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Alkyl Group Isomerization in the Oxidative Addition of Acyl Chlorides to Iridium(I) Complexes

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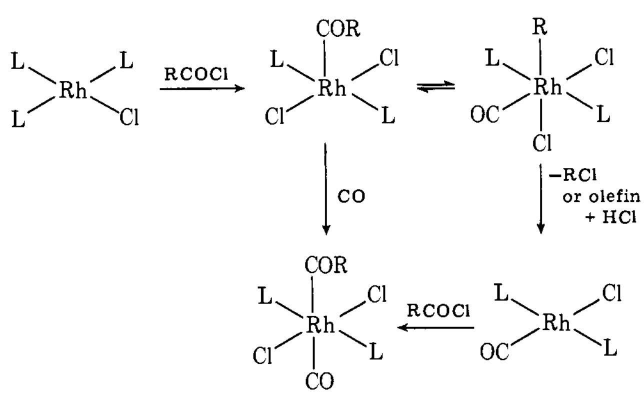
Abstract: Isomeric pairs of normal and α-branched acyl chlorides RCOCl [R = $(CH_2)_2CH_3$ or $CH(CH_3)_2$, $(CH_2)_3CH_3$ or $CH(CH_3)C_2H_5$, $(CH_2)_4CH_3$ or $CH(C_2H_5)_2$, and CH_2CH_2Ph or $CH(CH_3)Ph$] oxidatively add to $IrCl(PPh_3)_n$ (n = 2 or 3) to give the same n-alkyliridium(III) complexes $RIrCl_2(CO)(PPh_3)_2$ [R = $(CH_2)_2CH_3$, $(CH_2)_3CH_3$, $(CH_2)_4CH_3$, and CH_2CH_2Ph respectively], which contain *trans*-triphenylphosphine ligands. The α-branched acyl chlorides give $IrCl(CO)(PPh_3)_2$ and $IrHCl_2(PPh_3)_3$ as by-products. It is suggested that an initially formed *sec*-alkyl complex undergoes rapid β-hydride migration to form an olefin hydride which can either re-form the sterically more favorable n-alkyl or can decompose irreversibly to $IrCl(CO)(PPh_3)_2$, olefin, and HCl. In agreement, n-butanoyl chloride and 2-methylpropanoyl chloride add to the sterically less crowded cyclooctene complex $[IrCl(CO)(C_8H_{14})_2]_2$ to give respectively dimeric n- and isopropyliridium(III) complexes $[RIrCl_2(CO)_2]_2$ [R = $(CH_2)_2CH_3$, $CH(CH_3)_2$] which interconvert in hot benzene to give an approximately 3:2 mixture of n and iso complexes. The equilibrium between the similarly prepared n- and *sec*-butyl complexes is established rapidly even at 34 °C and favors the n-butyl complex. The alkyl complexes $[RIrCl_2(CO)_2]_2$ are formed from $[IrCl(CO)(C_8H_{14})_2]_2$ via acyls $[RCOIrCl_2(CO)(C_8H_{14})]_2$ which can be isolated [R = CH_3, $CH(CH_3)_2$]. Owing to reversible β-elimination, the ethyl complexes obtained from 2-dideuteropropanoyl chloride, CH_3CD_2COCl, and $IrCl(PPh_3)_2$ or $[IrCl(CO)(C_8H_{14})_2]_2$ have their deuterium atoms scrambled between methyl and methylene carbon atoms to an extent which depends on the reaction time. The oxidative additions of acyl chlorides to $IrCl(PPh_3)_3$ and $RhCl(PPh_3)_3$ are compared, and the alkyl group isomerizations observed in other reactions promoted or catalyzed by transition metal complexes are briefly discussed. In the complexes $CH_3(CH_2)_nIrCl_2(CO)(PPh_3)_2$ ($n > 3$) the protons on the third and fourth carbon atoms from the metal are abnormally shielded, as also are the phenethyl aromatic protons in $PhCH_2CH_2IrCl_2(CO)(PPh_3)_2$. These protons probably lie in the shielding zone of the aromatic rings of the *trans*-triphenylphosphine ligands.

