

Iron Carbonyl Complexes with Two Different Fluorocarbon Ligands

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Received September 16, 1977

The mixed fluorocarbon complex *trans*-(C₃F₇)(C₆F₅)Fe(CO)₄ has been obtained in good yield from the carbonylation of (C₃F₇)(C₆F₅)Fe(CO)₃(CH₃CN). The latter complex, together with small amounts of the tetracarbonyl, is formed in the reaction of C₃F₇Fe(CO)₄I with AgC₆F₅(CH₃CN) in dichloromethane solution. In acetonitrile solution, the bis(acetonitrile) complex (C₃F₇)(C₆F₅)Fe(CO)₂(CH₃CN)₂ is formed. These acetonitrile complexes are convenient precursors of (C₃F₇)(C₆F₅)Fe(CO)₃L and (C₃F₇)(C₆F₅)Fe(CO)₂L₂ derivatives (L = PPh₃, PPhMe₂, P(OMe)₃, P(OEt)₃, P(OPh)₃). Infrared spectra of the (C₃F₇)(C₆F₅)Fe(CO)₃L and (C₃F₇)(C₆F₅)Fe(CO)₃(CH₃CN) complexes indicate the presence of two or more isomers.

Introduction

Fluorocarbon complexes of the metal carbonyls have been studied in great detail over the past 15 years.¹ A recent development has been the synthesis of such complexes from fluorocarbon-silver reagents and metal carbonyl halide derivatives.^{2,3} This synthetic method, first introduced by King,² has afforded a variety of complexes which are not obtainable by more conventional routes.

In conjunction with our recent work⁴ involving perfluoro-*n*-propyliron carbonyl complexes, we have investigated the synthesis of the mixed perfluorocarbon complex (C₃F₇)(C₆F₅)Fe(CO)₄ from C₃F₇Fe(CO)₄I and perfluorophenylsilver. It was of interest to determine whether this complex would adopt the *cis* geometry^{3,5,6} of its symmetrical counterparts (C₃F₇)₂Fe(CO)₄ and (C₆F₅)₂Fe(CO)₄ or retain the *trans* geometry^{7,8} of C₃F₇Fe(CO)₄I. Retention of geometry is known to occur in the formation² of related *trans*-R(C₄F₇)Fe(CO)₄ complexes from *trans*-RFe(CO)₄I and AgC₄F₇ (R = C₂F₅, *n*-C₃F₇, *i*-C₃F₇). The geometry of these bis(perfluorocarbon) complexes and their configurational stability with respect to isomerization are related to the larger question of the stereochemistry of M(CO)₄X₂ molecules in general.⁹

Herein we report the preparation and characterization both of the desired complex and of several acetonitrile and phosphorus ligand-substituted derivatives. These complexes are additional examples of the relatively limited number of compounds² which contain two different fluorocarbon groups bonded to the same transition metal.

Experimental Section

General Procedures. All reactions were carried out under an atmosphere of nitrogen. Since AgC₆F₅(CH₃CN) is sensitive to light, all reactions involving this compound were carried out in flasks wrapped with aluminum foil. Microanalyses (Table I) were performed by Galbraith Laboratories, Knoxville, Tenn. Melting points (Table I) were taken in capillaries sealed under nitrogen and are uncorrected.

Materials. All solvents (reagent grade) were dried by appropriate methods and were saturated with nitrogen prior to use. The following compounds were purchased from commercial sources and were used without further purification: Fe(CO)₅, C₃F₇I, AgO₂CCF₃, PPh₃, PPhMe₂, P(OMe)₃, P(OEt)₃, and P(OPh)₃.

The method of King¹⁰ was used to prepare C₃F₇Fe(CO)₄I from Fe(CO)₅ and C₃F₇I. The compound AgC₆F₅(CH₃CN) was synthesized from AgO₂CCF₃ and LiC₆F₅ according to the literature method.¹¹ The ¹H NMR spectrum of AgC₆F₅(CH₃CN) in CD₃CN solution exhibited a sharp singlet at τ 7.80, confirming the previously suggested¹¹ complex formulation. For purposes of comparison, the methyl resonance of free CH₃CN occurs at τ 7.98 in CD₃CN solution.⁴

Spectra. Infrared spectra (Table II) were obtained on a Perkin-Elmer 180 spectrophotometer calibrated with carbon monoxide, polystyrene, and indene. Solution spectra were run in NaCl cells using *n*-heptane or dichloromethane as solvent. Mull spectra were recorded in Nujol and hexachlorobutadiene between NaCl plates.

Proton NMR spectra (Table II) were recorded at 60 MHz on a JEOL C-60-H instrument using internal Me₄Si as reference and

chloroform-*d*₁, acetone-*d*₆, or acetonitrile-*d*₃ as solvent. The ¹⁹F NMR spectra (Table III) were obtained at 56.4 MHz on the same instrument and were recorded for solutions in dichloromethane or acetone. Hexafluorobenzene was used as internal reference, and chemical shifts are presented relative to CFCl₃ using the conversion¹² φ_{CFCl₃} = δ_{C₆F₆} + 162.9 ppm.

Preparation of (C₃F₇)(C₆F₅)Fe(CO)₃(CH₃CN). Solid AgC₆F₅(CH₃CN) (3.56 g, 11.2 mmol) was added to a solution of C₃F₇Fe(CO)₄I (5.79 g, 12.5 mmol) in 100 mL of dichloromethane. The mixture was stirred for 6 h at room temperature and AgI was removed by filtration. Solvent was removed from the filtrate on the rotary evaporator to give a yellow-orange solid. Unreacted C₃F₇Fe(CO)₄I (0.37 g, 0.8 mmol) was removed from this solid by vacuum sublimation (0.01 mm) at 0 °C. The sublimation residue was extracted with 100 mL of *n*-heptane and the pale yellow filtrate was concentrated on the rotary evaporator to give a small amount of white crystalline (C₃F₇)(C₆F₅)Fe(CO)₄ (106 mg, 2% yield). The heptane-insoluble sublimation residue was crystallized from dichloromethane/*n*-heptane to give pure (C₃F₇)(C₆F₅)Fe(CO)₃(CH₃CN) as a bright yellow solid (3.48 g, 58%).

Preparation of (C₃F₇)(C₆F₅)Fe(CO)₄. A solution of (C₃F₇)(C₆F₅)Fe(CO)₃(CH₃CN) (1.10 g, 2.14 mmol) in dichloromethane (65 mL) was placed in a stainless steel Hoke bomb. The bomb was sealed, pressurized to 100 psi with carbon monoxide, and heated at 60 °C for 6 days. Solvent was removed on the rotary evaporator to give a tan solid which was recrystallized from dichloromethane/*n*-heptane to afford white crystalline (C₃F₇)(C₆F₅)Fe(CO)₄ (0.64 g, 59%).

