are easily produced in multigram quantities and are separable on silica gel columns. The isopropyl derivative crystallizes directly from the reaction mixture and requires no chromatography for purification. The following techniques were used for characterization: ^1H and ^{13}C NMR, IR, MS, and elemental analysis. The derivatives contain a plane of chirality causing NMR spectra to exhibit separate peaks for diastereotopic protons and carbons. Methylene protons α to the nitrogen of the alkyl derivatives give ^1H NMR peaks which are widely separated. The phenyl derivative shows these peaks closer together, but the coupling constant remains the same at 13 Hz.

The ferrocenes are tertiary amines and thioethers and thus act as bidentate ligands. The $PdCl_2$ complex of (η^5-C_5H_5)Fe(η^5-C_5H_3-1-CH_2NMe_2-2-S-i-Pr) was made and its potential as a catalyst explored. The $PdCl_2$ complex selectively hydrogenates 1,3-cyclooctadiene to cyclooctene under heterogeneous conditions in CH_2Cl_2 with H_2O present. Under homogeneous conditions in acetone with no H_2O this reaction is much faster. The $PdCl_2$ complex isomerizes and hydrogenates 1,5-cyclooctadiene to cyclooctene under homogeneous conditions in acetone.

PART II

A new (η^6-arene)$_2$chromium complex, bis(η^6-4-chloroanisole)chromium, has been prepared by metal vapor-ligand cocondensation and characterized spectroscopically. This compound exhibits some degree of air stability in the solid state, unlike many bis(arene)chromium species. A metal vapor reactor using resistive heating was built for this work and is described. Attempts to make new complexes bis(η^6-4-bromoanisole)chromium and bis(η^6-4-chloronitrobenzene)chromium by metal vapor-ligand cocondensation are detailed. Attempts to make the Grignard reagent of bis(η^6-4-chloroanisole)chromium are also described.

For Fritz Hembach, Art DeLaurier, Julie Biernat, Laurence LeGouge, Cynthia Hinds, Tom Dubovsky, Andy Bobrow, Mark Leis, Dan Schaefer, Claudia Donase, John Albert, Kathy Katovich, Dale Grover, Deirdre Weinberg, Mark Durbin, Mike Zack, Elizabeth Kupfer, Tom Jaworski, Sue Kujawa, Amy Matteson, Gabrielle Tazzia, Hojoon Kim, Janice Strait, Mary Ann Sweetland, Tom Carlson, Karen Mausser, Steve Baker, Linda Jackson, Dan Stouffer, and Silvia Blum,

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"Sine qua non."

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PART I. SYNTHESIS OF AND CATALYSIS BY USING 1-DIMETHYL-AMINOMETHYLFERROCENE-2-THIOETHERS

INTRODUCTION

Since dimethylaminomethylferrocene's first appearance in 1956,[1] much effort has been expended on the reactions of its lithiation product 2 (Figure 1). The chelating

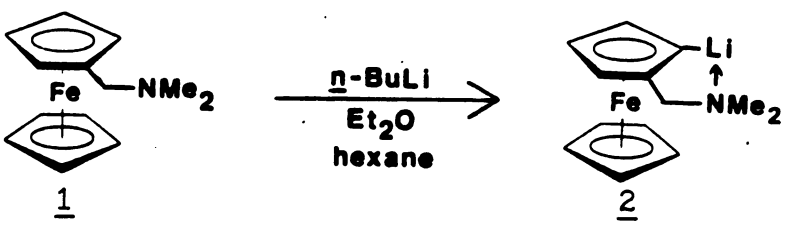

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Figure 1. Lithiation of dimethylaminomethylferrocene (1).

effect of the lone pair of electrons on nitrogen directs lithiation to the 2-position, giving 2 in high yield with minimal 3- and 1'-contamination. The coordination chemistry of 3 (Figure 2, available from 2 via nucleophilic substitution of chlorodiphenylphosphine) with chromium, molybdenum, tungsten, iron, and cobalt carbonyls has been investigated.[2] The ligand was bidentate with the group VIB carbonyls, but monodentate through phosphorus with Fe and Co. Compound 2 adds in Grignard fashion to carbonyl species giving 4,[3,4] and the addition products of acetylferrocene and acetaldehyde.[5,6] Pyridine undergoes a nucleo-

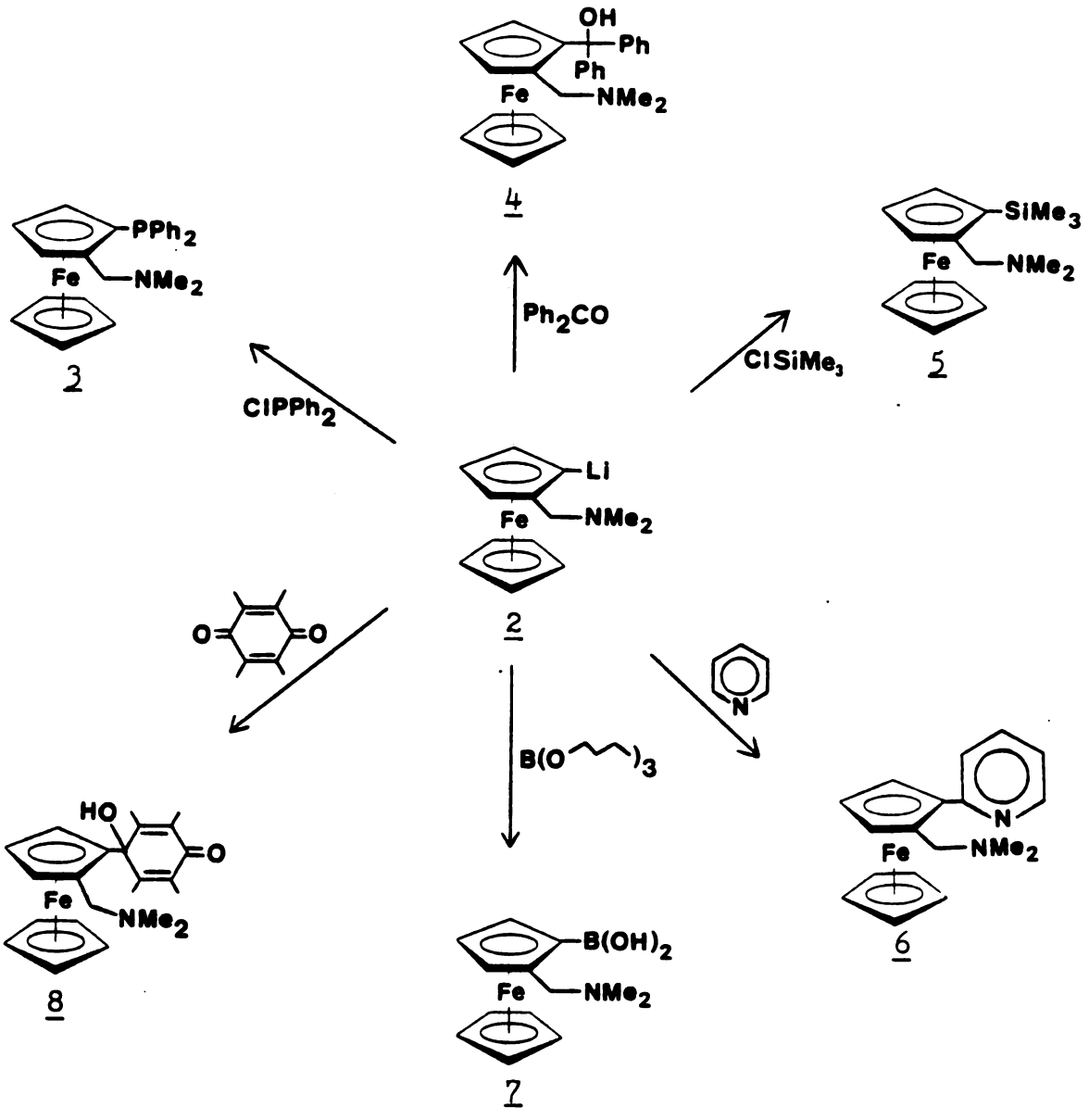

Figure 2. Selected reactions of 1-dimethylaminomethyl-2-lithioferrocene.

philic aromatic substitution to yield 6, whose CoX_2 complexes (X = Cl, Br, and SCN) have been studied.[6]

Marr et. al. have found that 2 reacts with paraformaldehyde and dimethylformamide giving 1-dimethylaminomethyl-2-hydroxymethylferrocene and 1-dimethylaminomethyl-2-formylferrocene, respectively.[7] Several derivatives of these compounds were reported. Trimethylchlorosilane reacts with 2 to give 5,[8] and 2 undergoes reaction with hexachloroethane to give the 2-chloro compound.[9] The latter reaction involves lithium-halogen exchange followed by β-elimination giving tetrachloroethylene. Tri-n-butyl borate reacts with 2 to yield, after hydrolysis, boronic acid 7,[10] which is an amino acid with the same properties as natural amino acids: it has an isoelectric point and is soluble in aqueous base and acid. More importantly, 7 undergoes replacement of the boronic acid portion with Cl, Br, and I using cupric chloride, cupric bromide, and I_2 as the reagents. Finally, various quinones have been added to 2 giving the corresponding keto alcohols, e.g., 8.[11] An excess of quinone was used, and no evidence was found for addition of 2 molecules of 2 to the quinone.

Thus, there are a multitude of electrophiles which will react with lithioferrocene 2. There are also many lithiated compounds which will react with disulfides.

The reaction of disulfides with anions has been known for years, and involves electrophilic rather than nucleophilic

sulfur. In organic chemistry, the reaction is used with enolate anions to produce α-sulfenyl carbonyl species (Figure 3), intermediates on the path to α,β-unsaturated

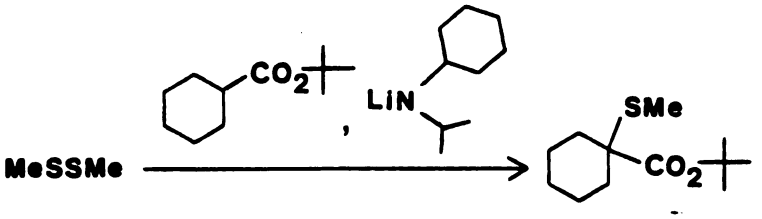

Figure 3. Reaction of methyldisulfide with a t-butyl ester enolate.

carbonyl compounds.[12-14] In 1981, bis(η^6-benzene)chromium was lithiated and the product reacted with methyl disulfide (Figure 4).[15] Thioether sandwich complex 9 acted as a chelating agent with $Mo(CO)_4$.

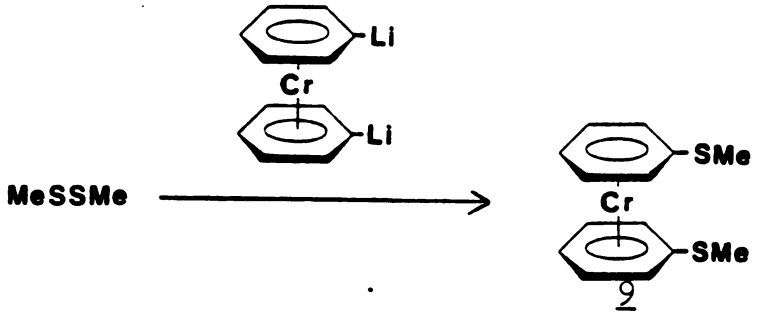

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Figure 4. Reaction of methyldisulfide with bis(η^6-phenyllithium)chromium.

Cava's group has found that phenyllithium and a number of lithiated aromatics react with tetraisopropylthiuram disulfide to give S-aryl-N,N-diisopropyldithiocarbamates

(10, Figure 5).[16] The bulk of the isopropyl groups prevents attack at the thione carbons, in contrast to the tetramethyl analog. With tetraisopropylthiuram disulfide replaced by tetramethylthiuram disulfide, a major side product is the thioamide. The authors hydrolyzed dithiocarbamates 10 to the thiols in high yield, so that the sequence represents a new synthesis of aromatic thiols.

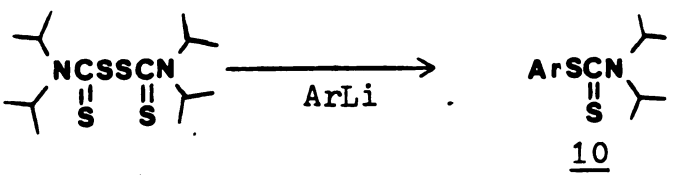

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Figure 5. Reaction of tetraisopropylthiuram disulfide with aryllithium species.

Recently in these laboratories[17-19] it was found that lithioferrocene and 1,1'-dilithioferrocene react with various disulfides to give thioethers and dithiocarbamates (Figure 6). Other ferrocene derivatives with sulfur in side chains have been made, but these were the products of a nucleophilic substitution in the side chain (Figure 7) or electrophilic aromatic substitution (Figure 8). Reaction of tetraalkylammonium iodide 11 (Figure 7) with sodium sulfide gave thioether 12 and disulfide 13.[20] Sulfur was introduced directly to a ferrocenyl ring via electrophilic sulfonation (Figure 8).[21] Sulfonic acid 14 was converted to the sulfonyl chloride and then the thiol. The thiol

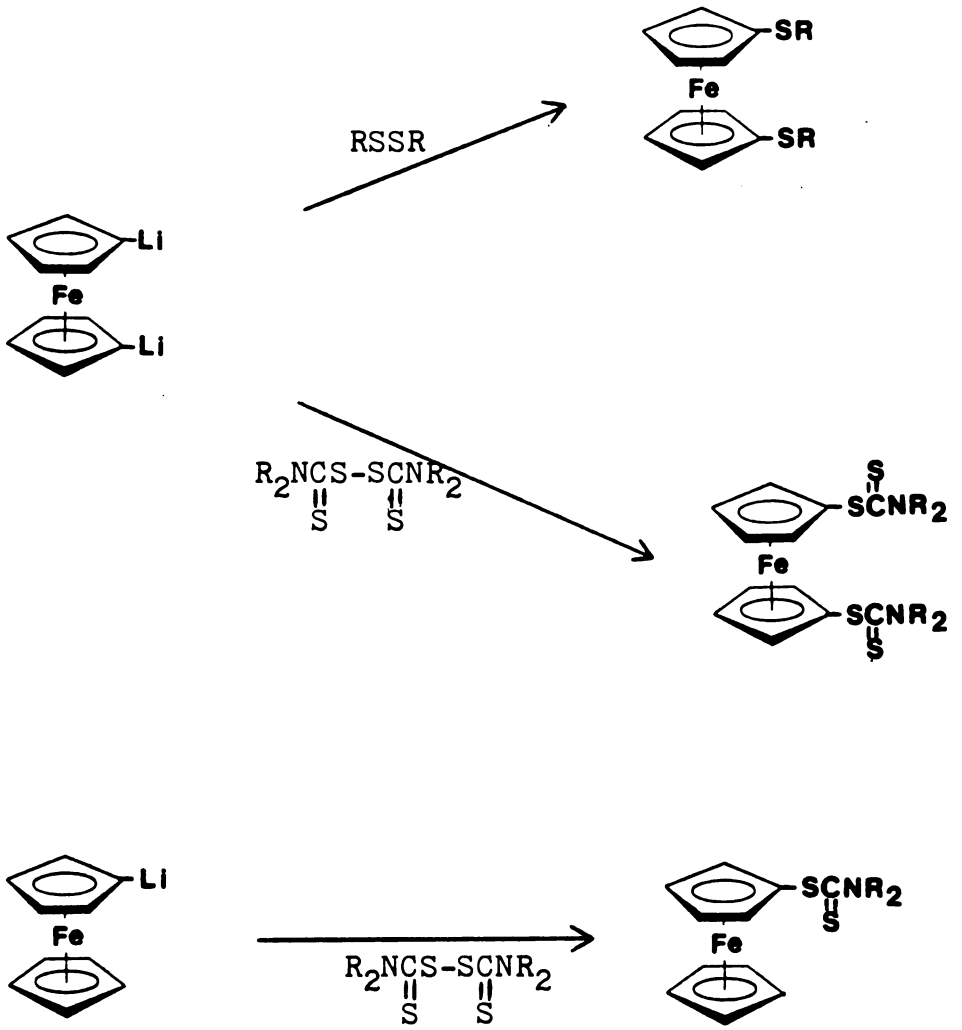

Figure 6. Reaction of lithiated ferrocenes with disulfides.

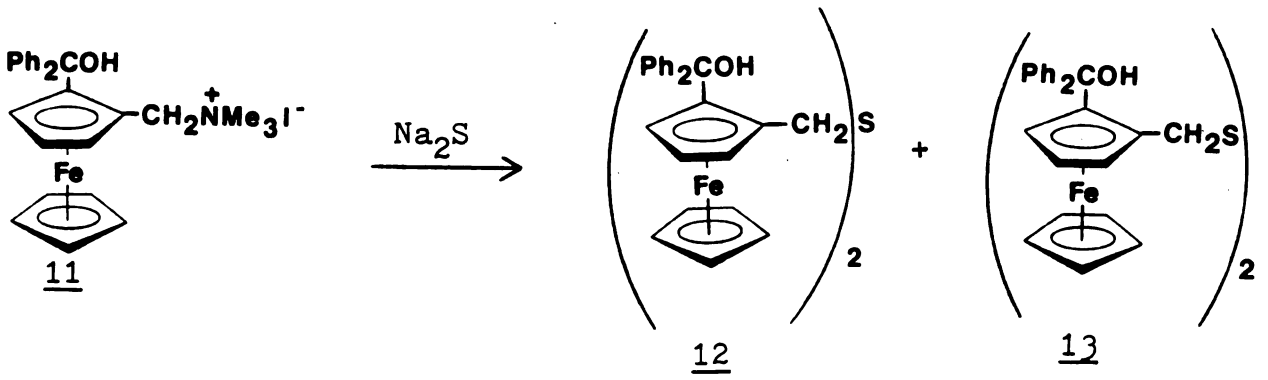

Figure 7. Nucleophilic substitution leading to ferrocenes with sulfur in the side chain.

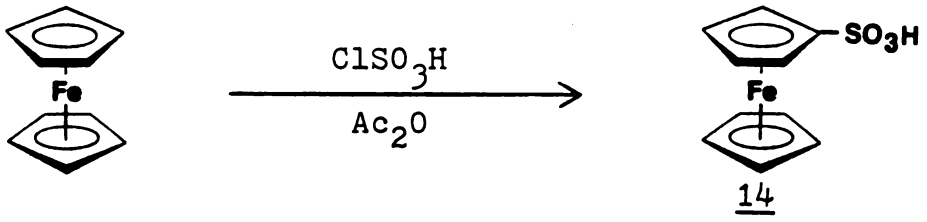

Figure 8. Introduction of sulfur to a ferrocene ring by electrophilic aromatic substitution.

was converted to its methyl thioether. The methyl thioether (15, Figure 9) was subjected to electrophilic substitution with bis(dimethylamino)methane.[22] All three possible monosubstituted products were obtained as was expected from the activating nature of the methylthio group.

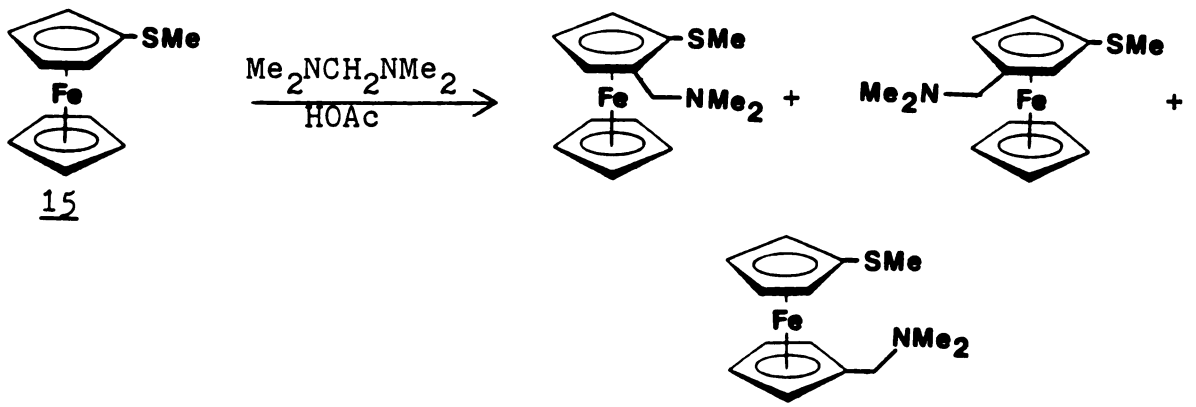

Figure 9. Aminomethylation of methylthioferrocene.

The lithiation procedure yielding 2 described above offers a distinct advantage over electrophilic substitution in that only a single lithiation product is obtained. Part I of this dissertation presents the reaction of a number of disulfides with lithioferrocene 2 to give several new ferrocene tertiary amine thioethers. The use of the $PdCl_2$ complex of one of these amine thioethers in isomerization and selective hydrogenation is also detailed.

This work represents an addition to the rich literature of ferrocene chemistry.[23-25]

EXPERIMENTAL

Proton and ^{13}C NMR's were obtained by use of a Bruker WM 250 spectrometer in chloroform-d except where noted, with TMS as internal standard. Infrared spectra were recorded by use of a Perkin-Elmer 457 machine. Mass spectra were obtained by means of a Finnigan 4021 instrument with INCOS data system. Elemental analyses were performed by Spang Microanalytical Laboratory, Eagle Harbor, Michigan, and Galbraith Laboratories, Knoxville, Tennessee. Gas chromatography was done by using a Hewlett-Packard 5880A instrument. Dimethylaminomethylferrocene was made by the standard method[26] or was purchased. The hydrogenation substrate 1,3-cyclooctadiene was obtained from Columbian Carbon Co., and 1,5-cyclooctadiene from Aldrich Chemical Co. The 1,4-isomer was made via the existing method.[27,28] Solvents were dried and distilled by standard methods.[29] Hydrogenations at 1 atm were followed by means of a barometer and manometer; at greater than 1 atm a pressure bottle with gauge was used.

1-Dimethylaminomethyl-2-methylthioferrocene (16, R = Me). To a magnetically stirred 500 mL Schlenk flask with a rubber septum were added 9.2 mL (0.046 mol) of dimethylaminomethylferrocene and 250 mL of dry ethyl ether under N_2. Via syringe, 32 mL (0.051 mol) of n-butyllithium (1.6 M in

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hexane) was slowly added. After stirring for 12 hrs, 4.1 mL (0.046 mol) of methyl disulfide was put in via cannula. Four hours later, 100 mL of H_2O was added, the mixture was filtered, and the organic layer was separated, dried over Na_2SO_4, and evaporated on the rotary evaporator. Methyl disulfide was removed on a vacuum pump and the residue was chromatographed on a 5 X 23 cm column of Al_2O_3, with CH_2Cl_2 as solvent. The first band gave the product as brown crystals: yield 2.27 g (17 %); mp 165° dec; ^1H NMR δ 2.27 (s, 3H, SCH_3), 2.31 (s, 6H, NMe_2), 3.47 (d, J = 13 Hz, 1H, NCH_2), 3.73 (d, J = 13 Hz, 1H, NCH_2), 4.12 (s, 5H, C_5H_5), 4.20 (m, 1H, H_3, H_4, H_5), 4.35 (m, 1H, H_3, H_4, H_5), 4.43 (m, 1H, H_3, H_4, H_5); ^{13}C NMR ppm (J_{CH}) 20.2 (140.4, SMe), 44.2 (137.4, NMe_2), 56.6 (140.8, NCH_2), 68.0 (176.9, C_3, C_4, C_5), 70.0 (173.6, C_5H_5), 70.8 (176.7, C_3, C_4, C_5), 71.9 (176.9, C_3, C_4, C_5), 83.6 (C_1), 84.3 (C_2); IR (Nujol, CsI) 719, 805 (ring-H bend perpendicular to ring), 888, 946, 996 (ring-H bend parallel to ring), 1102 cm^{-1} (antisymmetric ring breath); MS m/e (% RA) 44 (10, NMe_2), 47 (1, SMe), 56 (15, Fe), 58 (15, CH_2NMe_2), 65 (2, C_5H_5), 121 (41, C_5H_5Fe), 231 (2, $M^+ - CH_2NMe_2$), 242 (44, $M^+ - SMe$), 245 (37, $M^+ - NMe_2$), 289 (89, M^+).

1-Dimethylaminomethyl-2-ethylthioferrocene (16, R = Et). The lithioferrocene 2 was made as with 16, R = Me, using 8.1 mL (0.041 mol) of dimethylaminomethylferrocene, 100 mL of ethyl ether, and 28 mL (0.045 mol) of n-BuLi. The flask

was cooled to 0° and 5.1 mL (0.041 mol) of ethyl disulfide was added via cannula over 15 min. The suspension was unchanged on warming to 25°, so 100 mL of hexanes was added and the mixture was heated under reflux for 2 hrs. Distilled water (100 mL) was added and the mixture was filtered. The solid in the fritted glass funnel was washed with hexanes until the washings were colorless. The organic layer from the filtrate was washed with 2 X 200 mL of H_2O, dried over Na_2SO_4, and reduced on the rotary evaporator. Excess disulfide was removed on a vacuum pump. The residue was separated on a 5 X 24 cm column of alumina using hexanes/Et_2O, giving the product as golden crystals from the first band after 3 recrystallizations. Sublimation at 60°-108° gave the analytical sample of yellow crystals. Yield 5.60 g (45 %); mp 175° dec; ^1H NMR δ 1.19 (t, 3H, ethyl CH_3), 2.19 (s, 6H, NMe_2), 2.64 (m, 2H, ethyl CH_2), 3.21 (d, J = 13 Hz, 1H, NCH_2), 3.60 (d, J = 13 Hz, 1H, NCH_2), 4.09 (s, 5H, C_5H_5), 4.16 (t, 1H, H_3, H_4, H_5), 4.32 (d, 2H, H_3, H_4, H_5); ^{13}C NMR ppm (J_{CH}) 14.8 (126.9, $EtCH_3$), 30.7 (142.0, $EtCH_2$), 45.1 (133.9, NMe_2), 57.2 (131.7, NCH_2), 67.4 (169.9, 8.6, C_3, C_4, C_5), 69.8 (170.8, C_5H_5), 70.6 (179.9, C_3, C_4, C_5), 73.7 (177.1, 8.0, C_3, C_4, C_5), 80.5 (C_1), 87.0 (C_2); IR (Nujol, CsI) 720, 808 (ring-H bend perpendicular to ring), 888, 946, 998 (ring-H bend parallel to ring), 1103 (antisymmetric ring breath), 1178 (C-N stretch), 1264 cm^{-1} (alkyl C-H bend); MS m/e (% RA) 44 (23, NMe_2), 56 (61, Fe), 58

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(76, CH_2NMe_2), 65 (21, C_5H_5), 121 (100, FeCp), 242 (41, M^+ - SEt), 259 (20, M^+ - NMe_2), 274 (4, M^+ - Et), 303 (61, M^+). Anal. Calcd for $C_{15}H_{21}FeNS$: C, 59.41; H, 6.98; S, 10.57. Found: C, 59.61; H, 7.15; S, 10.48.