Decarbonylation of acyl halides catalyzed by planar d[8] metal complexes such as $RhCl(PPh_3)_3$, $RhCl(CO)(PPh_3)_2$, and $IrCl(CO)(PPh_3)_2$ is a potentially useful process in organic synthesis.[1] It is based on a sequence of reactions at the metal atom involving oxidative addition of the acyl halide, alkyl or aryl migration from the acyl group, and reductive elimination of alkyl or aryl halide, or of olefin and hydrogen halide, as illustrated in Scheme I for $RhCl(PPh_3)_3$.[2-11] Although oxidative additions of acyl halides to iridium(I) complexes of the type $IrCl(CO)L_2$ (L = various tertiary phosphines or arsines) are well documented,[5,12-15] corresponding reactions with $IrCl(PPh_3)_3$ have received little attention. This complex oxidatively adds hydrogen,[16] thiols,[17] silanes,[18] and 1-alkynes[19] more readily than either $IrCl(CO)(PPh_3)_2$ or $RhCl(PPh_3)_3$ and, compared with the latter, is less prone to lose triphenylphosphine; its reaction with acyl halides is of obvious interest for comparative purposes. Kubota et al.[15,20,21] have reported on the reaction of the closely related dinitrogen complex $IrCl(N_2)(PPh_3)_2$ with various acyl halides and on the reaction of acetyl chloride with $IrCl(PPh_3)_3$, and in a preliminary communication[22] we noted that oxidative addition of isomeric straight- and α-branched-chain acyl chlorides to $IrCl(PPh_3)_3$ affords exclusively n-alkyliridium(III) complexes. Full details of this work are presented herein.

Scheme I



Results

Straight-chain acyl halides RCOCl react with $IrCl(PPh_3)_3$ in refluxing benzene to give colorless, crystalline, monomeric octahedrally coordinated iridium(III) alkyls $RIrCl_2(CO)(PPh_3)_2$ (R = C_2H_5, C_3H_7, C_4H_9, C_5H_{11}, C_7H_{15}, and CH_2CH_2Ph) in 70–80% yield. In dichloromethane their IR spectra show one ν(CO) band in the range 2030–2040 cm^{-1}, and in Nujol mulls two such bands are occasionally observed, probably owing to solid state splitting (Table I). The far IR spectra show two strong ν(IrCl) bands at ca. 305 and 250 cm^{-1} assignable to Cl trans to CO and to σ-alkyl, respectively; these data are consistent with structure I. The ethyl complex obtained by this method is identical with that isolated from the reaction of $IrCl(N_2)(PPh_3)_2$ with propanoyl chloride.[15] The

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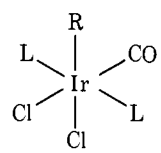
Table I. Analytical, IR, and ^{1}H NMR Data for Alkyliridium(III) Complexes $RIrCl_2(CO)(PPh_3)_2$[a]

R	% C		% H		% Cl		Mol wt		ν(CO)		ν(IrCl)	$\delta(^1H)$
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	CH_2Cl_2	Nujol		
C_2H_5	55.5	55.95	4.2	4.2	8.4	8.3	844	848	2035	2045, 2025	307, 252	0.78 (t, 3, CH_3), 1.54 (m, 2, CH_2, J_{HH} = 8 Hz)
C_3H_7	55.9	56.25	4.3	4.5	8.2	8.3	858	864	2030	2040, 2025	305, 254	0.12 (t, 3, CH_3), 1.10 (m, 4, $(CH_2)_2$, $J_{CH_2CH_3}$ = 7.5 Hz)
C_4H_9	56.4	56.7	4.5	4.6	8.1	8.3	872	893	2035	2040, 2030	306, 254	0.50 (m, 5, $CH_3 + CH_2$), 1.30 (m, 2, CH_2), 1.60 (m, 2, CH_2)[b]
C_5H_{11}	56.9	57.2	4.6	4.75	8.0	8.1	886	873	2035	2040, 2030	302, 252	0.3–1.7 (m, 11, $CH_3 + (CH_2)_4$)
C_7H_{15}	57.8	58.6	5.0	4.7	7.75	7.7	914	940	2025	2030, 2020	305, 253	0.75 (m, 7, $CH_3 + (CH_2)_2$), 1.25 (m, 8, $(CH_2)_4$)[b]
CH_2CH_2-C_6H_5	58.7	58.9	4.3	4.4	7.7	7.9	920	916	n.m.	2025	312, 250	1.90 (m, 2, CH_2), 2.40 (m, 2, CH_2), 6.15 (m, 2, C_6H_5), 6.95 (m, 3, C_6H_5)

[a] ν(IrCl) values refer to Nujol mulls. ^{1}H NMR spectra were measured in $CDCl_3$ at 32 °C except where stated. Chemical shifts (δ) are in parts per million downfield of internal $(CH_3)_4Si$. Abbreviation: n.m., not measured. [b] Measured in C_6D_6.