Preparation of (C₃F₇)(C₆F₅)Fe(CO)₂(CH₃CN)₂. Solid AgC₆F₅(CH₃CN) (5.54 g, 17.5 mmol) was added to a solution of C₃F₇Fe(CO)₄I (9.29 g, 20.0 mmol) in 120 mL of acetonitrile. The mixture was stirred for 2 h at room temperature and AgI was removed by filtration. The filtrate was evaporated to dryness in vacuo. Recrystallization of the resulting orange solid from dichloromethane/*n*-heptane afforded an orange powder (2.71 g, 34%).

Preparation of (C₃F₇)(C₆F₅)Fe(CO)₃PPh₃. Solid AgC₆F₅(CH₃CN) (0.63 g, 1.99 mmol) was added to a solution of C₃F₇Fe(CO)₄I (1.00 g, 2.16 mmol) and PPh₃ (1.37 g, 5.23 mmol) in 100 mL of benzene. The mixture was stirred at 50 °C for 24 h and the AgI was removed by filtration. Heptane was added to the filtrate and concentration of the solution on the rotary evaporator gave a bright yellow crystalline solid (0.71 g, 48%).

Preparation of (C₃F₇)(C₆F₅)Fe(CO)₃L (L = P(OMe)₃, P(OEt)₃, P(OPh)₃). A typical procedure is outlined for L = P(OEt)₃. Solid AgC₆F₅(CH₃CN) (0.63 g, 1.99 mmol) was added to a solution of C₃F₇Fe(CO)₄I (0.97 g, 2.09 mmol) and P(OEt)₃ (0.38 g, 2.30 mmol) in 100 mL of benzene. Immediate gas evolution was observed and precipitation of AgI occurred. The solution was heated at 50 °C for 26 h and AgI was removed by filtration. The yellow filtrate was evaporated to dryness in vacuo. The resulting orange oil was chromatographed on an alumina column using 2:1 petroleum ether/benzene as the eluting solvent. Concentration on the rotary evaporator gave a cream crystalline solid (0.52 g, 41%).

Preparation of (C₃F₇)(C₆F₅)Fe(CO)₃PPhMe₂. Solid AgC₆F₅(CH₃CN) (1.54 g, 4.87 mmol) was added to a solution of C₃F₇Fe(CO)₄I (2.57 g, 5.54 mmol) and PPhMe₂ (0.80 g, 5.97 mmol) in 120 mL of benzene. Immediate gas evolution was observed and precipitation of AgI occurred. The mixture was stirred at 40 °C for 8 h and AgI was removed by filtration. The filtrate was concentrated

Table I. Analytical Data and Melting Points

Complex	Mp, °C	Elemental analyses, calcd (found), %			
		C	H	P	Other
(C ₃ F ₇)(C ₆ F ₅)Fe(CO) ₄	137	30.98 (30.72)	0.00 (0.30)		F 45.28 (44.67); Fe 11.08 (10.79)
(C ₃ F ₇)(C ₆ F ₅)Fe(CO) ₃ (CH ₃ CN)	133	32.52 (32.81)	0.58 (0.54)		N 2.71 (3.04); F 44.10 (41.61); Fe 10.80 (10.38)
(C ₃ F ₇)(C ₆ F ₅)Fe(CO) ₂ (CH ₃ CN) ₂	116 dec	33.99 (32.88)	1.14 (1.11)		N 5.28 (5.14); F 43.01 (41.66)
(C ₃ F ₇)(C ₆ F ₅)Fe(CO) ₃ PPh ₃	128 dec	48.81 (48.84)	2.05 (2.17)	4.20 (4.31)	
(C ₃ F ₇)(C ₆ F ₅)Fe(CO) ₃ PPhMe ₂ -A ^a	109	39.12 (39.24)	1.81 (2.07)	5.04 (4.54)	
(C ₃ F ₇)(C ₆ F ₅)Fe(CO) ₃ PPhMe ₂ -B ^b	137	39.12 (38.97)	1.81 (1.80)	5.04 (5.13)	
(C ₃ F ₇)(C ₆ F ₅)Fe(CO) ₃ P(OMe) ₃	76	30.03 (30.15)	1.51 (1.55)	5.16 (4.98)	
(C ₃ F ₇)(C ₆ F ₅)Fe(CO) ₃ P(OEt) ₃	80	33.67 (33.81)	2.35 (2.35)	4.82 (4.06)	
(C ₃ F ₇)(C ₆ F ₅)Fe(CO) ₃ P(OPh) ₃	118	45.83 (45.44)	1.92 (2.03)	3.94 (3.56)	
(C ₃ F ₇)(C ₆ F ₅)Fe(CO) ₂ (PPhMe ₂) ₂	145 dec	44.78 (44.83)	3.06 (3.08)	8.55 (8.38)	
(C ₃ F ₇)(C ₆ F ₅)Fe(CO) ₂ [P(OMe) ₃] ₂	149	29.33 (29.23)	2.61 (2.59)	8.90 (8.84)	
(C ₃ F ₇)(C ₆ F ₅)Fe(CO) ₂ [P(OEt) ₃] ₂	120	35.40 (35.20)	3.88 (4.05)	7.94 (7.43)	
(C ₃ F ₇)(C ₆ F ₅)Fe(CO) ₂ [P(OPh) ₃] ₂	129	52.83 (52.96)	2.83 (2.80)	5.80 (5.46)	

^a Isomeric mixture A; see text. ^b Isomeric mixture B; see text.