1-Dimethylaminomethyl-2-isopropylthioferrocene (16, R = i-Pr). Lithioferrocene 2 was made as with 16, R = Me, using 16.3 mL (0.0823 mol) of dimethylaminomethylferrocene, 20 ml of ethyl ether, and 57 mL (0.090 mol) of n-BuLi. The orange suspension was stirred at 25° for 12 hrs. Isopropyl disulfide (13.1 mL, 0.0823 mol) was then added via cannula over 0.5 hr. A voluminous yellow precipitate appeared. After 1.5 hrs the reaction mixture was filtered and washed with 100 mL of H_2O, then 200 mL of ether. The red organic layer from the 2 phase filtrate was dried over Na_2SO_4 and reduced on the rotary evaporator to a red oil. The oil was dissolved in 50 mL of CH_2Cl_2, 25 mL of hexanes added, and the CH_2Cl_2 boiled off. Large brown prisms appeared after 10 days at 25°. Two recrystallizations gave 8.22 g (31.5 %) of 16, R = i-Pr: mp 82-83°; ^1H NMR δ 1.15 (d, J = 6 Hz, 3H, i-Pr CH_3), 1.19 (d, J = 7 Hz, 3H, i-Pr CH_3), 2.18 (s, 6H, NMe_2), 3.02 (m, 1H, i-Pr CH), 3.14 (d, J = 13 Hz, 1H, CH_2), 3.61 (d, J = 13 Hz, 1H, CH_2), 4.08 (s, 5H, C_5H_5), 4.16 (s, 1H, H_3, H_4, H_5), 4.32 (s, 2H, H_3, H_4, H_5); ^{13}C NMR ppm (J_{CH}) 22.8 (128.8, i-Pr CH_3), 23.6 (125.4, i-Pr CH_3), 39.4 (148.4, i-Pr CH), 45.3 (134.3, NMe_2), 57.3 (132.5, CH_2), 67.6 (179.5, 8.8, C_3, C_4, C_5), 69.9

(178.0, C_5H_5), 70.9 (174.0, C_3, C_4, C_5), 75.1 (185.0, 7.7, C_3, C_4, C_5), 79.0 (C_1), 88.0 (C_2); IR (Nujol, KBr) 662 (C-S stretch), 815 (ring-H bend perpendicular to ring), 891, 998 (ring-H bend parallel to ring), 1018, 1103 (anti-symmetric ring breath), 1180 (C-N stretch), 1260 (alkyl C-H bend), 3095 cm^{-1} (ring-H stretch); MS m/e (% RA) 43 (32, i-Pr), 44 (8, NMe_2), 56 (26, Fe), 58 (28, CH_2NMe_2), 65 (4, C_5H_5), 121 (52, C_5H_5Fe), 196 (9, $M^+ - C_5H_5Fe$), 242 (48, M^+ - S-i-Pr), 259 (3, $M^+ - CH_2NMe_2$), 273 (23, $M^+ - NMe_2$), 274 (24, M^+ - i-Pr), 302 (3, $M^+ - CH_3$), 317 (100, M^+). Anal. Calcd for $C_{16}H_{23}FeNS$: C, 60.57; H, 7.31; S, 10.10. Found: C, 60.54; H, 7.40; S, 10.16.

1-Dimethylaminomethyl-2-i-butylthioferrocene (16, R = i-Bu). The lithioferrocene 2 was made using the procedure for 16, R = Me, and a 500 mL Schlenk flask with 250 mL of Et_2O. After stirring for 6 hrs, 14.6 g (0.0823 mol) of isobutyl disulfide was added via cannula. Nine hours later, 100 mL of H_2O was added and the mixture was filtered. The solid remaining in the funnel was washed with 200 mL of Et_2O. The organic layer of the filtrate was washed with 2 X 100 mL of H_2O, dried over Na_2SO_4, and evaporated to a red oil. Vacuum distillation gave 5 mL of isobutyl disulfide and 5 mL of dimethylaminomethylferrocene in the receiver. The pot material was chromatographed on a 5 X 11 cm column of alumina with hexanes/CH_2Cl_2. The first band gave the product as yellow crystals from CH_2Cl_2/hexanes after 5 days. Two subsequent recrystallizations and a sublimation at 87°

gave the analytical sample: yield 12.0 g (43.9 %); mp 162-163° dec; ^{1}H NMR δ 0.94 (d, J = 7 Hz, 3H, i-Bu CH_3), 0.99 (d, J = 7 Hz, 3H, i-Bu CH_3), 1.77 (h, J = 7 Hz, 1H, 3° H), 2.19 (s, 6H, NMe_2), 2.45 (dd, J = 8 Hz, J = 12 Hz, 1H, SCH_2), 2.62 (dd, J = 6 Hz, J = 12 Hz, 1H, SCH_2), 3.20 (d, J = 13 Hz, 1H, NCH_2), 3.61 (d, J = 13 Hz, 1H, NCH_2), 4.09 (s, 5H, C_5H_5), 4.14 (t, 1H, H_3, H_4, H_5), 4.30 (m, 2H, H_3, H_4, H_5); ^{13}C NMR ppm (J_{CH}) 21.8 (123.1, i-Bu CH_3), 22.3 (126.8, i-Bu CH_3), 28.5 (125.7, i-Bu CH), 45.2 (132.0, NMe_2), 46.3 (132.0, i-Bu CH_2), 57.3 (137.7, NCH_2), 67.5 (173.0, C_3, C_4, C_5), 70.0 (170.4, C_5H_5), 70.6 (171.1, C_3, C_4, C_5), 73.3 (173.6, C_3, C_4, C_5), 81.9 (C_1), 87.1 (C_2); IR (Nujol, CsI) 718, 808 (ring-H bend perpendicular to ring), 888, 945, 993 (ring-H bend parallel to ring), 1103 cm^{-1} (anti-symmetric ring breath); MS m/e (% RA) 43 (8, i-Pr), 44 (11, NMe_2), 56 (45, Fe), 58 (48, CH_2NMe_2), 65 (6, C_5H_5), 121 (86, C_5H_5Fe, M^+ - C_5H_5Fe - S-i-Bu), 242 (97, M^+ - S-i-Bu), 331 (100, M^+). Anal. Calcd for $C_{17}H_{25}FeNS$: C, 61.63; H, 7.61; S, 9.68. Found: C, 61.17; H, 7.69; S, 9.82.

1-Dimethylaminomethyl-2-i-pentylthioferrocene (16, R = i-pentyl). Lithioferrocene 2 was made as with 16, R = Me, using 18.4 mL (0.0930 mol) of dimethylaminomethyl-ferrocene, 250 mL of ethyl ether, and 64 mL (0.10 mol) of n-BuLi. The suspension was stirred for 6 hrs and 19.2 g (0.0930 mol) of isopentyl disulfide was added via cannula. After 12 hrs 100 mL of H_2O was added and the mixture filtered.

The organic layer from the filtrate was dried over Na_2SO_4 and evaporated to a red oil. A vacuum distillation at 35-65° at this point gave 3 mL of red liquid in the receiver. Crystallization was induced in the pot with CH_2Cl_2/hexanes. The product was recrystallized twice, dissolved in CH_2Cl_2, deprotonated with 1 % aqueous Na_2CO_3, and chromatographed on a silica gel column with CH_2Cl_2/MeOH. The product was obtained as yellow crystals: yield 10.2 g (31.7 %); mp 175° dec; ^{1}H NMR δ 0.85 (d, J = 7 Hz, 3H, i-pentyl CH_3), 0.86 (d, J = 7 Hz, 3H, i-pentyl CH_3), 1.42 (m, 2H, i-propyl-CH_2), 1.65 (h, J = 7 Hz, 1H, i-pentyl CH), 2.19 (s, 6H, NMe_2), 2.59 (ddd, J_{gem} = 12 Hz, J_{vic} = 7 Hz, J_{vic} = 8 Hz, 1H, SCH_2), 2.70 (ddd, J_{gem} = 12 Hz, J_{vic} = 7 Hz, J_{vic} = 8 Hz, 1H, SCH_2), 3.17 (d, J = 13 Hz, 1H, NCH_2), 3.62 (d, J = 13 Hz, 1H, NCH_2), 4.08 (s, 5H, C_5H_5), 4.14 (t, 1H, H_3, H_4, H_5), 4.30 (d, 2H, H_3, H_4, H_5); ^{13}C NMR ppm (J_{CH}) 22.1 (119.7, i-pentyl CH_3), 22.4 (119.5, i-pentyl CH_3), 27.2 (125.6, i-pentyl CH), 35.1 (138.5, i-propyl-CH_2), 38.6 (128.0, SCH_2), 45.2 (129.9, NMe_2), 57.3 (136.3, NCH_2), 67.4 (177.4, C_3, C_4, C_5), 69.9 (170.8, C_5H_5), 70.7 (184.1, C_3, C_4, C_5), 73.6 (177.5, C_3, C_4, C_5), 81.2 (C_1), 87.2 (C_2); IR (Nujol, CsI) 720, 810 (ring-H bend perpendicular to ring), 888, 947, 995 (ring-H bend parallel to ring), 1103 cm^{-1} (antisymmetric ring breath); MS m/e (% RA) 56 (17, Fe), 53 (19, CH_2NMe_2), 65 (3, C_5H_5), 121 (20, FeCp, M^+ - FeCp - S-i-pentyl), 153 (3, M^+ - FeCp - i-pentyl), 242 (15, M^+ - S-i-pentyl), 274 (2, M^+ - i-pentyl),

301 (2, $M^+ - NMe_2$), 345 (20, M^+). Anal. Calcd for $C_{18}H_{27}FeNS$: C, 62.61; H, 7.88; S, 9.28. Found: C, 62.82; H, 8.07; S, 9.42.

1-Dimethylaminomethyl-2-phenylthioferrocene (16, R = phenyl). Lithioferrocene 2 was made using the procedure for 16, R = i-Pr, and a 1000 mL Schlenk flask with 250 ml of ethyl ether. After stirring for 8 hrs, a solution of 18.0 g (0.0823 mol) of phenyl disulfide in 250 mL of Et_2O was added via cannula. Sixteen hours later, 100 mL of H_2O was added. The mixture was filtered and filtrate's organic layer was dried over Na_2SO_4 and reduced to a red oil on the rotary evaporator. The oil was deprotonated with 1 % aqueous Na_2CO_3 and chromatographed repeatedly on silica gel with CH_2Cl_2/MeOH, then benzene/Et_2O, until an analytical sample was obtained. The product was exceedingly difficult to purify and the yield given represents that of the analytical sample, a yellow solid. Yield 0.030 g (0.10 %); mp 66-68°; ^1H NMR δ 2.02 (s, 6H, NMe_2), 3.40 (d, J = 13 Hz, 1H, NCH_2), 3.46 (d, J = 13 Hz, 1H, NCH_2), 4.16 (s, 5H, C_5H_5), 4.32 (t, 1H, H_3, H_4, H_5), 4.46 (m, 1H, H_3, H_4, H_5), 4.51 (m, 1H, H_3, H_4, H_5), 6.98-7.17 (m, 5H, Ph); ^{13}C NMR ppm (J_{CH}) 45.0 (132.6, NMe_2), 56.7 (134.5, CH_2), 69.0 (176.9, C_3, C_4, C_5), 70.3 (176.2, C_5H_5), 71.3 (175.2, C_3, C_4, C_5), 75.6 (179.8, C_3, C_4, C_5), 76.4 (C_1), 87.6 (C_2), 124.8 (157.5, para C), 126.2 (161.4, meta C), 128.4 (154.3, ortho C), 140.1 (substituted phenyl C); IR (neat) 690 (out-of-plane phenyl C-H

bend), 740 (out-of-plane phenyl C-H bend), 820 (C_5H_5 ring-H bend perpendicular to ring), 1000 (C_5H_5 ring-H bend parallel to ring), 1025, 1104 (antisymmetric C_5H_5 ring breath), 1176 (C-N stretch), 1260 (alkyl C-H bend), 1375 (methyl C-H bend), 1480 (phenyl C-C stretch), 1580 (phenyl C-C stretch), 2760, 2810, 2940 (alkyl C-H stretch), 3050-3100 cm^{-1} (phenyl C-H stretch); MS m/e (% RA) 56 (43, Fe), 58 (32, CH_2NMe_2), 121 (78, C_5H_5Fe), 242 (94, M^+ - SPh), 351 (92, M^+). Anal. Calcd for $C_{19}H_{21}FeNS$: C, 64.96; H, 6.03; S, 9.13. Found: C, 65.27; H, 5.87; S, 9.14.

1-Dimethylaminomethyl-2-isopropylthioferrocene palladium dichloride (17). A 125 mL Erlenmeyer flask with a stir bar was placed in a 100° oil bath. To this was added 1.00 g (0.00307 mol) of K_2PdCl_4 in 75 ml of H_2O. A solution of 0.973 g (0.00307 mol) of 16, R = i-Pr, in 45 mL of acetone was added dropwise over 15 min. The mixture was heated 10 minutes and left overnight at 25°. Filtration and washes with 20 mL of H_2O and 10 mL of hexanes gave fine brown crystals of the product: yield 0.902 g (59.6 %); mp 165-167°; IR (Nujol, CsI) 300 (Pd-S, Pd-Cl stretch), 331 (Pd-S, Pd-Cl stretch), 469 (Pd-N stretch), 718, 814 (ring-H bend perpendicular to ring), 992 (ring-H bend parallel to ring), 1103 (antisymmetric ring breath), 1168 (C-N stretch); MS m/e (% RA) 43 (41, i-Pr), 44 (55, NMe_2), 56 (21, Fe), 58 (18, CH_2NMe_2), 65 (24, C_5H_5), 106 (2, Pd), 121 (26, C_5H_5Fe), 196 (4, M^+ - C_5H_5Fe - $PdCl_2$), 242 (15, M^+ - S-i-Pr - $PdCl_2$), 273 (6, M^+ - NMe_2 - $PdCl_2$), 274 (7, M^+ - i-Pr - $PdCl_2$),

317 (20, $M^+ - PdCl_2$).

Attempted hydrogenation of 1,3-cyclooctadiene with 17 in benzene at 14.7 psi (Table 3, 1st entry). Ferrocene-palladium complex 17 (0.040 g, 0.000081 mol), benzene (100 mL), and Red-Al (1 mL, 0.003 mol, 3.4 M in toluene) were added to a 250 mL Schlenk flask with stir bar on a 1 atm hydrogenation line. Less than half of the catalyst went into solution. The system was evacuated and filled several times with H_2. Ten minutes passed during which no H_2 adsorption by the catalyst was observed. Via syringe 1.00 mL (0.00815 mol) of 1,3-cyclooctadiene was added. No hydrogen was absorbed in the next 36 hrs.

Attempted hydrogenation of 1,5-cyclooctadiene with 17 in methylene chloride at 14.7 psi (Table 3, 2nd entry). Ferrocene-palladium complex 17 (0.040 g, 0.000081 mol), CH_2Cl_2 (150 mL), Red-Al (0.50 mL, 0.0017 mol, 3.4 M in toluene), and 1,5-cyclooctadiene (1.00 mL, 0.00815 mol) were added under Ar to a 250 mL Schlenk flask with stir bar on a 1 atm hydrogenation line. The system was evacuated and filled several times with H_2. No H_2 uptake was observed in 12 hrs. The system was evacuated and filled with Ar and 1.99 mL (0.0000811 mol) of O_2 was added via syringe. The catalyst was stirred for 12 hrs and then the system was evacuated and flushed with H_2. No H_2 was absorbed in 18 hrs.

Attempted hydrogenation of 1,3-cyclooctadiene with 17 in toluene at 100 psi (Table 3, 3rd entry). Ferrocene-palladium complex 17 (0.010 g, 0.000020 mol), toluene (500 mL),

Red-Al (1.0 mL, 0.0034 mol, 3.4 M in toluene), and 1,3-cyclooctadiene (1.00 mL, 0.00815 mol) were placed in a 1000 mL Schlenk flask with a magnetic stirring bar under argon on a 1 atm hydrogenation line. The system was evacuated and filled several times with H_2. No H_2 uptake was observed in 20 hrs, so complex 17 (0.010 g, 0.000020 mol), Red-Al (1.0 mL, 0.0034 mol), 1,3-cyclooctadiene (1.00 mL, 0.00815 mol), and the 1 atm reaction mixture (9.0 mL) were placed in a 100 mL pressure bottle with a pressure gauge and stir bar. The bottle was evacuated and filled several times with H_2 to a pressure of 100 psi. No H_2 uptake was seen in 3 hrs at 30° or 12 hrs at 95°.

Hydrogenation of 1,3-cyclooctadiene with 17 in CH_2Cl_2 at 99 psi (Table 3, 4th entry; Figure 22). Ferrocene-palladium complex 17 (0.010 g, 0.000020 mol), methylene chloride (10.0 mL), and 1,3-cyclooctadiene (1.00 mL, 0.00815 mol) were added to a 100 mL pressure bottle with a pressure gauge and stir bar. The bottle was evacuated and filled several times with H_2 to a pressure of 99 psi. Uptake began in 30 minutes and slowed after absorption of 0.00815 mol of H_2. The initial turnover rate was 33 mol/mol Pd·hr. This reaction was later shown to be contaminated by H_2O.

Hydrogenation of 1,3-cyclooctadiene with 17 in CH_2Cl_2 at 101 psi (Figure 23). Ferrocene-palladium complex 17 (0.010 g, 0.000020 mol), methylene chloride (9.0 mL), and 1,3-cyclooctadiene (1.00 mL, 0.00815 mol) were added to a

100 mL pressure bottle with a pressure gauge and stir bar. The bottle was evacuated and filled several times with H_2 to a pressure of 101 psi. No H_2 uptake was observed in 27.4 hrs, so 0.0036 mL (0.00020 mol) of H_2O was added and the bottle was refilled with H_2. Uptake began immediately and slowed after absorption of 0.00815 mol of H_2. The initial turnover rate was 27 mol/mol Pd·hr.

Hydrogenation of 1,3-cyclooctadiene with 17 in acetone at 14.7 psi (Figure 24). Ferrocene-palladium complex 17 (0.010 g, 0.000020 mol), acetone (9.0 mL), and 1,3-cyclooctadiene (1.00 mL, 0.00815 mol) were added to a 100 mL round-bottomed magnetically-stirred flask on a 1 atm hydrogenation line with a mercury manometer. The system was evacuated and filled several times with H_2 to 1 atm. Uptake began after the red solution became cloudy and brown. The turnover rate in the linear region was 1.9 mol/mol Pd·hr. Product analysis at the end of reaction showed 0 % 1,3-cyclooctadiene, 100 % cyclooctene, and 0 % cyclooctane.

Hydrogenation of 1,3-cyclooctadiene with 17 in acetone at 61 psi (Figure 25). Ferrocene-palladium complex 17 (0.010 g, 0.000020 mol), acetone (9.0 mL) and 1,3-cyclooctadiene (1.00 mL, 0.00815 mol) were added to a 100 mL pressure bottle with a pressure gauge and stir bar. The bottle was evacuated and filled several times with H_2 to a pressure of 61 psi. Uptake began immediately and slowed after absorption of 0.0055 mol of H_2. The initial turnover rate was

422 mol/mol Pd·hr. Product analysis at the end of reaction showed 6.5 % 1,3-cyclooctadiene, 72.4 % cyclooctene, and 21.1 % cyclooctane.

Isomerization-hydrogenation of 1,5-cyclooctadiene with 17 (Figure 27). Ferrocene-palladium complex 17 (0.010 g, 0.000020 mol), acetone (9.5 mL), and 1,5-cyclooctadiene (0.50 mL, 0.0041 mol) were added to a 100 mL pressure bottle with a pressure gauge and stir bar. The bottle was evacuated and filled several times with H_2 to a pressure of 60 psi. Uptake began immediately and ceased after absorption of 0.0025 mol of H_2. The initial turnover rate was 9.0 mol/mol Pd·hr. Product analysis at the end of reaction showed 17.0 % 1,5-cyclooctadiene, 10.2 % 1,4-cyclooctadiene, 10.0 % 1,3-cyclooctadiene, 52.4 % cyclooctene, and 10.4 % cyclooctane.

RESULTS AND DISCUSSION

Ferrocenyl Sulfides 16

Several ferrocenyl tertiary amine thioethers 16, R = Me, Et, i-Pr, i-Bu, i-pentyl, and Ph, have been synthesized for the first time (Figure 10), via reaction of lithioferrocene amine 2 with the appropriate disulfide. These compounds are yellow solids which are soluble in polar solvents such as methylene chloride, acetone, and chloroform, and insoluble in nonpolar solvents such as hexane.

Dimethylaminomethylferrocene was lithiated using the procedure of Marr (Figure 1).[8] A hexane solution of n-BuLi was used. The n-BuLi was not titrated, although a procedure for this is available.[36] Instead, good results were obtained by use of 1.1 nominal equivalents of n-BuLi. Tetramethylethylenediamine is not necessary or desirable here. It is used in the lithiation of benzene and ferrocene.[37] Rausch's group has isolated ferrocenyllithium[38] in the solid state. Aminoferrocenyllithium 2 was not isolated here but rather was prepared fresh for each reaction.

Figure 11 shows the 250 MHz ^{1}H NMR of 16, R = Et. The most striking feature of this spectrum is the large shift (0.39 ppm) between the 2 diastereotopic protons of

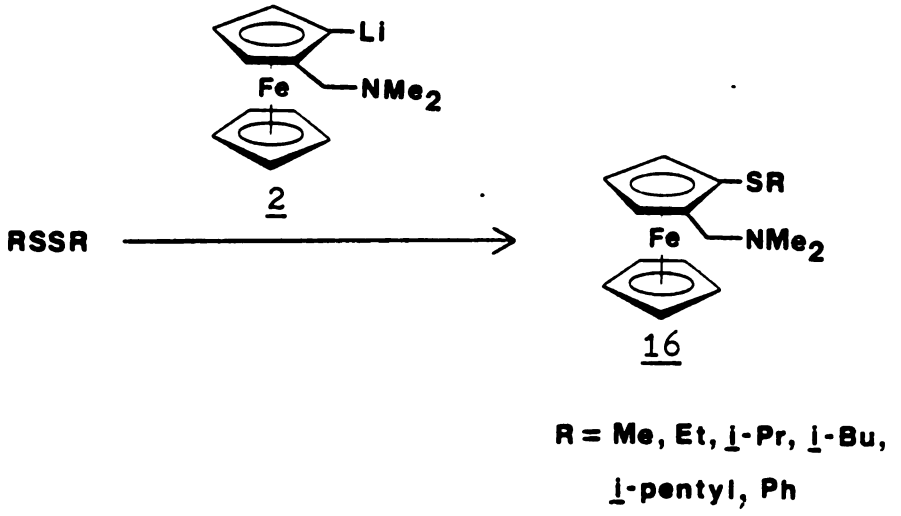


Figure 10. Synthesis of new ferrocenyl thioethers 16.

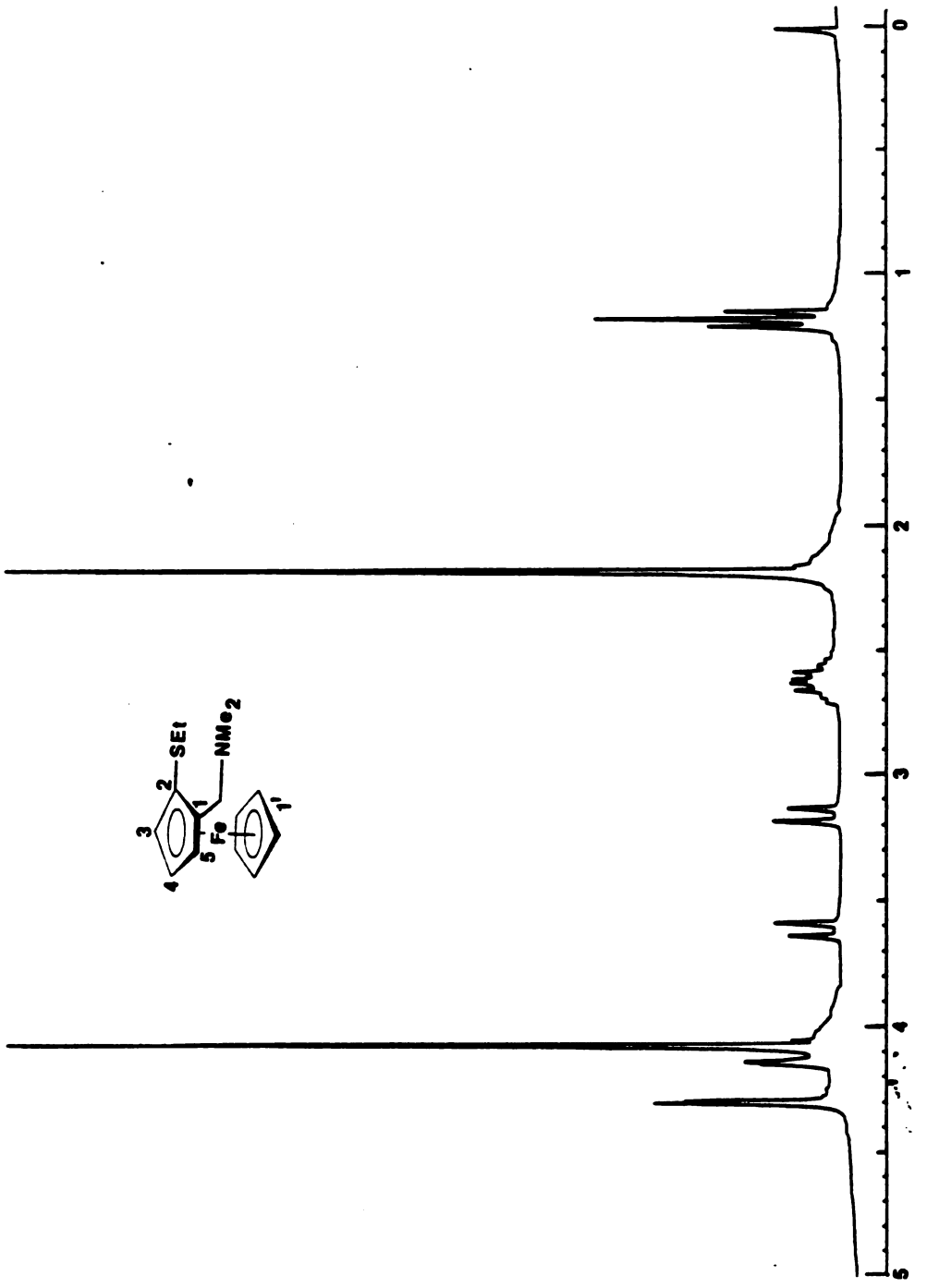


Figure 11. 250 MHz ^{1}H NMR of 16, R = Et.

the aminomethylene group in the δ 3-4 region. By contrast, the methylene protons of the ethylthio group at δ 2.64, although diastereotopic, appear overlapped. The large shift between aminomethylene protons has also been exhibited in 1-dimethylaminomethyl-2-diphenylphosphinoferrocene.[30] Inversion of the pyramidal N of 16, R = Et, is faster than the NMR time scale at this temperature, so the nitrogen methyls appear as a singlet at δ 2.19. Assignments of the substituted ring protons H_3, H_4, and H_5 have not been made since a number of ^1H NMR studies[31-33] have shown that a single substituent may deshield or shield position 2 and 5, and may deshield or shield positions 3 and 4, in any combination relative to ferrocene. Finally, Rosenblum and Woodward[34] have shown that there is free rotation about the Fe-Cp ring axis in ferrocenes. The barrier to rotation in ferrocene is only about one third that of the 2 methyls in ethane.[35] Thus, the unsubstituted C_5H_5 ring appears as a singlet at δ 4.09.