I

ethyl complex $C_2H_5IrCl_2(CO)(PPh_3)_2$ can also be isolated in 80% yield from the reaction of propanoyl chloride with a solution containing the cyclooctene complex $[IrCl(C_8H_{14})_2]_2$ (1 mol) and triphenylphosphine (4 mol).[23]

The ^{1}H NMR spectrum of $C_2H_5IrCl_2(CO)(PPh_3)_2$ shows a triplet at δ 0.78 ($J_{CH_2CH_3}$ = 8 Hz) due to the methyl protons and a multiplet at δ 1.54 due to the methylene protons which are coupled with ^{31}P ($^3J_{PH}$ = 8 Hz). The methyl triplet in the *n*-propyl complex is ca. 0.6 ppm to higher field than that in the ethyl complex and the methylene protons give rise to a complex multiplet at δ 1.10, i.e., ca. 0.4 ppm to higher field than in the ethyl complex. The ^{1}H NMR spectrum of the *n*-butyl complex consists of three complex multiplets at δ 0.50, 1.30, and 1.60 with relative intensities of 5:2:2. The two lower field resonances are clearly due to methylene protons while the highest field resonance corresponds to a methyl and one methylene group; the protons of the latter are at unexpectedly high field. A similar effect is evident in the ^{1}H NMR spectrum of the *n*-heptyl complex which consists of a pair of multiplets at δ 0.85 and 1.25 with relative intensities of 7:8. The highest field resonance must be due to a methyl group and four methylene protons which are ca. 0.4 ppm to higher field than might be expected. From these trends (Table I) it appears that in the alkyl chain $Ir-C_1-C_2-C_3-C_4-C_5\ldots$ of a complex $RIrCl_2(CO)(PPh_3)_2$ the protons on C3 and C4 are abnormally shielded. Molecular models indicate that these carbon atoms may be sandwiched between a pair of aromatic rings from the mutually trans triphenylphosphine ligands so that the hydrogen atoms are in the shielding zone of the aromatic rings. The magnitude of the effect is similar to that observed for the central methylene protons of 1,4-polymethylenebenzenes, $1,4-C_6H_4(CH_2)_n$ (n = 10–12).[24] The aromatic proton resonances of the 2-phenethyl group in $PhCH_2CH_2IrCl_2(CO)(PPh_3)_2$ appear as a pair of multiplets at δ 6.95 and 6.15 in an intensity ratio of 2:3, and are respectively 0.3 and 1.3 ppm to higher field than is usual for aromatic protons. A similar effect is observed[25] for the phenyl protons of 1,8-diphenylnaphthalene, which appear at δ 6.85, and we suggest by analogy with this example that the aromatic ring of the 2-phenethyl group is approximately plane parallel to one of the triphenylphosphine aromatic rings.

The aromatic resonances due to the *trans*-triphenylphosphine ligands in the $RIrCl_2(CO)(PPh_3)_2$ complexes consist of two multiplets of relative intensity 2:3 at δ 7.95 and 7.3. Although we have not proved the assignment, the lower field resonance is probably due to the ortho protons, as is the case for free triphenylphosphine.[26] The marked deshielding of these protons (ca. 0.6 ppm) on coordination contrasts with the shielding of the ortho protons in octahedral *cis*-bis(1,2-diphenylphosphino)ethane complexes of iridium(III), ruthenium(II), chromium(0), molybdenum(0), and tungsten(0).[27]

Reaction of 2-methylpropanoyl chloride, $(CH_3)_2CHCOCl$, with $IrCl(PPh_3)_3$ in refluxing benzene gives a 55% yield of the *n*-propyliridium(III) complex $CH_3CH_2CH_2IrCl_2(CO)(PPh_3)_2$ identical with that obtained using butanoyl chloride. Similarly, reaction of $IrCl(PPh_3)_3$ with 2-methylbutanoyl chloride, $CH_3CH_2CH(CH_3)COCl$, 2-ethylbutanoyl chloride, $(CH_3CH_2)_2CHCOCl$, and 2-phenylpropanoyl chloride, $PhCH(CH_3)COCl$, gives the *n*-butyl-, *n*-pentyl-, and 2-phenethyliridium(III) complexes, respectively. Lower yields of *n*-alkyls are obtained using α-branched acyl halides than with straight-chain acyl halides (30–40% compared with 70–80%), and variable amounts of $IrHCl_2(PPh_3)_3$ and $IrCl(CO)(PPh_3)_2$ are also formed. These two products are formed in 24 and 32% yield, respectively, in the reaction of 2-phenylpropanoyl chloride with $IrCl(PPh_3)_3$. Better yields of the *n*-alkyl complexes are obtained from the reaction of α-branched acyl halides with a mixture of $[IrCl(C_8H_{14})_2]_2$ (1 mol) and triphenylphosphine (4 mol); e.g., 2-ethylpropanoyl chloride gives the *n*-pentyl complex in 70% yield and 2-phenylpropanoyl chloride gives the 2-phenethyl complex in 53% yield.

