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ORGANOMETALLIC CHEMISTRY OF THE TRANSITION METALS XXV*. OXIDATIVE ADDITION REACTIONS OF (PENTAMETHYLCYCLOPENTADIENYL)DICARBONYLIRIDIUM WITH VARIOUS IODINE COMPOUNDS

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SUMMARY

Various oxidative addition reactions of $(CH_3)_5C_5Ir(CO)_2$ with iodine compounds are described. Iodine reacts with $(CH_3)_5C_5Ir(CO)_2$ in tetrahydrofuran at room temperature to give the red crystalline diiodide $(CH_3)_5C_5Ir(CO)I_2$. The perfluoroalkyl iodides, R_fI ($R_f = CF_3$, C_2F_5, and n-C_3F_7), react with $(CH_3)_5C_5Ir(CO)_2$ in benzene at room temperature to give the yellow-orange $(CH_3)_5C_5Ir(CO)(R_f)I$ ($R_f = CF_3$, C_2F_5, and n-C_3F_7). A similar reaction of methyl iodide with $(CH_3)_5C_5Ir(CO)_2$ gives a mixture of the yellow-orange σ-methyliridium derivatives $(CH_3)_5C_5Ir(CO)(CH_3)I$ and the diiodide $(CH_3)_5C_5Ir(CO)I_2$. Reaction of allyl iodide with $(CH_3)_5C_5Ir(CO)_2$ in tetrahydrofuran at room temperature gives a mixture of the unstable yellow ionic σ-allyl derivative $[(CH_3)_5C_5Ir(CO)_2CH_2CH{=}CH_2]$ I and the diiodide $(CH_3)_5C_5Ir(CO)I_2$. Reaction of ICF_2CF_2I with $(CH_3)_5C_5Ir(CO)_2$ in benzene at room temperature gives the cation $[(CH_3)_5C_5Ir(CO)_2CF_2CF_2I]^+$, which may be isolated as the yellow hexafluorophosphate salt. The IR, NMR, and mass spectra of these new (pentamethylcyclopentadienyl)iridium complexes are discussed.

INTRODUCTION

Within the last decade numerous oxidative addition reactions of the cyclopentadienylmetal dicarbonyls of cobalt and rhodium, $C_5H_5M(CO)_2$ (M = Co and Rh) have been reported[2-8]. Compounds prepared by this route include the cyclopentadienylmetal carbonyl diiodides, $C_5H_5M(CO)I_2$ (M = Co[4-6] and Rh[6]), the perfluoroalkyl derivatives $C_5H_5M(CO)(R_f)I$ (M = Co[2] or Rh[3]; $R_f = CF_3$, C_2F_5, C_3F_7, etc.) and the π-allyl derivatives[7,8] $[C_5H_5Co(C_3H_5)CO]^+$ and $C_5H_5Co(C_3H_5)I$. However, when this work was started, no comparable oxidative addition reactions of cyclopentadienyldicarbonyliridium[9], $C_5H_5Ir(CO)_2$, had been reported apparently because of the difficulty of preparing large quantities of $C_5H_5Ir(CO)_2$ not only because of the relatively high cost of iridium but also because of difficulties associated with obtaining large quantities of the $Ir(CO)_3Cl$ required for the preparation of $C_5H_5Ir(CO)_2$.

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Oxidative addition reactions of $C_5H_5Ir(CO)_2$ are of particular interest because of the greater strength of metal–carbon bonds in 5*d* transition metals as compared with 3*d* and 4*d* transition metals[10]. This suggests that iridium will form ionic dicarbonyl derivatives of the type $[C_5H_5Ir(CO)_2Y]X$ (Y = one-electron donor ligand such as halogen, alkyl or perfluoroalkyl; X = halogen) in cases where cobalt and rhodium form non-ionic monocarbonyl derivatives of the type $C_5H_5M(CO)YX$ (M = Co and Rh).

This dormant interest in the oxidative addition chemistry of $C_5H_5Ir(CO)_2$ was recently awakened by the discovery by Kang, Moseley, and Maitlis[11] of a convenient preparation of $(CH_3)_5C_5Ir(CO)_2$ using hydrated iridium trichloride and the now readily available hexamethylbicyclo[2,2,0]hexadiene ("hexamethyl-Dewar-benzene") as ultimate raw materials. This pentamethylcyclopentadienyl derivative $(CH_3)_5C_5Ir(CO)_2$ appeared to provide a suitable model compound for the study of oxidative addition reactions on cyclopentadienyliridium dicarbonyl derivatives since the presence of the five methyl groups rather than hydrogen atoms on the cyclopentadienyl ring would be expected to have relatively little influence upon oxidative addition reactions involving the metal atom. Accordingly we prepared several grams of $(CH_3)_5C_5Ir(CO)_2$ and studied its reactions with iodine, alkyl iodides, and perfluoroalkyl iodides. The details of this work are given in this paper.

After this work was essentially complete, we became aware of a parallel study by Kang and Maitlis[12] also concerning oxidative addition reactions on $(CH_3)_5C_5Ir(CO)_2$ but using different halides (mainly sulfonyl chlorides, RSO_2Cl) and/or different reaction conditions than the work described in this paper.

EXPERIMENTAL

Materials

The $(CH_3)_5C_5Ir(CO)_2$ used in this work was prepared by the procedure of Kang, Moseley, and Maitlis[11] utilizing as raw materials commercial samples of iridium trichloride trihydrate (Englehard Industries, Newark, New Jersey; 54.1% iridium) and hexamethylbicyclo[2,2,0]hexadiene ("hexamethyl-Dewar-benzene", Henley and Co., New York, New York) and $Fe_2(CO)_9$ prepared from $Fe(CO)_5$ (GAF Corp., New York, New York) by the published procedures[13] modified to fit the locally available photolysis apparatus. The iodine compounds used in this work all were commercial samples. Tetrahydrofuran was purified by distillation over lithium aluminum hydride. Benzene was dried by distillation over sodium.