The 250 MHz ^1H NMR of 16, R = i-pentyl is given in Figure 12. Several points can be made about this spectrum. The isopentyl methyls appear as 2 doublets due to their diastereotopic relationship to each other. This is remarkable in that they are 5 atoms removed from the chiral plane[39] of the molecule. The peaks in the δ 2.5-2.8 region are due to the SCH_2 protons. Their splitting pattern is given in diagrammatic form in Figure 13. Two singlets are split into

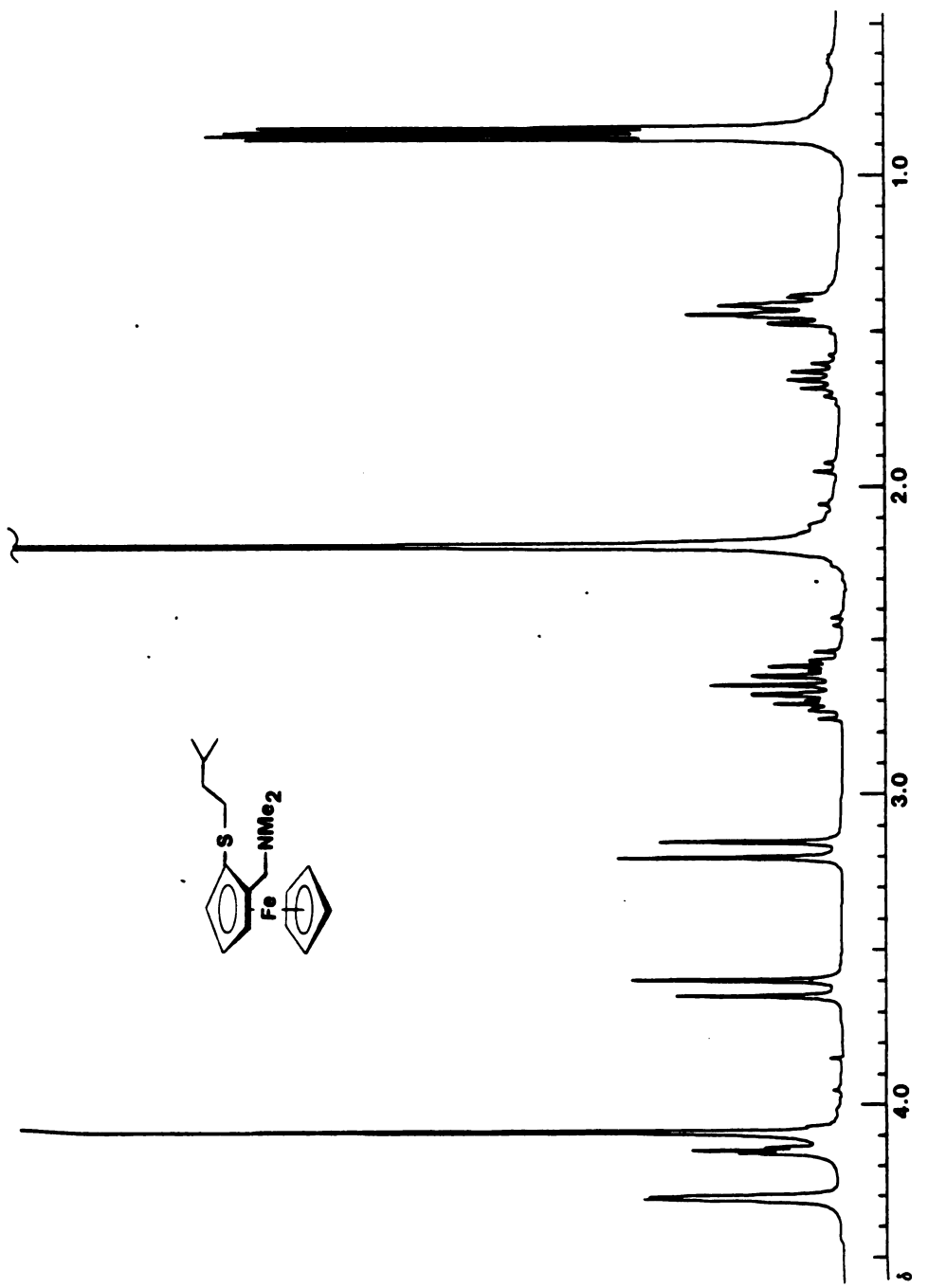


Figure 12. 250 MHz ^{1}H NMR of 16, R = i-pentyl.

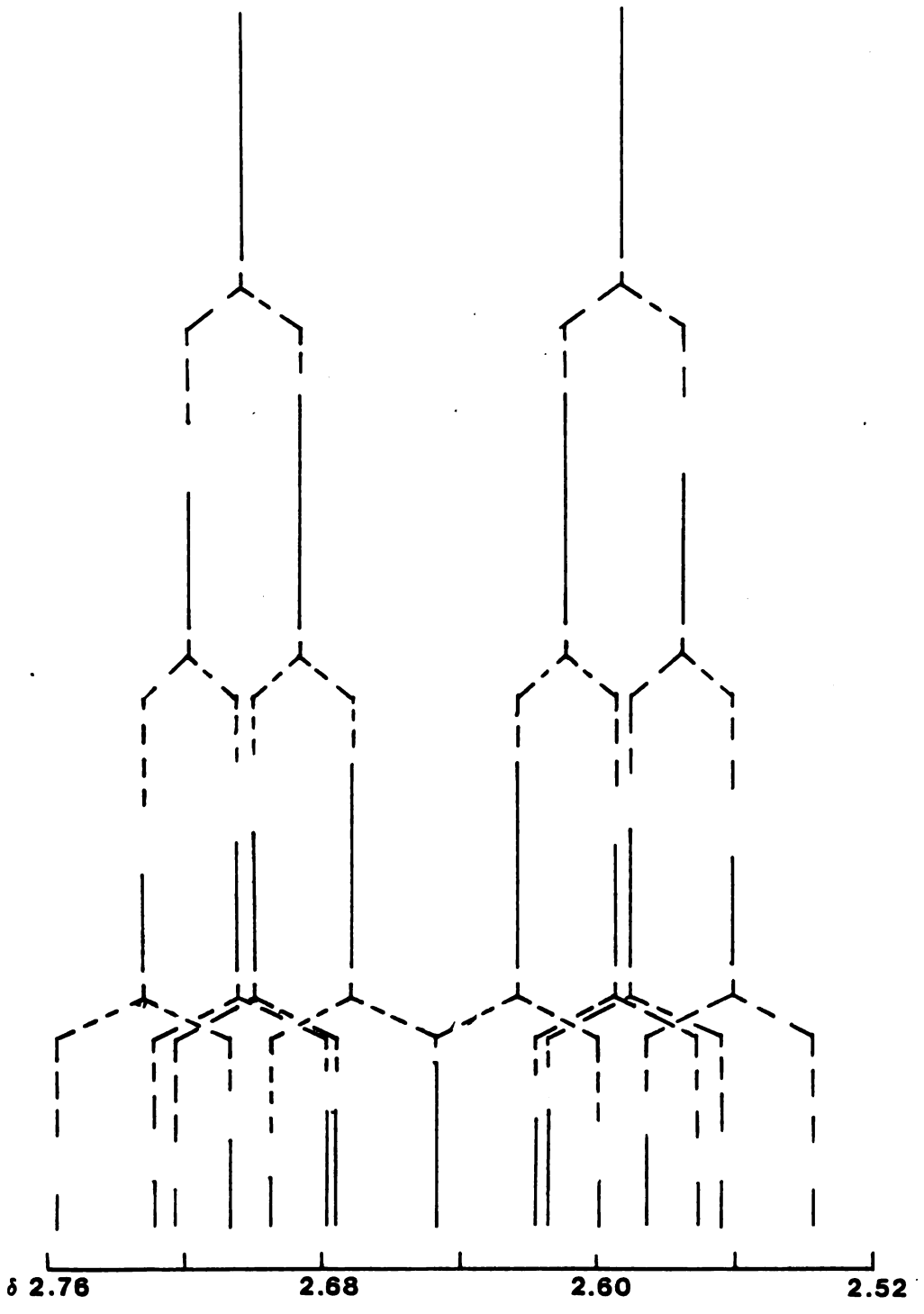


Figure 13. Splitting pattern of SCH_2 protons in 16, R = i-pentyl.

doublets by a vicinal coupling constant of 8 Hz (top), into doublets again by a vicinal constant of 7 Hz (middle), and into more doublets by a large geminal coupling constant of 12 Hz (bottom). The total number of peaks should be $2(2^3) = 16$. The actual number is 15 due to overlap of the central peaks.

Typical broadband and gated decoupled ^{13}C NMR spectra (those of 16, R = Et) are presented in Figures 14 and 15. All of the peaks in Figure 14 are singlets except those at 77.1 ppm downfield of TMS. This is a triplet due to the $CDCl_3$ solvent, with the nuclear spin of deuterium = 1. The compound in Figure 14 has a C_1 symmetry due to planar chirality but contains no diastereotopic carbons. Suitably substituted derivatives do contain diastereotopic carbons, however, which absorb at different chemical shifts (see, for example, Figure 50 in the Appendix). Assignments in Figure 14 were made with the help of the gated decoupled spectrum in Figure 15. A gated decoupled spectrum utilizes a pulse sequence which yields accurate, reproducible coupling constants without sacrifice of Nuclear Overhauser Enhancement; the result is a coupled spectrum with intense peaks.[40,41] Methyls appear as quartets in Figure 15, methylenes as triplets, methines as doublets, and substituted ring carbons as singlets. The four rightmost peaks in Figure 14 are thus assigned, right to left, to Et CH_3, Et CH_2, NMe_2, and NCH_2. As in the proton spectrum, the NMe_2 carbons are equivalent

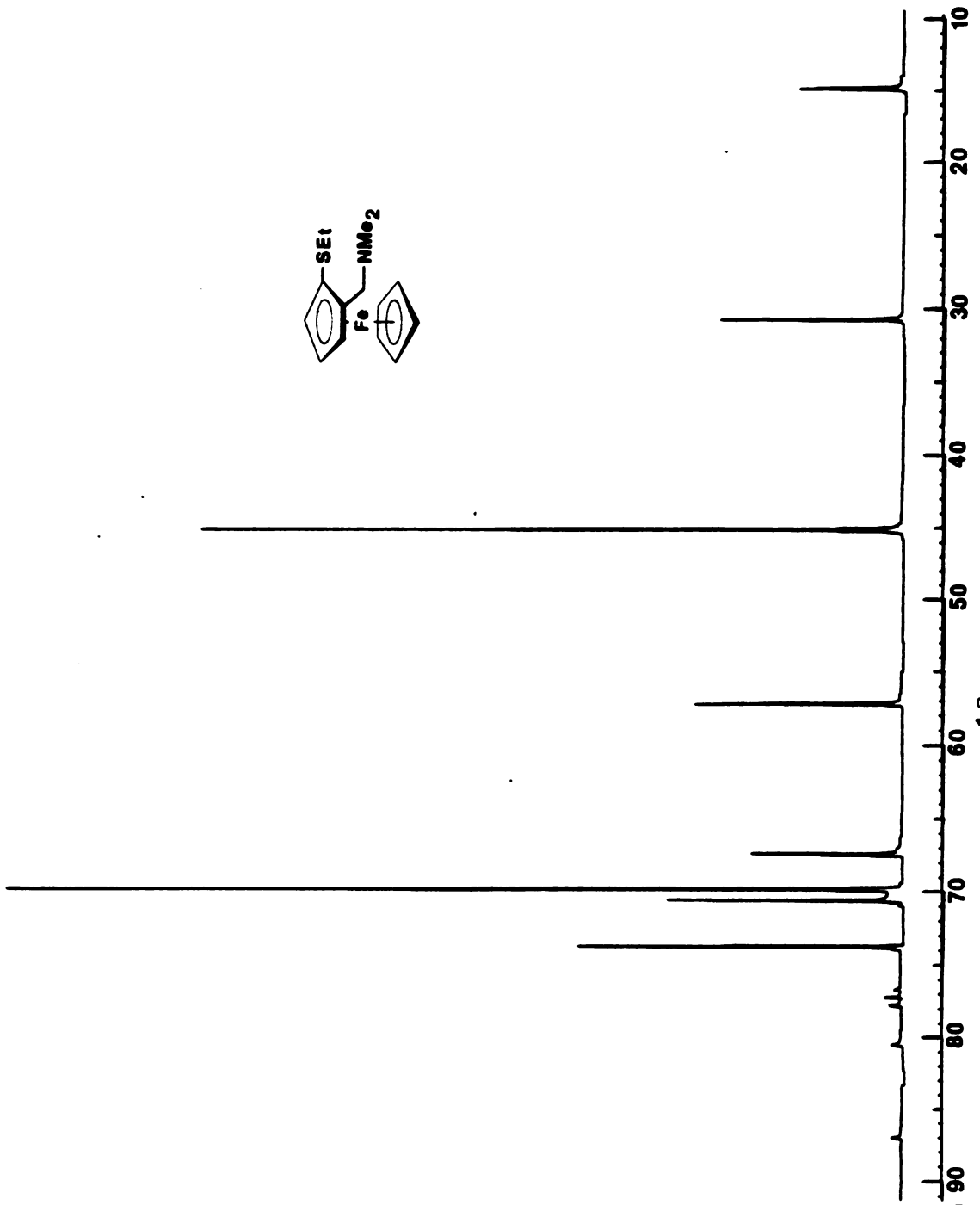


Figure 14. Broadband decoupled ^{13}C NMR of 16, R = Et.

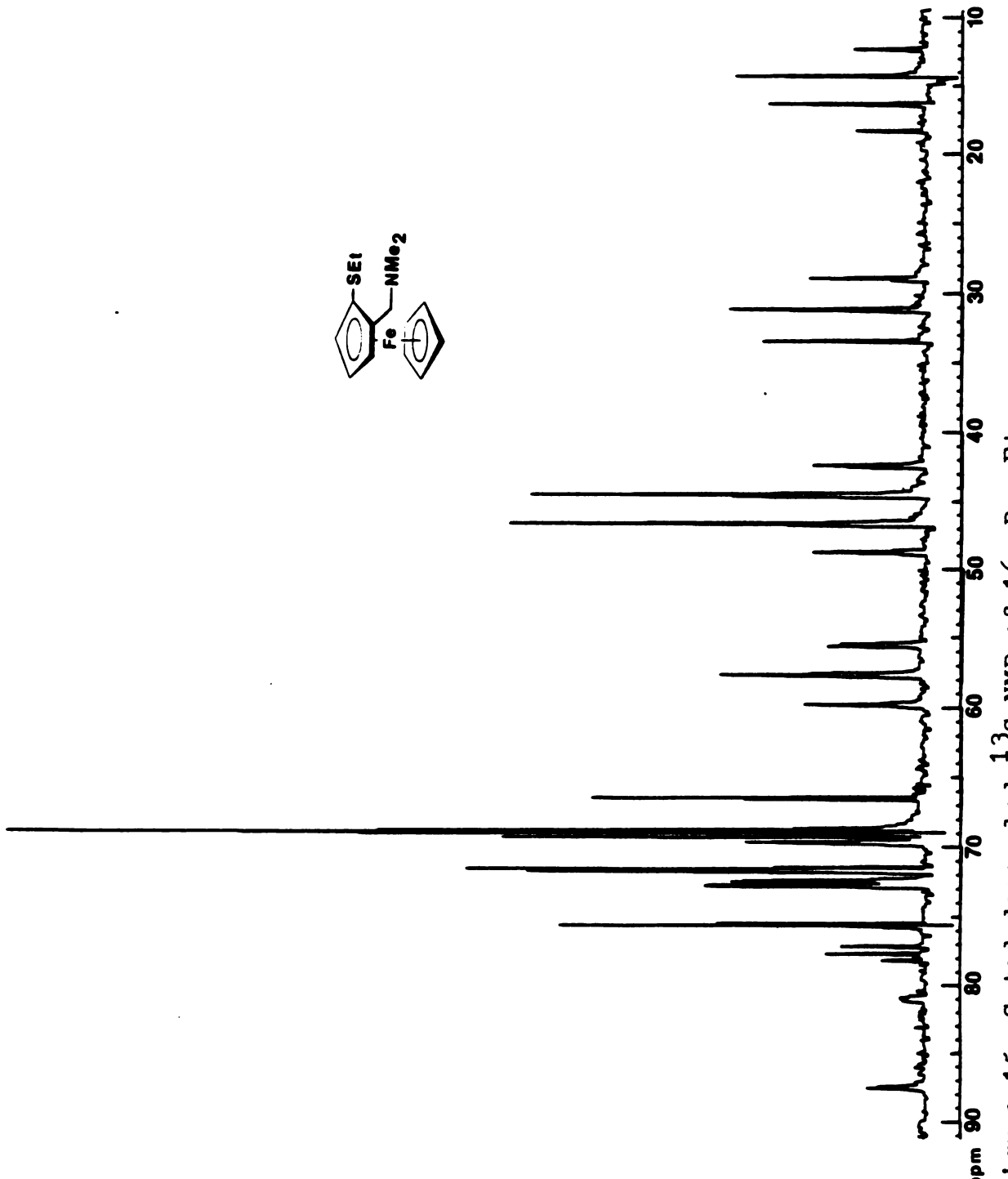


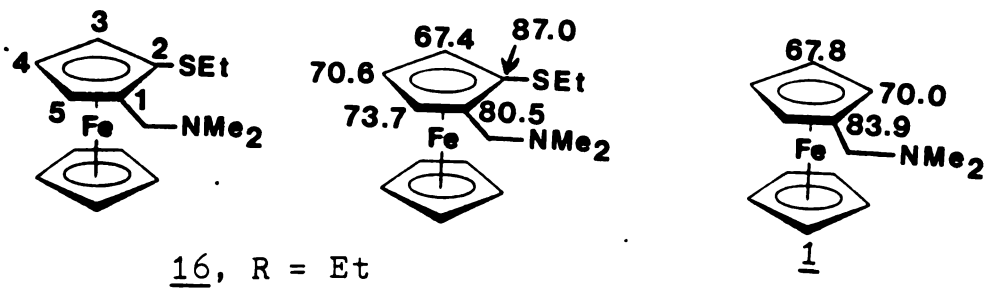
Figure 15. Gated decoupled ^{13}C NMR of 16, R = Et.

due to fast inversion and appear as singlets.

The peaks at 80.5 and 87.0 ppm are due to substituted ring carbons C_1 and C_2 respectively. These assignments are firm and are based on the following observations: 1) the gated decoupled spectrum reveals the 2 peaks as singlets (substituted carbons), 2) these peaks are the weakest in the spectrum due to the long spin-lattice relaxation time of substituted carbons,[42] 3) the more deshielded carbon is directly attached to a heteroatom, and 4) the upfield peak in Figure 15 is split by long-range coupling from CH_2 and is therefore broader and less intense than the downfield peak. The 2 peaks in Figure 14 are just barely above the baseline; their size can be increased by use of a longer relaxation delay (at expense of the acquisition time). Figure 14 was obtained with a relaxation delay of 1.0 sec.

The unsubstituted ring is easily assigned to the intense peak at 69.8 ppm, but carbons 3, 4, and 5 are more difficult. For this purpose the data in Figure 16 on 16, R = Et, and 1 are presented. Assignments in 1 are unequivocal and have been established by selective spin-spin proton decoupling.[43] Assignments of C_3, C_4, and C_5 in 16, R = Et, are tentative.

The ethylthio group exerts an inductive effect on C_2 in 16, R = Et, causing its shift to be downfield of that of the corresponding carbon in 1 (87.0 > 70.0). The other orderings are easily explained using the inductive π-polarization concept.[102,103] The C_2-S dipole (positive at C_2, negative at S) causes π-polarization of the C_4-C_3 and



16, R = Et

1

Figure 16. Substituted ring ^{13}C shifts in 16, R = Et, and 1.

C_5-C_1 bonds (positive at C_4 and C_5, negative at C_3 and C_1). Hence the relative chemical shifts of 16, R = Et, and 1 (C_1 in 16, R = Et, 80.5 < 83.9; C_3, 67.4 < 67.8; C_4, 70.6 > 67.8; C_5, 73.7 > 70.0).

As stated above, these assignments for C_3, C_4, and C_5 must be viewed as tentative at this time. In addition, it is incorrect to extrapolate ^{13}C data to ^{1}H data. In some cases the chemical shift ordering is the same, but in ferrocenylaldehyde, for example, the carbon order is $C_3 > C_2$,[44] whereas the proton order is $H_2 > H_3$.[31-33]

The 2 most important peaks in the infrared spectra of derivatives 16 are presented in Table 1. These compounds obey the "1000, 1100 rule"[46] which states that ferrocenes containing an unsubstituted ring will have 2 peaks, one near 1000 cm^{-1} due to C-H bend parallel to the ring, and another near 1100 cm^{-1} due to an antisymmetric ring-breath. The remainder of the IR assignments were made by using the available literature;[45-48] some of these peaks appear in the infrared spectrum of 16, R = i-Pr, given in Figure 17.

Absorptions near 890 cm^{-1} would be indicative of 1,2 (as opposed to 1,3) disubstitution, but these are too weak to be diagnostic. The 1,2/1,3 analysis using peaks in this region is most successful with acetyl, alkyls, and aryls as substituents[48-51] but is not as useful with 2-substituted dimethylaminomethylferrocenes.[52] The spectra are those of tertiary amines and thus lack peaks in the 3400 cm^{-1} region associated with N-H stretching in primary and secondary

Table 1. Infrared modes of the unsubstituted ring of compounds 16.

R	$\bar{\nu}$, cm^{-1}
Me	996, 1102
Et	998, 1103
i-Pr	998, 1103
i-Bu	993, 1103
i-pentyl	995, 1103
Ph	1000, 1104

amines. Sulfides have a C-S stretch near 660 cm^{-1} which is usually too weak to be of use; this is the case with compounds 16.

The mass spectrum of 16, R = i-Pr, is given in Figure 18 and is typical of the series. It shows peaks of high relative abundance due to i-Pr, Fe, CH_2NMe_2, C_5H_5Fe, M^+ - S-i-Pr, and a molecular ion which is also the parent peak. In addition to these fragments, peaks consistent with the less abundant isotopes ^{54}Fe, ^{57}Fe, and ^{34}S were present.

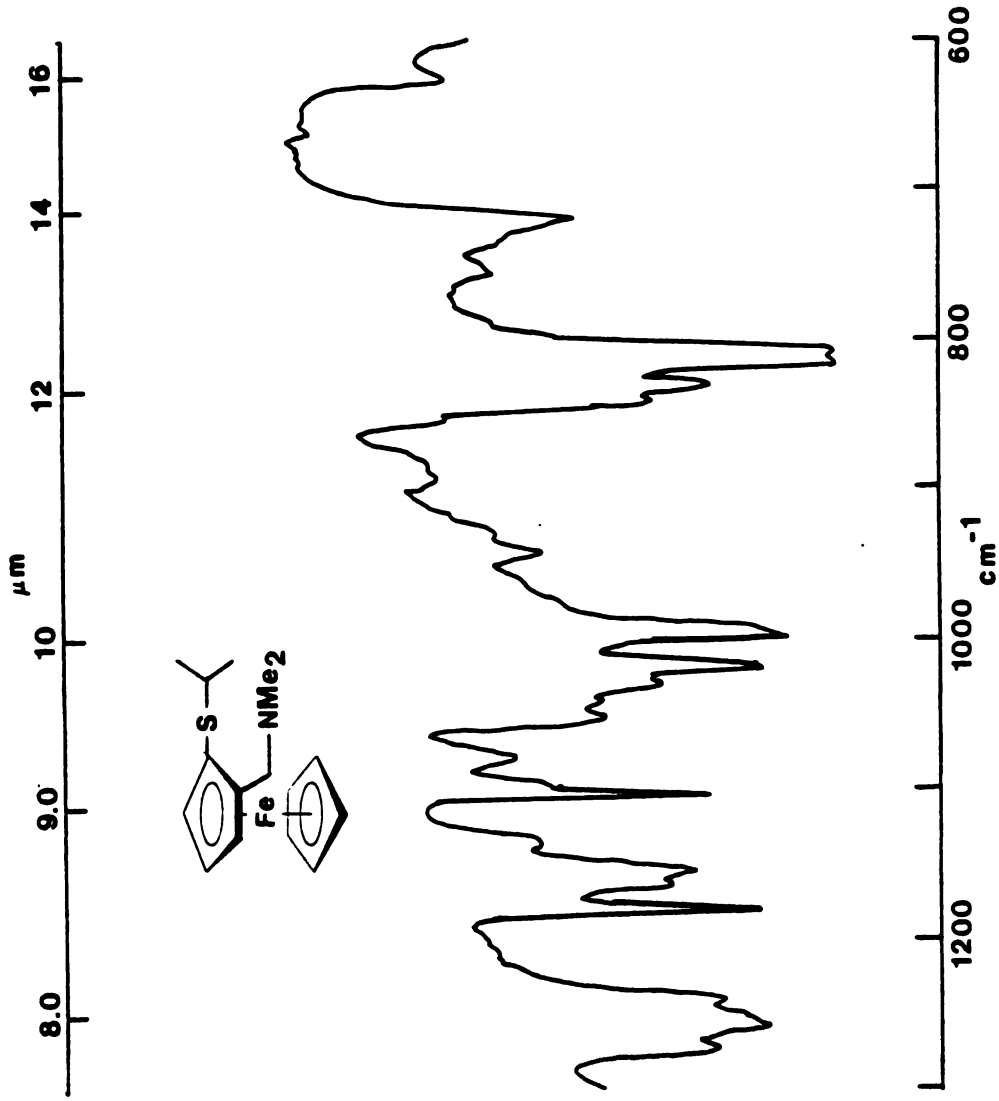


Figure 17. A portion of the infrared spectrum of 16, R = i-Pr.

