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PENTAMETHYLCYCLOPENTADIENYL DERIVATIVES OF TRANSITION METALS

V*. SOME PENTAMETHYLCYCLOPENTADIENYL AND ISOPROPENYLTETRAMETHYLCYCLOPENTADIENYLIRON CARBONYL DERIVATIVES

R.B. KING, W.M. DOUGLAS** and A. EFRATY***

Department of Chemistry, University of Georgia, Athens, Georgia, 30602 (U.S.A.)

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Summary

Acetylpentamethylcyclopentadiene, although it reacts with $Fe_2(CO)_9$ to give $[(CH_3)_5C_5Fe(CO)_2]_2$ as previously reported, has now been shown to react with $Fe(CO)_5$ in boiling 2,2,5-trimethylhexane to give the isopropenyltetramethylcyclopentadienyl derivative $[(CH_3C{=}CH_2)(CH_3)_4C_5Fe(CO)_2]_2$ contaminated with about 35% of the corresponding isopropyl derivative $[(CH_3CHCH_3)(CH_3)_4C_5Fe(CO)_2]_2$. The compounds $[R(CH_3)_4C_5Fe(CO)_2]_2$ ($R = CH_3$ and isopropenyl) react with sodium amalgam to form the corresponding sodium salts $Na[R(CH_3)_4C_5Fe(CO)_2]$ which react with appropriate halides to form the corresponding $R(CH_3)_4C_5Fe(CO)_2R'$ derivatives (R = methyl or isopropenyl; $R' = CH_3$, $Sn(C_6H_5)_3$, and $C(O)CH_3$). Halogenation of the compounds $[R(CH_3)_4C_5Fe(CO)_2]_2$ ($R = CH_3$ and isopropenyl) by various methods gives the corresponding halides $R(CH_3)_4C_5Fe(CO)_2X$ ($R = CH_3$, X = Br; R = isopropenyl, X = Cl and I).

Introduction

The reactions between acetylpentamethylcyclopentadiene and various iron carbonyls [2] make the pentamethylcyclopentadienyliron carbonyl derivative $[(CH_3)_5C_5Fe(CO)_2]_2$ readily available for the first time. This availability of $[(CH_3)_5C_5Fe(CO)_2]_2$ allows a comparison of its chemistry with that of the unsubstituted cyclopentadienyl derivative $[C_5H_5Fe(CO)_2]_2$.

In orders to study the chemistry of $[(CH_3)_5C_5Fe(CO)_2]_2$ we first attempted

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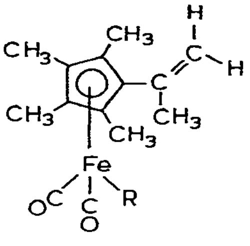
[*] For part IV of this series, see ref. 1.

[**] Post-doctoral research associate, 1971 - 1973.

[***] Post-doctoral research associate, 1968 - 1971. Present address: School of Chemistry, Rutgers University, New Brunswick, New Jersey, 08903 (U.S.A.).

to prepare this compound by treatment of acetylpentamethylcyclopentadiene with $Fe(CO)_5$, the most readily available iron carbonyl. We obtained a pentaalkylcyclopentadienyliron dicarbonyl dimer of the type $[R_5C_5Fe(CO)_2]_2$ with an infrared spectrum in the $\nu(CO)$ region essentially identical to that of the pentamethylcyclopentadienyl derivative $[(CH_3)_5C_5Fe(CO)_2]_2$. The proton NMR spectrum, although broadened by paramagnetic impurities, appeared to show only the expected single resonance for $[(CH_3)_5C_5Fe(CO)_2]_2$. We therefore used this material to prepare derivatives by methods such as halogenation or sodium amalgam reduction followed by addition of a halide. However, the NMR spectra of these derivatives and the mass spectrum of the methyl derivative $R_5C_5Fe(CO)_2CH_3$ were inconsistent with the formulation of these compounds as pentamethylcyclopentadienyl derivatives. This paper presents evidence supporting the formulation of these products derived from the $[R_5C_5Fe(CO)_2]_2$ obtained from iron pentacarbonyl and acetylpentamethylcyclopentadiene in boiling 2,2,5-trimethylhexane as mixtures of isopropenyltetramethylcyclopentadienyl derivatives of the type I (R = Cl, CH_3, $(C_6H_5)_3Sn$, etc.) and isopropyltetramethylcyclopentadienyl derivatives of the type II.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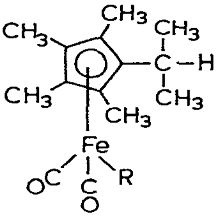
(II)

Once we determined, contrary to what we had earlier believed, that the treatment of acetylpentamethylcyclopentadiene with $Fe(CO)_5$ did not provide a satisfactory synthesis of $[(CH_3)_5C_5Fe(CO)_2]_2$, we turned to the treatment of acetylpentamethylcyclopentadiene with the more reactive $Fe_2(CO)_9$ to prepare authentic $[(CH_3)_5C_5Fe(CO)_2]_2$. Studies on the chemistry of these compounds indicated that the pentaalkylated cyclopentadienyl derivatives $[(CH_3)_5C_5Fe(CO)_2]_2$ and $[(CH_2{=}CCH_3)(CH_3)_4C_5Fe(CO)_2]_2$ undergo metal—metal bond cleavage with halogens and with sodium metal analogous to the unsubstituted derivative $[C_5H_5Fe(CO)_2]_2$, but the pentaalkylated cyclopentadienyl derivatives do not undergo as readily as the unsubstituted cyclopentadienyl derivative those reactions involving carbonyl loss such as formation of the corresponding $[R_5C_5FeCO]_4$ and $[R_5C_5FeCOSR']_2$ derivatives.

Experimental

Microanalyses (Tables 1 and 2) were carried out by Pascher Mikroanalytisches Laboratorium, Bonn, Germany; Meade Microanalytical Laboratory, Amherst, Massachusetts; and Mr. W. Swanson and co-workers of the microanalytical laboratory at the University of Georgia. Molecular weight determinations (Table 2) were determined by the commercial laboratories listed above using vapor pressure osmometry. Infrared spectra in the $\nu(CO)$ region (Tables 1 and 2)

TABLE 1

SOME NEW PENTAMETHYLCYCLOPENTADIENYL IRON CARBONYL DERIVATIVES

Compound	Color	M.p. (°C)	Analyses found (calcd.) (%)					Infrared spectrum [a]
			C	H	O	Fe	Other	ν(CO) cm^{-1}
$Me_5C_5Fe(CO)_2Me$	yellow	72 - 74	59.5 (59.5)	6.9 (6.9)	12.3 (12.2)	21.3 (21.4)		1988 s, 1936 s
$Me_5C_5Fe(CO)_2C_6F_5$	yellow	104 - 106	52.6 (52.2)	3.7 (3.6)		13.2 (13.5)		2023 s, 1965 s
$Me_5C_5Fe(CO)_2Sn(C_6H_5)_3$	yellow	150 - 152	60.4 (60.3)	5.1 (5.0)	5.4 (5.4)	9.5 (9.4)	20.2(Sn) (19.9(Sn))	1974 s, 1923 s
$Me_5C_5Fe(CO)_2Br$	red-brown	160 - 162	44.1 (44.2)	4.7 (4.6)	9.3 (9.8)	16.5 (17.1)	24.5(Br) (24.5(Br))	2033 s, 1978 s

[a] The ν(CO) frequencies of $(CH_3)_5C_5Fe(CO)_2CH_3$ were determined in cyclohexane solution. The remaining ν(CO) frequencies were determined in CH_2Cl_2 solutions.