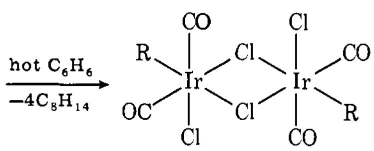
The branched- to straight-chain alkyl isomerization described above led us to reexamine the oxidative addition of acyl chlorides to the dimeric cyclooctene-iridium(I) complex $[IrCl(CO)(C_8H_{14})_2]_2$. Shaw and Singleton[28] reported that acetyl chloride, propanoyl chloride, and 2-methylpropanoyl chloride react with this complex in hot benzene to give dimeric σ-alkyliridium(III) complexes (II) (eq 1), the structure of which was confirmed by single-crystal x-ray study of the methyl complex.[29] The ^{1}H NMR spectrum of the isopropyl complex $[(CH_3)_2CHIrCl_2(CO)_2]_2$ in $CDCl_3$ is as expected (Table II), but on heating in benzene for 1.5 h an equilibrium mixture of

Table II. Spectroscopic Data for Alkyliridium(III) Complexes $[RIrCl_2(CO)_2]_2$ and Related Acyls[a]

	IR		
	ν(CO)	ν(C=O)	^{1}H NMR, δ
$[CH_3COIrCl_2(CO)(C_8H_{14})]_2$	2080	1720	1.82 (s, CH_3),[b] 2.63 (s, $COCH_3$), 4.8 (br, m, =CH of coord C_8H_{14}), 5.58 (t, =CH of free C_8H_{14}, J = 5 Hz)
$[(CH_3)_2CHCOIrCl_2(CO)(C_8H_{14})]_2$	2070	1700	*c*
$[CH_3CH_2CH_2IrCl_2(CO)_2]_2$	2135, 2085		0.99 (t, 3, CH_3), 1.68 (sxt, 2, CH_3CH_2, $J_{CH_2CH_3}$ = 8.0 Hz), 2.66 (m, 2, CH_2Ir)[d]
$[(CH_3)_2CHIrCl_2(CO)_2]_2$	2130, 2080		1.45 (d, 6, CH_3), 3.28 (m, 1, CH, J = 7.5 Hz)
$[CH_3CH_2CH_2CH_2IrCl_2(CO)_2]_2$	2140, 2085		0.91 (t, 3, CH_3, J = 8.0 Hz), 1.46 (m, 4, CH_2CH_2), 2.69 (m, 2, CH_2Ir)
$[CH_3CH_2CH(CH_3)IrCl_2(CO)_2]_2$	2135, 2085		0.86 (t, 3, CH_3CH_2, J = 9.0 Hz), 1.45 (d, 3, CH_3CH, J = 7.5 Hz), 2.10 (m, 2, CH_2), 3.20 (m, 1, CH)
$[CH_3CH_2CH_2CH_2CH_2IrCl_2(CO)_2]_2$	2130, 2085		0.99 (t, 3, CH_3, J = 7.5 Hz), 1.46 (m, 2, CH_2), 1.69 (m, 2, CH_2), 2.68 (m, 2, CH_2)
$[C_6H_5CH_2CH_2IrCl_2(CO)_2]_2$	2135, 2085		2.85 (m, 4, CH_2CH_2), 7.1–7.3 (m, 5, C_6H_5)
$[C_6H_5CH(CH_3)IrCl_2(CO)_2]_2$	2135, 2085		1.70 (d, 3, CH_3), 4.50 (q, 1, CH, J = 7.5 Hz), 7.1–7.5 (m, 5, C_6H_5)
$CH_3CH_2CH_2COIrCl_2(CO)(PPh_3)_2$	2060	1630	*e*
$CH_3CH_2CH_2COIrCl_2(CO)(PMePh_2)_2$	2060	1630	0.04 (t, 3, CH_3CH_2, J_{HH} = 7 Hz), 0.40 (m, 2, CH_2), 0.94 (m, 2, CH_2), 2.50 (t, 3, PCH_3, $^2J_{PH} + {}^4J_{PH}$ = 6 Hz)
$(CH_3)_2CHCOIrCl_2(CO)(PPh_3)_2$	2045	1670	0.10 (t, 6, CH_3), 2.99 (m, 1, CH, J_{HH} = 7.5 Hz)