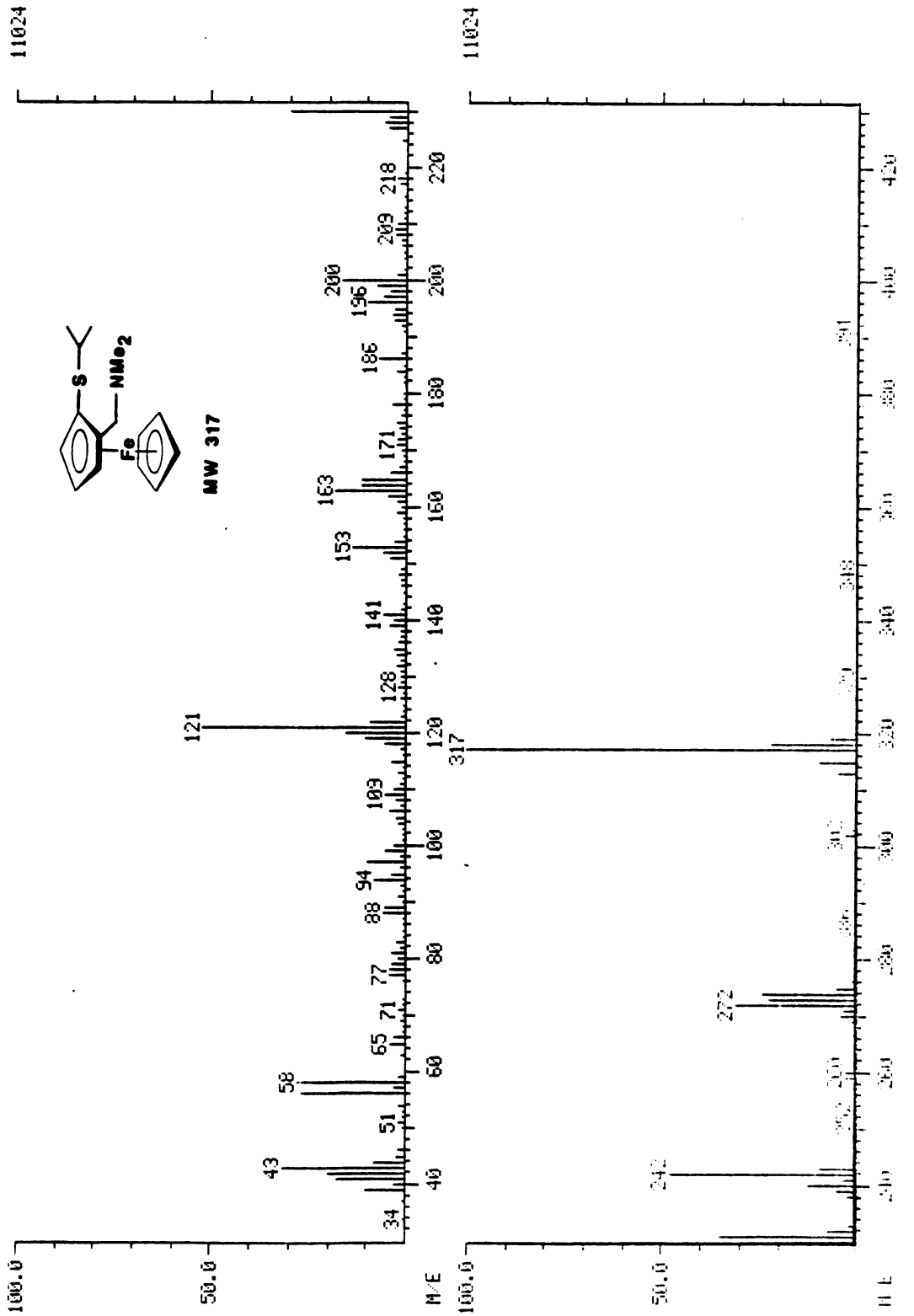
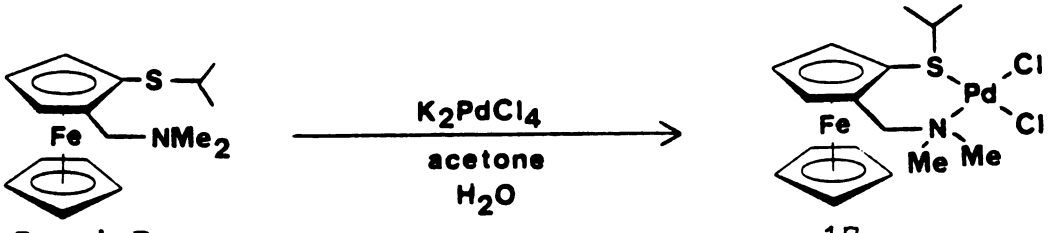


Figure 18. Mass spectrum of 16, R = i-Pr.

Palladium Complex 17

Palladium complex 17 was made by using the same procedure as for o-methylthioaniline.[53] An acetone solution of the ferrocene was added dropwise to a hot aqueous solution of potassium tetrachloropalladate (Figure 19). The acetone boiled off and the product precipitated immediately as fine brown crystals. The product 17 did not have a molecular ion in its mass spectrum. This was expected based on previous findings from this laboratory.[19] The mass spectrum had fragments consistent with those of the starting material 16, R = i-Pr. That the product was different from the starting material was established based on clearly defined melting points: 16, R = i-Pr; 82-83°; 17, 165-167°. S-Dealkylation was not observed here as with similar complexes.[54] The elemental analysis of 17 supports its structure rather than that of various dimers similar to 18 (Figure 20), for example, with Pd-N chelation only. It is not likely that a Pd-S bond is not formed when the amine thioether reacts with K_2PdCl_4. Low spin d^8 ions, e.g. Pd^{2+}, form strong σ bonds with soft ligands such as thioethers and also dπ-dπ



16, R = i-Pr 17

Figure 19. Synthesis of amine-thioether-palladium complex 17.

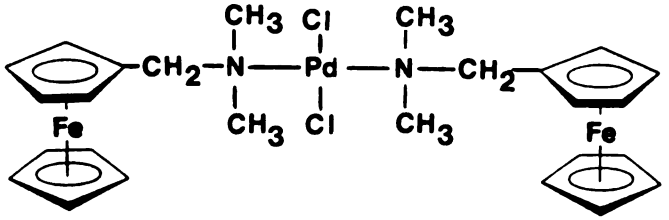


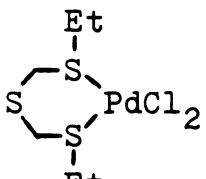
Figure 20. Dimer 18.[59]

bonds by donation of electron density to S.[57] The π-acceptor capacity of thioethers, although somewhat lower than that of 3° phosphines or arsines,[58,60,61] is still substantial. Complex 17 gave an elemental analysis with carbon outside the ± 0.4 % range. This is consistent with other results obtained recently on similar amine-thioether-palladium and amine-selenoether-palladium complexes.[55]

Chromatography of 17 on silica gel left a gray deposit distributed throughout the column. The complex did not give a simple ^{1}H NMR spectrum. Deposition of a black precipitate began immediately on dissolution in chloroform-d.

The metal-S, metal-N, and metal-Cl stretching modes of several complexes including 17 are given in Table 2. Metal-S bands are often weak and occur in a region similar to metal-Cl bands. Consequently the absorptions at 300 and 331 cm^{-1} in 17 have been assigned to Pd-S and/or Pd-Cl stretches. Metal-N stretches occur at a higher frequency so the 469 cm^{-1} peak is assigned to Pd-N. These assignments are tentative since in complex molecules of low symmetry more than one fundamental mode often contributes to a given

Table 2. Metal-S, metal-N, and metal-Cl stretching modes of several complexes.

Compound	$\bar{\nu}$, cm^{-1}	Stretching mode	Ref.
17	300	Pd-S, Pd-Cl	This work
	331	Pd-S, Pd-Cl	
	469	Pd-N	
	273	Pd-Cl	56
	316	Pd-Cl	
	349	Pd-S	
	396	Pd-S	
thioether-metal complexes	280-400	M-S	57
unidentate amine-metal complexes	370-500	M-N	57

peak.[58]

The reader is directed to reference 62 for more information on ferrocene-palladium complexes.

Hydrogenation and Isomerization Using Palladium Complex 17

Hydrogenation by homogeneous catalysts is a well-developed discipline.[63] Of the many known complexes, those of Group VIII metals with amines and sulfides have been used with varying degrees of success. In 1967 $PtCl_2(SPh_2)_2$ was found to be selective for the hydrogenation of dienes to monoenes in the presence of $SnCl_2$.[64] Treatment of $PdCl_2$ or Na_2PdCl_4 with tertiary amines resulted in an active selective catalyst.[65] The same was true of $PdCl_2$ when treated with 2,2'-bipyridine and $NaBH_4$.[66] Palladium chloride and thioethers gave complexes which, upon reduction by diisobutylaluminum hydride, were selective catalysts.[67] The thioether-rhodium complex $RhCl_3(SEt_2)_3$ hydrogenates maleic acid, provided maleic acid is present in excess.[68-71] Finally, $RuCl_3(PhS\text{-}\underline{n}\text{-}Pr)_3$ has been synthesized and is inactive in catalytic hydrogenation.[72]

In view of the selective hydrogenation activity of amine-palladium and thioether-palladium complexes when treated with hydride reducing agents[66,67] (Figure 21), a number of similar procedures were tried by using ferrocene-palladium complex 17 and $NaH_2Al(OCH_2CH_2OCH_3)_2$ in various solvents at various temperatures and pressures (Table 3). All of the hydrogenations with reducing agent present failed. Pretreatment of Pd complexes with O_2 has given increased rates of hydrogenation.[73,74] Treatment with O_2 here (Table 3, 2nd entry) did not. When the reducing agent was left out in a blank

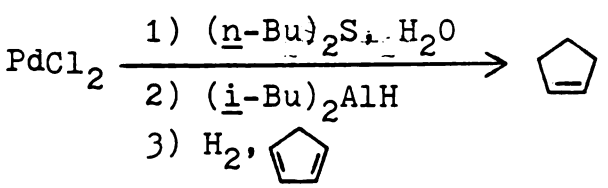


Figure 21. Selective hydrogenation using $(\underline{n}\text{-Bu})_2S$.

Table 3. Selective hydrogenation: initial attempts. Red-Al = $NaH_2Al(OCH_2CH_2OCH_3)_2$. COD = cyclooctadiene.

Conditions	Result
17, PhH, Red-Al, 14.7 psi, 25°, 1,3-COD	No H_2 uptake
17, CH_2Cl_2, Red-Al, 14.7 psi, 25°, 1,5-COD, O_2	No H_2 uptake
17, toluene, Red-Al, 100 psi, 95°, 1,3-COD	No H_2 uptake
17, CH_2Cl_2, 99 psi, 25°, 1,3-COD, Figure 22	One double bond hydrogenated

experiment, however, hydrogen uptake was observed (Table 3, 4th entry; Figure 22). This experiment was repeated with carefully distilled CH_2Cl_2 (Figure 23). The horizontal part of Figure 23 shows that before H_2O was added the system was inactive. Therefore the solvent in the initial successful experiment (Figure 22) was contaminated by water. After 10 mol of H_2O/mol of 17 was added in Figure 23, a black precipitate appeared and 1,3-cyclooctadiene was hydrogenated to cyclooctene, but only at a slow rate. The complex also forms an active heterogeneous system in acetone at 1 atm (Figure 24). The original red solution became cloudy after 36 hrs and H_2 uptake began. The selectivity was excellent (0 % diene, 100 % monoene, and 0 % alkane) but the rate was again low (1.9 mol/mol Pd·hr).

Hydrogenation of 1,3-cyclooctadiene became conveniently fast in acetone at 61 psi (Figure 25). This is a homogeneous system with no H_2O or reducing agents and reaction proceeds at a useful rate (422 mol/mol Pd·hr). As time passed the red solution became brown but remained homogeneous. Most of the product at the end of reaction was cyclooctene, but some cyclooctane was present.

The compounds present after each of the above reactions were 1,3-cyclooctadiene, cyclooctene, and cyclooctane. The (diene + monoene):alkane ratio was determined by gas chromatography, the two peaks being separated typically by more than 1.1 minutes. The diene:monoene ratio was

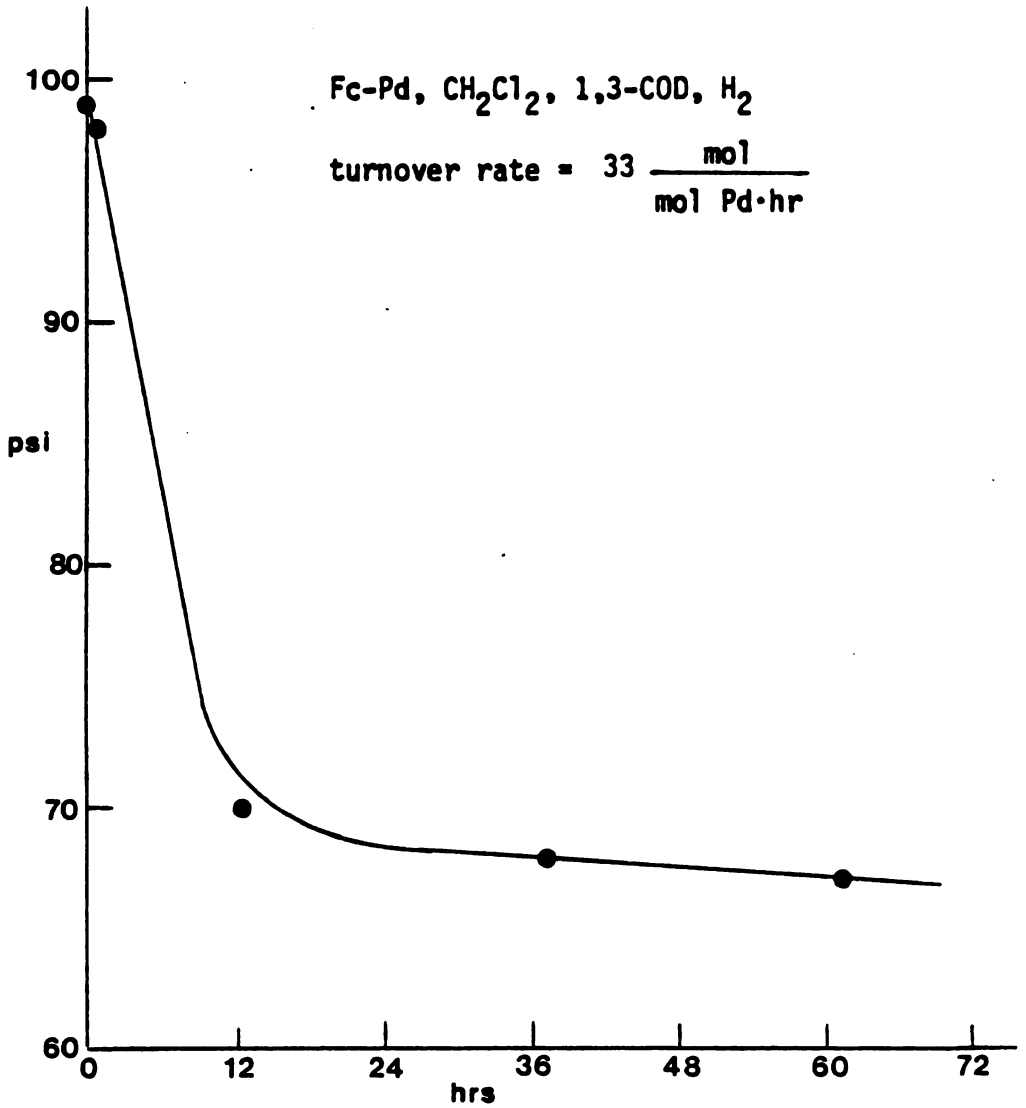


Figure 22. Selective hydrogenation of 1,3-cyclooctadiene in CH_2Cl_2 at 25°C using Fc-Pd (17) (Table 3, 4th entry).

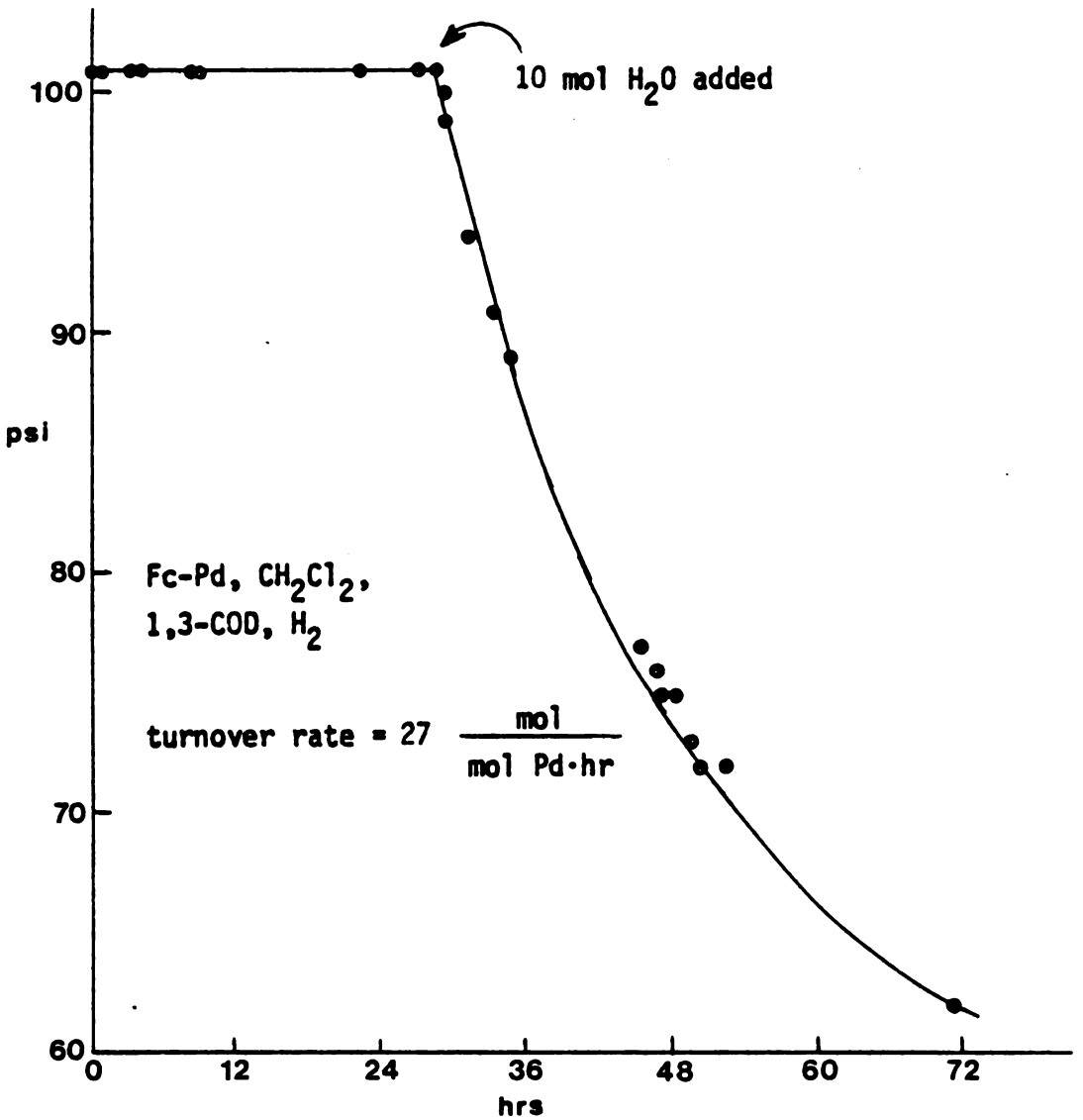


Figure 23. Selective hydrogenation of 1,3-cyclooctadiene in CH_2Cl_2 at 24°C using Fc-Pd (17).

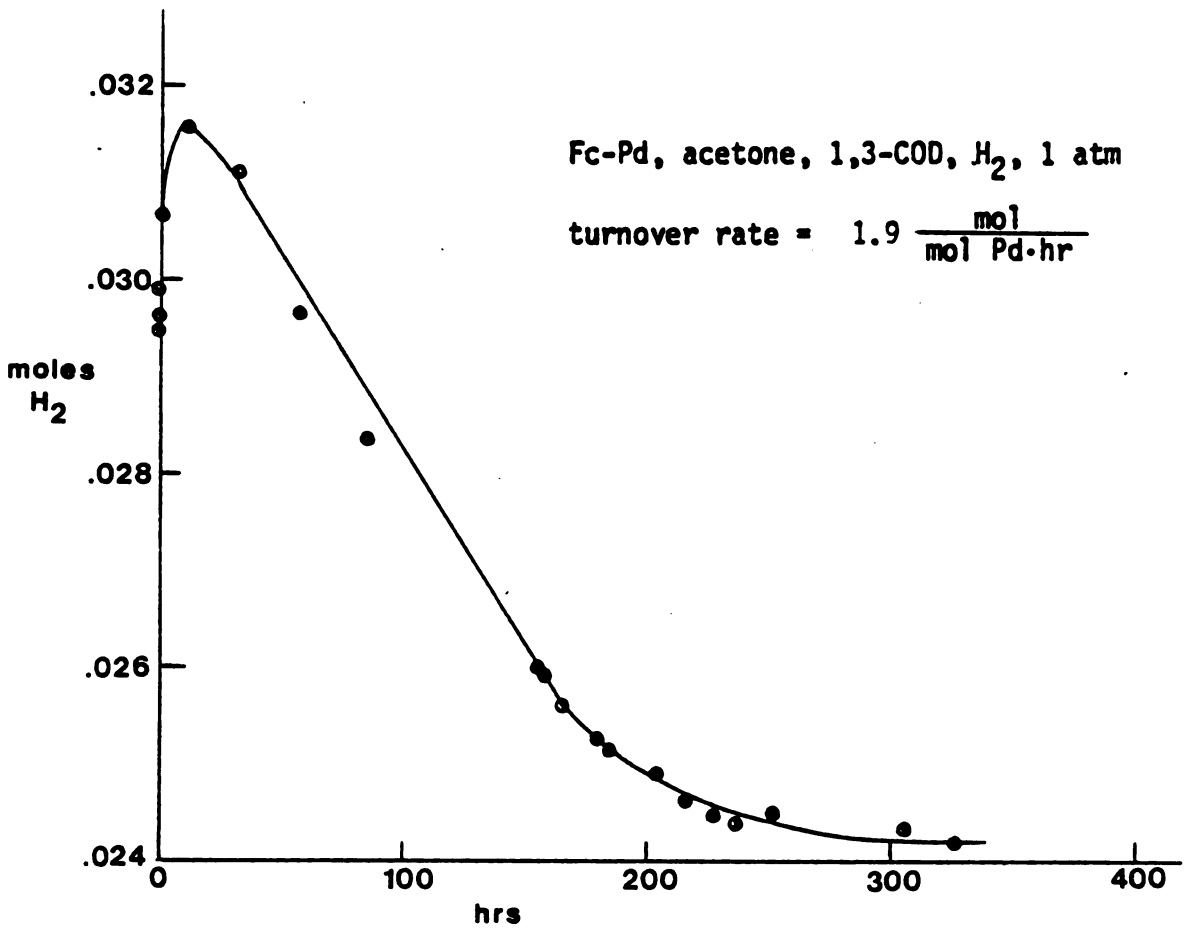


Figure 24. Selective hydrogenation of 1,3-cyclooctadiene in acetone at 28°C and 14.7 psi using Fc-Pd (17).