TABLE 2

SOME ISOPROPENYLTETRAMETHYLCYCLOPENTADIENYLIRON CARBONYL DERIVATIVES

Compound [a]	Color	M.p. (°C)	Analyses found (calcd.) (%)						Infrared spectrum [c]	
			C	H	O	Fe	Other	Mol.wt.	ν(C=C)	ν(CO)
$[(MeCCH_2)Me_4C_5Fe(CO)_2]_2$	dark red	184 - 186	62.1 (61.5)	6.6 (6.2)						1934 s, 1765 s
$(MeCCH_2)Me_4C_5Fe(CO)_2Me$	yellow	59 - 64	62.2 (62.5)	7.2 (6.9)		19.1 (19.4)			1648 vvw	1993 s, 1939 s
$(MeCCH_2)Me_4C_5Fe(CO)_2(COMe)$	orange	liquid, b.p. 50°/0.001mm	60.8 (60.7)	6.4 (6.3)	15.1 (15.2)	17.7 (17.7)			[b]	2002 s, 1945 s, 1647 m [b]
$(MeCCH_2)Me_4C_5Fe(CO)_2$-$Sn(C_6H_5)_3$	yellow	140 - 143	61.0 (61.6)	4.4 (5.1)		9.1 (9.0)	19.3(Sn) (19.1(Sn))	617 (623)	~1630 vvw	1973 s, 1923 s
$(MeCCH_2)Me_4C_5Fe(CO)_2Cl$	red-orange	144 - 146	53.7 (54.5)	5.7 (5.5)		18.5 (18.1)	11.8(Cl) (11.5(Cl))	304 (308.5)	1646 vvw	2035 s, 1980 s
$(MeCCH_2)Me_4C_5Fe(CO)_2I$	brown	127 - 129	41.3 (42.1)	4.4 (4.2)	7.8 (8.0)	14.2 (14.0)	32.7(I) (31.9(I))		1648 vvw	2028 s, 1981 s

[a] These isopropenyltetramethylcyclopentadienyl derivatives are contaminated with 30 to 40% of the corresponding isopropyltetramethylcyclopentadienyl derivatives as indicated in Table 3.

[b] Acyl ν(CO) frequency. This obscures the much weaker ν(C=C) frequency.

[c] The ν(C=C) frequencies were determined in KBr pellets. The ν(CO) frequencies of $(CH_3CCH_2)(CH_3)_4C_5Fe(CO)_2CH_3$ and $(CH_3CCH_2)(CH_3)_4C_5Fe(CO)_2$-$(COCH_3)$ were determined in cyclohexane solution. The remaining ν(CO) frequencies were determined in CH_2Cl_2 solutions.

TABLE 3

PROTON NMR SPECTRA OF SOME ISOPROPENYLTETRAMETHYLCYCLOPENTADIENYLIRON CARBONYL DERIVATIVES

Compound	Proton NMR spectrum (τ(ppm))						
	Solvent	Olefinic =CHR	$CH_3C(R)=$	$(CH_3)_4C_5$	Other [a]	Isopropyl [b]	Isopropyl [c] (%)
$[(MeCCH_2)Me_4C_5Fe(CO)_2]_2$	$CDCl_3$	4.67, 4.97	7.91	8.36, 8.48		8.69d (7)	40
$(MeCCH_2)Me_4C_5Fe(CO)_2Me$	$CDCl_3$	4.85, 5.07	8.10	8.31, 8.36	10.15(CH_3Fe)	8.69d (7)	35
$(MeCCH_2)Me_4C_5Fe(CO)_2C(O)Me$	neat	4.73, 4.96	8.08	8.26	7.58 ($CH_3C(O)Fe$)	8.76d (7)	30
$(MeCCH_2)Me_4C_5Fe(CO)_2Cl$	$CDCl_3$	4.71, 4.94	8.09	8.23, 8.26		8.75d (7)	40
$(MeCCH_2)Me_4C_5Fe(CO)_2I$	$CDCl_3$	4.79, 5.02	8.04	8.04		8.78d (7)	35

[a] The resonance from the R group is listed here. [b] This refers to the position of the doublet (J = 7 Hz) methyl resonance of the isopropyl group in the $[(CH_3)_2CH](CH_3)_4C_5Fe(CO)_2R$ impurity. [c] This refers to the amount of the isopropyltetramethylcyclopentadienyl impurity in the isopropenyltetramethylcyclopentadienyl derivative. This was obtained by integration of the olefinic protons versus the isopropyl methyl protons (see text).

were taken in the indicated solvents and recorded on a Perkin—Elmer Model 621 spectrometer with grating optics. The proton NMR spectra (Table 3) were taken in $CDCl_3$ solution, unless otherwise indicated, and recorded at 60 MHz on a Perkin—Elmer Hitachi R-20 spectrometer. Melting points were taken on samples in capillaries and are uncorrected.

A nitrogen atmosphere was routinely provided for the following operations: (a) carrying out reactions with metal carbonyl derivatives; (b) handling filtered solutions of organometallic compounds; (c) filling evacuated vessels containing organometallic compounds. Tetrahydrofuran was purified by distillation over sodium benzophenone ketyl under nitrogen.

The $[(CH_3)_5C_5Fe(CO)_2]_2$ used in this work was prepared essentially according to the previously described [2] procedure using the reaction of $Fe_2(CO)_9$ [3] with acetylpentamethylcyclopentadiene in boiling 2,2,5-trimethylhexane. A reaction between 20 g (55 mmoles) of $Fe_2(CO)_9$ and 8.0 g (45 mmoles) of acetylpentamethylcyclopentadiene in 250 ml of degassed 2,2,5-trimethylhexane for 18 h at the boiling point gave 5.3 g (48% yield based on $(CH_3)_5C_5COCH_3$) of $[(CH_3)_5C_5Fe(CO)_2]_2$. The reaction between $Fe(CO)_5$ and pentamethylcyclopentadiene [4] according to the published procedure [5] was also used to prepare $[(CH_3)_5C_5Fe(CO)_2]_2$.

References to the preparations of the analogous unsubstituted cyclopentadienyliron carbonyl derivatives are cited after the titles of the preparations of the pentamethylcyclopentadienyl and isopropenyltetramethylcyclopentadienyl derivatives given below.