Table II. Infrared and ¹H NMR Data

Complex	$\nu(\text{CO}), \text{cm}^{-1}$ ^a	¹ H NMR ^{b,c}
(C ₃ F ₇)(C ₆ F ₅)Fe(CO) ₄	2155 vw, 2118 vw, 2094 s, 2090 s	
(C ₃ F ₇)(C ₆ F ₅)Fe(CO) ₃ (CH ₃ CN)	2129 w, 2075 s, 2073 s, 2064 m, 2058 m	CH ₃ CN, 7.66 s ^d
(C ₃ F ₇)(C ₆ F ₅)Fe(CO) ₂ (CH ₃ CN) ₂	2066 s, 2025 s ^e	CH ₃ CN, 7.58 s ^d
(C ₃ F ₇)(C ₆ F ₅)Fe(CO) ₃ PPh ₃	2107 m, 2051 vs, 2031 s, 2023 s	C ₆ H ₅ , 2.46 s
(C ₃ F ₇)(C ₆ F ₅)Fe(CO) ₃ PPhMe ₂ -A ^f	2102 m, 2043 vs, 2035 s, 2020 s	CH ₃ , 8.26 d, <i>J</i> _{PH} = 11.6 Hz; C ₆ H ₅ , 2.74 m ^d
(C ₃ F ₇)(C ₆ F ₅)Fe(CO) ₃ PPhMe ₂ -B ^g	2107 m, 2065 m, 2060 s, 2042 vs, 2037 s	CH ₃ , 8.03 d, <i>J</i> _{PH} = 10.4 Hz; C ₆ H ₅ , 2.79 m ^d
(C ₃ F ₇)(C ₆ F ₅)Fe(CO) ₃ P(OMe) ₃	2118 m, 2076 s, 2069 s, 2056 vs, 2050 vs	CH ₃ , 6.19 d, <i>J</i> _{PH} = 13.6 Hz
(C ₃ F ₇)(C ₆ F ₅)Fe(CO) ₃ P(OEt) ₃	2117 m, 2073 s, 2066 s, 2054 vs, 2048 vs	CH ₃ , 8.73 t; <i>J</i> _{HH} = 8.4 Hz; CH ₂ , 5.86 qt; <i>J</i> _{PH} = 8.4 Hz
(C ₃ F ₇)(C ₆ F ₅)Fe(CO) ₃ P(OPh) ₃	2120 m, 2066 vs, 2052 s, 2047 s	C ₆ H ₅ , 2.75 m
(C ₃ F ₇)(C ₆ F ₅)Fe(CO) ₂ (PPhMe ₂) ₂	2055 w, 1985 s	CH ₃ , 8.22 vct; C ₆ H ₅ , 2.82 m
(C ₃ F ₇)(C ₆ F ₅)Fe(CO) ₂ [P(OMe) ₃] ₂	2076 w, 2013 s	CH ₃ , 6.38 vct
(C ₃ F ₇)(C ₆ F ₅)Fe(CO) ₂ [P(OEt) ₃] ₂	2076 w, 2010 s	CH ₃ , 8.81 t; <i>J</i> _{HH} = 8.5 Hz; CH ₂ , 6.02 m
(C ₃ F ₇)(C ₆ F ₅)Fe(CO) ₂ [P(OPh) ₃] ₂	2089 w, 2032 s	C ₆ H ₅ , 2.84 m

^a *n*-Heptane solution unless otherwise noted. ^b Acetone-*d*₆ solution unless otherwise noted; chemical shifts on τ scale. ^c Abbreviations: s, singlet; d, doublet; t, triplet; qt, quintet; m, multiplet; vct, virtual-coupled triplet. ^d CDCl₃ solution. ^e CH₂Cl₂ solution. ^f Isomeric mixture A; see text. ^g Isomeric mixture B; see text.

Table III. ¹⁹F NMR Data^a

Complex	C ₃ F ₇ group				C ₆ F ₅ group		
	$\alpha\text{-CF}_2$	$\beta\text{-CF}_2$	CF ₃	⁴ <i>J</i> _{F₀F₁F₂F₃, Hz}	<i>o</i> -F	<i>m</i> -F	<i>p</i> -F
(C ₃ F ₇)(C ₆ F ₅)Fe(CO) ₄	67.7	117.5	81.4	10.1	107.8	164.5	160.5
(C ₃ F ₇)(C ₆ F ₅)Fe(CO) ₃ (CH ₃ CN) ^b	78.6	117.1	79.8	11.0	109.4	162.7	159.3
(C ₃ F ₇)(C ₆ F ₅)Fe(CO) ₂ (CH ₃ CN) ₂	82.2	117.9	79.4	10.7	112.5	164.8	162.5
(C ₃ F ₇)(C ₆ F ₅)Fe(CO) ₃ PPh ₃	66.8	114.1	77.9	12.1	100.1	161.9	159.7
(C ₃ F ₇)(C ₆ F ₅)Fe(CO) ₃ PPhMe ₂ -A ^c	74.2	118.3	82.0	11.8	105.6	165.4	163.3
(C ₃ F ₇)(C ₆ F ₅)Fe(CO) ₃ PPhMe ₂ -B ^d	72.0	114.1	78.1	12.3	102.3	161.3	159.2
(C ₃ F ₇)(C ₆ F ₅)Fe(CO) ₃ P(OMe) ₃	72.2	117.4	81.5	12.4	106.8	165.2	161.9
(C ₃ F ₇)(C ₆ F ₅)Fe(CO) ₃ P(OEt) ₃ ^b	70.1	115.3	79.8	12.1	104.2	162.8	159.3
(C ₃ F ₇)(C ₆ F ₅)Fe(CO) ₃ P(OPh) ₃ ^b	70.6	115.7	79.6	11.8	102.7	162.6	159.5
(C ₃ F ₇)(C ₆ F ₅)Fe(CO) ₂ (PPhMe ₂) ₂	67.2	112.3	77.5	13.5	99.5	162.1	162.1
(C ₃ F ₇)(C ₆ F ₅)Fe(CO) ₂ [P(OMe) ₃] ₂	65.8	113.8	78.1	13.1	101.5	163.9	161.2
(C ₃ F ₇)(C ₆ F ₅)Fe(CO) ₂ [P(OEt) ₃] ₂	66.1	113.1	77.7	12.6	100.5	164.7	162.4
(C ₃ F ₇)(C ₆ F ₅)Fe(CO) ₂ [P(OPh) ₃] ₂	65.8	113.1	77.3	13.1	100.0	163.3	160.4

^a Chemical shifts in ppm from CFCl₃; acetone solution unless otherwise noted. ^b Dichloromethane solution. ^c Isomeric mixture A; see text. ^d Isomeric mixture B; see text.

in vacuo to a red-orange oil which was chromatographed on alumina using 2:1 petroleum ether/benzene as the eluting solvent. Two yellow-orange bands eluted. Both fractions were crystallized from dichloromethane/heptane to afford pale yellow solids, each of which was shown to be an isomeric mixture of products by infrared spectroscopy. The first band eluted corresponds to isomeric mixture B (0.20 g, 7%) while the second band corresponds to isomeric mixture A (0.60 g, 20%).

Preparation of (C₃F₇)(C₆F₅)Fe(CO)₂L₂ (L = P(OMe)₃, P(OEt)₃, P(OPh)₃). A typical procedure is outlined for the P(OEt)₃ derivative. A solution of (C₃F₇)(C₆F₅)Fe(CO)₂(CH₃CN)₂ (0.97 g, 1.83 mmol) and P(OEt)₃ (0.99 g, 5.96 mmol) in 75 mL of benzene was heated at 60 °C for 109 h. Solvent was removed in vacuo to give an orange oily solid which was dissolved in dichloromethane/heptane. Con-

centration of this solution on the rotary evaporator gave the product as an off-white powder (0.38 g, 24%).

Preparation of (C₃F₇)(C₆F₅)Fe(CO)₂(PPhMe₂)₂. Solid AgC₆F₅(CH₃CN) (1.12 g, 3.54 mmol) was added to a solution of C₃F₇-Fe(CO)₄I (1.86 g, 4.01 mmol) and PPhMe₂ (1.01 g, 7.32 mmol) in 100 mL of benzene. The solution was heated at 50 °C for 72 h and AgI was removed by filtration. The yellow filtrate was evaporated to dryness in vacuo to give an orange oily solid. Chromatography on alumina gave a yellow-orange band which was eluted with 2:1 petroleum ether/benzene. Recrystallization of the resulting solid from dichloromethane/heptane afforded a bright yellow crystalline solid (1.30 g, 51%).