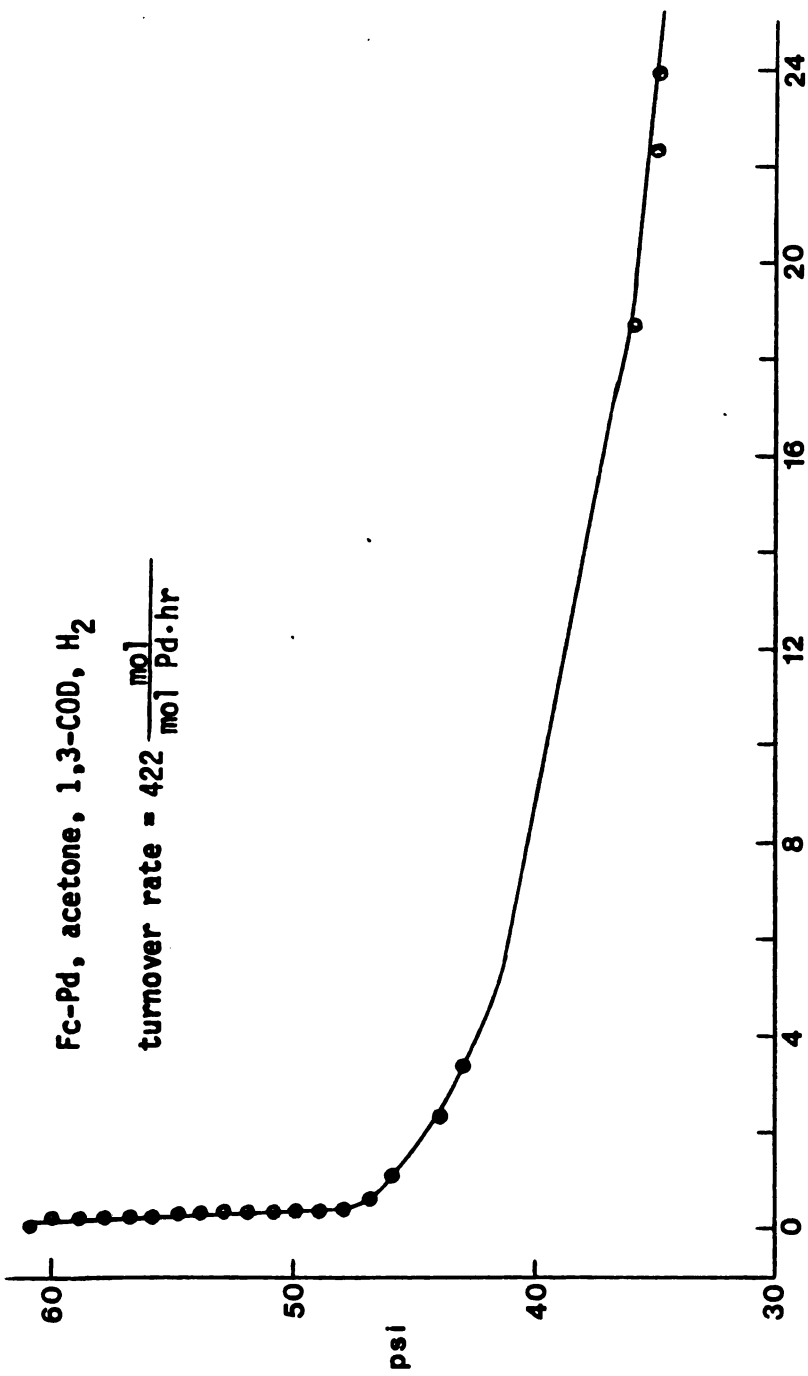


Figure 25. Selective hydrogenation of 1,3-cyclooctadiene in acetone at 27°C and 61 psi using Fc-Pd (17).

determined by ^1H NMR, as illustrated in Figure 26. The central olefinic protons of the diene appear near δ 5.8, and the outer protons near 5.6. The olefinic protons of the monoene are near δ 5.6. The ratio of monoene to diene is therefore given by

$$\frac{\text{monoene}}{\text{diene}} = \frac{A_{5.6} - A_{5.8}}{A_{5.8}}$$

where A = area. In the case of Figure 26, the ratio was

$$\frac{\text{monoene}}{\text{diene}} = \frac{91.8}{8.2}$$

which with the GC data gave diene:monoene:alkane = 6.5 : 72.4 : 21.1.

Complex 17 isomerized and hydrogenated 1,5-cyclooctadiene (Figure 27) according to the scheme:

1,5-COD → 1,4-COD → 1,3-COD → cyclooctane

The isomerizations were slow compared to the hydrogenation, as evidenced by the relative rates of Figures 25 and 27:

$$\frac{\text{Rate}_{25}}{\text{Rate}_{27}} = \frac{422}{9.0} = 47$$

The isomerization-hydrogenation is a homogeneous reaction.

In order to assess its effectiveness as a selective hydrogenation catalyst, complex 17 is compared to previous homogeneous Pd catalysts in Table 4. The initial rates have been normalized as much as possible by dividing by the number of moles of Pd and the pressure. The catalyst in this work and that of the 2nd entry ($PdCl_2$ complexed by undecylamine, reduced by diisobutylaluminum hydride, and

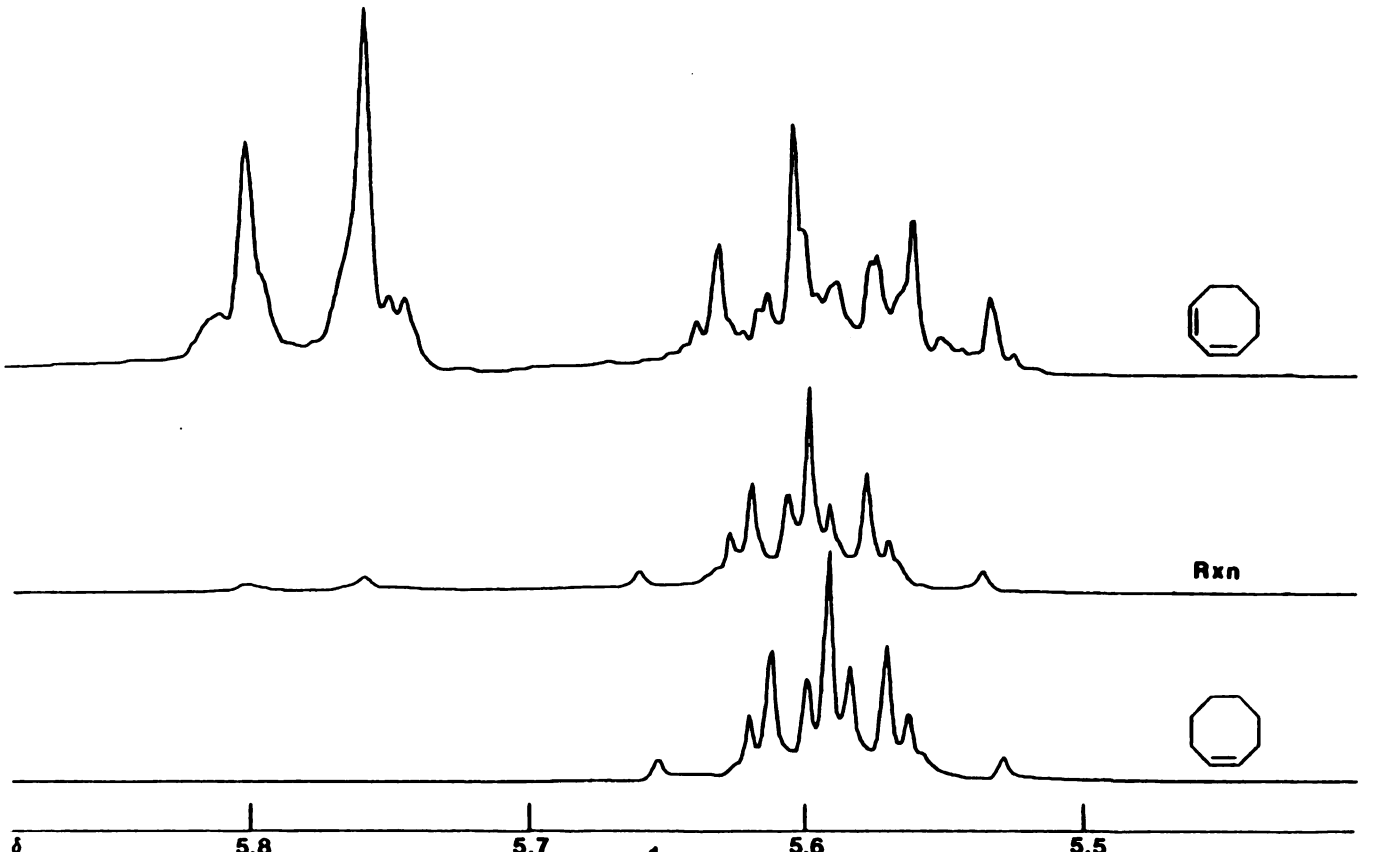


Figure 26. Olefinic region of 250 MHz ^{1}H NMR of 1,3-cyclooctadiene (top), reaction mixture of Figure 25 (middle), and cyclooctene (bottom).

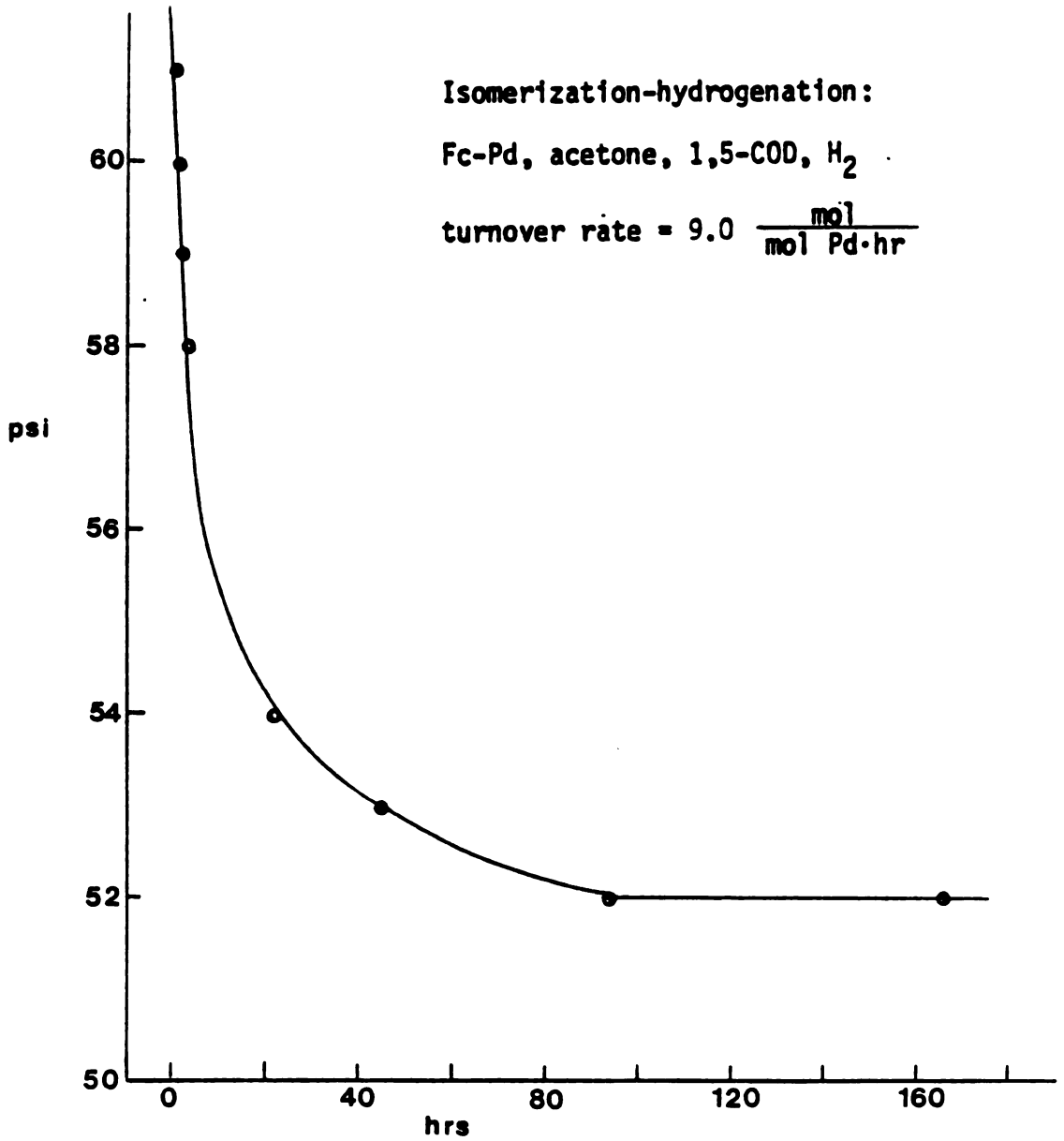


Figure 27. Isomerization-hydrogenation of 1,5-cyclooctadiene in acetone at 25° and 61 psi using Fc-Pd (17).

Table 4. Homogeneous selective hydrogenation of dienes to monoenes. COD = cyclooctadiene. Ligands vary from case to case. Complex 17 was used in the first entry.

Initial rate, mol/mol Pd•hr•psi	Substrate	T, °C	Metal	Solvent	Additive	Ref.
6.92	1,3-COD	27	Pd^{2+}	acetone	---	This work
8.99	1,3-COD	22	Pd^{0}	toluene	H_2O	67
3.45-5.52	isoprene	22	Pd^{0}	toluene	---	65
0.0011	1,4-cyclo-hexadiene	65	Pd^{2+}	toluene	---	73

hydrolyzed)[67] have rates of the same order of magnitude with 1,3-cyclooctadiene. The 3rd (catalyst = $PdCl_2$ complexed by trialkylamines)[65] and 4th (catalyst = $(Ph_2PCH_2PPh_2)PdCl_2$)[73] entries are not as comparable to this work as the 2nd entry. As has been pointed out,[73] rates and selectivities are affected most by substrates, and to a smaller extent by ligands, oxidation state of the metal, and solvents. With this in mind, the catalyst in this work appears to be at least as fast as the amine catalyst in entry 3, and 3 orders of magnitude faster than the chelating bisphosphine in entry 4.

Figure 28 presents a mechanistic scheme for the homogeneous selective hydrogenation of 1,3-cyclooctadiene using 17, This scheme accounts for 2 observations: 1) that the hydrogenation proceeds in acetone but not methylene chloride, and 2) that 1,3- cyclooctadiene is hydrogenated much faster than cyclooctene.

Complex 17 dissolves completely in dry CH_2Cl_2, forming a red solution. This solution is, however, catalytically inactive since H_2 is unable to oxidatively add to Pd. When 17 is dissolved in acetone, acetone replaces the amine. That the N-Pd bond and not the S-Pd bond breaks is supported by the mechanism of the Grignard cross-coupling reaction of the $PdCl_2$ complex of a similar ferrocenyl tertiary amine thioether,[55] in which N-Pd bond breakage is a necessary prerequisite to N-Mg bond formation. Catalysts for hydrogenation, dimerization, and carbonylation tend to be low

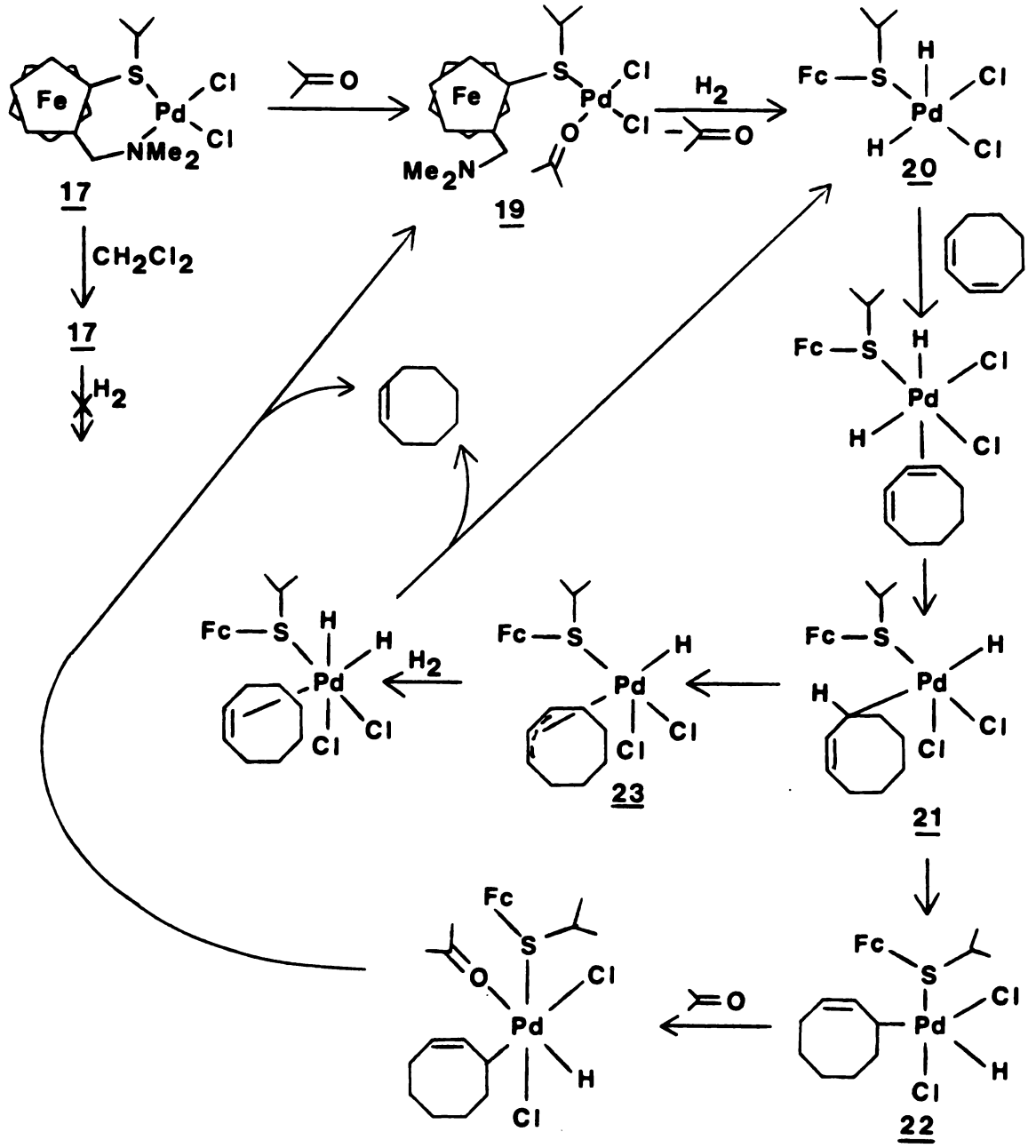


Figure 28. Possible mechanisms of the homogeneous selective hydrogenation of 1,3-cyclooctadiene using complex 17. Fc- = 2-dimethylaminomethylferrocenyl.

valent complexes stabilized by soft, polarizable ligands such as thioethers.[63] Also, the transition metal hydrides formed subsequently in Figure 28 can exist only if they are stabilized by a π acceptor.[64] Sulfur is a π acceptor and nitrogen is not.

Hydrogen is able to add to 19 in contrast to 17. The hydrogenation therefore proceeds in acetone. Complexation of the diene and olefin insertion give σ complex 21. At this point rearrangement could give 22 or complexation to the second double bond could give 23. The cycle 19, 20, 21, 22, 19 is the less probable cycle. The energy requirements for each step would be similar whether 1 or 2 double bonds were present, so the monoene would be hydrogenated as easily as the diene. The other cycle (20, 21, 23, 20) is more likely. It contains 2 steps (21→23 and the subsequent step) which are impossible in the hydrogenation of the monoene. If either of these steps is rate-determining it could explain why the diene is hydrogenated faster. The rate-determining step in this type of reaction may involve a hydrido-metal-olefin complex such as 23.[64]

It should be pointed out that the hydrogenation of cyclooctene could proceed by a route analagous to the 1st cycle (19, 20, 21, 22, 19), which is similar to an accepted route involving Wilkinson's catalyst.[75] Also, the possibility of binuclear catalysis[76] in the diene hydrogenation has not been ruled out.

One explanation of the heterogeneous reactions of Figures 22 and 23 is presented in Figure 29. The quaternary ammonium salt may precipitate and act as the catalyst, or a Pd^{2+} hydroxide species dissociated from the thioether may be the precipitate. Hydrolysis as in Figure 29 has been previously observed.[67]

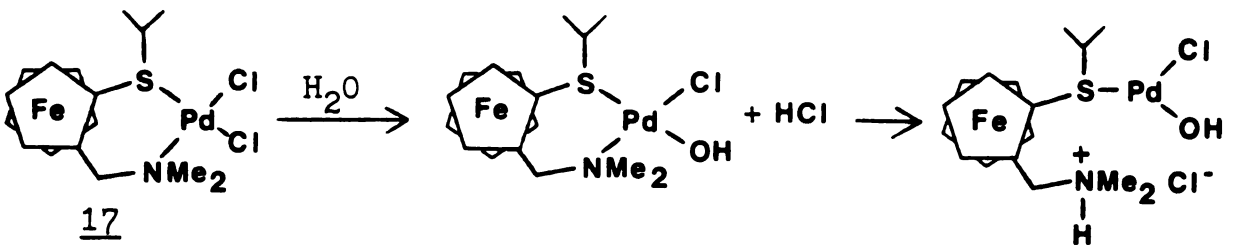


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Figure 29. Hydrolysis of complex 17 prior to heterogeneous selective hydrogenation.

PART II. BIS(η^6-4-CHLOROANISOLE)CHROMIUM

INTRODUCTION

There are a number of useful methods available for the synthesis of π-bis(arene)chromium complexes, including the Grignard synthesis,[45] the Fischer-Hafner aluminum synthesis,[77] and Fischer-Hafner variations.[78-80] These methods cannot be used, however, when the arene rings contain substituents with lone pairs of electrons. Some of the Grignard reagents are impossible to make, and in the Fischer-Hafner-type reactions, either the substituent withdraws too much electron density from the ring, or the heteroatoms complex with the Lewis acid present in each case. Alkylarenes are dealkylated and isomerized under Fischer-Hafner conditions. For alkylated arenes and arenes with heteroatom substituents, chromium vapor-ligand cocondensation must be employed.

In a cocondensation reaction[81-84] (illustrated for bis(benzene)chromium in Figure 30) metal vapor is produced

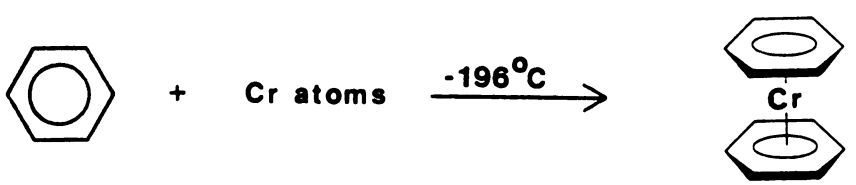
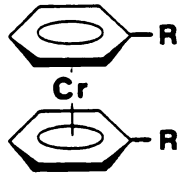


Figure 30. Synthesis of bis(η^6-benzene)chromium.

in a high vacuum. Chromium is easily vaporized and a resistively heated tungsten filament or boat is generally used, although electron gun setups are available. An organic compound (the ligand) is vaporized at the same time by slow admission through an addition funnel (liquids) or resistive heating (solids). The metal and ligand vapors are cocondensed on the flask walls, which are kept near -196°C by liquid nitrogen. The flask contents are subsequently warmed and the products removed.

Many bis(η^6-arene)chromium derivatives have been made by metal vapor-ligand cocondensation. Some of these are presented in Figure 31 and include 1,1'-disubstituted compounds 24, R = H,[85] Me, Et,[86] C≡C-Ph,[87] F, Cl,[86] OMe, CO_2Me, NMe_2,[88] PPh_2,[89] and $SiMe_3$,[90] dodecamethyl substituted 25,[86] bis(η^6-naphthalene)chromium (26),[91] and bis(η^6-1,4-difluorobenzene)chromium (27).[86] Elschenbroich and Heck have discovered that the reaction of biphenyl with chromium atoms gives monometallated compound 28, dimetallated compound 29, and a small amount of dimetallated compound 30 with side-by-side chromium atoms (Figure 32).[92] The unusual [2.2]paracyclophane derivatives 31 and 32 (Figure 33) have also been made.[93]

A series of fluorinated bis(arene)chromium compounds 33 (and the o and m isomers) has been made (Figure 34) and studied by ^{19}F NMR.[94] The results showed that the electron-withdrawing effect of the Cr is similar to the effect of



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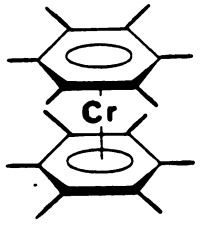
R = H, Me, Et, C≡C-Ph, F, Cl, OMe, CO_2Me, NMe_2, PPh_2, $SiMe_3$



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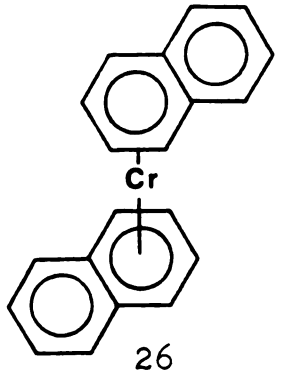

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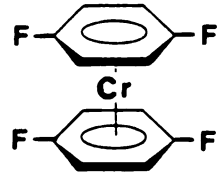

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Figure 31. Bis(η^6-arene)chromium compounds made by metal vapor-ligand cocondensation.