Preparation of the sodium salt $Na[(CH_3)_5C_5Fe(CO)_2]_2$ *[6]*

A solution of $[(CH_3)_5C_5Fe(CO)_2]_2$ (0.5 to 0.6 g) in tetrahydrofuran (400 ml per gram of iron complex) was stirred at room temperature for at least 4 h with excess dilute sodium amalgam. After removing the excess sodium amalgam, the resulting solution of the sodium salt $Na[(CH_3)_5C_5Fe(CO)_2]$ was used for the experiments described below. For the purpose of calculating the amount of sodium salt present, the yield was assumed to be quantitative.

Preparation of $(CH_3)_5C_5Fe(CO)_2CH_3$ *[6]*

A solution of 2 mmoles of $Na[(CH_3)_5C_5Fe(CO)_2]$ in 200 ml of tetrahydrofuran, prepared as described above, was treated dropwise with a solution of excess (1.5 ml, 3.42 g, 24 mmoles) of methyl iodide in 50 ml of tetrahydrofuran. After the addition of the methyl iodide was completed, the reaction mixture was stirred for 30 minutes at room temperature. Solvent was then removed at ~ 25°/35 mm. The residue was extracted with two 25 ml portions of hexane. The hexane extracts were concentrated to ~ 25 ml and then chromatographed on a 1.5 × 60 cm Florisil column. The main yellow band was eluted with hexane. Solvent was removed from the hexane eluate at ~ 25°/35 mm. Sublimation of the solid residue three times at ~ 30°/0.5 mm with careful removal of the first oily fractions gave 0.20 g (38% yield) of yellow $(CH_3)_5C_5Fe(CO)_2CH_3$, m.p. 72 - 74°, NMR ($CDCl_3$ solution): $\tau[(CH_3)_5C_5]$ 8.30, $\tau(CH_3Fe)$ 10.19.

Preparation of $(CH_3)_5C_5Fe(CO)_2(COCH_3)$ *[7]*

A solution of 1.1 mmoles of $Na[(CH_3)_5C_5Fe(CO)_2]$ in 200 ml of tetrahydrofuran, prepared as described above, was treated at −78° with 0.2 ml (0.22 g, 2.8 mmoles) of acetyl chloride. The reaction mixture was then allowed to warm to room temperature and stirred for 25 h at room temperature. Solvent was removed at 25°/35 mm. An extract of the residue in 50 ml of boiling hexane was chromatographed on a 1.5 × 60 cm Florisil column. The major yellow band was eluted with dichloromethane. Evaporation of this eluate followed by sublimation at 60°/0.1 mm gave 0.087 g (27% yield) of yellow $(CH_3)_5C_5Fe(CO)_2$-$(COCH_3)$, m.p. 70 - 71° (lit. [2] m.p. 72 - 73°). The infrared spectrum of this sample was identical to that of a sample of $(CH_3)_5C_5Fe(CO)_2(COCH_3)$ prepared from $Fe_2(CO)_9$ according to the published procedure [2].

Preparation of $(CH_3)_5C_5Fe(CO)_2Sn(C_6H_5)_3$ *[8]*

A solution of ~ 2 mmoles of $Na[(CH_3)_5C_5Fe(CO)_2]_2$ in 250 ml of tetrahydrofuran, prepared as described above, was treated dropwise with a solution of 1.0 g (2.7 mmoles) of triphenyltin chloride in 50 ml of tetrahydrofuran. The reaction mixture was then stirred for 1 h at room temperature. Chromatography of the reaction mixture as described above for the preparation of $(CH_3)_5C_5Fe$-$(CO)_2CH_3$ gave a single yellow band. Elution of this band with a 1/4 dichloromethane—hexane mixture followed by evaporation of the eluate and crystallization of the residue from boiling hexane gave 0.76 g (54% yield) of yellow $(CH_3)_5C_5Fe(CO)_2Sn(C_6H_5)_3$. The proton NMR spectrum of $(CH_3)_5C_5Fe(CO)_2$-$Sn(C_6H_5)_3$ ($CDCl_3$ solution) exhibited phenyl resonances at τ 2.51 and 2.87 and a methyl resonance at τ 8.34.

Preparation of $(CH_3)_5C_5Fe(CO)_2Br$ *[9]*

A solution of 1.0 g(~ 2.0 mmoles) of $[(CH_3)_5C_5Fe(CO)_2]_2$ in 50 ml of dichloromethane was treated dropwise with a solution of 0.325 g (2 mmoles) of bromine in 20 ml of dichloromethane. After stirring at room temperature for 4 h, solvent was removed at ~ 25°/35 mm. The product was purified by recrystallization from a mixture of dichloromethane and hexane to give 0.75 g (57% yield) of red-brown $(CH_3)_5C_5Fe(CO)_2Br$. The analytical sample, m.p. 160 - 162°, proton NMR: $\tau(CH_3)$ in $CDCl_3$ 8.17, was purified by sublimation at 65 - 70°/ 0.01 mm.

Preparation of $(CH_3)_5C_5Fe(CO)_2C_6F_5$ *[10]*

A solution of pentafluorophenyllithium was prepared by stirring at −78° for 40 minutes 0.25 g (~ 1.5 mmoles) of pentafluorobenzene with 0.7 ml (~ 1.1 mmoles) of a 1.6 *M* hexane solution of n-butyllithium in 7 ml of dry diethyl ether. This pentafluorophenyllithium solution was treated dropwise with a solution of 0.33 g (1 mmole) of $(CH_3)_5C_5Fe(CO)_2Br$ in 30 ml of diethyl ether while keeping the reaction mixture at −78°. The reaction mixture was stirred at −78° for 2 h and at 25° for an additional 12 h. Solvent was removed at ~ 25°/35 mm. A solution of the residue in pentane was chromatographed on a Florisil column. The major yellow band was eluted with pentane. Solvent was removed from this eluate at ~ 25°/35 mm. The residue was recrystallized by dissolving in pentane at room temperature and cooling the filtered solution to −78° to give 0.185 g. (41% yield) of yellow $(CH_3)_5C_5Fe(CO)_2C_6F_5$, m.p. 104 - 106°. The proton NMR spectrum of $(CH_3)_5C_5Fe(CO)_2C_6F_5$ ($CDCl_3$ solution) exhibited a singlet methyl resonance at τ 8.26. The ^{19}F NMR spectrum of $(CH_3)_5C_5Fe(CO)_2C_6F_5$ exhibited resonances at ϕ 108.8, ~ 160, and 164.8 corresponding to the *ortho*, *para*, and *meta* fluorine atoms, respectively, of the pentafluorophenyl group.