The corresponding P(OMe)₃, P(OEt)₃, and P(OPh)₃ complexes could also be prepared using this general procedure. However, the

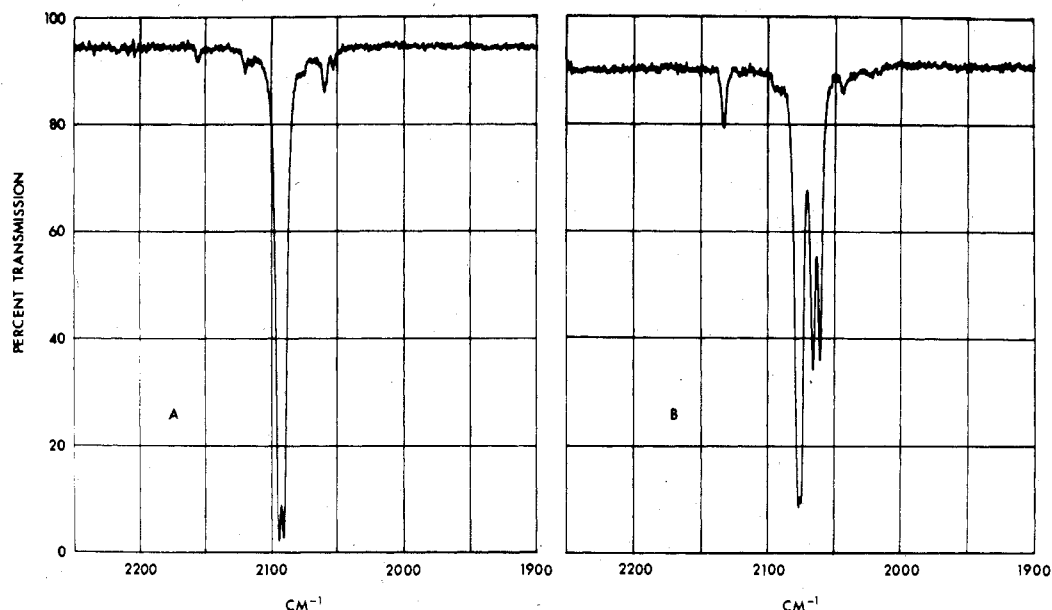


Figure 1. (A) Infrared spectrum in *n*-heptane of *trans*-(C₃F₇)(C₆F₅)Fe(CO)₄. The band at 2059 cm⁻¹ is due to ¹³CO in natural abundance. (B) Infrared spectrum in *n*-heptane of (C₃F₇)(C₆F₅)Fe(CO)₃(CH₃CN) (saturated solution).

yields were significantly lower than for the alternative method of preparing these compounds from (C₃F₇)(C₆F₅)Fe(CO)₂(CH₃CN)₂.

Results and Discussion

Since attempts to prepare uncomplexed AgC₆F₅ from the acetonitrile complex by the published method¹¹ led only to extensive decomposition, all of our studies were carried out with AgC₆F₅(CH₃CN). The acetonitrile ligand was observed to be a surprisingly noninnocent participant in the reactions of the silver reagent. Thus, the reaction of C₃F₇Fe(CO)₄I with AgC₆F₅(CH₃CN) in dichloromethane at room temperature afforded the mono(acetonitrile) derivative (C₃F₇)(C₆F₅)Fe(CO)₃(CH₃CN) in ~60% yield. A very low yield (~2%) of the unsubstituted complex (C₃F₇)(C₆F₅)Fe(CO)₄ was also formed. The presence of carbon monoxide at 1 atm had a negligible effect on the relative amounts of (C₃F₇)(C₆F₅)Fe(CO)₃(CH₃CN) and (C₃F₇)(C₆F₅)Fe(CO)₄ produced.

The facile replacement of CO by CH₃CN is surprising since equivalent amounts of (C₃F₇)(C₆F₅)Fe(CO)₄ and free acetonitrile did not react under similar conditions. This suggests that the labilization of CO is a direct result of acetonitrile being coordinated to silver.

The reaction of C₃F₇Fe(CO)₄I and AgC₆F₅(CH₃CN) followed a different course in acetonitrile solution at room temperature. Under these conditions, further replacement of CO by *free* acetonitrile took place to afford the bis(acetonitrile) complex (C₃F₇)(C₆F₅)Fe(CO)₂(CH₃CN)₂. No other carbonyl-containing product was formed, in contrast to the results obtained in dichloromethane.

The mono- and bis(acetonitrile) complexes are nonvolatile yellow solids. They are virtually insoluble in aliphatic hydrocarbon solvents but are soluble in benzene and in polar solvents such as dichloromethane, acetonitrile, and acetone. Although the solid complexes are stable in air at room temperature, solutions of the complexes decompose within a few hours.

Substantially improved yields (~60%) of the unsubstituted tetracarbonyl complex (C₃F₇)(C₆F₅)Fe(CO)₄ were obtained from prolonged carbonylation (100 psi CO) of (C₃F₇)(C₆F₅)Fe(CO)₃(CH₃CN) in dichloromethane solution. The complex is a white volatile solid which is soluble in most organic solvents. Such properties resemble those of related bis(perfluorocarbon)tetracarbonyliron derivatives.^{2,3,5}

Other substituted derivatives of (C₃F₇)(C₆F₅)Fe(CO)₄ were prepared by carrying out the reaction of C₃F₇Fe(CO)₄I and AgC₆F₅(CH₃CN) in the presence of the phosphorus-donor ligands (L) PPh₃, PPhMe₂, P(OMe)₃, P(OEt)₃, and P(OPh)₃. Thus, reaction of equivalent amounts of C₃F₇Fe(CO)₄I, AgC₆F₅(CH₃CN), and L in benzene at 50 °C gave mono-substituted (C₃F₇)(C₆F₅)Fe(CO)₃L complexes. The use of excess L and longer reaction times afforded low yields of the corresponding disubstituted (C₃F₇)(C₆F₅)Fe(CO)₂L₂ complexes for all ligands except PPh₃. The disubstituted complexes were also synthesized from (C₃F₇)(C₆F₅)Fe(CO)₂(CH₃CN)₂ under similar conditions. In general, this latter method gave improved yields (~30–50%). Attempts to isolate a mixed disubstituted intermediate of the type (C₃F₇)(C₆F₅)Fe(CO)₂(CH₃CN)L were unsuccessful.

All of the (C₃F₇)(C₆F₅)Fe(CO)₃L and (C₃F₇)(C₆F₅)Fe(CO)₂L₂ complexes are air-stable, white-to-yellow solids which are soluble in nonpolar and polar solvents. Although similar mono- and disubstituted derivatives of the chelate complex (CF₂)₄Fe(CO)₄ have been prepared,¹³ previous attempts¹⁴ to synthesize analogous nonchelate bis(perfluorocarbon) complexes have been unsuccessful. For example, Plowman and Stone¹⁴ reported that PPh₃ and P(OMe)₃ both vigorously degrade (C₃F₇)₂Fe(CO)₄ into products which no longer contain the perfluoropropyliron group. Our results on the (C₃F₇)(C₆F₅)Fe(CO)₄ system suggest that the lack of corresponding isolable (C₃F₇)₂Fe(CO)_{4-x}L_x derivatives is probably due to the reaction conditions used rather than any inherent instability of such nonchelate complexes.