Reaction of $(CH_3)_5C_5Ir(CO)_2$ with iodine

A mixture of 0.25 g (0.653 mmole) of $(CH_3)_5C_5Ir(CO)_2$, 0.166 g (0.653 mmole) of iodine, and 10 ml of redistilled tetrahydrofuran was kept for three days at room temperature (~25°). Solvent was removed at ~25°/40 mm. The residue was recrystallized three times from mixtures of dichloromethane and hexane to give 0.336 g (85% yield) of red crystalline air-stable $(CH_3)_5C_5Ir(CO)I_2$. The properties of this compound and the other compounds prepared in this work are summarized in Table 1.

Reactions of $(CH_3)_5C_5Ir(CO)_2$ with the perfluoroalkyl iodides

A mixture of 0.15 to 0.25 g of $(CH_3)_5C_5Ir(CO)_2$, excess (3 to 4 g) of the perfluoroalkyl iodide, and 3 to 4 ml of benzene was kept in a sealed tube for 50 h at room temperature (~25°). Excess perfluoroalkyl iodide and benzene were then removed at ~25°/40 mm. The residue was recrystallized twice from mixtures of dichloromethane and hexane to give the yellow-orange air-stable $(CH_3)_5C_5Ir(CO)(R_f)I$ derivative in 78–88% yield.

Reaction of $(CH_3)_5C_5Ir(CO)_2$ with methyl iodide

A mixture of 0.15 g (0.39 mmole) of $(CH_3)_5C_5Ir(CO)_2$, 3 g (21.2 mmoles) of methyl iodide, and 3 ml of benzene was kept at room temperature (~25°) in a sealed tube for 73 h. A pale yellow precipitate appeared 10 min after mixing the reagents but after 24 h this precipitate had disappeared and the reaction mixture had turned deep red. After the reaction period was over, excess methyl iodide and benzene were removed at 25°/40 mm. The dry residue was dissolved in a mixture of 8 ml of dichloromethane and 24 ml of hexane and the resulting solution chromatographed on a 1.5 × 20 cm florisil column under nitrogen. The chromatogram was developed with a mixture of dichloromethane and hexane to give a yellow band of $(CH_3)_5C_5Ir(CO)(CH_3)I$ and an orange band of $(CH_3)_5C_5Ir(CO)I_2$. The $(CH_3)_5C_5Ir(CO)(CH_3)I$ was eluted with a 1/2 mixture of dichloromethane and hexane and the $(CH_3)_5C_5Ir(CO)I_2$ was eluted with a 1/1 mixture of dichloromethane and hexane. Both eluates were evaporated and the products recrystallized from the same solvent mixture to give ultimately 0.047 g (24% yield) of yellow-orange $(CH_3)_5C_5Ir(CO)(CH_3)I$ and 0.025 g (11% yield) of red $(CH_3)_5C_5Ir(CO)I_2$.

Reaction of $(CH_3)_5C_5Ir(CO)_2$ with 1,2-diiodotetrafluoroethane

A mixture of 0.15 g (0.39 mmole) of $(CH_3)_5C_5Ir(CO)_2$, 0.35 g (1.0 mmoles) of 1,2-diiodotetrafluoroethane, and 5 ml of dry benzene was kept at room temperature (~25°) for 4 days. The orange precipitate was removed by filtration, washed with four 5 ml portions of benzene, and dried to give 0.205 g (80% yield) of orange $[(CH_3)_5C_5Ir(CO)_2CF_2CF_2I]I$, identified by its ν(CO) frequencies at 2119 and 2087 cm^{-1} (CH_2Cl_2 solution). This crude product also contained some of the iodide $(CH_3)_5C_5Ir(CO)I_2$ as indicated by the ν(CO) frequency at 2044 cm^{-1}. For this reason it was converted in quantitative yield to the corresponding yellow hexafluorophosphate salt by treatment with a ten-fold excess of ammonium hexafluorophosphate in acetone followed by recrystallization of the hexafluorophosphate salt from a mixture of dichloromethane and hexane.

Reaction of $(CH_3)_5C_5Ir(CO)_2$ with allyl iodide

A mixture of 0.30 g (0.78 mmole) of $(CH_3)_5C_5Ir(CO)_2$, 0.50 g (3.0 mmoles) of allyl iodide, and 3 ml of redistilled tetrahydrofuran was kept at room temperature (~25°) for 24 h. A yellow precipitate contaminated with some red crystals separated. This yellow precipitate was removed by filtration, freed from the red contaminant by washing with four 3 ml portions of tetrahydrofuran, and dried to give 0.257 g (60% yield) of yellow $[(CH_3)_5C_5Ir(CO)_2CH_2CH{=}CH_2]I$. Upon standing or dissolution in organic solvent (*e.g.* dichloromethane) this allyl derivative decomposed to give the red halides $(CH_3)_5C_5Ir(CO)X_2$ (X = Cl or I). For this reason, a meaningful proton NMR spectrum could not be obtained.

The tetrahydrofuran filtrate and washings from the isolation of $[(CH_3)_5C_5Ir$-