Preparation of $[(CH_3C{=}CH_2)(CH_3)_4C_5Fe(CO)_2]_2$

The isopropenyltetramethylcyclopentadienyl derivative $[(CH_3C{=}CH_2)(CH_3)_4C_5Fe(CO)_2]_2$ was prepared by boiling under reflux acetylpentamethylcyclopentadiene with excess $Fe(CO)_5$ in 2,2,5-trimethylhexane for 20 - 24 h using a procedure essentially identical to that previously reported [2] for the reaction of acetylpentamethylcyclopentadiene with $Fe(CO)_5$ to give $[(CH_3)_5C_5Fe(CO)_2]_2$. The $[(CH_3C{=}CH_2)(CH_3)_4C_5Fe(CO)_2]_2$ was purified by chromatography on alumina in dichloromethane solution. Yields were 50 to 65%.

Preparations of $(CH_3C{=}CH_2)(CH_3)_4C_5Fe(CO)_2CH_3$ *[6] and* $(CH_3C{=}CH_2)(CH_3)_4C_5Fe(CO)_2Sn(C_6H_5)_3$ *[8]*

The procedures used for conversion of $[(CH_3C{=}CH_2)(CH_3)_4C_5Fe(CO)_2]_2$ to the methyl derivative $(CH_3C{=}CH_2)(CH_3)_4C_5Fe(CO)_2CH_3$ and the triphenyltin derivative $(CH_3C{=}CH_2)(CH_3)_4C_5Fe(CO)_2Sn(C_6H_5)_3$ were essentially identical to the procedures described above for conversions of $[(CH_3)_5C_5Fe(CO)_2]_2$ to the corresponding derivatives $(CH_3)_5C_5Fe(CO)_2CH_3$ and $(CH_3)_5C_5Fe(CO)_2Sn(C_6H_5)_3$.

Preparation of $(CH_3C{=}CH_2)(CH_3)_4C_5Fe(CO)_2(COCH_3)$ *[7]*

The conversion of $[(CH_3C{=}CH_2)(CH_3)_4C_5Fe(CO)_2]_2$ to the acetyl derivative $(CH_3C{=}CH_2)(CH_3)_4C_5Fe(CO)_2(COCH_3)$ was carried out in a manner essentially identical to the conversion of $[(CH_3)_5C_5Fe(CO)_2]_2$ to the corresponding acetyl derivative $(CH_3)_5C_5Fe(CO)_2(COCH_3)$ until completion of the chromatography. However, since the acetyl derivative $(CH_3C{=}CH_2)(CH_3)_4C_5Fe(CO)_2(COCH_3)$ is liquid rather than solid at room temperature, evaporative distillation at ~ 50°/0.001 mm rather than vacuum sublimation was used for the final purification.

Preparation of $(CH_3C{=}CH_2)(CH_3)_4C_5Fe(CO)_2Cl$

(a) From $[(CH_3C{=}CH_2)(CH_3)_4C_5Fe(CO)_2]_2$ *and* $FeCl_3 \cdot 6H_2O$ *[11]*. A solution of 0.5 g (0.92 mmoles) of $[(CH_3C{=}CH_2)(CH_3)_4C_5Fe(CO)_2]_2$ in 25 ml of acetone was treated dropwise with a solution of 0.55 g (2 mmoles) of $FeCl_3 \cdot 6H_2O$ in 25 ml of acetone. After stirring for 90 minutes the reaction mixture was treated dropwise with a solution of 1.75 g (30 mmoles) of sodium chloride in 50 ml of water. The acetone was then removed at ~ 25°/35 mm. The resulting aqueous solution was extracted with 100 ml of dichloromethane. After drying over anhydrous magnesium sulfate the filtered dichloromethane solution was treated with 150 ml of hexane. The solution was then concentrated to ~ 25 ml at 25°/35 mm. Cooling to ~ —78° precipitated 0.27 g (47% yield) of red-orange crystalline $(CH_3C{=}CH_2)(CH_3)_4C_5Fe(CO)_2Cl$, m.p. 137 - 139°. The analytical sample, m.p. 144 - 146°, was purified by sublimation at ~ 90°/0.01 mm and crystallization from a mixture of dichloromethane and hexane.

(b) From $Na[(CH_3C{=}CH_2)(CH_3)_4C_5Fe(CO)_2]$ *and* $HgCl_2$. The chloride $(CH_3C{=}CH_2)(CH_3)_4C_5Fe(CO)_2Cl$ was isolated in minor quantities from numer-

ous reactions of $Na[(CH_3C{=}CH_2)(CH_3)_4C_5Fe(CO)_2]$ with various chlorides such as acetyl chloride, diphenylchlorophosphine, disulfur dichloride, and mercuric chloride. The reaction of $Na[(CH_3C{=}CH_2)(CH_3)_4C_5Fe(CO)_2]$ with mercuric chloride is given as representative of reactions of this type.

A solution of ~ 2.3 mmoles of $Na[(CH_3C{=}CH_2)(CH_3)_4C_5(CO)_2]$ in 200 ml of tetrahydrofuran was treated dropwise with a solution of 0.4 g (1.47 mmoles) of mercuric chloride in 50 ml of tetrahydrofuran. After stirring for 1 h at room temperature, solvent was removed at ~ 25°/35 mm. The residue was extracted with a hot 2/3 dichloromethane—hexane mixture and the extract was chromatographed on a 1.5 × 60 cm Florisil column. A red band of $[(CH_3C{=}CH_2)(CH_3)_4C_5Fe(CO)_2]_2$ was first eluted with a 2/3 mixture of dichloromethane and hexane. The orange band of $(CH_3C{=}CH_2)(CH_3)_4C_5Fe(CO)_2Cl$ was next eluted with pure dichloromethane. Evaporation of the eluate followed by crystallization from a mixture of dichloromethane and hexane gave 0.08 g (~ 11% yield) of $(CH_3C{=}CH_2)(CH_3)_4C_5Fe(CO)_2Cl$.

Preparation of $(CH_3C{=}CH_2)(CH_3)_4C_5Fe(CO)_2I$ *[12]*

A solution of 5.0 g (9.2 mmoles) of $[(CH_3C{=}CH_2)(CH_3)_4C_5Fe(CO)_2]_2$ in 100 ml of chloroform was treated dropwise with a solution of 2.5 g (10 mmoles) of iodine in 250 ml of chloroform over a period of 2½ h. The reaction mixture was then stirred an additional 2 h at room temperature and boiled under reflux for 1 h. Solvent was removed at 40°/35 mm and the product washed with 50 ml of pentane to give 7.0 g (95% yield) of black $(CH_3C{=}CH_2)(CH_3)_4C_5Fe(CO)_2I$. The analytical sample, m.p. 142 - 144°, was obtained by chromatography on Florisil in a 1/3 mixture of dichloromethane and hexane followed by several recrystallizations from mixtures of dichloromethane and hexane.

The iodide $(CH_3C{=}CH_2)(CH_3)_4C_5Fe(CO)_2I$ was also obtained in ~ 5% yield by reaction of ~ 2.2 mmoles of $Na[(CH_3C{=}CH_2)(CH_3)_4C_5Fe(CO)_2]$ with 2.5 ml (3.1 g, ~ 10 mmoles) of 2-iodoheptafluoropropane by a procedure similar to that given above for the reaction of $Na[(CH_3C{=}CH_2)(CH_3)_4C_5Fe(CO)_2]$ with mercuric chloride.