[a] IR spectra measured as Nujol mulls; ^{1}H NMR spectra measured in $CDCl_3$. [b] Due to CH_3 of $[CH_3IrCl_2(CO)_2]_2$ (see text). [c] Could not be measured owing to rapid conversion into $[(CH_3)_2CHIrCl_2(CO)_2]_2$. [d] Irradiation of the peak at δ 2.66 collapsed the signal at δ 1.68 to a triplet (J = 8.0 Hz) leaving the methyl triplet unchanged, and irradiation at the δ 1.68 peak collapsed the methyl triplet to a singlet, thus confirming the assignment of the methylene resonances. [e] Not sufficiently soluble for ^{1}H measurement.

$[IrCl(CO)(C_8H_{14})_2]_2$ + RCOCl



(1)

II

R = CH_3, C_2H_5, $CH(CH_3)_2$

isopropyl and *n*-propyl complexes (ca. 2:3) is obtained (Figure 1). Addition of butanoyl chloride to $[IrCl(CO)(C_8H_{14})_2]_2$ in hot benzene gives the pure *n*-propyliridium(III) complex $[CH_3CH_2CH_2IrCl_2(CO)_2]_2$ which resembles the other members of the series in showing two ν(CO) bands at 2135 and 2085 cm^{-1} in its IR spectrum. Its ^{1}H NMR spectrum exhibits typical *n*-propyl resonances at δ 0.99 (t, CH_3, J_{HH} = 8 Hz), 1.68 (m, CH_2), and 2.66 (m, CH_2). On heating in benzene for 1.5 h it isomerizes to the same equilibrium mixture of isopropyl and *n*-propyl complexes as obtained starting from the isopropyl complex. On prolonged heating in benzene both complexes decompose giving bronze needles of the polymeric or dimeric hydride $[IrHCl_2(CO)_2]_n$.[28] Attempts to study the kinetics of isomerization of the *n*- and isopropyl complexes by IR monitoring of bands in the 1170-cm^{-1} region due to isopropyl skeletal vibrations were frustrated by deposition of $[IrHCl_2(CO)_2]_n$ on the cell windows.

Reaction of pentanoyl and 2-methylbutanoyl chlorides with $[IrCl(CO)(C_8H_{14})_2]_2$ in hot benzene gives the expected *n*- and *sec*-butyl complexes $[RIrCl_2(CO)_2]_2$ [R = $CH_2CH_2CH_2CH_3$, $CH(CH_3)CH_2CH_3$], respectively. The ^{1}H NMR spectrum of the *n*-butyl complex in $CDCl_3$ shows signals at δ 0.91 (t, CH_3, J_{HH} = 8 Hz), 1.46 (m, CH_2), and 2.69 (m, CH_2) with relative intensities of 3:4:2; the resonance at lowest field is tentatively assigned to the methylene group attached to the metal. The chemical shift of the other methylene protons is