TABLE 1

(PENTAMETHYLCYCLOPENTADIENYL)IRIDIUM CARBONYL DERIVATIVES PREPARED IN THIS WORK

Compound[a]	Color	M.p.[b] (°C)	Yield[c] (%)	Analyses, found (calcd.) (%)[d]					IR[e] ν(CO)	NMR[f] τ(CH_3)
				C	H	O	I	F		
$Me_5C_5Ir(CO)I_2$	Red	305–306	85	21.9 (21.7)	2.5 (2.5)	2.7 (2.6)	41.4 (41.6)		2044	7.72
$Me_5C_5Ir(CO)(CF_3)I$	Yellow-orange	228–230 (dec.)	78	26.4 (26.2)	2.8 (2.7)		23.1 (23.1)	10.4 (10.3)	2050	7.79
$Me_5C_5Ir(CO)(C_2F_5)I$	Yellow-orange	235–236	88	26.1 (26.0)	2.5 (2.5)		21.2 (21.2)	15.8 (15.8)	2048	7.84
$Me_5C_5Ir(CO)(C_3F_7)I$	Yellow-orange	161–162	88	25.9 (25.9)	2.5 (2.3)		19.6 (19.5)	20.5 (20.4)	2049	7.82
$Me_5C_5Ir(CO)(CH_3)I$	Yellow-orange	190–191 (dec.)	24	29.1 (28.9)	3.6 (3.6)	3.3 (3.2)	25.9 (25.6)		2002	7.92 8.67[g]
$[Me_5C_5Ir(CO)_2C_3H_5]I$	Yellow	125–127	60	32.7 (32.7)	3.8 (4.0)	6.4 (6.4)	23.1 (23.1)		2103, 2063	[h]
$[Me_5C_5Ir(CO)_2CF_2CF_2I][PF_6]$	Yellow	172–173	80	22.1 (22.3)	2.3 (2.0)	[i]	16.8 (16.8)	25.3 (25.2)	2131, 2100	7.52[j]

[a] Me=methyl. [b] These melting and decomposition points were determined in capillaries and are uncorrected. [c] These yields were obtained from preparations carried out as described in the Experimental Section. [d] These microanalyses were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany. [e] These IR spectra were obtained in dichloromethane solution and recorded on a Perkin-Elmer Model 621 Spectrometer with grating optics. Frequencies are given in cm^{-1}. [f] These proton NMR spectra were run in CH_2Cl_2 solution (unless otherwise indicated) and recorded on a Perkin-Elmer Hitachi Model R-20 Spectrometer. [g] This resonance arises from the methyl group directly bonded to iridium. [h] This compound was too unstable in solution for a meaningful proton NMR spectrum to be obtained. [i] Found: P, 4.2. Calcd.: P, 4.1%. [j] This spectrum was run in $(CD_3)_2CO$ solution.

$(CO)_2CH_2CH{=}CH_2]I$ were combined and then evaporated at ~25°/40 mm to give 0.06 g (13% yield) of red crystalline $(CH_3)_5C_5Ir(CO)I_2$. (Found: C, 21.9; H, 2.5; O, 2.8. $C_{11}H_{15}I_2IrO$ calcd.: C, 21.7; H, 2.5; O, 2.6%.)

An analogous reaction was carried out between $(CH_3)_5C_5Ir(CO)_2$ and allyl chloride in tetrahydrofuran for 10 days. However, unreacted $(CH_3)_5C_5Ir(CO)_2$ was the only iridium compound that could be isolated from the reaction mixture.

The reaction between $(CH_3)_5C_5Ir(CO)_2$ and allyl iodide was also carried out in benzene rather than tetrahydrofuran but otherwise employing the same reaction conditions. In this case, no $[(CH_3)_5C_5Ir(CO)_2CH_2CH{=}CH_2]I$ was obtained. The only (pentamethylcyclopentadienyl)iridium derivative found in this reaction mixture was $(CH_3)_5C_5Ir(CO)I_2$, which was isolated in 33% yield.

Reactions of $(CH_3)_5C_5Ir(CO)_2$ with other alkyl iodides

The reactions between $(CH_3)_5C_5Ir(CO)_2$ and the iodides RI (R = ethyl, propyl, and phenyl) were carried out in benzene solution utilizing the same procedure described above for the reaction between $(CH_3)_5C_5Ir(CO)_2$ and methyl iodide. In the cases of the ethyl, propyl and phenyl iodides, chromatography on Florisil after a 10 day reaction period gave only a high recovery of unreacted $(CH_3)_5C_5Ir(CO)_2$. Similar results were obtained in the reaction between 1,2-diiodobenzene and $(CH_3)_5C_5Ir(CO)_2$. The reactions between $(CH_3)_5C_5Ir(CO)_2$ and the iodides C_2H_5I, n-C_3H_7I, and 1,2-$C_6H_4I_2$ in pentane (rather than benzene) for 7 days at room temperature (~25°) gave a 10 to 20% yield of $(CH_3)_5C_5Ir(CO)I_2$ as well as some unreacted $(CH_3)_5C_5Ir(CO)_2$.

IR spectra

The IR spectra were taken in the indicated media and recorded on a Perkin-Elmer Model 621 or Model 257 IR spectrometer with grating optics. The ν(CO) frequencies are given in Table 1. Each compound exhibited an exceedingly weak ν(CH) frequency at ~2915 cm^{-1}. The other IR frequencies in the region 1600 to 700 cm^{-1} obtained from spectra taken in potassium bromide pellets are listed below for some of the compounds.

A. $(CH_3)_5C_5Ir(CO)I_2$

Bands at 1498 w, 1491 w, 1471 w, 1455 w, 1449 w, 1438 vw, 1402 w, 1382 m, 1374 m, 1358 w, 1160 w, 1080 w, 1027 m, 1021 m, and 727 vw cm^{-1}.

B. $(CH_3)_5C_5Ir(CO)(CF_3)I$

ν(CF) frequencies at 1081 s and 1012 s cm^{-1}; other bands at 1500 vw, 1474 vw, 1453 w, 1402 w, 1387 m, 1382 m, 1362 vw, 1160 vw, 1040 w, 1020 w, and 711 w cm^{-1}.

C. $(CH_3)_5C_5Ir(CO)(C_2F_5)I$

ν(CF) frequencies at 1302 s, 1280 w, 1191 s, 1170 s, 1064 s, 1057 m, 1010 s, and 919 s cm^{-1}; other bands at 1500 vw, 1480 vw, 1472 vw, 1453 w, 1400 w, 1381 w, 1360 vw, 1075 w, 1026 w, and 731 m cm^{-1}.

D. $(CH_3)_5C_5Ir(CO)(C_3F_7)I$

ν(CF) frequencies at 1323 s, 1293 m, 1215 s, 1192 s, 1162 s, 1085 s, 1052 m, and 1012 s cm^{-1}; other bands at 1500 vw, 1473 vw, 1454 vw, 1398 w, 1385 m, 1380 m, 1361 w, 1077 w, 1030 w, 813 s, and 725 s cm^{-1}.