Mass spectra

The following mass spectra were run on the University of Georgia Perkin—Elmer Hitachi RMU-6 mass spectrometer at 70 eV with a chamber temperature of 110° and sample temperatures of 60 - 70°. Relative intensities are given in parentheses.

A. $(CH_3)_5C_5Fe(CO)_2CH_3$: $C_{10}H_{15}Fe(CO)_2CH_3^+$ (18), $C_{10}H_{15}Fe(CO)_2^+$ (3), $C_{10}H_{15}FeCOCH_3^+$ (19), $C_{10}H_{15}FeCO^+$ (7), $C_{11}H_{18}Fe^+$ (11), $C_{10}H_{15}Fe^+$ (28), $C_{10}H_{14}Fe^+$ (100), $C_9H_{10}Fe^+$ (15), $C_8H_{10}Fe^+$ (2), $C_8H_8Fe^+$(2), $C_7H_{10}Fe^+$ (2), $C_7H_8Fe^+$ (1), $C_{10}H_{15}^+$ (6), $C_{10}H_{14}^+$ (4), $C_{10}H_{13}^+$ (20), $C_{10}H_{12}^+$ (4), $C_9H_{11}^+$ (11), $C_9H_{10}^+$ (3), $C_9H_9^+$ (6), $C_9H_7^+$ (2), $C_8H_{11}^+$ (2), $C_8H_9^+$ (8), $C_8H_7^+$ (2), $C_7H_{11}^+$ (2), $C_7H_9^+$ (2), $C_7H_7^+$ (7), $C_6H_7^+$ (3), $C_6H_5^+$ (4), Fe^+ (8), $C_3H_5^+$ (4), $C_3H_3^+$ (2), $C_{10}H_{15}FeCO^{++}$ (1), $C_{10}H_{15}Fe^{++}$ (2). Metastable ions: *m/e* 209 s ($C_{10}H_{15}Fe(CO)_2$-$CH_3^+ \rightarrow C_{10}H_{15}FeCOCH_3^+ + CO$), *m/e* 194.2 w ($C_{10}H_{15}Fe(CO)_2^+ \rightarrow C_{10}H_{15}FeCO^+ + CO$), *m/e* 181 m ($C_{10}H_{15}FeCOCH_3^+ \rightarrow C_{11}H_{18}Fe^+ + CO$), *m/e* 166.5 m ($C_{10}H_{15}FeCO^+ \rightarrow C_{10}H_{15}Fe^+ + CO$), *m/e* 159.5 s ($C_{10}H_{14}Fe^+ \rightarrow C_9H_{10}Fe^+ + CH_4$), *m/e* 139.5 m ($C_{10}H_{15}Fe(CO)_2CH_3^+ \rightarrow C_{10}H_{15}Fe^+ + 2CO + CH_3$), and *m/e* 113 w ($C_9H_9^+ \rightarrow C_9H_7^+ + H_2$).

B. $(CH_3C{=}CH_2)(CH_3)_4C_5Fe(CO)_2CH_3$. $C_{12}H_{19}Fe(CO)_2CH_3^+$ (2), $C_{12}H_{17}Fe(CO)_2CH_3^+$ (6), $C_{12}H_{17}Fe(CO)_2^+$ (1), $C_{10}H_{15}Fe(CO)_2CH_3^+$ (21), $C_{12}H_{17}FeCOCH_3^+$ (6), $C_{10}H_{15}Fe(CO)_2^+$ (4), $C_{12}H_{17}FeCO^+$ (3), $C_{10}H_{15}FeCOCH_3^+$ (23), $C_{13}H_{20}Fe^+$ (7), $C_{10}H_{15}FeCO^+$ (9), $C_{12}H_{18}Fe^+$ (6), $C_{12}H_{17}Fe^+$ (9), $C_{12}H_{16}Fe^+$ (26), $C_{11}H_{18}Fe^+$ (10), $C_{11}H_{14}Fe^+$ (41), $C_{10}H_{15}Fe^+$ (34), $C_{10}H_{14}Fe^+$ (100), $C_9H_{12}Fe^+$ (12), $C_9H_{10}Fe^+$ (20), $C_{11}H_{18}^+$ (8), $C_{10}H_{15}^+$ (15), $C_{10}H_{13}^+$ (26), $C_9H_{15}^+$ (6), $C_9H_{13}^+$ (5), $C_9H_{11}^+$ (21), $C_9H_9^+$ (8), $C_9H_7^+$ (6), $C_8H_{11}^+$ (6), $C_8H_9^+$ (11), $C_7H_7^+$ (14), $C_6H_7^+$ (6), $C_6H_5^+$ (7), Fe^+ (11), $C_3H_7^+$ (17), $C_3H_5^+$ (9), $C_3H_3^+$ (6), $C_{10}H_{15}FeCO^{2+}$ (0.5), $C_{12}H_{17}Fe^{2+}$ (0.4), and $C_{10}H_{15}Fe^{++}$ (1). Metastable ions at 209 w, 181 w, 159.1 m (same assignments as the corresponding metastable ions in the mass spectrum of $(CH_3)_5C_5Fe(CO)_2CH_3$ above), 175.3 m ($C_{11}H_{18}Fe^+ \rightarrow C_{10}H_{14}Fe^+ + CH_4$), and 143.5 m ($C_{11}H_{18}Fe^+ \rightarrow C_9H_{12}Fe^+ + C_2H_6$).

Discussion

The dark red crystalline product from the reaction of acetylpentamethylcyclopentadiene and $Fe(CO)_5$ previously [2] believed to be $[(CH_3)_5C_5Fe(CO)_2]_2$ had the reactivity expected for an $[R_5C_5Fe(CO)_2]_2$ derivative. For example, it reacted with sodium amalgam to give a solution with the appearance expected for a sodium salt of the type $Na[R_5C_5Fe(CO)_2]$. This solution reacted with halides such as methyl iodide and triphenyltin chloride to give compounds with the expected colors and general physical properties for the corresponding $R_5C_5Fe(CO)_2R'$ ($R' = Sn(C_6H_5)_3$ and CH_3) derivatives. Also, reaction of this product from acetylpentamethylcyclopentadiene and $Fe(CO)_5$ with halogens or other halogenating agents gave products with the expected colors and general physical properties for the corresponding $R_5C_5Fe(CO)_2X$ (X = Cl and I) derivatives.