Spectra and Structures. The ¹⁹F NMR spectra of all complexes exhibited the expected pattern of three resonances due to the α-CF₂ (φ 65.8–82.2), β-CF₂ (φ 112.3–118.3), and CF₃ (φ 77.3–82.0) groups of the *n*-C₃F₇ moiety. The coupling constant between the α-CF₂ and CF₃ fluorine atoms, ⁴J_{F_αF_β, was 10–14 Hz. Three additional resonances corresponded to the ortho (φ 99.5–112.5), meta (φ 161.3–165.4), and para (φ 159.2–163.3) fluorines of the C₆F₅ group. The ¹⁹F NMR spectra thus closely resemble the spectra of other perfluoropropyl^{2,4,15} and perfluorophenyl-metal^{3,12,16} complexes.}

The infrared spectrum of (C₃F₇)(C₆F₅)Fe(CO)₄ in the ν(CO) region exhibited two closely spaced strong bands at 2094 and 2090 cm⁻¹ together with two very weak bands at 2155 and 2118 cm⁻¹ (Figure 1). This observation suggests

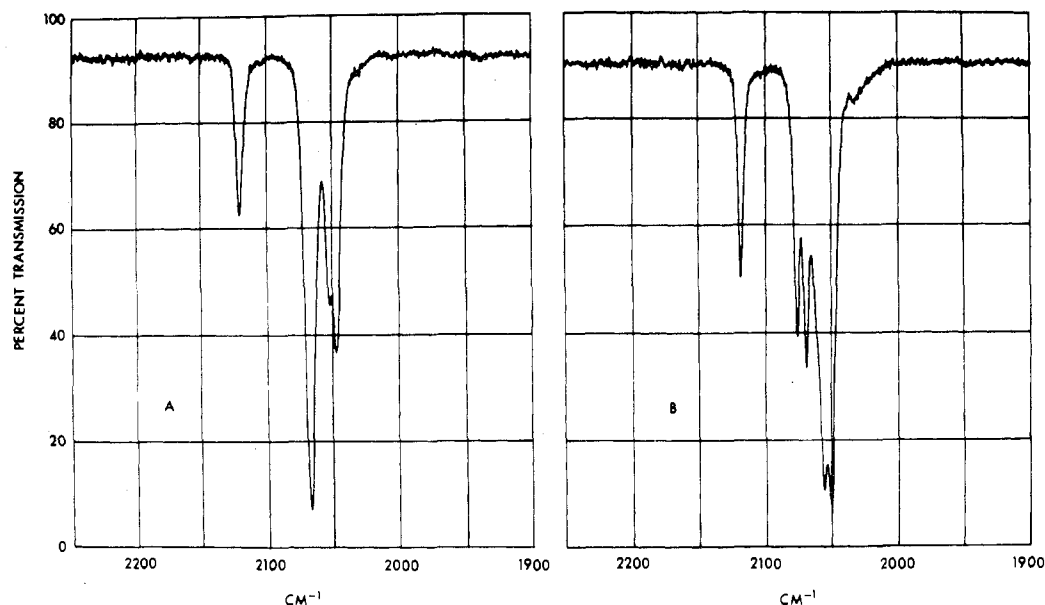
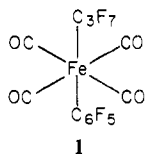


Figure 2. Infrared spectra in *n*-heptane of (A) $(C_3F_7)(C_6F_5)Fe(CO)_3P(OPh)_3$ and (B) $(C_3F_7)(C_6F_5)Fe(CO)_3P(OEt)_3$.

that the two fluorocarbon groups occupy mutually trans positions about iron (**1**). A cis structure would be expected



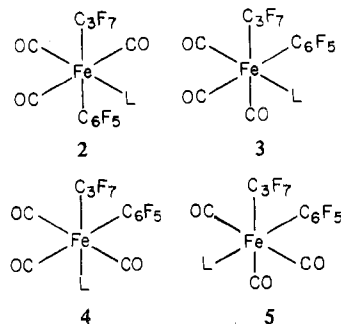
to have an infrared spectrum similar to that^{6,13} of the chelate derivative $(CF_2)_4Fe(CO)_4$, in contrast to actual observation.

Structure **1** should give rise to one very weak (A_1) and one strong (E) infrared-active $\nu(CO)$ band under rigorous C_{4v} symmetry. However, the lack of axial symmetry of the C_3F_7 group causes the E mode to be split into two components ($2094, 2090\text{ cm}^{-1}$).^{17,18} The removal of degeneracy of the E mode is usually accompanied¹⁷ by appearance of the normally only Raman-active B_1 mode which has gained a slight infrared intensity in the reduction of symmetry from strict C_{4v} . We thus assign the two very weak bands at 2155 and 2118 cm^{-1} as the A_1 and B_1 modes, respectively. This interpretation of the infrared spectrum of $(C_3F_7)(C_6F_5)Fe(CO)_4$ is consistent with the spectral assignments² for related mixed fluorocarbon complexes of the type *trans*- $R(C_4F_7)Fe(CO)_4$ ($R = C_2F_5, n-C_3F_7, i-C_3F_7$).

It is interesting to note the difference in stereochemistry between the mixed fluorocarbon complex *trans*- $(C_3F_7)(C_6F_5)Fe(CO)_4$ and its symmetrical counterparts $(C_3F_7)_2Fe(CO)_4$ ^{5,6} and $(C_6F_5)_2Fe(CO)_4$.³ The published^{3,6} infrared spectra of the latter complexes indicate the cis isomer to be present, although the simultaneous presence of the trans isomer cannot be unambiguously ruled out. Significantly, $(C_3F_7)(C_6F_5)Fe(CO)_4$ was isolated from a 6-day reaction at 60°C , conditions which might have caused isomerization of any initially formed cis isomer to the observed trans form. The question naturally arises as to whether $(C_3F_7)_2Fe(CO)_4$ and $(C_6F_5)_2Fe(CO)_4$ are configurationally unstable with respect to cis \rightarrow trans isomerization. We are presently investigating this possibility via appropriate infrared and variable-temperature ^{13}C NMR studies.

The infrared spectra of the $(C_3F_7)(C_6F_5)Fe(CO)_3L$ complexes were surprisingly complicated and exhibited four or five $\nu(CO)$ bands. Typical spectra are shown in Figure 2. Since

only three $\nu(CO)$ bands are predicted for each of the four possible isomers of $(C_3F_7)(C_6F_5)Fe(CO)_3L$ (**2-5**), the complex



infrared spectra must be interpreted in terms of the presence of at least two isomers. The composition of the isomeric mixture is clearly dependent on the nature of L , as illustrated by the quite different $\nu(CO)$ band patterns observed for the $(C_3F_7)(C_6F_5)Fe(CO)_3P(OPh)_3$ and $(C_3F_7)(C_6F_5)Fe(CO)_3P(OEt)_3$ complexes (Figure 2). For purposes of comparison, the infrared spectra of the PPh_3 and $P(OMe)_3$ complexes resemble those of the $P(OPh)_3$ and $P(OEt)_3$ derivatives, respectively.