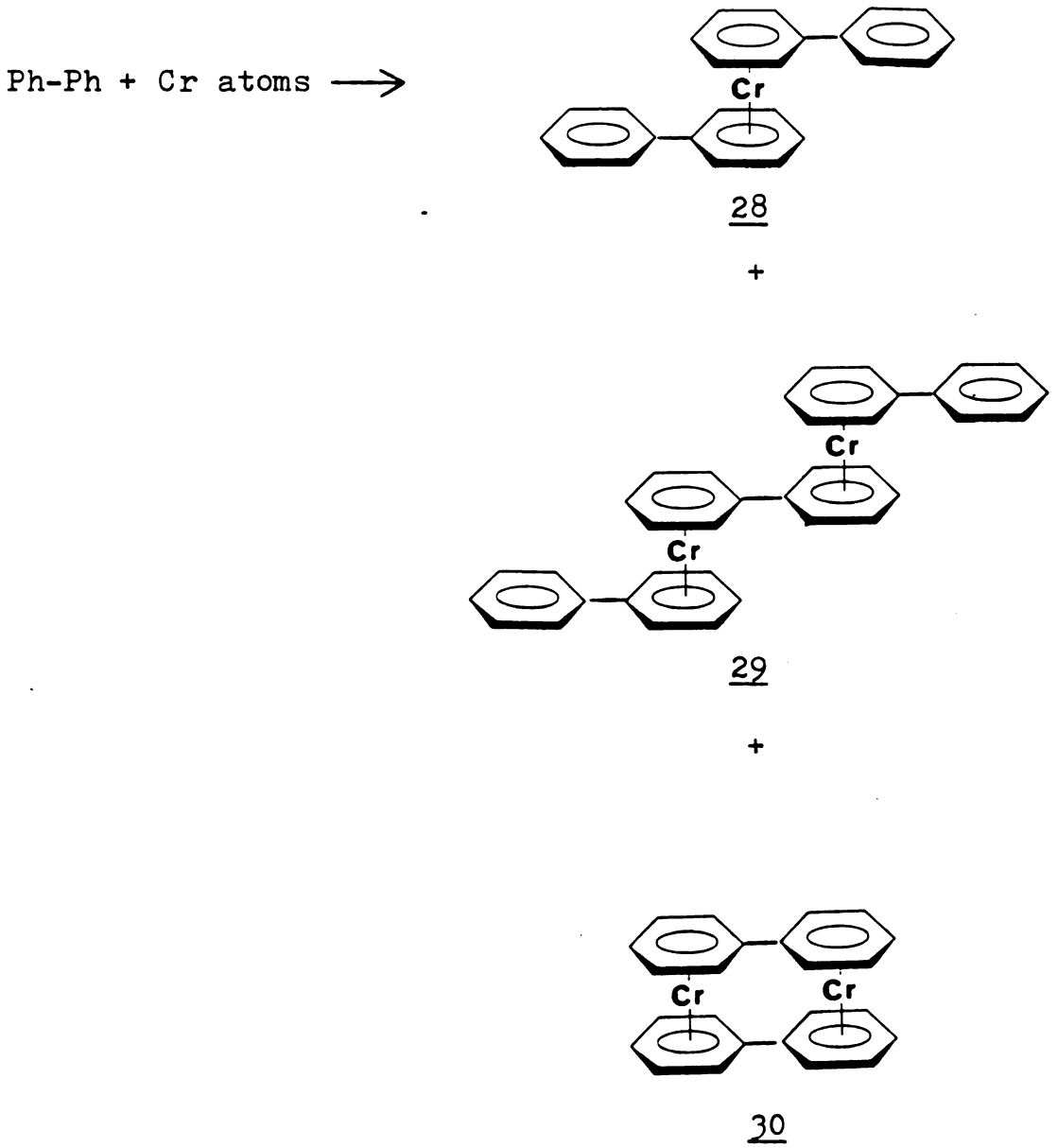
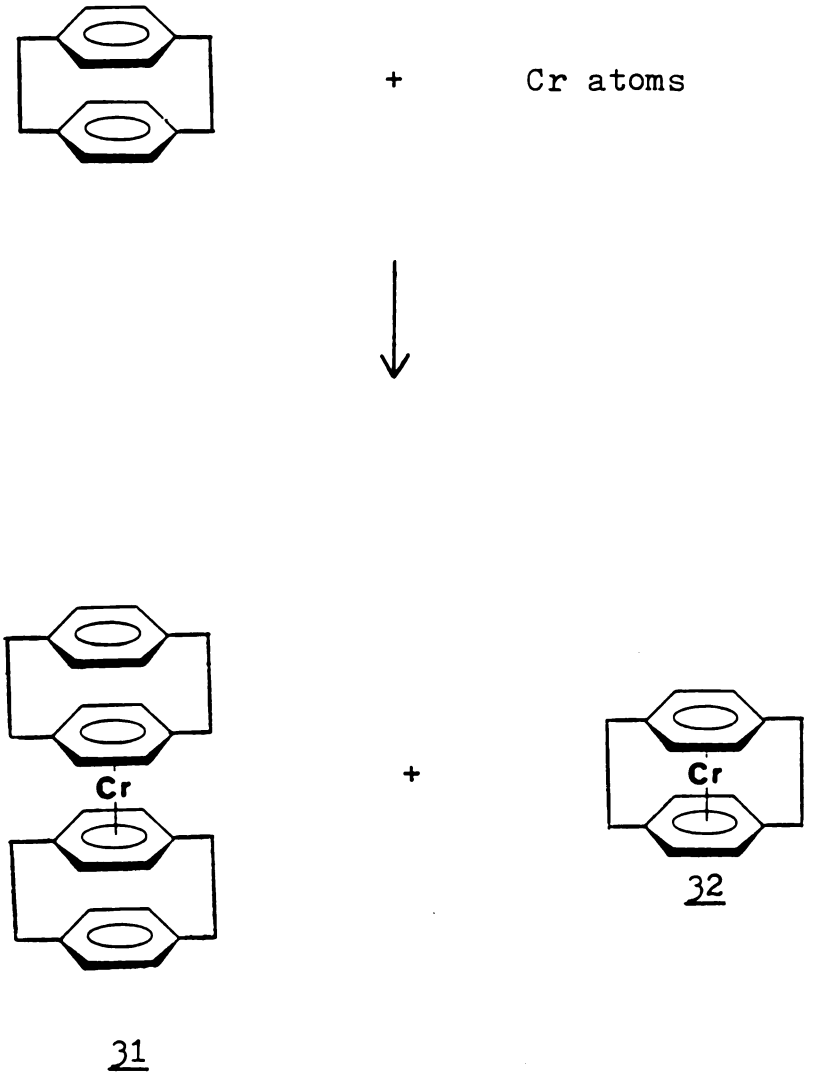


Figure 32. Reaction of biphenyl with Cr atoms.



31 32

Figure 33. Reaction of [2.2]paracyclophane with Cr atoms.

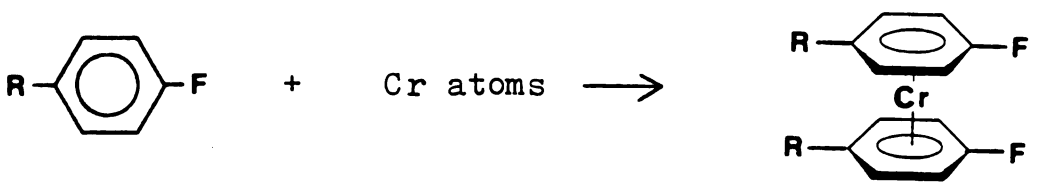
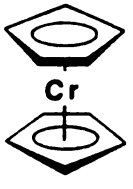


Figure 34. Fluorinated bis(arene)chromium derivatives.

4 fluorines together.

Other compounds besides benzene derivatives have been condensed with chromium vapor. These include cyclopentadiene, giving chromocene (34, Figure 35),[86] 2,6-dimethylpyridine, giving pyridine sandwich compound 35,[95] and PF_3, giving complex 36.[85]

This portion of the thesis describes the synthesis and characterization of a new bis(η^6-arene)chromium compound, the metal vapor system used, and attempts to make other bis(arene)chromium species.



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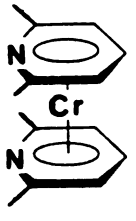

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$Cr(PF_3)_6$

36

Figure 35. Chromium complexes from metal vapor-ligand cocondensation using non-benzene ligands.

EXPERIMENTAL

Proton NMR's were obtained by use of a Bruker WM 250 spectrometer in benzene-d_6 or chloroform-d, with TMS as internal standard. Infrared spectra were recorded by use of a Perkin-Elmer 457 machine. Mass spectra were obtained by means of a Finnigan 4021 instrument with INCOS data system. Elemental analyses were performed by Spang Microanalytical Laboratory, Eagle Harbor, Michigan.

Bis(η^6-4-chloroanisole)chromium (37). Chromium chips (1.8 g, 0.035 mol) were placed in a B12B.040W conical tungsten basket[96] connected to the electrodes. The flask was evacuated and surrounded by liquid nitrogen. After the chromium was degassed at a low voltage setting, metal vapor was produced at 40 amps, 7 V AC. Over a period of 3 hrs, 50 mL (0.41 mol) of 4-chloroanisole was added through an addition funnel equipped with high vacuum stopcocks. After reaction, the liquid N_2 was removed, excess arene was pumped away, and the electrodes were replaced with a cold finger under a strong flow of Ar. The product was sublimed twice under high vacuum giving 37 as brown crystals: yield 0.31 g (6.0 % based on Cr evaporated); mp 47-48 °C; ^{1}H NMR (benzene-d_6, TMS) δ 3.14 (s, 6H, CH_3), 4.38 (d, 4H, J = 5.2 Hz, ring H), 4.63 (d, 4H, J = 5.2 Hz, ring H); IR (Nujol, CsI plates) 462 (asymmetric Cr-ring stretch or ring tilt), 615, 792,

989, 1025, 1060 (C-H deformation), 1173 (C-C stretch), 1225 (C-O stretch), 1515 cm^{-1}; MS m/e (% RA) 52 (29, Cr), 99, 101 (60, 20, 5-chloro-1,3-cyclopentadienyl cation), 107 (4, $C_6H_4OCH_3$), 127, 129 (55, 18, ClC_6H_4O), 142, 144 (100, 32, $ClC_6H_4OCH_3$), 194, 196 (5, 2, $M^+ - ClC_6H_4OCH_3$), 336, 338 (2, 1, M^+); UV (1.9×10^{-4} M in cyclohexane) λ_{max} 317 nm. Anal. Calcd for $C_{14}H_{14}Cl_2CrO_2$: C, 49.87; H, 4.19; Cl, 21.03. Found: C, 49.68; H, 4.26; Cl, 20.94.

Bis(η^6-toluene)chromium (24, R = Me). Freshly cut chromium chips (1 g, 0.02 mol) were placed in a B12B.060W conical tungsten basket connected to the electrodes. The flask was evacuated and placed in a Dewar flask of liquid nitrogen. Degassing was done at 2.1 V, 24 A, and metal vapor produced at 9 V, 64 A for 2.0 hrs, during which time 41 mL (0.39 mol) of toluene was added. The product was sublimed as usual giving 1.7 g (37 % based on Cr evaporated) of 24, R = Me, with a proton NMR spectrum identical to that previously reported.[86]

Attempted synthesis of bis(η^6-1,3,5-trimethylbenzene)-chromium (38). An S20A-.005W tungsten boat[96] was fixed to the electrodes using set screws. Chromium chips (0.511 g, 0.00983 mol) were placed in the boat. The system was evacuated and the flask was cooled with liquid nitrogen. Exiting cooling water became hot when the potential was 8 V. Through the addition funnel 15 mL (0.11 mol) of 1,3,5-trimethylbenzene was added over a 3 hr period. When the liquid

nitrogen was removed it was apparent that no metal had evaporated.

Attempted synthesis of bis(η^6-4-bromoanisole)chromium (39). Chromium chips (1.2 g, 0.023 mol) were placed in a B12B.040W conical tungsten basket connected to the electrodes. The flask was evacuated and surrounded by liquid N_2. The chromium was degassed and metal vapor was produced at 40 amps. Over a period of 3 hrs, 30 mL (0.24 mol) of 4-bromoanisole was added. Afterwards the liquid N_2 was removed, excess arene was pumped away, and the electrodes were replaced with a cold finger. Nothing appeared on the cold finger after sublimation for 36 hrs at 25° and 12 hrs at 100°.

Attempted synthesis of bis(η^6-4-chloronitrobenzene)-chromium (40). Method A. Chromium chips (1.76 g, 0.0338 mol) were placed in a B12B.040W tungsten basket. The rest of the procedure was similar to that for 37, except that the solid ligand (mp 83°) was kept in the liquid state with heating tape. The ligand clogged the inlet tube early in the addition. No product was obtained on sublimation of the reaction mixture.

Attempted synthesis of bis(η^6-4-chloronitrobenzene)-chromium (40). Method B. In this case 1.7 g (0.033 mol) of chromium chips, and 20.0 g (0.127 mol) of 4-chloronitrobenzene in 32 mL of diethylene glycol dimethyl ether were used. The ligand inlet tube did not clog, but evaporation of the solvent left the ligand at the bottom of the tube

in a ball. Chromium continued to evaporate for 30 minutes after addition of the ligand, during which time the ball of ligand disappeared. Removal of solvent and excess arene with the vacuum pump gave a black tar which did not sublime.

Attempted synthesis of bis(η^6-4-chloronitrobenzene)-chromium (40). Method C. Chromium chips (1.5 g, 0.029 mol) were placed in a B12B.040W tungsten basket. A solution of 20.0 g (0.127 mol) of 4-chloronitrobenzene in 32 mL of diethylene glycol dimethyl ether was placed in the bottom of the flask with a stirring bar and the flask was immersed in Dry Ice/isopropyl alcohol. Chromium vapor was condensed into the stirred solution for 4 hours. The rate of Cr evaporation was slow. No product was obtained on workup.

Attempted synthesis of bis(η^6-4-chloronitrobenzene)-chromium (40). Method D. A stainless steel crucible was suspended from the ligand inlet tube. In it was placed 18.5 g (0.117 mol) of 4-chloronitrobenzene. Chromium was evaporated from a B12B.040W basket. The ligand melted and evaporated quickly 35 minutes after the chromium began to vaporize. Chromium was evaporated for 10 more minutes then stopped. No product was obtained on sublimation. Brief exposure of the reaction mixture to air did not result in formation of a cationic complex.

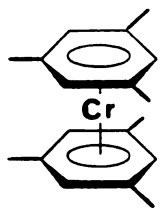
Attempted synthesis of bis(η^6-4-methoxyphenylmagnesium chloride)chromium (41). In a 3-necked 200 mL round-bottomed flask under Ar with a condenser, addition funnel, and stirring

bar was placed 0.032 g (13 X 10^{-4} mol) of Mg turnings. Complex 37 (0.204 g, 6.07 X 10^{-4} mol) in 100 mL of ether was placed in the addition funnel. The complex was added slowly to the magnesium. No reaction occurred at 25° or with gentle heat. Addition of Mg activated by reaction with bromobenzene caused no change. A change of solvent to THF, then to dimethoxyethane, did not produce any visible reaction.

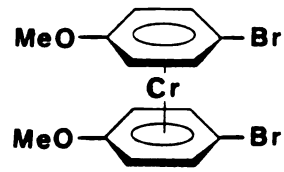
RESULTS AND DISCUSSION

A stationary metal vapor system including water-cooled electrodes and a Pyrex flask was designed and built for this work. To assess the effectiveness of this system in metal vapor-ligand cocondensation, known complex bis(η^6-toluene)-chromium (24, R = Me, Figure 31) was made. The electrodes were modified to accept tungsten boats in an attempt to circumvent the problem of chromium chips falling through the basket. The synthesis of bis(η^6-1,3,5-trimethylbenzene)-chromium (38, Figure 36) using a boat was then tried. The new complex bis(η^6-4-chloroanisole)chromium (37, Figure 37) was successfully made using a tungsten basket and characterized by ^{1}H NMR, IR, MS, UV, and elemental analysis. Efforts to make 39 (the bromo analog of 37) and nitro derivative 40 were unsuccessful. Chloro compound 37 did not form Grignard reagent 41 at 25° or 35° in ether, THF, or dimethoxyethane.

The electrodes designed for this work are shown in Figure 38. The flask with electrodes and addition funnel in place is shown in Figure 39. The system consists of electrodes, a rubber O-ring, and a Pyrex flask. The electrodes are of stainless steel throughout except the copper blocks, plastic insulator, and solder. They are made from a round 3/8 inch plate through which three 1/4 inch tubes are inserted. Two of the tubes are silver-soldered to the plate; the third is insulated from the plate by a plastic ring.



38



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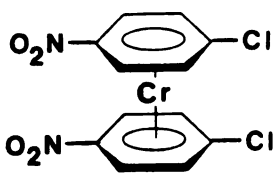
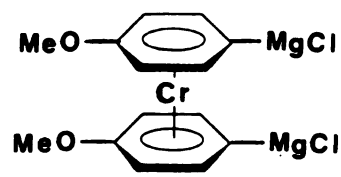
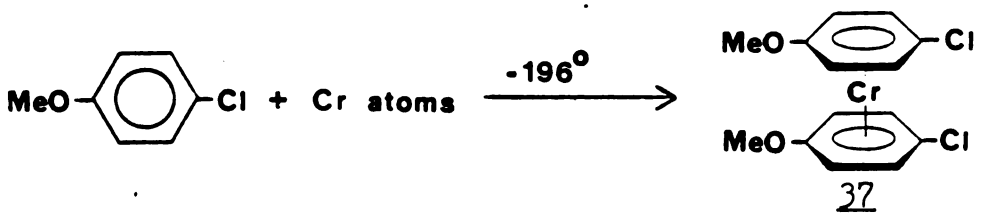


40



41

Figure 36. Complexes 38, 39, 40, and 41.



37

Figure 37. Synthesis of bis(η^6-4-chloroanisole)chromium (37).

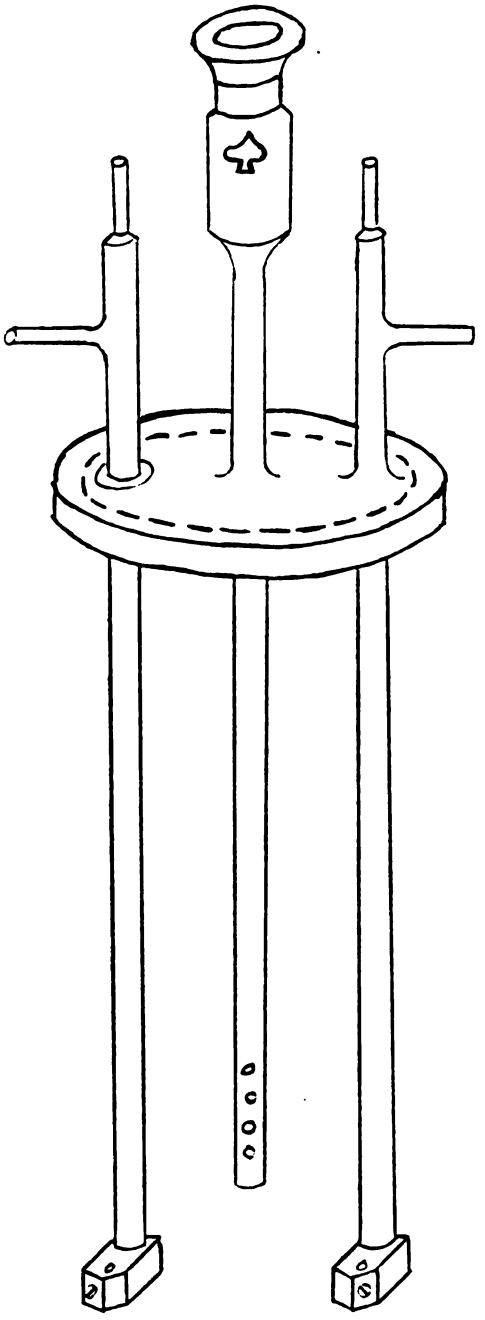


Figure 38. Stainless steel electrodes.

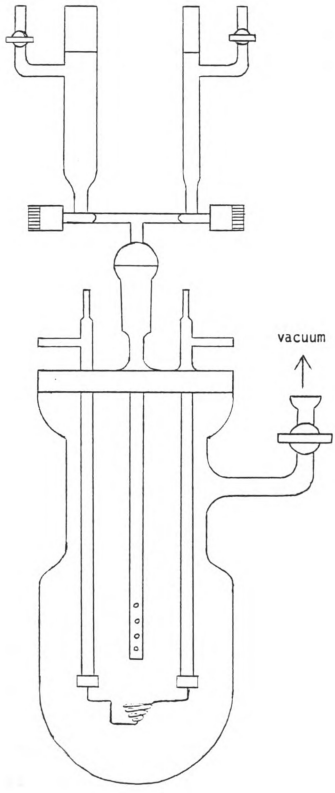


Figure 39. Metal vapor reactor.

The plastic-steel interfaces are made vacuum tight with epoxy glue. The center ligand inlet tube is fitted with an 18/9 socket joint for connection with the addition funnel. Sixteen holes (4 X 4) are drilled in the bottom inch of the inlet tube. The two side tubes are water-cooled with inner 1/8 inch tubes. A 3/8 X 1/2 X 1/2 inch copper block with a hole for the heating element is attached to the bottom of each side tube. An O-ring groove is cut into the underside of the 3/8 inch plate. The flask is made with a commercially available 75 mm inside diameter O-ring joint and has a test tube-shaped bottom of 120 mm diameter. A side arm with a high vacuum 8 mm stopcock provides for evacuation of the reactor. Other nonrotating systems similar to this have been previously described.[82,83,97]

Bis(toluene)chromium (24, R = Me) was made using the new metal vapor system. A tungsten basket of 0.060 inch diameter wire was used. A large amount (1700 mg) of product was obtained but two problems became apparent: 1) chromium chips fell through the basket, making accurate yield determinations difficult, and 2) the current requirement for this large diameter wire was high. The limiting factor at high currents in the system was the melting temperature of the epoxy glue.

To correct the first problem 2 grooves were made in the copper blocks of the electrodes so a tungsten boat could be attached. However, the current required was too high and

no metal evaporated in an attempted synthesis of hexamethyl derivative 38.

The second problem was corrected in the successful synthesis of bis(η^6-4-chloroanisole)chromium (37) using a tungsten basket of 0.040 inch diameter wire. The 250 MHz proton NMR of 37 (Figure 40) was done in a sealed NMR tube in benzene-d_6. This compound is air-sensitive in solution and decomposes in chloroform-d. The spectrum shows the expected ring proton doublets (J = 5.2 Hz) of this AA'XX' system and a methyl singlet. The ring protons appear upfield of their uncomplexed position due to reduction of electron density in the ring π orbitals upon complex formation or to other effects.[98] That deoxygenation of the ether linkage has not occurred is shown by the presence of a C-O stretch at 1225 cm^{-1} in the IR (Figure 41). The infrared also shows an asymmetric Cr-ring stretch or ring tilt[99] at 462 cm^{-1}. The base peak in the mass spectrum (Figure 42) is due to 4-chloroanisole (m/e 142) and there is a peak at m/e 144 of the correct relative abundance (32) due to ^{37}Cl. The compound exhibits molecular ions at m/e 336 and 338. A metal to ligand ($4e_{2g} \rightarrow 4e_{2u}$) charge transfer band at 317 nm in cyclohexane solution is present in the UV spectrum.

Like many bis(arene)chromium complexes compound 37 is air-sensitive. However, the presence of the electronegative Cl and O retards oxidation so that 37 may be left

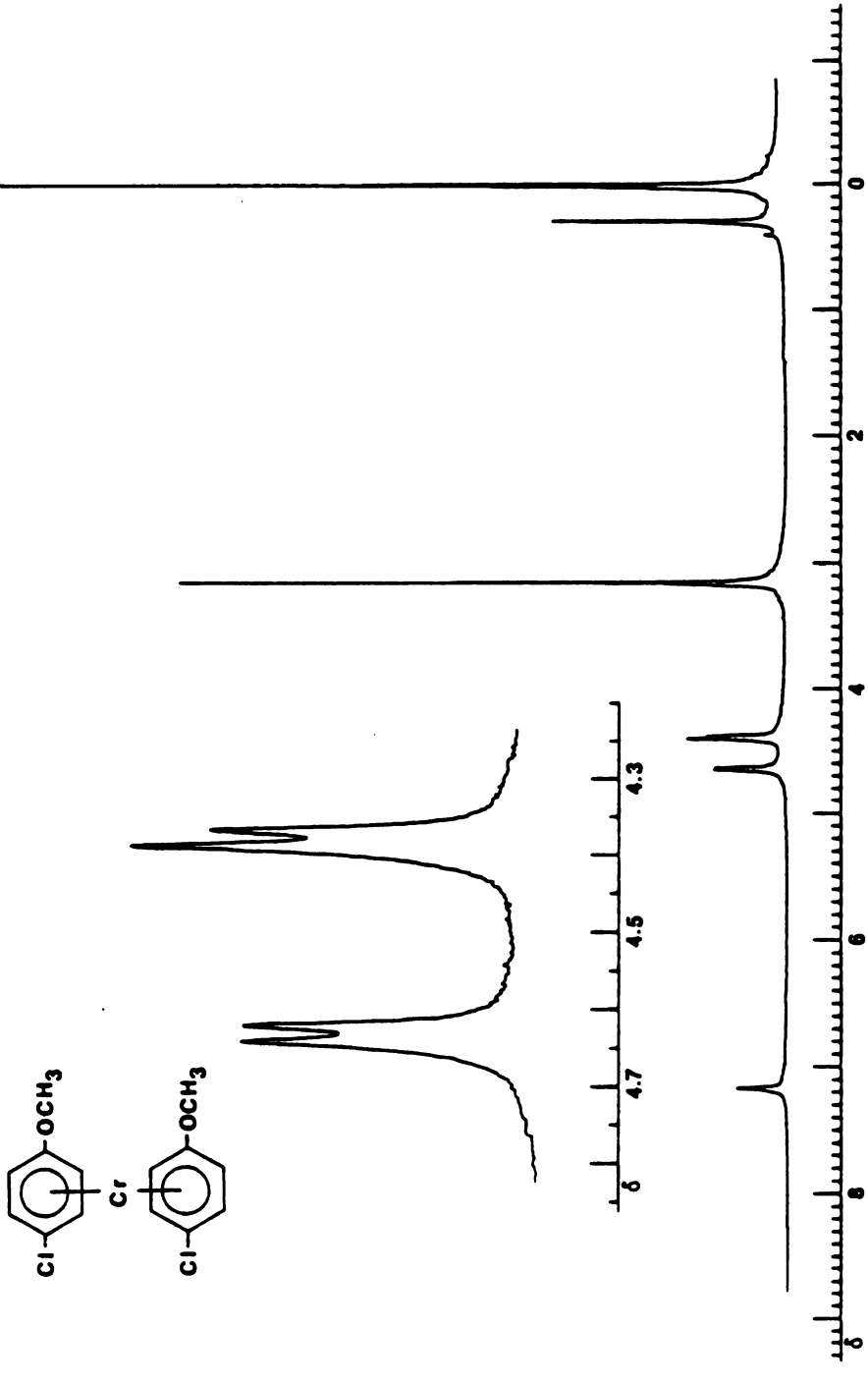


Figure 40. 250 MHz ^{1}H NMR of bis(η^{6}-4-chloroanisole)chromium (37).

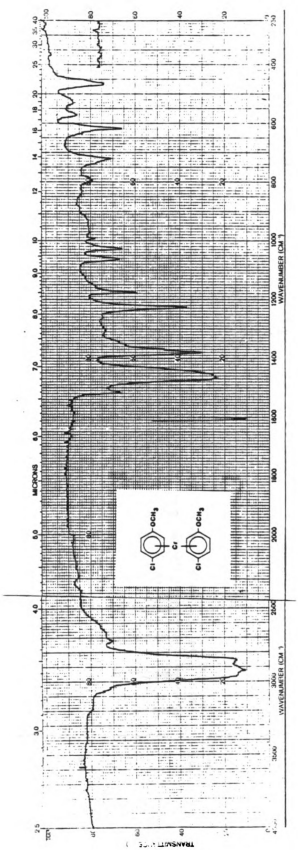


Figure 41. Infrared spectrum of complex 27.