E. $[(CH_3)_5C_5Ir(CO)_2CF_2CF_2I][PF_6]$

ν(CF) frequencies (?) at 1114 w, 1077 w, 1032 m, and 1014 w cm^{-1}; ν(PF) frequency at 835 vs cm^{-1}; other bands at 1460 m, 1417 m, 1396 m, 1384 m, 1160 vw, (br), 820 vw, and 792 vw cm^{-1}.

F. $[(CH_3)_5C_5Ir(CO)_2CH_2CH{=}CH_2]I$

ν(C=C) frequencies at 1619 w and 1599 vw cm^{-1}; other bands at 1486 w, 1454 w, 1425 vw, 1393 m, 1374 m, 1129 m, 1071 w, 1037 vw, 1020 m, 990 w, and 903 m cm^{-1}.

NMR spectra

The proton NMR spectra (Table 1) were taken in dichloromethane or acetone-d_6 solutions and recorded at 60 MHz on a Perkin–Elmer Hitachi Model R-20 spectrometer. The ^{19}F NMR spectra were taken in dichloromethane solution with 1,2-difluoro-1,1,2,2-tetrachloroethane (ϕ 67.8) as an internal standard and recorded at 56.456 MHz on the same spectrometer. The observed ^{19}F NMR resonances are listed below.

A. $(CH_3)_5C_5Ir(CO)(CF_3)I$

CF_3 group. ϕ 5.0 (singlet).

B. $(CH_3)_5C_5Ir(CO)(C_2F_5)I$

(*a*). *CF_2 group.* AB pattern (four peaks) centered at ϕ 70.5 with splittings of 269 Hz between peaks 1 and 2 and between peaks 3 and 4 and a splitting of 437 Hz between peaks 2 and 3. This corresponds[14] to $J_{gem}(FF) = 269.5$ Hz and $\delta = 651$ Hz or 11.6 ppm. The experimental values for the relative intensity ratios I_b/I_a and I_c/I_d were 2.02 ± 0.03 as compared with the value of 2.24 for this ratio calculated[14] from the chemical shift and coupling constant data.

(*b*). *CF_3 group.* ϕ 82.3 [triplet, $J_{\alpha\beta}$ (FF) = 2.0 Hz].

C. $(CH_3)_5C_5Ir(CO)(C_3F_7)I$

(*a*). *α-CF_2 group.* AB pattern barely distinguishable from the noise and with additional fine structure centered at ϕ 65.6 with splittings of 280 Hz between peaks 1 and 2 and between peaks 3 and 4 and a splitting of 425 Hz between peaks 2 and 3. This corresponds[14] to J_{gem} (FF) = 280 Hz and $\delta = 647$ Hz or 11.5 ppm.

(*b*). *β-CF_2 group.* ϕ 115.3 (apparent doublet with 60 Hz separation, possibly the two inner lines of an AB quartet[3]).

(*c*). *CF_3 group.* ϕ 79.4 (triplet, $J = 12$ Hz).

D. $[(CH_3)_5C_5Ir(CO)_2CF_2CF_2I][PF_6]$ *[$(CD_3)_2CO$ solution; PF region not scanned]*

(*a*). *α-CF_2 group.* ϕ 65.7 (apparent singlet).

(*b*). *β-CF_2 group.* ϕ 75.2 (apparent singlet).

Mass Spectra

Mass spectra of the non-ionic compounds prepared in this work were taken at 70 eV on a Perkin–Elmer Hitachi RMU-6 mass spectrometer with a chamber temperature of 220°. The spectra were relatively complicated because of the tendency for ions such as $(CH_3)_5C_5Ir^+$ to undergo dehydrogenation and loss of individual carbon atoms to give a large variety of ions of the type $C_mH_nIr^+$. However, only the ions with a complete pentamethylcyclopentadienyl ($C_{10}H_{15}$) unit are listed below (except for $(CH_3)_5C_5Ir(CO)_2$). Relative intensities and sample temperatures are given in parentheses with the designation *D* in place of a relative intensity value indicating ions that are found mixed with dehydrogenation products.

A. $(CH_3)_5C_5Ir(CO)_2$ (105°)

$C_{10}H_{15}Ir(CO)_2^+$ (74), $C_{10}H_{15}IrCO^+$ (52), $C_{10}H_{13}IrCO^+$(60), $C_{10}H_{11}IrCO^+$ (~110), $C_{10}H_{15}Ir^+$ (10), $C_{10}H_{13}Ir^+$ (21), $C_{10}H_{11}Ir^+$ (79), and $C_{10}H_9Ir^+$ (36).

B. $(CH_3)_5C_5Ir(CO)I_2$ (~140°)

$C_{10}H_{15}Ir(CO)I_2^+$ (6), $C_{10}H_{15}IrI_2^+$ (144), $C_{10}H_{15}IrCOI^+$ (13), $C_{10}H_{15}IrI^+$ (*D*), $C_{10}H_{15}Ir(CO)_2^+$ (190), $C_{10}H_{15}IrCO^+$ (*D*), $C_{10}H_{15}Ir^+$ (*D*), $C_{10}H_{15}IrI^{++}$ (*D*), and $C_{10}H_{15}Ir^{++}$ (*D*).

C. $(CH_3)_5C_5Ir(CO)(CH_3)I$ (~120°)

$C_{10}H_{15}IrI_2^+$ (1.5), $C_{10}H_{15}Ir(CO)(CH_3)I^+$ (107), $C_{10}H_{15}Ir(CO)I^+$ (94), $C_{10}H_{15}Ir(CH_3)I^+$ (16), $C_{10}H_{15}IrI^+$ (*D*), $C_{10}H_{15}Ir(CO)(CH_3)^+$ (5), $C_{10}H_{15}Ir(CH_3)^+$ (14), $C_{10}H_{15}Ir^+$ (*D*), $C_{10}H_{15}Ir(CH_3)I^{++}$ (13), $C_{10}H_{15}IrI^{++}$ (*D*), and $C_{10}H_{15}Ir^{++}$ (*D*).