A more detailed investigation of these $R_5C_5Fe(CO)_2R'$ derivatives revealed properties inconsistent with their formulation as simple pentamethylcyclopentadienyl derivatives. Their carbon and hydrogen analyses were consistently high for the expected $(CH_3)_5C_5Fe(CO)_2R'$ derivatives. Their proton NMR spectra did not exhibit only a single sharp methyl resonance in addition to any resonances expected for the R′ group. The σ-acetyl derivative $R_5C_5Fe(CO)_2(COCH_3)$ was a liquid at room temperature in contrast to the reported [2] $(CH_3)_5C_5$-$Fe(CO)_2(COCH_3)$ from the reaction of acetylpentamethylcyclopentadiene with $Fe_2(CO)_9$ which is a yellow crystalline solid at room temperature. The mass spectrum of the σ-methyl derivative $R_5C_5Fe(CO)_2CH_3$ (i.e. $R' = CH_3$) exhibited an apparent molecular ion at 26 *m/e* units above the expected position for the molecular ion of $(CH_3)_5C_5Fe(CO)_2CH_3$. In addition, this apparent molecular ion underwent the fragmentations such as losses of CO and CH_3 which would be expected for the molecular ion of a compound of the type $R_5C_5Fe(CO)_2CH_3$.

The failure of the $[R_5C_5Fe(CO)_2]_2$ product from $Fe(CO)_5$ and acetylpentamethylcyclopentadiene to be the desired $[(CH_3)_5C_5Fe(CO)_2]_2$ forced us to use less convenient methods for the preparation of the $[(CH_3)_5C_5Fe(CO)_2]_2$ required for this work. Most of this $[(CH_3)_5C_5Fe(CO)_2]_2$ was obtained from acetylpentamethylcyclopentadiene and $Fe_2(CO)_9$ [2] although material prepared from the more difficultly accessible pentamethylcyclopentadiene [4] and

$Fe(CO)_5$ [5] was also used. Reactions of the $[(CH_3)_5C_5Fe(CO)_2]_2$ prepared by either of these two methods gave $R_5C_5Fe(CO)_2R'$ derivatives with properties completely consistent with their formulations as the pentamethylcyclopentadienyl derivatives $(CH_3)_5C_5Fe(CO)_2R'$. This indicated that the difficulties in obtaining $(CH_3)_5C_5Fe(CO)_2R'$ derivatives from the $[R_5C_5Fe(CO)_2]_2$ compound from $Fe(CO)_5$ and acetylpentamethylcyclopentadiene arose from the failure of this product to be the desired $[(CH_3)_5C_5Fe(CO)_2]_2$ rather than from some peculiar transformation of $[(CH_3)_5C_5Fe(CO)_2]_2$ under the influence of the reagents used to prepare the $R_5C_5Fe(CO)_2R'$ derivatives, generally sodium amalgam to prepare the sodium salt $Na[R_5C_5Fe(CO)_2]$ or halogenating agents to prepare the halides $R_5C_5Fe(CO)_2X$.

The simple reactions of pure $[(CH_3)_5C_5Fe(CO)_2]_2$ prepared either from $Fe_2(CO)_9$ and acetylpentamethylcyclopentadiene [2] or from $Fe(CO)_5$ and pentamethylcyclopentadiene [5] were unexceptional. Reaction of $[(CH_3)_5C_5$-$Fe(CO)_2]_2$ with sodium amalgam in tetrahydrofuran gave an orange-brown solution containing the expected $Na[(CH_3)_5C_5Fe(CO)_2]$, since it reacted with methyl iodide to give $(CH_3)_5C_5Fe(CO)_2CH_3$ and with triphenyltin chloride to give $(CH_3)_5C_5Fe(CO)_2Sn(C_6H_5)_3$. Reaction of the solution of $Na[(CH_3)_5C_5$-$Fe(CO)_2]$ with acetyl chloride gave yellow crystalline $(CH_3)_5C_5Fe(CO)_2(COCH_3)$ shown to be identical to the product of this formulation obtained in low yield from $Fe_2(CO)_9$ and acetylpentamethylcyclopentadiene [2], thereby confirming further this previously proposed formulation of the latter product. Reaction of $[(CH_3)_5C_5Fe(CO)_2]_2$ with bromine in an inert solvent gave the bromide $(CH_3)_5C_5Fe(CO)_2Br$. This reacted with pentafluorophenyllithium to give the corresponding pentafluorophenyl derivative $(CH_3)_5C_5Fe(CO)_2C_6F_5$.

The major question arising from this work is the nature of the peculiar $[R_5C_5Fe(CO)_2]_2$ compound from $Fe(CO)_5$ and acetylpentamethylcyclopentadiene. The mass spectrum of the σ-methyl derivative obtained from this $[R_5C_5Fe(CO)_2]_2$ compound indicates the stoichiometry $C_{12}H_{17}Fe(CO)_2CH_3$; this stoichiometry is also consistent with the analytical data. The following inteteresting features of the NMR spectrum of $C_{12}H_{17}Fe(CO)_2CH_3$ are not found in the much simpler NMR spectrum of $(CH_3)_5C_5Fe(CO)_2CH_3$: (1) two olefinic resonances around τ 5; (2) a methyl resonance around τ 8 distinctly separated from the methyl resonances at slightly higher chemical shifts associated with methyl groups bonded to the cyclopentadienyl ring; (3) a doublet (J 7 Hz) around τ 8.7. The first two features of the proton NMR spectrum of $C_{12}H_{17}Fe(CO)_2CH_3$ may be interpreted on the basis of its formulation as the isopropenyltetramethylcyclopentadienyl derivative I ($R = CH_3$) which has the required stoichiometry. The olefinic resonances around τ 5 can be assigned to the two non-equivalent olefinic protons of the isopropenyl substituent on the cyclopentadienyl ring. Similarly, the "isolated" methyl resonance around τ 8 may be assigned to the methyl group bonded to an uncomplexed olefinic carbon atom in the isopropenyl substituent. In the isopropenyltetramethylcyclopentadienyl derivative $(CH_3C{=}CH_2)(CH_3)_4C_5Fe(CO)_2CH_3$ (I: $R = CH_3$) the four methyl substituents on the cyclopentadienyl ring occur in two non-equivalent pairs consistent with the observation of two methyl resonances of approximately equal relative intensities around τ 8.3.