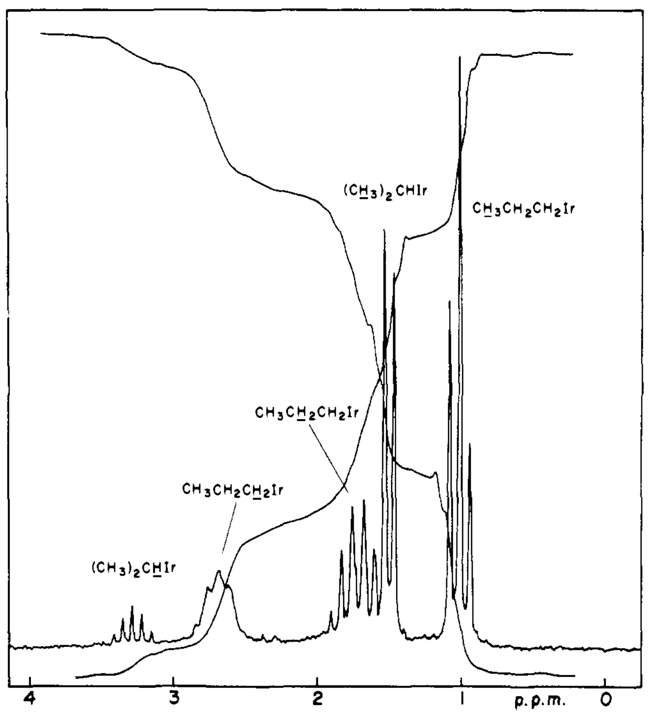


Figure 1. ^{1}H NMR spectrum of equilibrium mixture of $[CH_3CH_2CH_2IrCl_2(CO)_2]_2$ and $[(CH_3)_2CHIrCl_2(CO)_2]_2$.

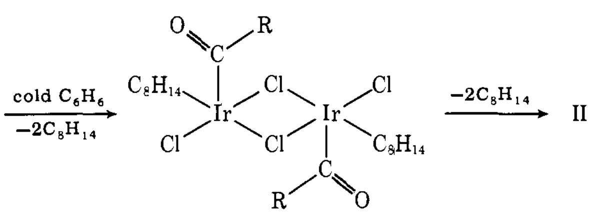
normal, which supports the idea that the abnormal shielding of one of the *n*-butyl methylene groups in $CH_3CH_2CH_2CH_2IrCl_2(CO)(PPh_3)_2$ is due to the aromatic rings of the triphenylphosphine ligands. A freshly prepared solution of the *sec*-butyl complex shows typical *sec*-butyl proton resonances (Table II), but in the course of 3 h these disappear almost completely and are replaced by those of the *n*-butyl complex.

Over a longer period, or on heating in benzene, the solution deposits insoluble $[IrHCl_2(CO)_2]_n$.

2- and 3-phenylpropanoyl chlorides react with $[IrCl(CO)(C_8H_{14})_2]_2$ in hot benzene to give the 1- and 2-phenethyliridium(III) complexes $[RIrCl_2(CO)_2]_2$ [R = $PhCHCH_3$, CH_2CH_2Ph], respectively, The aromatic proton resonances of the latter are in the normal region, in contrast with those of $PhCH_2CH_2IrCl_2(CO)(PPh_3)_2$ discussed above. Attempts to interconvert the phenethyl complexes led only to decomposition.

There is convincing evidence[15,20,21] that acyl chlorides react with $IrCl(N_2)(PPh_3)_2$ to give initially five-coordinate acyls $RCOIrCl_2(PPh_3)_2$ which subsequently undergo alkyl migration to give the six-coordinate alkyls, $RIrCl_2(CO)(PPh_3)_2$. Acyl precursors can also be detected in the addition of acyl halides to $[IrCl(CO)(C_8H_{14})_2]_2$. The latter reacts with acetyl chloride in cold benzene for 5 min to give a colorless complex $[CH_3COIrCl_2(CO)(C_8H_{14})]_2$ which shows IR bands at 2080 and 1720 cm^{-1} (Nujol) assignable respectively to terminal ν(CO) and acyl ν(C═O) modes. Over a 20-min period in chloroform solution the acyl band disappears and is replaced by a ν(CO) band at 2130 cm^{-1}. The final spectrum has a pair of ν(CO) bands at 2130 and 2080 cm^{-1} due to $[CH_3IrCl_2(CO)_2]_2$ (eq 2). The course of the reaction can also be fol-

$[IrCl(CO)(C_8H_{14})_2]_2$ + RCOCl



(2)

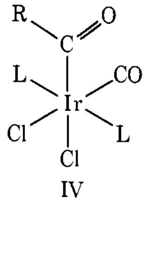
III

R = CH_3, $CH(CH_3)_2$

lowed by ^{1}H NMR spectroscopy. A freshly prepared solution of the acetyl complex in $CDCl_3$ shows sharp singlets at δ 2.63 and 1.82 due to acetyl and methyl protons, respectively, in addition to multiplets at δ 5.58 and 4.8 due to the olefinic protons of free and coordinated cyclooctene. Over a 20-min period the methyl resonance increases at the expense of the acetyl resonance and the resonance at δ 5.58 increases at the expense of that at δ 4.83. Similar behavior is observed for the complex multiplets at δ 2.2 and 1.5 due to the methylene groups of free and coordinated cyclooctene, respectively.