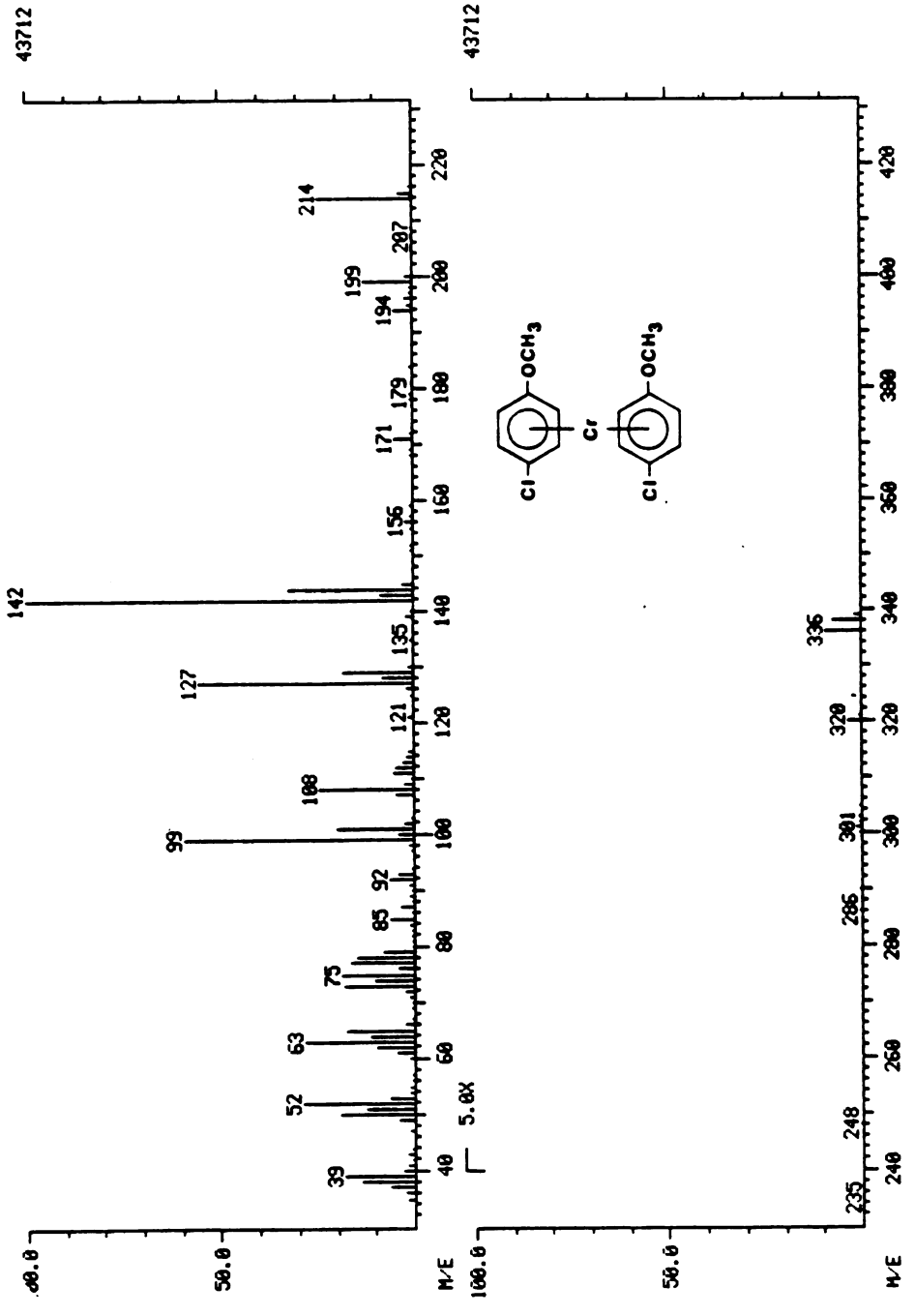


Figure 42. Mass spectrum of complex 27.

exposed to air for short periods in the solid state without significant decomposition.

The bromo analog of 37 is 39. It has been previously found[100] that bromobenzene fails to form a π complex with Cr atoms, the product being $CrBr_3$. In accordance with this, no 39 could be found after cocondensation of 4-bromoanisole with chromium.

The metal vapor reactor here is best suited for liquid ligands. The solid ligand used in the attempted syntheses of bis(4-chloronitrobenzene)chromium (40) created problems. Four methods were used: 1) addition of hot liquid ligand, 2) addition of a diglyme solution of the ligand, 3) condensation of chromium vapor into a cold diglyme solution of the ligand in a procedure similar to that described by Kündig and Timms,[101] and evaporation of the ligand from a stainless steel crucible inside the flask. These reactions failed for a variety of reasons, mostly related to failure of the ligand to mix evenly with Cr atoms.

Finally, chloro derivative 37 did not form Grignard reagent 41 under a variety of conditions. The magnesium turnings failed to give any visible reaction. Addition of Mg activated by reaction with bromobenzene did not help.

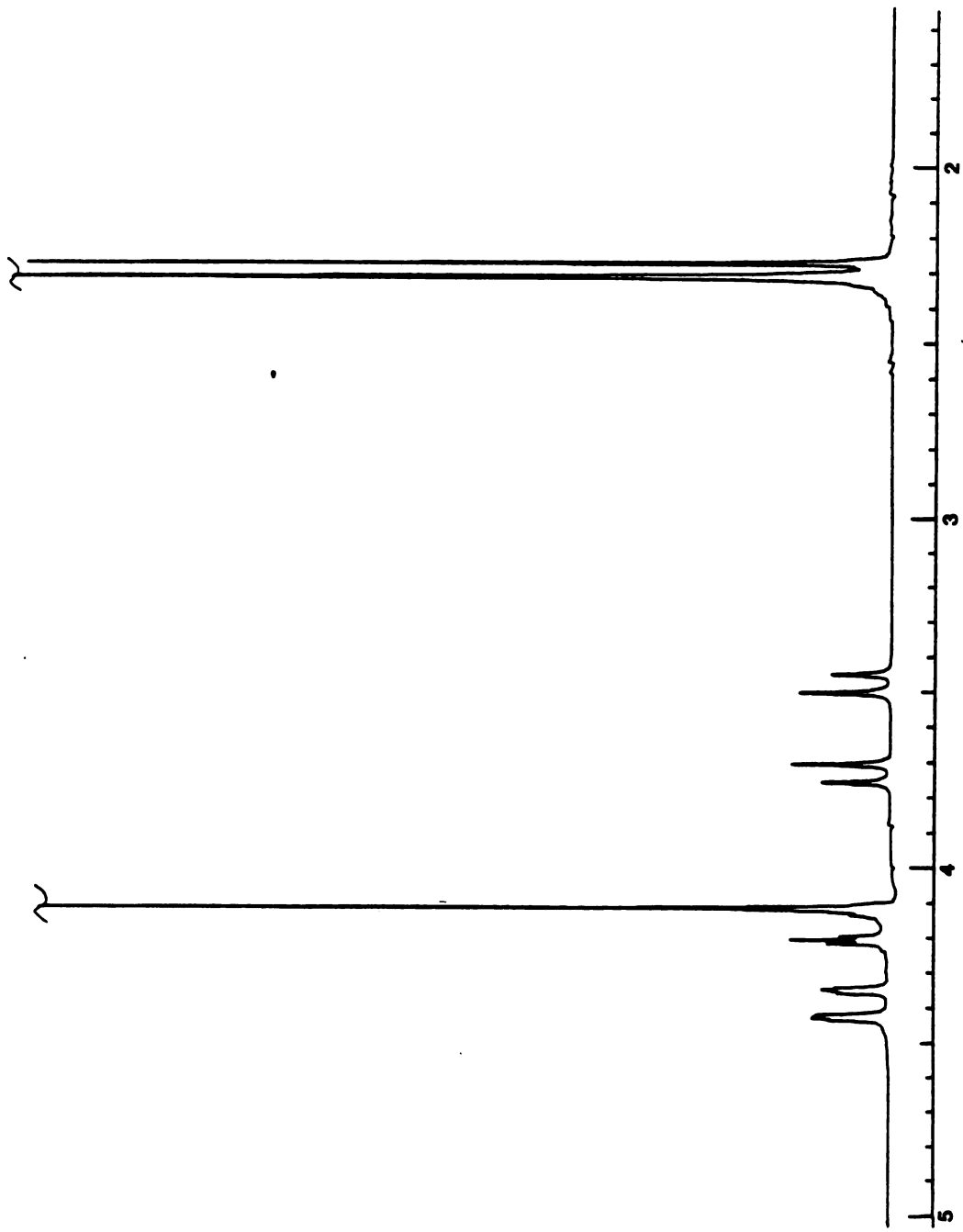


Figure 43. 250 MHz ^{1}H NMR of 16, R = Me.

Figure 44. Broadband decoupled ^{13}C NMR of 16, R = Me.

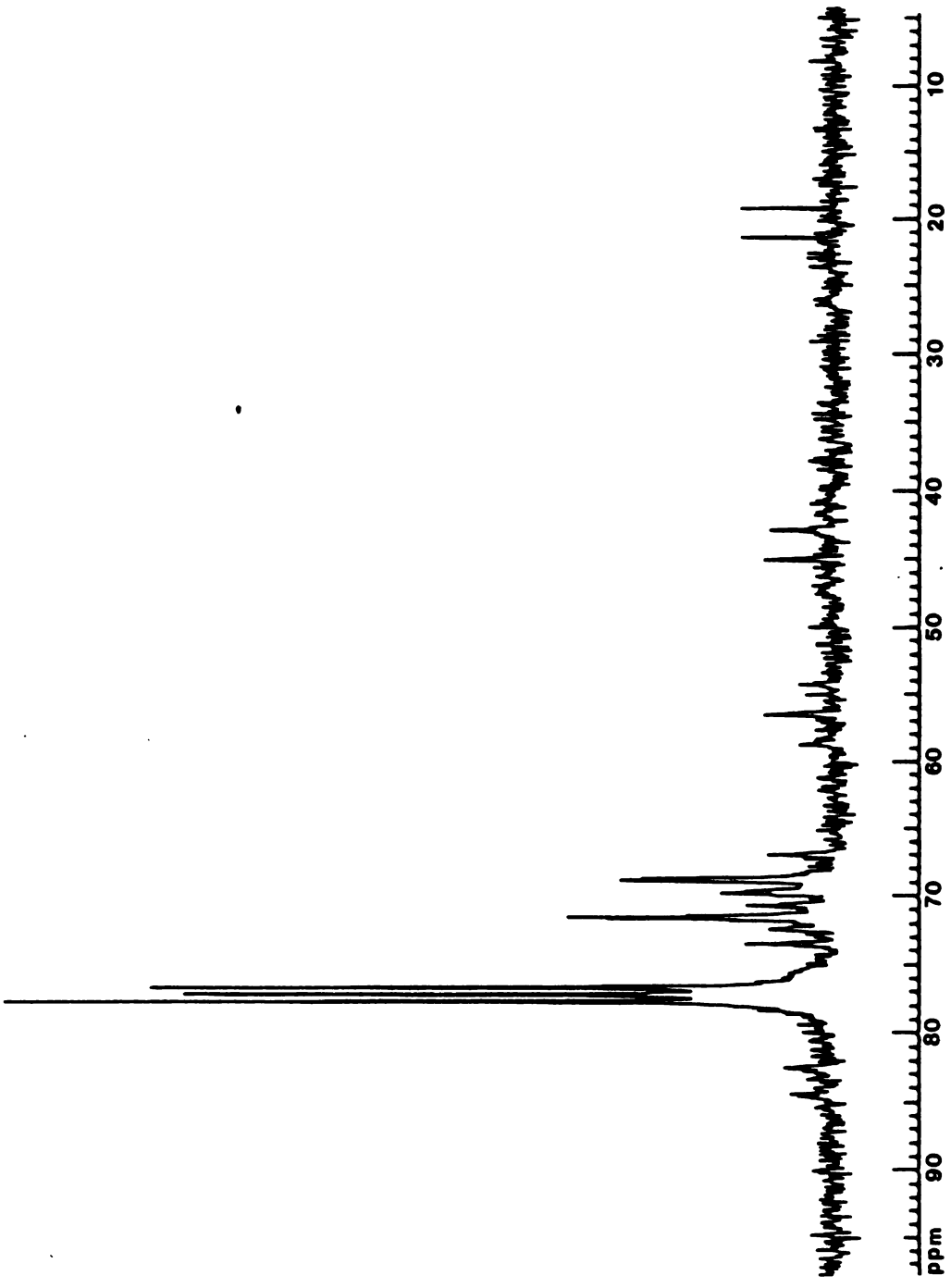


Figure 45. Gated decoupled ^{13}C NMR of 16, R = Me.

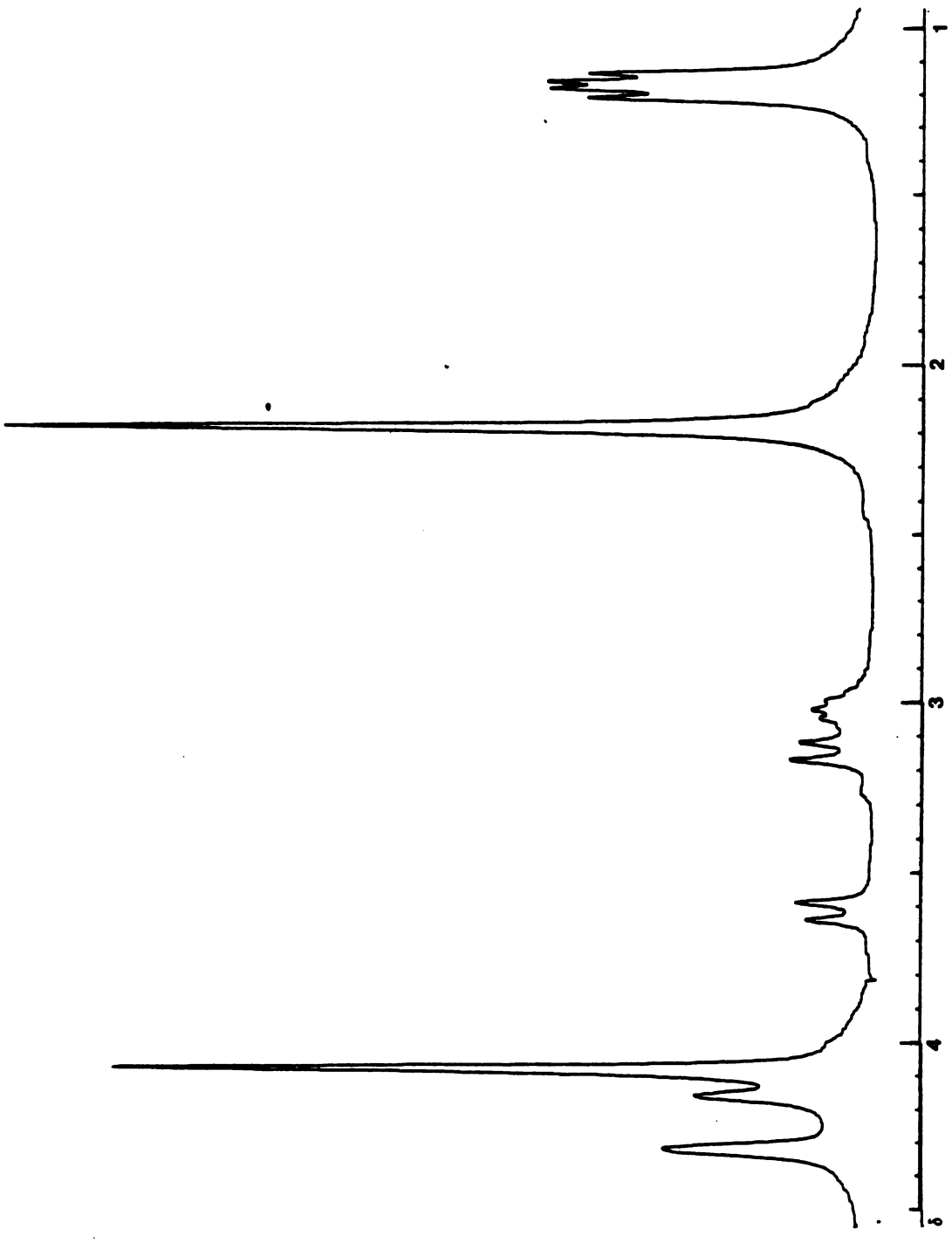


Figure 46. 250 MHz ^{1}H NMR of 16, R = i-Pr.

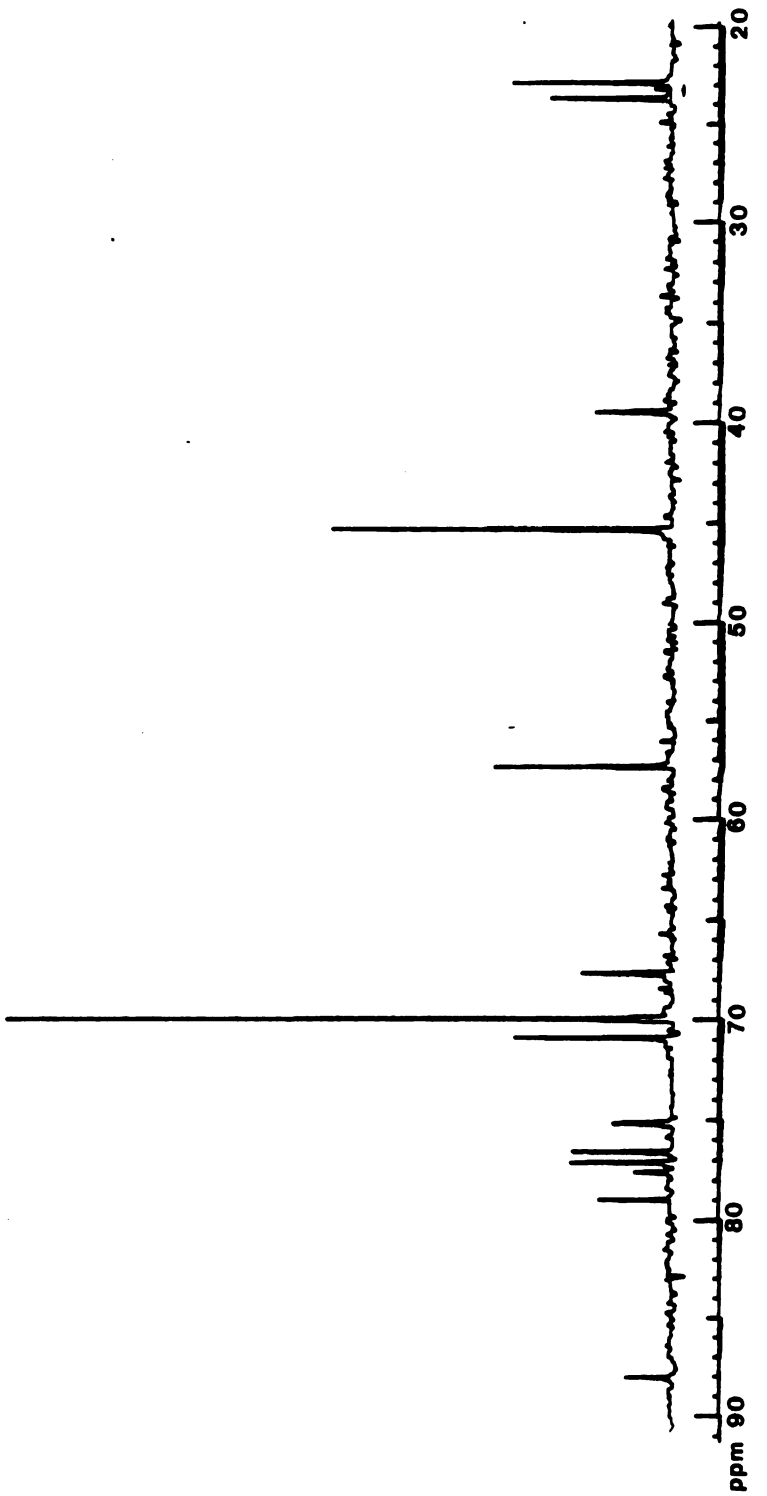


Figure 47. Broadband decoupled ^{13}C NMR of 16, R = i-Pr.

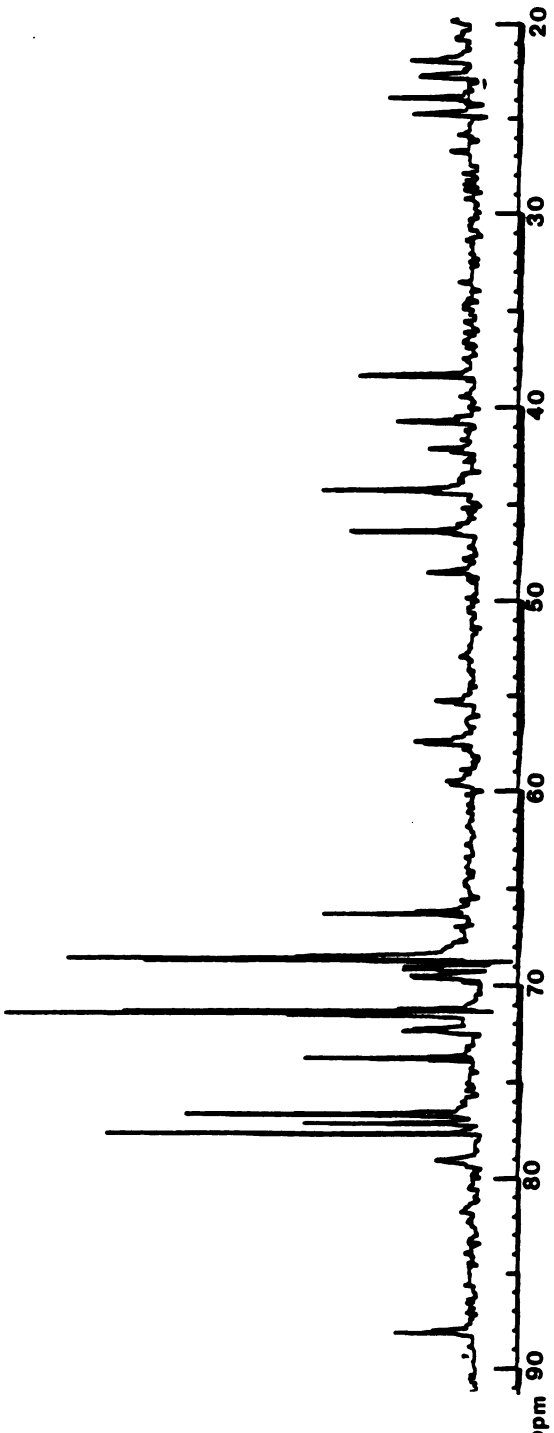


Figure 48. Gated decoupled ^{13}C NMR of 16, R = i-Pr.

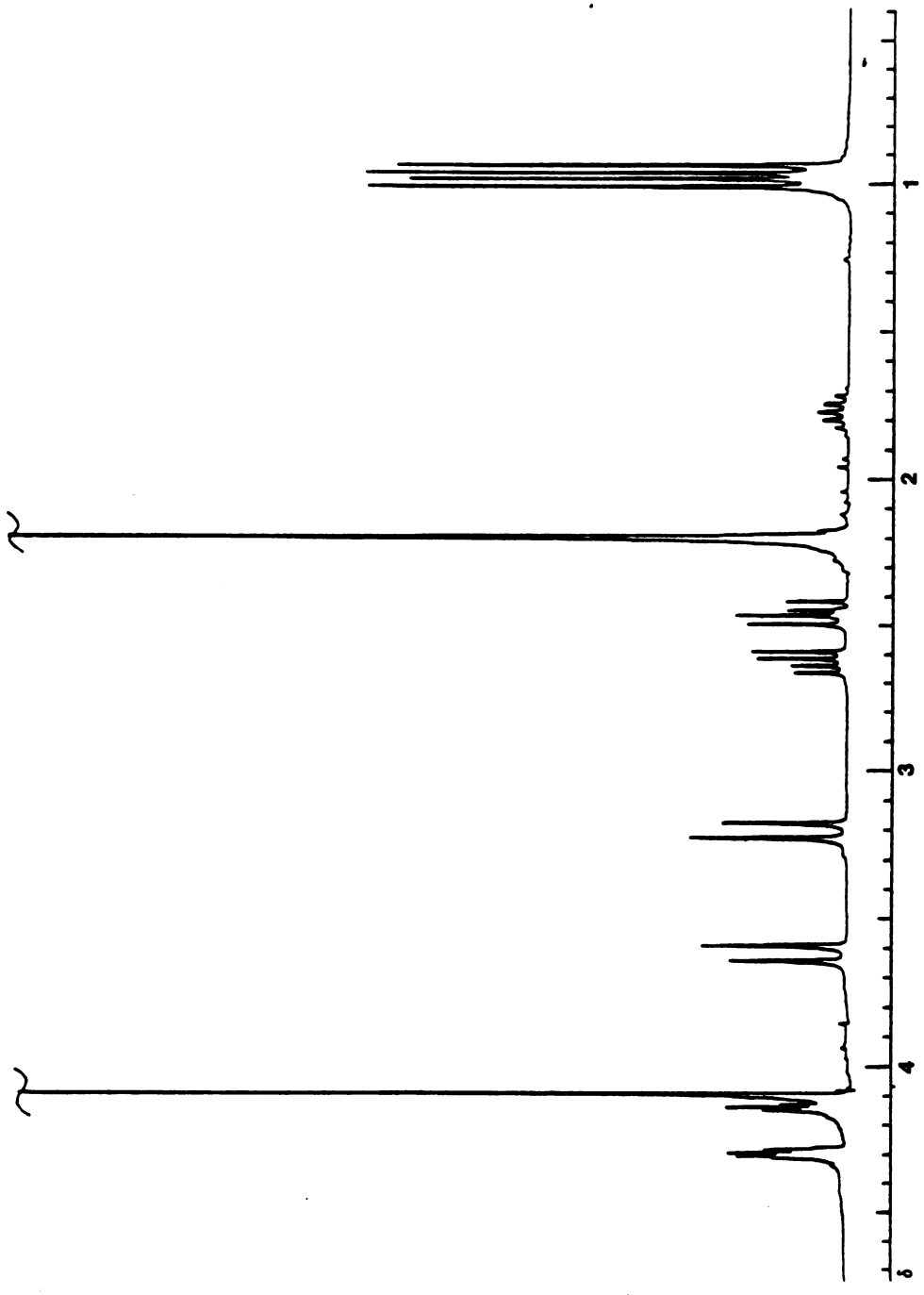


Figure 49. 250 MHz ^{1}H NMR of 16, R = i-Bu.