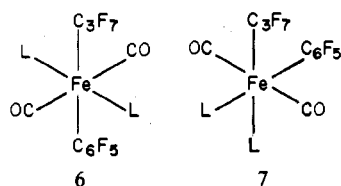
Only in the case of $(C_3F_7)(C_6F_5)Fe(CO)_3PPhMe_2$ was it possible to achieve even partial separation of the individual isomeric components. Chromatography afforded two separate products each of which was in fact an isomeric mixture as evidenced by infrared spectroscopy. The infrared spectrum of the minor product (isomeric mixture A) was very similar to that of $(C_3F_7)(C_6F_5)Fe(CO)_3P(OPh)_3$, while the infrared spectrum of the major product (isomeric mixture B) resembled that of the $P(OEt)_3$ complex.

It is highly probable that some of the observed $\nu(CO)$ bands of a particular $(C_3F_7)(C_6F_5)Fe(CO)_3L$ complex are fortuitously common to two or more isomers.¹⁹ This is particularly true for **4** and **5** since the electronic effects of the C_3F_7 and C_6F_5 groups should be very similar.²⁰ Thus, infrared spectroscopy cannot be used to determine the number of isomers present. Unfortunately, ^1H and ^{19}F NMR spectroscopy also proved to be of limited use in this respect. Although the two isomeric mixtures of $(C_3F_7)(C_6F_5)Fe(CO)_3PPhMe_2$ exhibited quite different ^1H and ^{19}F NMR spectra (Tables II, III), evidence for more than a single component within each mixture

was not obtained. It is, of course, possible that within each isomeric mixture only one isomer is present in high enough concentration to be detected by ^1H and ^{19}F NMR spectroscopy. However, infrared spectra seem inconsistent with this interpretation. A more reasonable explanation is that the individual components of a given isomeric mixture have fortuitously coincident ^1H and ^{19}F chemical shifts.²²

A similar explanation could account for the failure to observe more than one set of resonances in the ^1H and ^{19}F NMR spectra of the other $(\text{C}_3\text{F}_7)(\text{C}_6\text{F}_5)\text{Fe}(\text{CO})_3\text{L}$ derivatives.²² The inability of ^1H NMR spectroscopy to distinguish among isomers *except* in the case of the PPhMe_2 complex is not surprising in view of studies on related systems. For example, the methyl resonances of the *fac* and *mer* isomers of $\text{BrMn}(\text{CO})_3(\text{PPhMe}_2)_2$ differ in chemical shift by 0.20 ppm, but the ligand resonances in the corresponding $\text{P}(\text{OEt})_3$ complexes are virtually identical.²³ Similar observations have been noted²⁴ for the ^1H NMR spectra of *fac* and *mer* $\text{CH}_3\text{COMn}(\text{CO})_3\text{L}_2$ complexes of PPhMe_2 and $\text{P}(\text{OMe})_3$.

In contrast to the monosubstituted derivatives, the disubstituted complexes were formed as a single isomer. The infrared spectra of all $(\text{C}_3\text{F}_7)(\text{C}_6\text{F}_5)\text{Fe}(\text{CO})_2\text{L}_2$ complexes exhibited the same simple pattern of one weak and one strong $\nu(\text{CO})$ band, indicating the presence of *trans* CO groups. Possible structures for $(\text{C}_3\text{F}_7)(\text{C}_6\text{F}_5)\text{Fe}(\text{CO})_2\text{L}_2$ are thus limited to **6** and **7**. The ^1H NMR spectra of the PPhMe_2 and

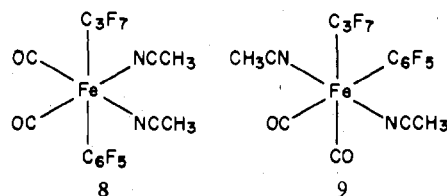


$\text{P}(\text{OMe})_3$ complexes both showed virtual-coupled triplet patterns for the methyl resonances, an observation usually attributed to mutually *trans* phosphorus ligands.^{25,26} Unfortunately, an unambiguous structural assignment cannot be made on this basis since virtual coupling has also been observed for *cis*-oriented PPhMe_2 and $\text{P}(\text{OMe})_3$ ligands.^{23,27}

The appearance of five $\nu(\text{CO})$ bands in the infrared spectrum of $(\text{C}_3\text{F}_7)(\text{C}_6\text{F}_5)\text{Fe}(\text{CO})_3(\text{CH}_3\text{CN})$ (Figure 1) suggests the same type of isomer problem (**2–5**; $\text{L} = \text{CH}_3\text{CN}$) associated with the monosubstituted $(\text{C}_3\text{F}_7)(\text{C}_6\text{F}_5)\text{Fe}(\text{CO})_3\text{L}$ complexes. Since only one of these isomers (**2**) has a *trans* arrangement of the fluorocarbon groups, a stereochemical rearrangement must necessarily take place during the carbonylation of $(\text{C}_3\text{F}_7)(\text{C}_6\text{F}_5)\text{Fe}(\text{CO})_3(\text{CH}_3\text{CN})$ to form exclusively *trans*- $(\text{C}_3\text{F}_7)(\text{C}_6\text{F}_5)\text{Fe}(\text{CO})_4$. As in the case of the $(\text{C}_3\text{F}_7)(\text{C}_6\text{F}_5)\text{Fe}(\text{CO})_3\text{L}$ complexes, ^1H and ^{19}F NMR spectroscopies were of no use in determining the number of isomers present. For example, the ^1H NMR spectrum in CDCl_3 solution revealed only a single sharp resonance (τ 7.66) attributable to coordinated acetonitrile.

The presence of two intense $\nu(\text{CO})$ bands in the infrared spectrum of $(\text{C}_3\text{F}_7)(\text{C}_6\text{F}_5)\text{Fe}(\text{CO})_2(\text{CH}_3\text{CN})_2$ is consistent with a *cis* arrangement of the two CO ligands, in contrast to their *trans* orientation in the $(\text{C}_3\text{F}_7)(\text{C}_6\text{F}_5)\text{Fe}(\text{CO})_2\text{L}_2$ complexes. The ^1H NMR spectrum of the complex in CDCl_3 solution showed a sharp singlet at τ 7.58 indicating that the two acetonitrile groups are equivalent. Of the six possible isomers of $(\text{C}_3\text{F}_7)(\text{C}_6\text{F}_5)\text{Fe}(\text{CO})_2(\text{CH}_3\text{CN})_2$ only two (**8** and **9**) are consistent with both the infrared and ^1H NMR results. A further distinction between **8** and **9** is not possible from the spectroscopic evidence at hand.