Formulation of $C_{12}H_{17}Fe(CO)_2CH_3$ as the isopropenyltetramethylcyclopentadienyl derivative $(CH_3C{=}CH_2)(CH_3)_4C_5Fe(CO)_2CH_3$ (I: R = CH_3) accounts for all of the "unusual" features of its NMR spectrum except for the doublet (J 7 Hz) around τ 8.7. This doublet can arise from the isopropyl methyl protons of an isopropyltetramethylcyclopentadienyl contaminant $(CH_3CHCH_3)(CH_3)_4C_5Fe(CO)_2CH_3$ (II: R = CH_3). The expected resonance from the single saturated proton of the isopropyl substituent in the isopropyltetramethylcyclopentadienyl contaminant II (R = CH_3) was not observed, but it would be expected to be split (J 7 Hz) by the six isopropyl methyl protons and hence would be too weak to be observed above the noise. Integration of the NMR spectrum of $C_{12}H_{17}Fe(CO)_2CH_3$ indicated that the isopropyl derivative $(CH_3CHCH_3)(CH_3)_4C_5Fe(CO)_2CH_3$ (II: R = CH_3) represented about 35% of the material. The presence of the isopropyltetramethylcyclopentadienyl derivative II (R = CH_3) in the sample of $C_{12}H_{17}Fe(CO)_2CH_3$ is also supported by an ion in the mass spectrum corresponding to $C_{12}H_{19}Fe(CO)_2CH_3^+$. The intensity of $C_{12}H_{19}Fe(CO)_2CH_3^+$ relative to $C_{12}H_{17}Fe(CO)_2CH_3^+$ in the mass spectrum of $C_{12}H_{17}Fe(CO)_2CH_3$ is about 1/3 consistent with the analysis by NMR integration of the $C_{12}H_{17}Fe(CO)_2CH_3$ cited above. Elucidation of the fragmentation pattern of the isopropyltetramethylcyclopentadienyl derivative II (R = CH_3) is prevented by the coincidence of the nominal m/e values of ions containing $C_{12}H_{19}Fe$ units and the corresponding ions containing $C_{10}H_{15}FeCO$ units. These spectroscopic observations all indicate that the isopropenyltetramethylcyclopentadienyl derivative $(CH_3C{=}CH_2)(CH_3)_4C_5Fe(CO)_2CH_3$ prepared from the $[R_5C_5Fe(CO)_2]_2$ compound from $Fe(CO)_5$ and acetylpentamethylcyclopentadiene is not pure but instead is contaminated with about 35% of the corresponding isopropyltetramethylcyclopentadienyl derivative $(CH_3CHCH_3)(CH_3)_4C_5Fe(CO)_2CH_3$ which cannot be separated by the normal chromatographic purification techniques used in this work and which would have a negligible effect on the elemental analyses of the $(CH_3C{=}CH_2)(CH_3)_4C_5Fe(CO)_2CH_3$. The inability to separate by normal techniques two $R(CH_3)_4C_5Fe(CO)_2CH_3$ derivatives with only slightly different alkyl groups for the R substituents is scarcely surprising.

A further test of the proposed structure of the isopropenyltetramethylcyclopentadienyl derivative $(CH_3C{=}CH_2)(CH_3)_4C_5Fe(CO)_2CH_3$ (I: R = CH_3) would be the ability to hydrogenate catalytically the uncomplexed carbon—carbon double bond of the isopropenyl substituent to give the corresponding isopropyltetramethylcyclopentadienyl derivative $(CH_3CHCH_3)(CH_3)_4C_5Fe(CO)_2CH_3$ (II: R = CH_3) which would be identical to the observed contaminant. However, the isopropenyltetramethylcyclopentadienyl derivative I (R = CH_3) was inert to catalytic atmospheric pressure hydrogenation using either 10% palladium on charcoal in ethanol or $[(C_6H_5)_3P]_3RhCl$ in benzene as catalysts. The isopropenyl double bond in I (R = CH_3) may be blocked too much by large substituents to be susceptible to catalytic hydrogenation under conditions mild enough to maintain the basic organometallic structural features.

These observations on the methyl derivative $C_{12}H_{17}Fe(CO)_2CH_3$ demonstrate clearly that the product from the reaction of $Fe(CO)_5$ with acetylpentamethylcyclopentadiene is primarily the isopropenyltetramethylcyclopentadienyl derivative $[(CH_3C{=}CH_2)(CH_3)_4C_5Fe(CO)_2]_2$ rather than the pentamethylcyclopentadienyl derivative $[(CH_3)_5C_5Fe(CO)_2]_2$. Reinvestigation of the proton NMR spectrum of a sample of the dark red product from the reaction between $Fe(CO)_5$ and acetylpentamethylcyclopentadiene which had been carefully purified by column chromatography (Table 3) revealed the same basic features found in the NMR spectrum of the methyl derivative $C_{12}H_{17}Fe(CO)_2$-CH_3, i.e. the olefinic resonances around $\tau 5$, the non-equivalent methyl resonances, and the relatively weak isopropyl methyl doublet around τ 8.7. These had been overlooked in the proton NMR spectrum of the product obtained in our previously published [2] study of the reaction of $Fe(CO)_5$ with acetylpentamethylcyclopentadiene because of small amounts of paramagnetic impurities in the earlier sample which broadened the spectrum sufficiently to prevent separation of the non-equivalent methyl resonances and which reduced the signal-to-noise ratio sufficiently to prevent observation of the olefinic resonances and the much weaker methyl resonances from the isopropyltetramethylcyclopentadienyl impurity.

Our observation of isopropenyltetramethylcyclopentadienyl and isopropyltetramethylcyclopentadienyl derivatives as products from the reaction of $Fe(CO)_5$ with acetylpentamethylcyclopentadiene can be rationalized by the reaction scheme depicted in Fig. 1. Deoxygenation of acetylpentamethylcyclopentadiene with $Fe(CO)_5$ gives (pentamethylcyclopentadienyl)methylcarbene IIIa. This carbene can then undergo a methyl migration to give 1,2,3,4,6,6-hexamethylfulvene IIIb. This fulvene can react with $Fe(CO)_5$ either by loss of a hydrogen atom to give an isopropenyltetramethylcyclopentadienyliron carbonyl unit IIIc or by abstraction of a hydrogen atom from excess hydrocarbon or solvent to give an isopropyltetramethylcyclopentadienyl iron carbonyl unit IIId. Various ways of coupling the units IIIc and IIId can give

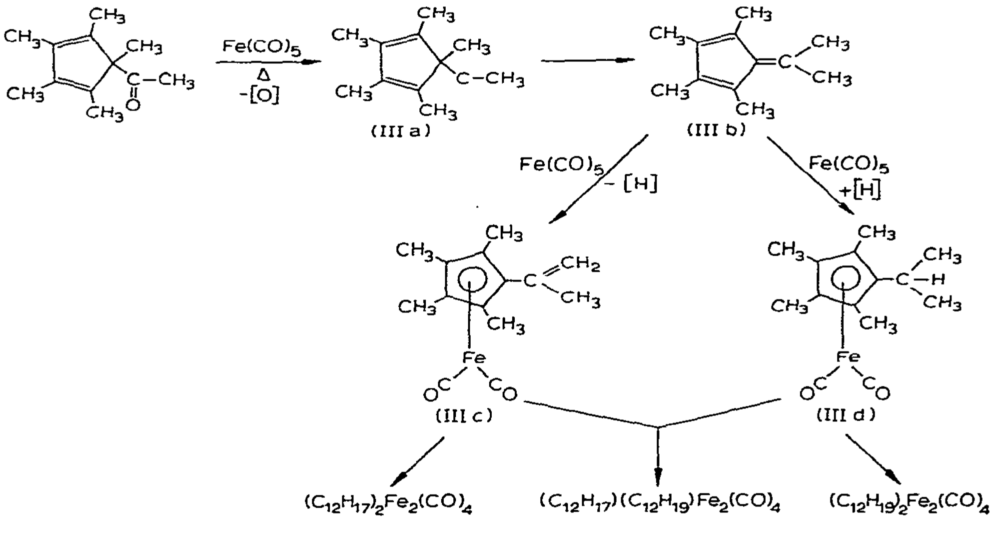

Fig. 1. A possible scheme for the formation of isopropenyl-and isopropyl-tetramethylcyclopentadienyl derivatives from pentacarbonyliron and acetylpentamethylcyclopentadiene.