Metastable ions at *m/e* 428 [$C_{10}H_{15}Ir(CO)I^+ \rightarrow C_{10}H_{15}IrI^{++} + CO$] and *m/e* 312 [$C_{10}H_{15}Ir(CH_3)^+ \rightarrow C_{10}H_{15}Ir^+ + CH_3$].

D. $(CH_3)_5C_5Ir(CO)(CF_3)I$ (100°)

$C_{10}H_{15}Ir(CO)I_2^+$ (2), $C_{10}H_{15}IrI_2^+$ (86), $C_{10}H_{15}Ir(CO)(CF_3)I^+$ (640), $C_{10}H_{15}Ir(CO)(CF_2)I^+$ (4), $C_{10}H_{15}Ir(CF_3)I^+$ (90), $C_{10}H_{15}Ir(CF_2)I^+$ (71), $C_{10}H_{15}Ir(CO)I^+$ (370), $C_{10}H_{15}IrFI^+$ (16), $C_{10}H_{15}IrI^+$ (*D*), $C_{10}H_{15}Ir(CO)CF_3^+$ (37), $C_{10}H_{15}Ir(CO)CF_2^+$ (36), $C_{10}H_{15}IrCF_3^+$ (200), $C_{10}H_{15}Ir(CO)_2^+$ (11), $C_{10}H_{15}IrCF_2^+$ (*D*), $C_{10}H_{15}IrCO^+$ (*D*), $C_{10}H_{15}IrF^+$ (54), $C_{10}H_{15}Ir^+$ (*D*), $C_{10}H_{15}Ir(CF_2)I^{++}$ (10), $C_{10}H_{15}Ir(CO)I^{++}$ (4), $C_{10}H_{15}IrI^{++}$ (*D*), and $C_{10}H_{15}Ir^{++}$ (*D*).

Metastable ions at *m/e* 496 [$C_{10}H_{15}Ir(CO)(CF_3)I^+ \rightarrow C_{10}H_{15}Ir(CF_3)I^+ + CO$], *m/e* 430 [$C_{10}H_{15}Ir(CO)I^+ \rightarrow C_{10}H_{15}IrI^+ + CO$], and *m/e* 303 [$C_{10}H_{15}IrCO^+ \rightarrow C_{10}H_{15}Ir^+ + CO$].

E. $(CH_3)_5C_5Ir(CO)(C_2F_5)I$ (110°)

$C_{10}H_{15}Ir(CO)(C_2F_5)I^+$ (85), $C_{10}H_{15}IrI_2^+$ (7), $C_{10}H_{15}Ir(C_2F_5)I^+$ (14), $C_{10}H_{15}Ir(C_2F_4)I^+$ (5), $C_{10}H_{15}Ir(CO)(CF_3)I^+$ (4), $C_{10}H_{15}Ir(CO)I^+$ (78), $C_{10}H_{15}IrFI^+$ (9), $C_{10}H_{15}IrI^+$ (*D*), $C_{10}H_{15}IrC_2F_5^+$ (13), $C_{10}H_{15}IrC_2F_4^+$ (8), $C_{10}H_{15}IrCF_3^+$ (2), $C_{10}H_{15}IrCO^+$ (*D*), $C_{10}H_{15}IrF^+$ (59), $C_{10}H_{15}Ir^+$ (*D*), $C_{10}H_{15}Ir(CO)I^{++}$ (2), $C_{10}H_{15}IrI^{++}$ (*D*), and $C_{10}H_{15}Ir^{++}$ (*D*).

Metastable ion at *m/e* 387 [$C_{10}H_{15}Ir(CO)(C_2F_5)I^+ \rightarrow C_{10}H_{15}Ir(CO)I^+ + C_2F_5$].

F. $(CH_3)_5C_5Ir(CO)(C_3F_7)I$ (~140°)

$C_{10}H_{15}Ir(CO)(C_3F_7)I^+$ (18), $C_{10}H_{15}Ir(C_3F_7)I^+$ (7), $C_{10}H_{15}Ir(C_3F_6)I^+$ (4), $C_{10}H_{15}IrI_2^+$ (6), $C_{10}H_{15}Ir(CO)(C_3F_7)^+$ (4), $C_{10}H_{15}Ir(CO)(C_3F_7)^+$ (77), $C_{10}H_{15}IrC_3F_7^+$ (8), $C_{10}H_{15}Ir(CO)I^+$ (53), $C_{10}H_{15}IrC_3F_6^+$ (19), $C_{10}H_{15}IrI^+$ (220), $C_{10}H_{15}IrCO^+$ (*D*), $C_{10}H_{15}IrF^+$ (350), $C_{10}H_{15}Ir^+$ (*D*), $C_{10}H_{15}IrI^{++}$ (*D*), and $C_{10}H_{15}Ir^{++}$ (*D*).

Metastable ion at *m/e* 428 [$C_{10}H_{15}Ir(CO)I^+ \rightarrow C_{10}H_{15}IrI^+ + CO$].

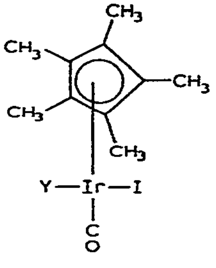
DISCUSSION

Oxidative addition reactions of cyclopentadienylmetal dicarbonyl derivatives $R_5C_5M(CO)_2$ ($R = H$ or CH_3, $M = CO$, Rh, or Ir) with a halide of the type YX ($X =$ halogen, $Y =$ halogen, alkyl, or perfluoroalkyl group) proceed according to the following two step sequence:

$$R_5C_5M(CO)_2 + YX \rightarrow [R_5C_5M(CO)_2Y]X \qquad (1)$$

$$[R_5C_5M(CO)_2Y]X \rightarrow R_5C_5M(CO)YX + CO \qquad (2)$$

The formation of the salt $[R_5C_5M(CO)_2Y]X$ by simple addition of the halide to the $R_5C_5M(CO)_2$ derivative with fission of the X–Y bond in step (1) above is completely analogous to the formation of an "onium" salt by addition of an alkyl halide to an amine, phosphine, sulfide, or similar Lewis base. Indeed the Lewis basicity of C_5H_5-$Co(CO)_2$ towards Lewis acids such as mercuric chloride has previously been demonstrated[15]. In step (2) above the halide ion generated by fission of the X–Y bond acts as a Lewis base replacing one carbonyl group to form a non-ionic R_5C_5M-(CO)YX derivative. The tendency for step (2) to occur is highly dependent upon the strength of the metal–carbonyl bonds. In the reported reactions of the cobalt and rhodium derivatives $C_5H_5M(CO)_2$ (M = Co and Rh) with iodine[4–6] or perfluoroalkyl iodides[2,3] the only isolable products were the non-ionic compounds of the type R_5C_5-M(CO)YX (R = H, M = Co or Rh, Y = I, CF_3, C_2F_5, C_3F_7, etc.) apparently because the metal–carbonyl bond strengths in the presumed ionic intermediates $[R_5C_5M$-$(CO)_2Y]X$ are so low that the step (2) occurs very rapidly under conditions that step (1) takes place. The iridium systems $R_5C_5Ir(CO)_2$ (R = H or CH_3) should be better cases than their cobalt or rhodium analogues for inhibiting step (2) of the above sequence and thus for isolating and characterizing the ionic intermediates $[R_5C_5M(CO)_2Y]X$ formed in step (1) because of the greater strength of metal–carbon bonds to carbonyl groups formed by *5d* transition metals such as iridium as compared with *3d* transition metals such as cobalt or *4d* transition metals such as rhodium[10]. Similar differences in behavior have been noted for oxidative addition reactions with analogous triphenylphosphine complexes of the type $[(C_6H_5)_3P]_2M(CO)_3$ of the iron, ruthenium, and osmium triad[16].



(I)

The oxidative addition reactions of iodine and perfluoroalkyl iodides to the iridium derivative $(CH_3)_5C_5Ir(CO)_2$ in benzene solution proceed to the same extent as the corresponding oxidative addition reactions to the cobalt and rhodium derivatives $C_5H_5M(CO)_2$ (M = Co and Rh). Steps (1) and (2) both occur giving ultimately products of the type $(CH_3)_5C_5Ir(CO)YI$ [(I), Y = I, CF_3, C_2F_5, and C_3F_7]. In these cases the additional strength of the iridium–carbon bonds relative to analogous cobalt–carbon and rhodium–carbon bonds does not inhibit step (2) sufficiently to allow isolation of stable ionic $[(CH_3)_5C_5Ir(CO)_2Y]I$ derivatives.

The oxidative addition of methyl iodide to $(CH_3)_5C_5Ir(CO)_2$ in benzene solution at room temperature first gave an unstable yellow precipitate presumed to be the ionic $[(CH_3)_5C_5Ir(CO)_2CH_3]I$, the expected reaction product from step (1); Kang and Maitlis[12] independently prepared this ionic compound from methyl iodide and $(CH_3)_5C_5Ir(CO)_2$ in diethyl ether. In the case of the reaction between methyl iodide and $(CH_3)_5C_5Ir(CO)_2$ in benzene solution, the original yellow precipitate soon redissolved to form a red solution from which the step (2) non-ionic oxidative addition product $(CH_3)_5C_5Ir(CO)(CH_3)I$ could be isolated as well as the iodide $(CH_3)_5C_5Ir(CO)I_2$. The preparation of the iridium σ-methyl derivative $(CH_3)_5C_5Ir(CO)(CH_3)I$ is unusual since similar cobalt and rhodium σ-methyl derivatives of the type $C_5H_5M(CO)(CH_3)I$ (M = Co and Rh) have apparently been isolated neither from the reactions of methyl iodide with the cyclopentadienylmetal dicarbonyls $C_5H_5M(CO)_2$ nor from other likely reactions. This may again reflect the greater stability of iridium–carbon bonds relative to analogous cobalt–carbon and rhodium–carbon bonds.

The higher alkyl iodides C_2H_5I and n-C_3H_7I failed to react with $(CH_3)_5C_5Ir(CO)_2$ in benzene at room temperature for several days. These alkyl iodides reacted slowly with $(CH_3)_5C_5Ir(CO)_2$ in pentane at room temperature to give the diiodide $(CH_3)_5C_5Ir(CO)I_2$. The failure to obtain ethyl and n-propyl derivatives of the types $[(CH_3)_5C_5Ir(CO)_2R]I$ and $(CH_3)_5C_5Ir(CO)RI$ is probably a consequence of the relative weakness of transition metal–carbon σ-bonds to ethyl and higher alkyl groups. This is consistent with other observations such as the instability of the ethyl derivative $C_2H_5Mn(CO)_5$ relative to the corresponding methyl derivative $CH_3Mn(CO)_5$[17].

The cobalt derivative $C_5H_5Co(CO)_2$ reacts with allyl iodide to give both the ionic[7] π-allyl derivative $[C_5H_5Co(CO)(C_3H_5)]I$ and the non-ionic[8] π-allyl derivative $C_5H_5Co(C_3H_5)I$. This suggests the following three-step sequence for the reaction between cyclopentadienylmetal dicarbonyl derivatives and allyl iodide:

$$R_5C_5M(CO)_2 + C_3H_5I \rightarrow [R_5C_5M(CO)_2(\sigma\text{-}C_3H_5)]I \tag{1}$$

$$[R_5C_5M(CO)_2(\sigma\text{-}C_3H_5)]I \rightarrow [R_5C_5M(CO)(\pi\text{-}C_3H_5)]I + CO \tag{2A}$$

$$[R_5C_5M(CO)(\pi\text{-}C_3H_5)]I \rightarrow [R_5C_5M(\pi\text{-}C_3H_5)]I + CO \tag{3A}$$

The products $[C_5H_5Co(CO)(C_3H_5)]I$ and $C_5H_5Co(C_3H_5)I$ from the reaction between $C_5H_5Co(CO)_2$ and allyl iodide are the products from steps (2A) and (3A) respectively, in the sequence listed above.