The acetonitrile ligands in $(\text{C}_3\text{F}_7)(\text{C}_6\text{F}_5)\text{Fe}(\text{CO})_3(\text{CH}_3\text{CN})$ and $(\text{C}_3\text{F}_7)(\text{C}_6\text{F}_5)\text{Fe}(\text{CO})_2(\text{CH}_3\text{CN})_2$ were observed by ^1H NMR to undergo exchange with free CD_3CN in CDCl_3 solution. Thus, addition of CD_3CN to a solution of the mono-



or bis(acetonitrile) complex led to the appearance and further growth of a resonance at τ 7.99 attributable to free acetonitrile. A concomitant decrease in intensity of the methyl resonance of coordinated acetonitrile was also observed. An interesting feature of this exchange process is the marked difference in rate observed for the two complexes. For the bis(acetonitrile) complex, exchange was complete within about 5 min at ambient temperature. In contrast, complete exchange was not observed for the mono(acetonitrile) complex after 12 h. The rapid exchange of acetonitrile by $(\text{C}_3\text{F}_7)(\text{C}_6\text{F}_5)\text{Fe}(\text{CO})_2(\text{CH}_3\text{CN})_2$ suggests that the two CH_3CN ligands are mutually *cis*; previous studies²⁸ involving related octahedral systems have indicated that mutually *trans* CH_3CN ligands are extremely inert with respect to exchange. On this basis we tentatively favor structure **8** for $(\text{C}_3\text{F}_7)(\text{C}_6\text{F}_5)\text{Fe}(\text{CO})_2(\text{CH}_3\text{CN})_2$.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the partial support of this research. Additional research support from the Research Corp. is also gratefully acknowledged. We thank the Faculty Research Committee, Miami University, for research support and for a research assistantship to D.W.H.

Registry No. *trans*- $(\text{C}_3\text{F}_7)(\text{C}_6\text{F}_5)\text{Fe}(\text{CO})_4$, 65466-02-6; $(\text{C}_3\text{F}_7)(\text{C}_6\text{F}_5)\text{Fe}(\text{CO})_3(\text{CH}_3\text{CN})$, 65466-01-5; $(\text{C}_3\text{F}_7)(\text{C}_6\text{F}_5)\text{Fe}(\text{CO})_2(\text{CH}_3\text{CN})_2$, 65466-00-4; $(\text{C}_3\text{F}_7)(\text{C}_6\text{F}_5)\text{Fe}(\text{CO})_3\text{PPh}_3$, 65465-99-8; $(\text{C}_3\text{F}_7)(\text{C}_6\text{F}_5)\text{Fe}(\text{CO})_3\text{PPhMe}_2$, 65465-98-7; $(\text{C}_3\text{F}_7)(\text{C}_6\text{F}_5)\text{Fe}(\text{CO})_3\text{P}(\text{OMe})_3$, 65465-97-6; $(\text{C}_3\text{F}_7)(\text{C}_6\text{F}_5)\text{Fe}(\text{CO})_3\text{P}(\text{OEt})_3$, 65465-96-5; $(\text{C}_3\text{F}_7)(\text{C}_6\text{F}_5)\text{Fe}(\text{CO})_3\text{P}(\text{OPh})_3$, 65465-95-4; $(\text{C}_3\text{F}_7)(\text{C}_6\text{F}_5)\text{Fe}(\text{CO})_2(\text{PPhMe}_2)_2$, 65465-94-3; $(\text{C}_3\text{F}_7)(\text{C}_6\text{F}_5)\text{Fe}(\text{CO})_2[\text{P}(\text{OMe})_3]_2$, 65465-93-2; $(\text{C}_3\text{F}_7)(\text{C}_6\text{F}_5)\text{Fe}(\text{CO})_2[\text{P}(\text{OEt})_3]_2$, 65466-09-3; $(\text{C}_3\text{F}_7)(\text{C}_6\text{F}_5)\text{Fe}(\text{CO})_2[\text{P}(\text{OPh})_3]_2$, 65466-08-2; $\text{AgC}_6\text{F}_5(\text{CH}_3\text{CN})$, 65466-07-1; $\text{C}_3\text{F}_7\text{Fe}(\text{CO})_4\text{I}$, 65529-00-2.

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- A similar E-mode splitting has been observed⁸ for the related complex $\text{C}_3\text{F}_7\text{Mn}(\text{CO})_5$, but not¹⁷ for $\text{C}_6\text{F}_5\text{Mn}(\text{CO})_5$. This suggests that the E-mode splitting in $(\text{C}_3\text{F}_7)(\text{C}_6\text{F}_5)\text{Fe}(\text{CO})_4$ is a consequence of the C_3F_7 group rather than the C_6F_5 group.

- (19) For a related example, see the elegant infrared study of isomeric $\text{Fe}(\text{CO})_2\text{L}_2$ complexes: M. Pankowski and M. Bigorgne, *J. Organomet. Chem.*, **125**, 231 (1977).
- (20) For example, the $\nu(\text{CO})$ bands of $\text{C}_3\text{F}_7\text{Fe}(\text{CO})_4\text{I}^6$ and $\text{C}_3\text{F}_7\text{Mn}(\text{CO})_5^8$ are within $\pm 5 \text{ cm}^{-1}$ of the corresponding bands of $\text{C}_6\text{F}_5\text{Fe}(\text{CO})_4\text{I}^{21}$ and $\text{C}_6\text{F}_5\text{Mn}(\text{CO})_5^{16}$ respectively.
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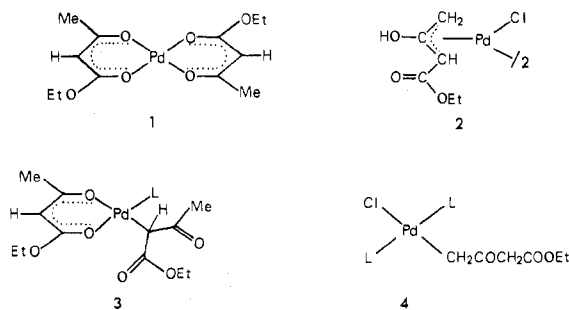
η^3 and η^1 Terminal-Carbon-Bonded Complexes of 2,4-Pentanedione with Palladium(II)

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Received July 21, 1977

Dichlorobis(benzonitrile)palladium(II) reacts with 2,4-pentanedione (acacH) in acetone at 0°C to afford $[\text{PdCl}(\text{acac-}O,O)]_2$ (**5**), which turns to a η^3 acac complex $[\text{PdCl}(\text{acac-C}^1\text{-C}^3)]_2$ (**6**) during a prolonged reaction at room temperature. Bridge-splitting reactions of **5** with triphenylphosphine and triphenylarsine yield $\text{PdCl}(\text{acac-}O,O)\text{L}$, where L is PPh_3 (**7a**) or AsPh_3 (**7b**). Corresponding mononuclear complexes $\text{PdCl}(\text{acac-C}^1\text{-C}^3)\text{L}$ (L = PPh_3 (**8a**) or AsPh_3 (**8b**)) and $\text{M}[\text{PdCl}_2(\text{acac-C}^1\text{-C}^3)]$ (M = PPh_4 (**9a**) or AsPh_4 (**9b**)) are similarly derived from **6**. The isomeric pairs **7a-8a** and **7b-8b** manifest a novel type of linkage isomerism. The reaction of **6** with 2,2'-bipyridine results in $\text{PdCl}(\text{acac-C}^1)(\text{bpy})$, which exhibits the keto-enol tautomerism of the terminal-carbon-bonded acac, the equilibrium quotient $[\text{enol}]/[\text{keto}]$ being 0.7 in CDCl_3 at 25°C .