$[R_5C_5Fe(CO)_2]_2$ derivatives with the observed properties. The presence of both isopropenyl- and isopropyl-tetramethylcyclopentadienyliron carbonyl derivatives in the observed product is strongly suggestive of the fulvene intermediate IIIb. Furthermore, reactions of 6,6-dimethylfulvene with metal carbonyls to give isopropylcyclopentadienylmetal carbonyl derivatives have been reported [13].

Since $[(CH_3C{=}CH_2)(CH_3)_4C_5Fe(CO)_2]_2$ is actually somewhat more readily available than $[(CH_3)_5C_5Fe(CO)_2]_2$, its chemistry was investigated in somewhat greater detail as representative of the chemistry of a completely alkylated $[R_5C_5Fe(CO)_2]_2$ derivative. The solution obtained by reduction of $[(CH_3C{=}CH_2)(CH_3)_4C_5Fe(CO)_2]_2$ with sodium amalgam in tetrahydrofuran was shown to contain the anion $[(CH_3C{=}CH_2)(CH_3)_4C_5Fe(CO)_2]^-$ by its reaction with methyl iodide to give the σ-methyl derivative $(CH_3C{=}CH_2)(CH_3)_4C_5Fe(CO)_2CH_3$ and by its reaction with triphenyltin chloride to give the triphenyltin derivative $(CH_3C{=}CH_2)(CH_3)_4C_5Fe(CO)_2Sn(C_6H_5)_3$. Reaction of the anion $[(CH_3C{=}CH_2)(CH_3)_4C_5Fe(CO)_2]^-$ with acetyl chloride gave a liquid acetyl derivative $(CH_3C{=}CH_2)(CH_3)_4C_5Fe(CO)_2(COCH_3)$ in contrast to the crystalline $(CH_3)_5C_5Fe(CO)_2(COCH_3)$.

The cyclopentadienyliron dicarbonyl anion $C_5H_5Fe(CO)_2^-$ is of interest because of its extremely high nucleophilicity relative to other metal carbonyl anions [14]. The anion $[(CH_3C{=}CH_2)(CH_3)_4C_5Fe(CO)_2]^-$ in which the hydrogen atoms of $C_5H_5Fe(CO)_2^-$ are replaced with electron-releasing methyl and isopropenyl groups should have a still higher nucleophilicity. Reactions of the anion $[(CH_3C{=}CH_2)(CH_3)_4C_5Fe(CO)_2]^-$ with numerous organic and inorganic halides were investigated in order to see whether its presumed very high nucleophilicity would lead to interesting new chemistry. In many such reactions complex mixtures were obtained which after chromatography gave insufficient quantities of pure products even for minimal characterization. Especially noticeable, however, was the frequent appearance of the chloride $(CH_3C{=}CH_2)(CH_3)_4C_5Fe(CO)_2Cl$ as one of the products from reactions of $[(CH_3C{=}CH_2)(CH_3)_5C_5Fe(CO)_2]^-$ with various chlorides. The reaction of $[(CH_3C{=}CH_2)(CH_3)_4C_5Fe(CO)_2]^-$ with mercuric chloride was particularly unusual in giving the chloride $(CH_3C{=}CH_2)(CH_3)_4C_5Fe(CO)_2Cl$ rather than an iron—mercury derivative which is often formed extremely easily in reactions of $C_5H_5Fe(CO)_2^-$ prepared with sodium amalgam [15]. The tendency of $[(CH_3C{=}CH_2)(CH_3)_4C_5Fe(CO)_2]^-$ to form the chloride $(CH_3C{=}CH_2)(CH_3)_4C_5Fe(CO)_2Cl$ when treated with various chlorine compounds may be a consequence of the very high electron density on the iron atom from the electron-releasing alkyl groups which causes $[(CH_3C{=}CH_2)(CH_3)_4C_5Fe(CO)_2]^-$ to function more frequently as a strong reducing agent than as a nucleophile.

The chloride $(CH_3C{=}CH_2)(CH_3)_4C_5Fe(CO)_2Cl$ besides being a product of reactions of $Na[(CH_3C{=}CH_2)(CH_3)_4C_5Fe(CO)_2]$ with various chlorides could also be obtained by oxidative chlorination of $[(CH_3C{=}CH_2)(CH_3)_4C_5Fe(CO)_2]_2$ with ferric chloride. The iodide $(CH_3C{=}CH_2)(CH_3)_4C_5Fe(CO)_2I$ could be obtained either from the reaction of $[(CH_3C{=}CH_2)(CH_3)_4C_5Fe(CO)_2]_2$ with iodine or from the reaction of $Na[(CH_3C{=}CH_2)(CH_3)_4C_5Fe(CO)_2]_2$ with 2-iodoheptafluoropropane. These preparative techniques for the isopropenyltetramethylcyclopentadienyliron dicarbonyl halides have been well-established for similar unsubstituted cyclopentadienyliron dicarbonyl derivatives and related compounds.

Several other reactions of $[(CH_3C{=}CH_2)(CH_3)_4C_5Fe(CO)_2]_2$ were investigated. Prolonged boiling of $[(CH_3C{=}CH_2)(CH_3)_4C_5Fe(CO)_2]_2$ in n-octane or xylene failed to give any new isopropenyltetramethylcyclopentadienyliron dicarbonyl derivatives in contrast to the unsubstituted $[C_5H_5Fe(CO)_2]_2$ which gives the green tetramer [16] $[C_5H_5FeCO]_4$ under comparable conditions. Similarly no new product could be obtained in characterizable quantities from $[(CH_3C{=}CH_2)(CH_3)_4C_5Fe(CO)_2]_2$ and dimethyl disulfide in boiling cyclohexane or methylcyclohexane in contrast to the unsubstituted $[C_5H_5Fe(CO)_2]_2$ which gives either $C_5H_5Fe(CO)_2SCH_3$ or $[C_5H_5FeCOSCH_3]_2$ with dimethyl disulfide depending upon the reaction conditions [17]. The difficulty in effecting many reactions of $[(CH_3C{=}CH_2)(CH_3)_4C_5Fe(CO)_2]_2$ which involve displacement of one or more carbonyls may relate to stronger iron—carbonyl bonds in the pentaalkylcyclopentadienyl derivative arising from increased retrodative bonding from the iron atom to the carbonyl groups in order to remove some of the electron density transferred to the iron atom from the ring by the five electron-releasing alkyl groups.

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