Allyl iodide (but not allyl chloride) reacts with $(CH_3)_5C_5Ir(CO)_2$ in tetrahydrofuran solution to give a yellow precipitate shown by its IR spectrum and elemental analyses to be the ionic σ-allyl derivative $[(CH_3)_5C_5Ir(CO)_2CH_2CH{=}CH_2]I$, the expected reaction product from step (1). In addition some $(CH_3)_5C_5Ir(CO)I_2$ can be isolated from the reaction mixture. No π-allyl derivatives such as the expected products from steps (2A) and (3A) above were isolated from the reaction between allyl iodide and $(CH_3)_5C_5Ir(CO)_2$. Apparently, the *5d* transition metal iridium forms such strong bonds with carbon monoxide[10] that decarbonylation according to reaction (2A) is inhibited to the extent that it cannot compete with the homolytic cleavage of the allyl–iridium σ-bond. This parallels the behavior of the σ-allylmolybdenum derivative $C_3H_5Mo(CO)_3C_5H_5$ which upon heating forms $[C_5H_5Mo(CO)_3]_2$ by homolytic cleavage of the allyl–molybdenum bond rather than the π-allylmolybdenum derivative $C_3H_5Mo(CO)_2C_5H_5$ by decarbonylation, even though the π-allyl derivative is known to be a relatively stable compound[18].

The σ-allyl derivative $[(CH_3)_5C_5Ir(CO)_2CH_2CH{=}CH_2]I$, although initially yellow, gradually becomes red, particularly in solution. The IR spectrum of decomposed $[(CH_3)_5C_5Ir(CO)_2CH_2CH{=}CH_2]I$ in the ν(CO) region (CH_2Cl_2 solution) suggests the presence of $(CH_3)_5C_5Ir(CO)I_2$, $(CH_3)_5C_5Ir(CO)_2$, and a third compound possibly the non-ionic acyl derivative $(CH_3)_5C_5Ir(CO)(COCH_2CH{=}CH_2)I$ on the basis of a single terminal ν(CO) frequency at ~2000 cm^{-1} and a single acyl ν(CO) frequency at ~1650 cm^{-1}. The $(CH_3)_5C_5Ir(CO)(COCH_2CH{=}CH_2)I$ is isomeric with the $[(CH_3)_5C_5Ir(CO)_2(CH_2CH{=}CH_2)]I$ and closely related to a rhodium compound $(CH_3)_5C_5Rh(CO)(COCH_3)I$ prepared by Kang and Maitlis[12]; it can be formed by a decarbonylation reaction similar to step (2) discussed above but with the liberated carbon monoxide inserting into the relatively weak allyl–iridium σ-bond by the usual alkyl migration mechanism[19].

The reaction between $C_5H_5Co(CO)_2$ and 1,2-diiodo-1,1,2,2-tetrafluoroethane, $C_2F_4I_2$, in benzene at ~50° gives $C_5H_5Co(CO)I_2$ with apparent elimination of tetrafluoroethylene[20]. The reaction between $(CH_3)C_5Ir(CO)_2$ and $C_2F_4I_2$ in benzene at room temperature gives in addition to a small amount of the analogous $(CH_3)_5C_5Ir(CO)I_2$ a larger quantity of the cation $[(CH_3)_5C_5Ir(CO)_2CF_2CF_2I]^+$, the reaction product from step (1) given above; this cation is best isolated as its hexafluorophosphate salt $[(CH_3)_5C_5Ir(CO)_2CF_2CF_2I]$ $[PF_6]$. Thus, 1,2-diiodo-1,1,2,2-tetrafluoroethane, like allyl iodide, can be made to stop at simple addition [step (1) above] in its reaction with $(CH_3)_5C_5Ir(CO)_2$. Further decomposition of the cations $[R_5C_5M(CO)_2CF_2CF_2I]^+$ clearly results in the elimination of one mole of tetrafluoroethylene and one mole of carbon monoxide to give $R_5C_5M(CO)I_2$ in the presence of iodide, but presently available data are insufficient to determine the sequence of these two elimination processess.

The IR spectra of the new (pentamethylcyclopentadienyl)iridium carbonyl derivatives are in accord with the proposed formulations. The monocarbonyls $(CH_3)_5C_5Ir(CO)YX$ exhibit the expected single ν(CO) band at a frequency similar to that of the single ν(CO) band in related cobalt[2,4–6] and rhodium[3,5] derivatives. The dicarbonyls $[(CH_3)_5C_5Ir(CO)_2Y]X$ ($Y = CH_2CH{=}CH_2, X = I; Y = CF_2CF_2I, X = PF_6$) exhibit the expected two strong ν(CO) bands at higher frequencies than those observed for similar monocarbonyls $(CH_3)_5C_5Ir(CO)YX$. This is an indication of less retrodative bonding from the iridium atom to the carbonyl group(s) in the dicarbonyls $[(CH_3)_5C_5Ir(CO)_2Y]^+$ than in the monocarbonyls $(CH_3)_5C_5Ir(CO)YX$, an expected effect of the positive charge and the second strongly retrodative bonding carbonyl group in the cation. A comparison of the infrared spectrum of $(CH_3)_5C_5Ir(CO)I_2$ with the IR spectra of the perfluoroalkyl derivatives $(CH_3)_5C_5Ir(CO)(R_f)I$ ($R_f = CF_3$, C_2F_5, and C_3F_7) allows unequivocal assignment of the ν(CF) frequencies in the 1350–900 cm^{-1} region of the latter compounds. The ν(CF) bands arising from the fluorine atoms attached to the α-carbon atom of the perfluoroalkyl group *i.e.*, the carbon atom bonded directly to the metal atom) exhibit the expected downward shift[21–23] attributed to weakening of the carbon–fluorine bond by retrodative bonding from the transition metal atom into antibonding orbitals of the perfluoroalkyl group.