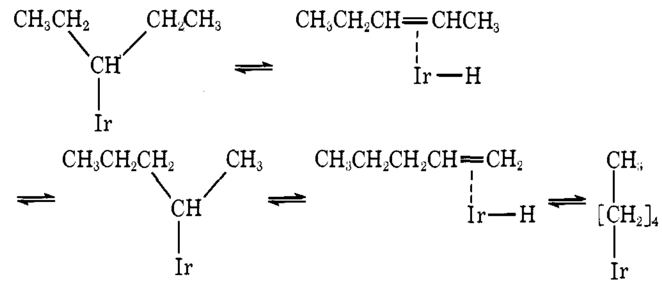
Reaction of 2-methylpropanoyl chloride with $[IrCl(CO)(C_8H_{14})_2]_2$ in cold benzene gives the acyl complex $[(CH_3)_2CHCOIrCl_2(CO)(C_8H_{14})]_2$, which shows IR bands at 2070 [ν(CO)] and 1700 cm$^-$ [ν(C═O)] in a Nujol mull. However, in chloroform solution, only the two typical ν(CO) bands of the isopropyl complex are observed and the acyl band is absent. Evidently alkyl migration occurs even more rapidly in this case than in the acetyl chloride reaction.

As noted previously,[28-30] acyls are re-formed when the $[RIrCl_2(CO)_2]_2$ complexes are treated with tertiary phosphines or arsines. Addition of 2 equiv of ligand to the isopropyl or *n*-propyl complexes gives monomeric $RCOIrCl_2(CO)L_2$ [R = $CH(CH_3)_2$, L = PPh_3; R = $CH_2CH_2CH_3$, L = PPh_3, $PMePh_2$] (IV) which exhibit an acyl ν(C═O) band at 1670

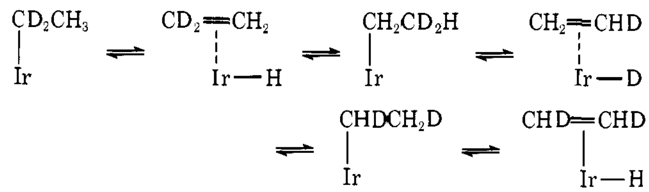


IV

Scheme II



Scheme III



cm^{-1} in their IR spectra. The 1:2:1 triplet resonance for the methyl protons of coordinated diphenylmethylphosphine indicates that these ligands are mutually trans, and the ^{1}H NMR spectra confirm that no alkyl group isomerization occurs during the migration. The same conclusions hold for the previously prepared dimethylphenylphosphine complex [R = $CH(CH_3)_2$, L = PMe_2Ph].[28]

The alkyl group isomerizations are presumed to occur via a series of reversible β-eliminations in an initially formed secondary alkyl. This is illustrated in Scheme II for the formation of the *n*-pentyl complex from 2-ethylbutanoyl chloride via 2-ethylpropyl and 2-methylbutyl complexes. An indication that the reversible hydrogen migration occurs while the olefin is coordinated is provided by the lack of influence of external ethylene (1 atm) on the reactions of 2-methylpropanoyl chloride with $IrCl(PPh_3)_2$ and $[IrCl(CO)(C_8H_{14})_2]_2$; there is no evidence for the formation of ethyliridium(III) complexes under these conditions. This result shows that the intermediate hydride does not react with external ethylene and that ethylene does not displace the olefin formed by β-elimination (in this case, propene) under the reaction conditions. Once propene is lost from the coordination sphere, alkyl group isomerization ceases. Our conclusions are similar to those drawn for the thermal decomposition by β-elimination of $(CH_3CH_2CD_2CH_2)_2Pt(PPh_3)_2$,[31] and for the isomerization of the *tert*-butylgold complex $(CH_3)_3CAu(CH_3)_2(PPh_3)$ to the isobutyl complex $(CH_3)_2CHCH_2Au(CH_3)_2(PPh_3)$.[32]