2,4-Pentanedione and other β -dicarbonyl compounds are very versatile ligands exhibiting various modes of bonding to metal ions.¹ In recent years four kinds of coordination modes of ethyl acetoacetate have been observed in palladium(II) complexes: O,O' chelation (**1**, **3**),² η^3 -allylic bonding (**2**),³ η^1 central carbon bonding (**3**),² and terminal carbon bonding (**4**).⁴



In order to clarify the factors which make the ligand prefer a particular bonding mode, many more comparative studies are necessary employing other β -dicarbonyl compounds and various coexisting ligands. 2,4-Pentanedione (acacH), the most representative β -dicarbonyl compound, usually coordinates to a metal ion through the two oxygen atoms forming a six-membered chelate ring.⁵ The central-carbon-bonded palladium(II) complexes of acacH similar to **3** were obtained by the reactions of $\text{Pd}(\text{acac})_2$ with Lewis bases (L) such as triphenylphosphine, pyridine, and diethylamine.⁶ The present paper reports the preparation and characterization of several palladium(II) complexes of acacH exhibiting η^3 bonding a little different from the delocalized η -allylic coordination in **2** and those containing terminal σ bonding similar to that in **4**.

Experimental Section

Di- μ -chloro-bis(2,4-pentanedionato)dipalladium(II), $[\text{PdCl}(\text{acac-}O,O)]_2$ (5**).** Dichlorobis(benzonitrile)palladium(II) (1 g, 2.6 mmol) prepared by the method of Kharasch et al.⁷ was dissolved in 25 mL of a mixture (1:1 by volume) of acetone and acacH. The solution was stirred in an ice bath for 1–2 h to separate out a brown fuzzy precipitate in 22% yield, which was filtered, washed with acetone, and dried in vacuo. The compound is sparingly soluble in the usual

solvents. Anal. Calcd for $[\text{PdCl}(\text{C}_5\text{H}_7\text{O}_2)]_2$: C, 24.92; H, 2.93; Cl, 14.71. Found: C, 24.50; H, 2.86; Cl, 15.25.

Di- μ -chloro-bis(η^3 -1-acetyl-2-hydroxyallyl)palladium(II), $[\text{PdCl}(\text{acac-C}^1\text{-C}^3)]_2$ (6**).** The above-mentioned reaction between $\text{PdCl}_2(\text{PhCN})_2$ and acacH was performed at room temperature for about 24 h. The brown precipitate once formed was gradually converted into a yellow powder, which was filtered, washed with acetone, and dried in vacuo. The yield was 40%. The compound is also sparingly soluble in usual solvents. Anal. Calcd for $[\text{PdCl}(\text{C}_5\text{H}_7\text{O}_2)]_2$: C, 24.92; H, 2.93; Cl, 14.71. Found: C, 25.37; H, 2.99; Cl, 14.88.

Chloro(2,4-pentanedionato)(triphenylphosphine)palladium(II), $\text{PdCl}(\text{acac-}O,O)\text{PPh}_3$ (7a**).** A benzene solution (8 mL) containing triphenylphosphine in amounts (0.1821 g) equimolar with palladium was added drop by drop with stirring to a suspension of complex **5** (0.1682 g) in benzene (3 mL). The mixture turned to a clear solution upon reaction. After filtration the solution was concentrated to ca. 5 mL by vacuum evaporation at room temperature. Ethyl ether was added to the solution to precipitate a yellow powder, which was filtered and washed with ether. The yield was 60%. Red-orange needles were obtained by recrystallization from dichloromethane–petroleum ether. Anal. Calcd for $\text{PdCl}(\text{C}_5\text{H}_7\text{O}_2)\text{P}(\text{C}_6\text{H}_5)_3$: C, 54.89; H, 4.41; mol wt, 503. Found: C, 54.60; H, 4.76; mol wt, 532.

Chloro(2,4-pentanedionato)(triphenylarsine)palladium(II), $\text{PdCl}(\text{acac-}O,O)\text{AsPh}_3$ (7b**).** The bridge-splitting reaction of complex **5** with triphenylarsine in a similar fashion as above afforded red-orange needles in a 79.6% yield. Anal. Calcd for $\text{PdCl}(\text{C}_5\text{H}_7\text{O}_2)\text{As}(\text{C}_6\text{H}_5)_3$: C, 50.48; H, 4.05; Cl, 6.48; mol wt, 547. Found: C, 51.04; H, 4.11; Cl, 7.82; mol wt, 593.

Chloro(η^3 -1-acetyl-2-hydroxyallyl)(triphenylphosphine)palladium(II), $\text{PdCl}(\text{acac-C}^1\text{-C}^3)\text{PPh}_3$ (8a**), and Chloro(η^3 -1-acetyl-2-hydroxyallyl)(triphenylarsine)palladium(II), $\text{PdCl}(\text{acac-C}^1\text{-C}^3)\text{AsPh}_3$ (**8b**).** The bridge-splitting reactions of complex **6** with triphenylphosphine or triphenylarsine were carried out in benzene at room temperature to obtain yellow powders in 84.7 and 79.4% yields, respectively. Both of them were recrystallized from dichloromethane–petroleum ether. Anal. Calcd for $\text{PdCl}(\text{C}_5\text{H}_7\text{O}_2)\text{P}(\text{C}_6\text{H}_5)_3$: C, 54.89; H, 4.41; Cl, 7.04; P, 6.15; mol wt, 503. Found: C, 54.61; H, 4.39; Cl, 7.20; P, 5.68; mol wt, 540. Calcd for $\text{PdCl}(\text{C}_5\text{H}_7\text{O}_2)\text{As}(\text{C}_6\text{H}_5)_3$: C, 50.48; H, 4.05; Cl, 6.48; mol wt, 547. Found: C, 50.41; H, 4.03; Cl, 7.36; mol wt, 584.

Di- μ -bromo-bis(η^3 -1-acetyl-2-hydroxyallyl)palladium(II), $[\text{PdBr}(\text{acac-C}^1\text{-C}^3)]_2$ (6'**).** Dibromobis(benzonitrile)palladium(II) was allowed to react in an acetone–acacH solution at room temperature