The proton NMR spectra of the new (pentamethylcyclopentadienyl)iridium derivatives each exhibit a singlet methyl resonance from the fifteen equivalent protons of the five methyl groups of the pentamethylcyclopentadienyl ring. The proton NMR spectrum of the σ-methyl derivative $(CH_3)_5C_5Ir(CO)(CH_3)I$ exhibits the expected two methyl resonances in an approximate 5/1 ratio with the higher field resonance corresponding to the protons of the single methyl group directly bonded to the iridium atom. The instability of the σ-allyl derivative $[(CH_3)_5C_5Ir(CO)_2CH_2CH{=}CH_2]I$ prevented observation of its proton NMR spectrum.

The ^{19}F NMR spectra of the perfluoroalkyliridium derivatives were entirely analogous to those previously[23,24] observed for other similar perfluoroalkyl transition metal derivatives. The ^{19}F NMR spectra of the α-CF_2 fluorines of both the pentafluoroethyl derivative $(CH_3)_5C_5Ir(CO)(C_2F_5)I$ and the heptafluoropropyl derivative $(CH_3)_5C_5Ir(CO)(C_3F_7)I$ exhibited an AB pattern similar to reported AB patterns in the rhodium derivative[3] $C_5H_5Rh(CO)(C_2F_5)I$ and certain substituted cobalt derivatives[25] of the type $[C_5H_5CoLL'R_f]^+$ [$L=CO$, $L'=(C_6H_5)_3P$, $R_f=C_2F_5$ or C_3F_7; $L=CH_3CN$ $L'=(C_6H_5)_3P$, $R_f=C_2F_5$]. The chemical shift differences and coupling constants calculated from the AB patterns of the α-CF_2 groups in the iridium derivatives $(CH_3)_5C_5Ir(CO)(R_f)I$ ($R_f=C_2F_5$ or C_3F_7) were very similar to each other (see Experimental Section) confirming the assignment of the observed peaks in the ^{19}F NMR spectrum of the heptafluoropropyl derivative where additional coupling ($J=12$ Hz determined from the CF_3 resonance) of the α-CF_2 group with the CF_3 group broadened the individual peaks of the AB pattern so that they were barely observable above the noise level. The observed AB pattern of the α-CF_2 fluorine atoms in the perfluoroalkyliridium derivatives $(CH_3)_5C_5Ir(CO)(R_f)I$ as in the other cases[3,25] is a consequence of restricted rotation around the iridium–carbon (perfluoroalkyl) bond combined with the asymmetry generated by the non-equivalence of the ligands bonded to the iridium atom.

The mass spectra of all of the monocarbonyl derivatives $(CH_3)_5C_5Ir(CO)YI$ prepared in this work confirmed the proposed formulations. Strong molecular ions were observed in all cases. The molecular ions underwent fragmentation by several parallel pathways including iodine, carbon monoxide and alkyl loss, and, in the cases of the perfluoroalkyl derivatives, fluorine loss. However, in no case was the loss of the pentamethylcyclopentadienyl ring the first fragmentation step of the molecular ion; furthermore no significant concentrations of iridium ions not containing a pentamethylcyclopentadienyl ring or some identifiable fragment thereof were observed. For (pentamethylcyclopentadienyl)iridium derivatives of the type $(CH_3)_5C_5Ir(CO)RI$ ($R=CH_3$, CF_3, C_2F_5, or C_3F_7) the relative abundances of ions formed by cleavage of various fragments from the molecular ion (abbreviated as P^+) decreased according to the fragment eliminated in the following sequence: $(P\text{–}R)^+$ (most abundant) $>(P\text{–}CO)^+ > (P\text{–}I)^+ \gg (P\text{–}F)^+$ (for perfluoroalkyl derivatives $\ggg [P\text{–}(CH_3)_5C_5]^+$ (not observed at all). All of the mass spectra of the iridium alkyls and perfluoroalkyls of the type $(CH_3)_5C_5Ir(CO)RI$ ($R=CH_3$, CF_3, C_2F_5, and C_3F_7) exhibit the ion $(CH_3)_5C_5IrI_2^+$ which probably arises from $(CH_3)_5C_5Ir(CO)I_2$ produced by pyrolysis in the mass spectrometer. However, no evidence was observed for the formation of any dialkyls of the type $(CH_3)_5C_5Ir(CO)R_2$ by pyrolysis or other processes in the mass spectra of any of the $(CH_3)_5C_5Ir(CO)RI$ derivatives.

The observed ions in the mass spectra of the $(CH_3)_5C_5Ir(CO)RI$ derivatives ($R=CH_3$, CF_3, C_2F_5, C_3F_7, or I) with intact (pentamethylcyclopentadienyl)iridium groups all arise from one or more of the following processes: (1) Elimination of an alkyl, iodine, or carbonyl ligand; (2) Elimination of a fluorine atom from a perfluoroalkyl group, a process observed in numerous other fluorocarbon derivatives of transition metals[26]; (3) Pyrolysis to give $(CH_3)_5C_5Ir(CO)I_2$ as discussed above; (4) Shift of a fluorine atom from a perfluoroalkyl group to an iridium atom, another process frequently observed in fluorocarbon derivatives of transition metals[26]; (5) Shift of a fluorine atom to an α-carbon atom as required to form the ion $(CH_3)_5C_5Ir(CO)(CF_3)I^+$ in the mass spectrum of $(CH_3)_5C_5Ir(CO)(C_2F_5)I$, another previously observed process[27]. The doubly charged ions $(CH_3)_5C_5Ir^{++}$ and $(CH_3)_5C_5IrI^{++}$ were observed in all of the mass spectra. Metastable ions could be observed for certain carbon monoxide (CO) and alkyl eliminations from some of the more abundant ions (see Experimental Section), but the presence of two iridium isotopes (^{191}Ir and ^{193}Ir) in significant abundances broadened the metastable ions so that their detection and interpretation were more difficult than in the case of metastable ions for processes involving ions containing only essentially monoisotopic elements.

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