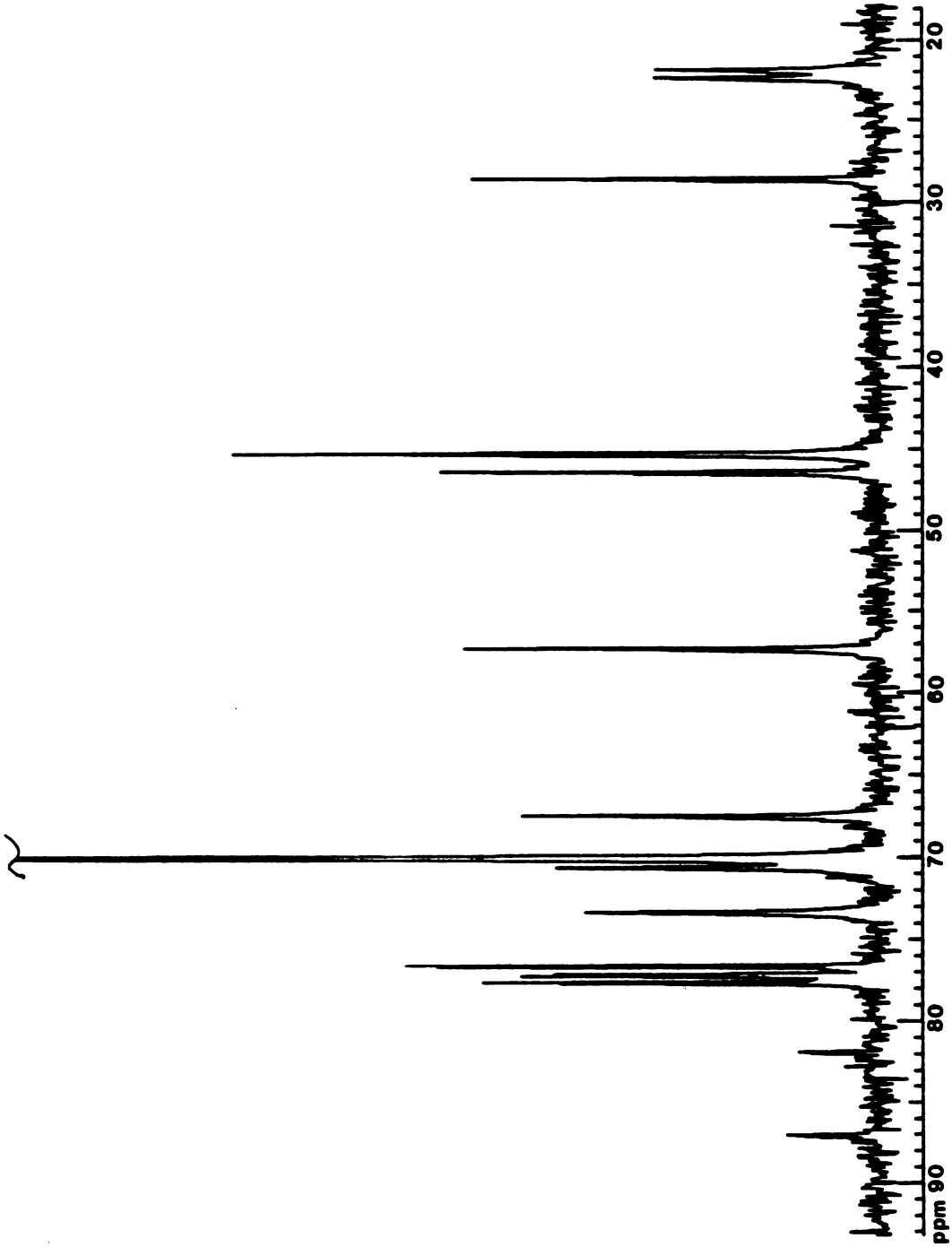


Figure 50. Broadband decoupled ^{13}C NMR of 16, R = i-Bu.

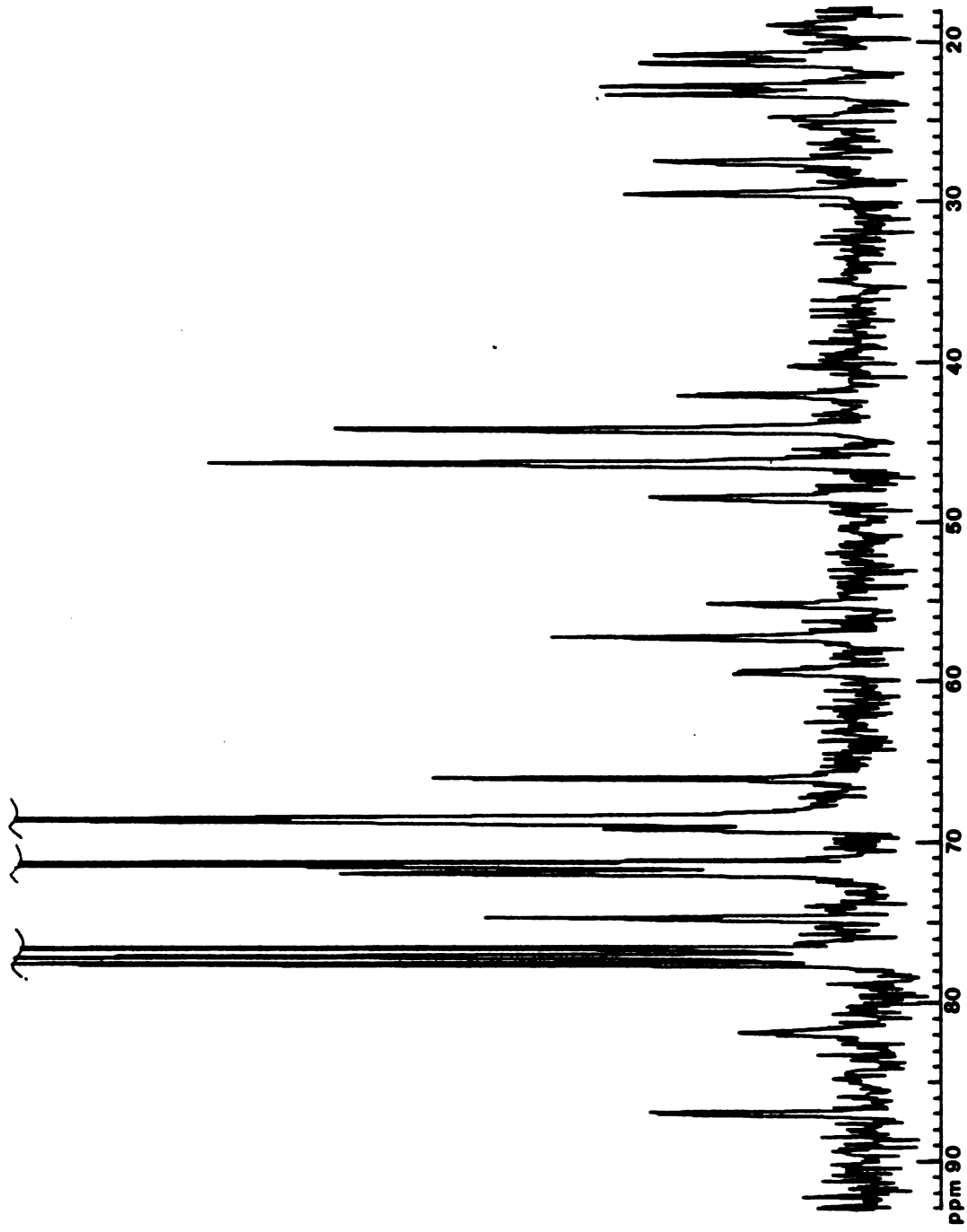


Figure 51. Gated decoupled ^{13}C NMR of 16, R = i-Bu.

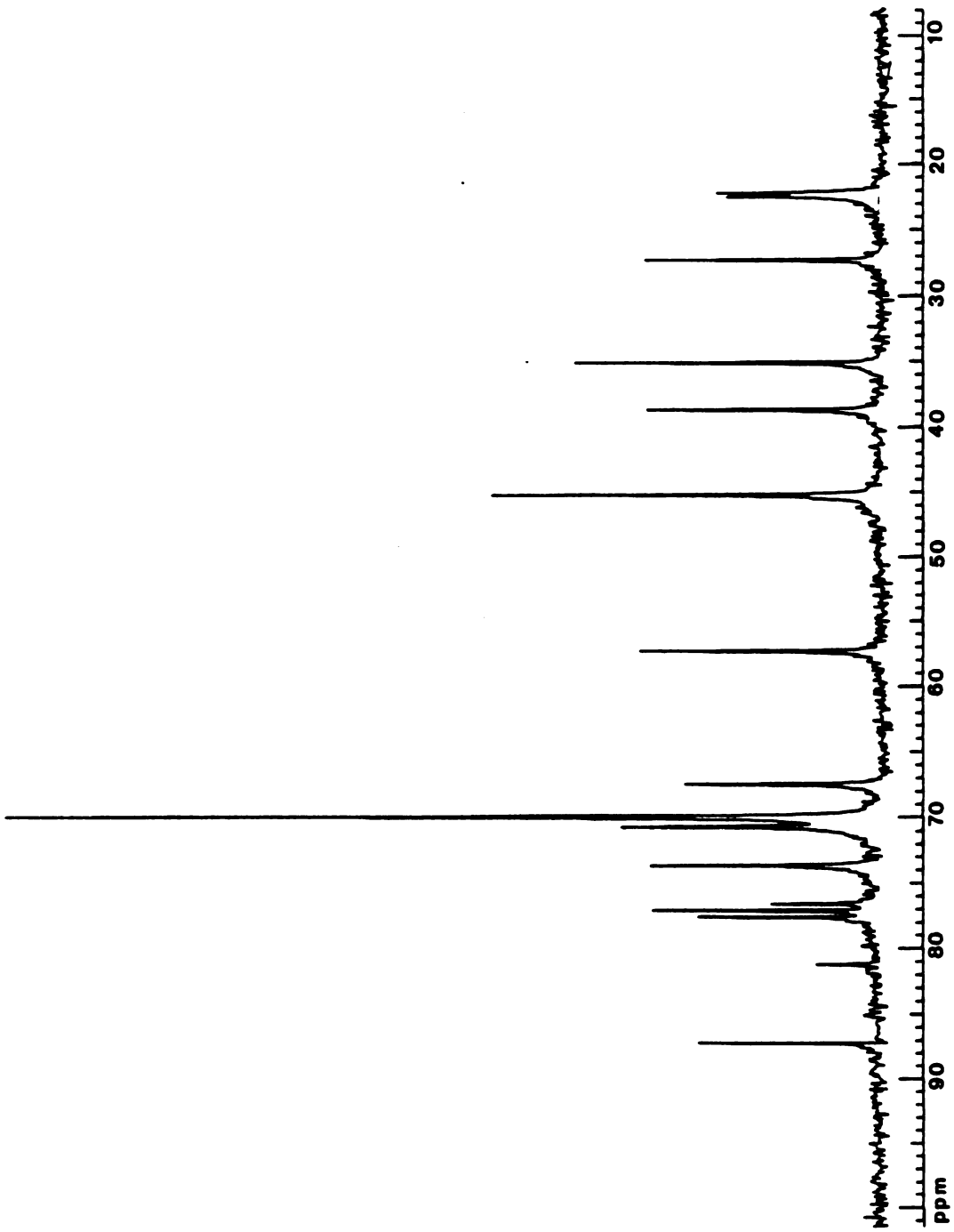


Figure 52. Broadband decoupled ^{13}C NMR of 16, R = i-pentyl.

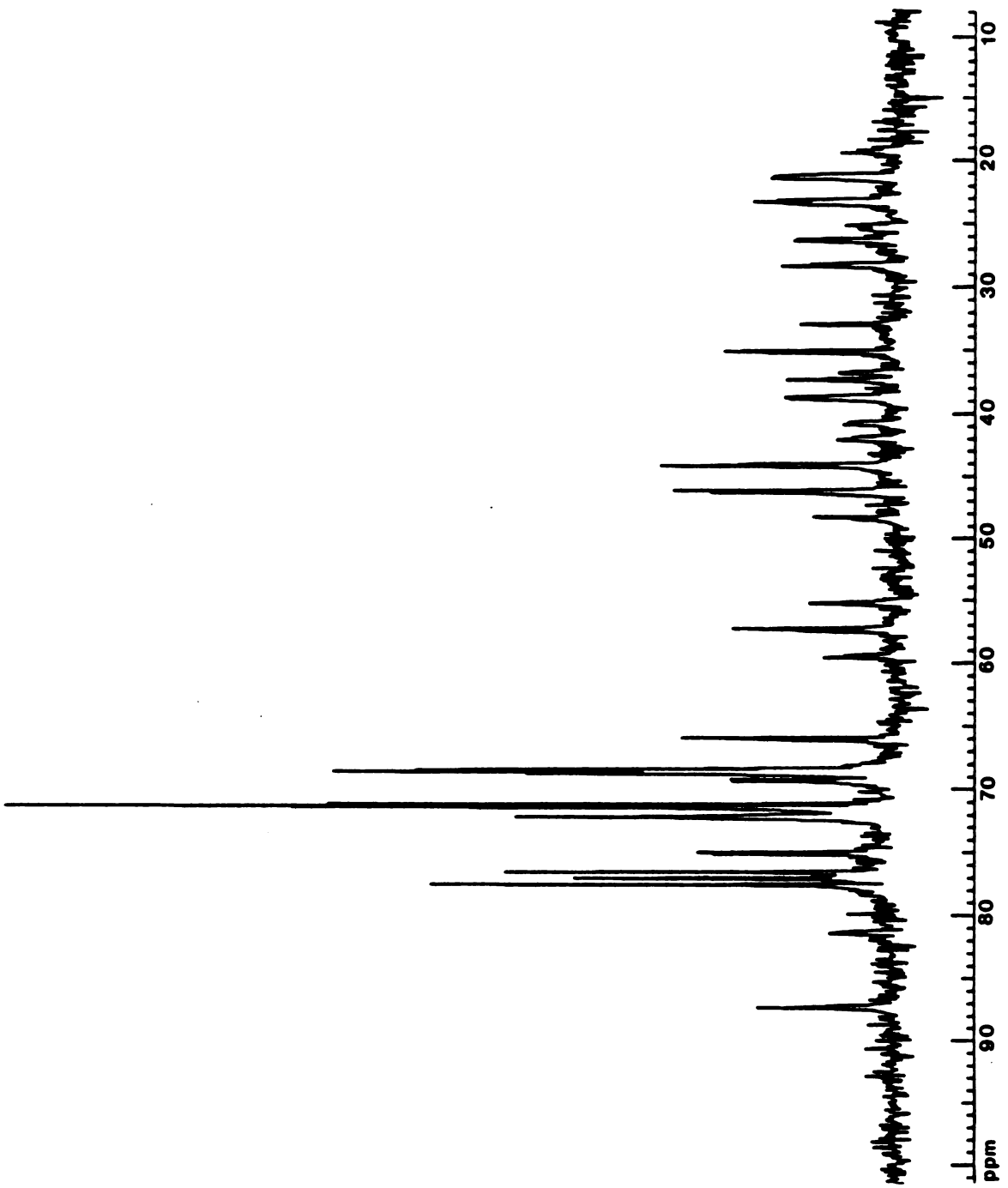


Figure 53. Gated decoupled ^{13}C NMR of 16, R = i-pentyl.

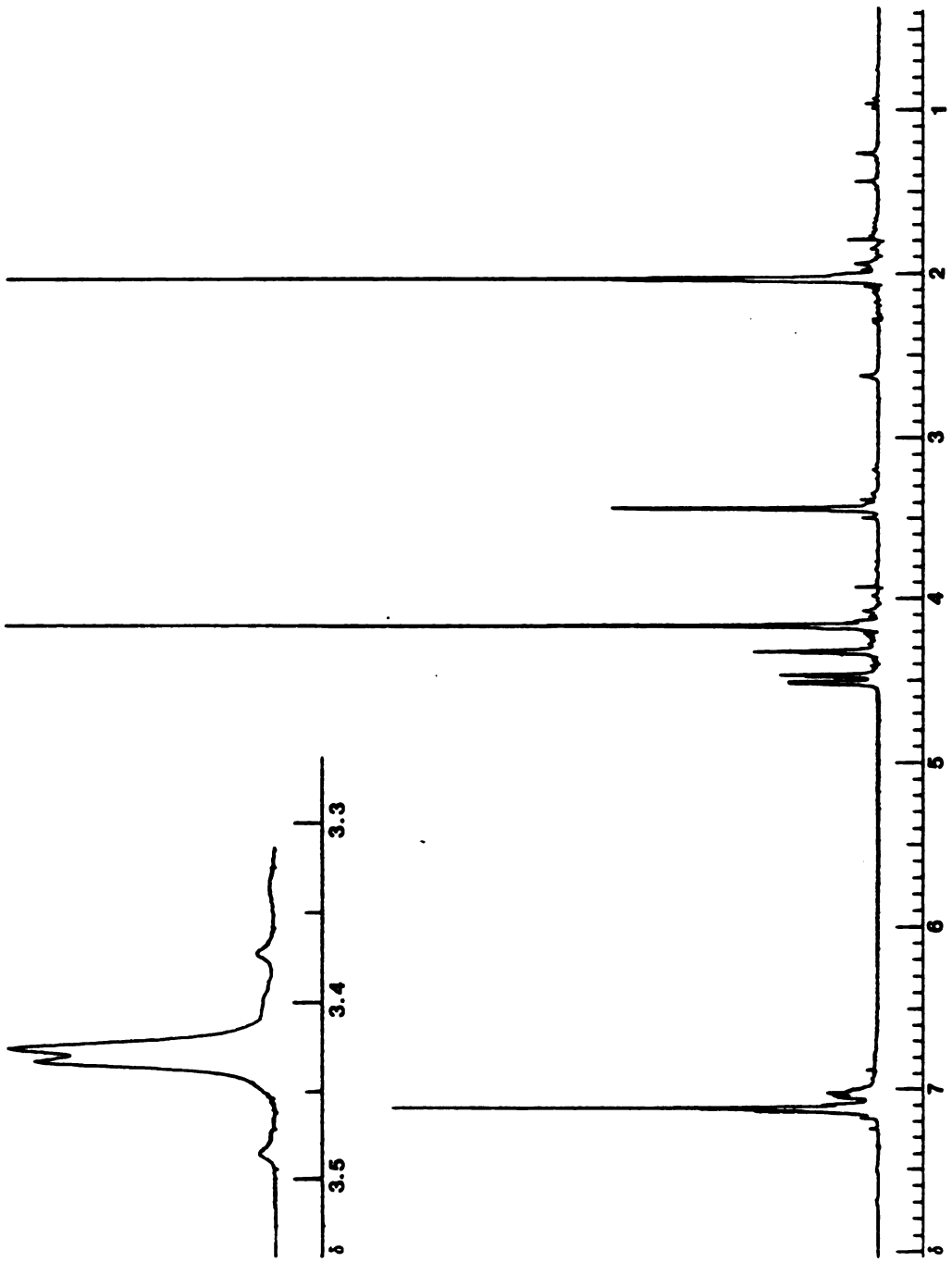


Figure 54. 250 MHz ^{1}H NMR of 16, R = Ph.

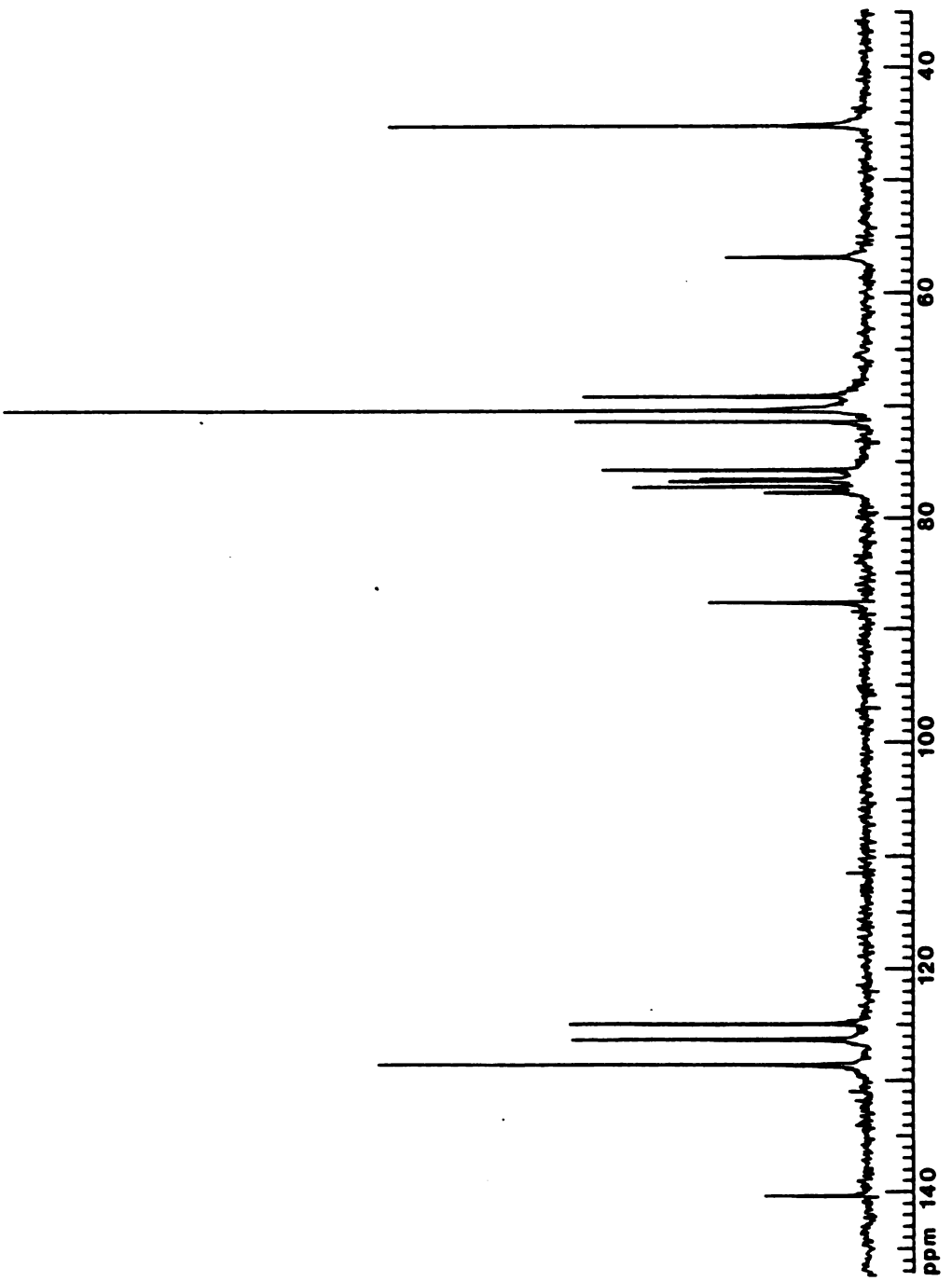


Figure 55. Broadband decoupled ^{13}C NMR of 16, R = Ph.

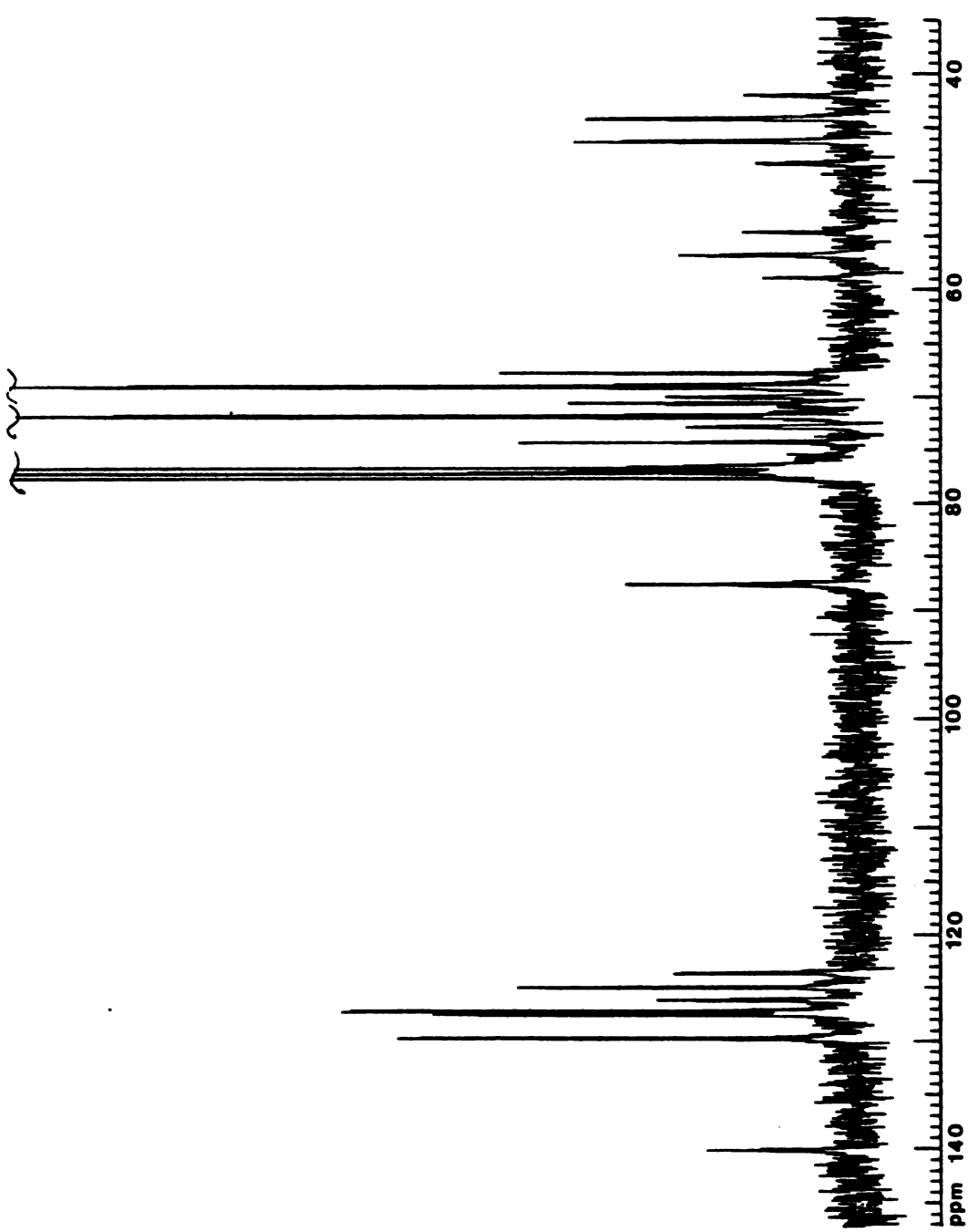


Figure 56. Gated decoupled ^{13}C NMR of 16, R = Ph.

Infrared spectral data for 1,1'-bis(phenylseleno)ferrocene (42, Figure 57)

This compound was made by Mr. Lie-Hang Shen. IR (Nujol, CsI) 466 (antisymmetric ring-Fe stretch), 493 (antisymmetric ring tilt), 685 (out-of-plane phenyl C-H bend), 729 (out-of-plane phenyl C-H bend), 820 (C-H bend perpendicular to Cp ring), 1010, 1150, 1575 cm^{-1} (phenyl C-C stretch).

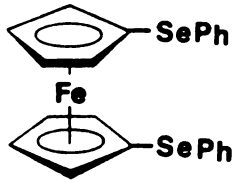


Figure 57. 1,1'-Bis(phenylseleno)ferrocene (42).

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