Reaction of a mixture of di- and monodeuteriopropanoyl chlorides, CH_3CD_2COCl and $CH_3CHDCOCl$ (ratio of 3:1 estimated from observed 12:1 ratio of CH_3:CH resonances), with $[IrCl(C_8H_{14})_2]_2$ + $4PPh_3$ for 1 h in refluxing benzene gives deuterated ethyl complex $C_2H_5IrCl_2(CO)(PPh_3)_2$ in which the intensity ratio of resonances originally due to CH_3 and to (CH_2 + CH) is ca. 5:1; after a 4.5-h reaction period the ratio has changed to ca. 2.5:1. This result is consistent with a series of β-eliminations which lead to deuterium scrambling between the two carbon atoms of the ethyl group (Scheme III). The complex isolated from the reaction of the same acid chloride with $[IrCl(CO)(C_8H_{14})_2]_2$ in refluxing benzene for 12 min is essentially unscrambled $[CH_3CD_2IrCl_2(CO)_2]_2$, since the intensity ratio of CH_3 to (CH_2 + CH) resonances is identical with that of the precursor. On heating in benzene this complex decomposed to give $[IrH(D)Cl_2(CO)_2]_n$ and the β-elimination reaction leading to isomerization could not be monitored. However, the ethyl complex isolated from the reaction of the acid chloride with $[IrCl(CO)(C_8H_{14})_2]_2$ in refluxing benzene after 4 h has a "CH_3" to "CH_2 + CH" intensity ratio of only 3:1, and a reaction period of 8 h reduces this still further to 1.5:1. We do not know why the ethyl complex should be more stable to loss of olefin when it is kept in the reaction mixture but the result provides additional evidence for reversible β-elimination. Similar H–D scrambling has been observed during thermal decomposition of the labeled alkyls $(CH_3CH_2CD_2CH_2)_2Pt(PPh_3)_2$,[31] $CH_3CD_2PtBr(PEt_3)_2$,[33a] $CH_3CH_2CD_2Fe(\eta^5\text{-}C_5H_5)(CO)(PPh_3)$,[33b] $CD_3CH_2Ni(acac)(PPh_3)$,[34] and $(CD_3CH_2)_2Co(acac)(PMe_2Ph)_2$.[35]

Discussion

The reactions of $IrCl(PPh_3)_3$ and $RhCl(PPh_3)_3$ with straight-chain acyl halides are basically similar (Scheme I). Compared with their rhodium analogues, the initially formed iridium(III) acyls rearrange more rapidly to the six-coordinate alkyls and the latter do not so readily undergo reductive elimination to $MCl(CO)(PPh_3)_2$. The reaction of $IrCl(PPh_3)_3$ with α-branched acyl halides probably proceeds via a *sec*-alkyliridium(III) complex such as I which then undergoes rapid reversible β-eliminations to give the *n*-alkyliridium(III) isomer. The equilibrium between *sec*- and *n*-alkyl in type I complexes must favor the *n*-alkyl even more than is the case for type II complexes, because we have been unable to detect an isopropyliridium(III) intermediate in the reaction of $IrCl(PPh_3)_3$ with 2-methylpropanoyl chloride, $(CH_3)_2CHCOCl$, to give $CH_3CH_2CH_2IrCl_2(CO)(PPh_3)_2$. The position of equilibrium is determined by the direction of addition of hydrogen to olefin in the presumed olefin hydride intermediate, the same factor which is responsible for the formation of straight-chain or branched aldehydes from olefins in hydroformylation;[36] our observations are probably related to the fact that tertiary phosphine-based hydroformylation catalysts such as $[Co(CO)_3(PBu_3)_2]_2$[37] and $RhH(CO)(PPh_3)_3$[36] give higher normal:branched aldehyde ratios than $Co_2(CO)_8$. As discussed previously,[36] replacement of CO by tertiary phosphine can reduce the acidity of the hydride species as a consequence of the good σ-donor/poor π-acceptor properties of the tertiary phosphine, thus rendering the hydride more hydridic, $M^+\text{-}H^-$, and more likely to add to an olefin in the anti-Markownikoff sense. Alternatively, the bulky tertiary phosphine can exert a steric effect which is particularly pronounced if two phosphines are trans to each other and cis to the hydride. Models indicate that in type I complexes there is considerable steric hindrance between a *sec*-alkyl group R and the aromatic rings of the triphenylphosphine ligands; hence the preference for a *n*-alkyl group is not surprising.

The nature of the intermediate olefin hydride cannot be specified at present. The simplest formulation would be seven-coordinate $IrHCl_2(CO)(olefin)(PPh_3)_2$, and, although seven-coordinate iridium(III) hydrido complexes are known, viz., IrH_5L_2 ($L = PEt_2Ph, PEt_3$),[38] most are six coordinate. Since the β-eliminations in $(CH_3CH_2CD_2CH_2)_2Pt(PPh_3)_2$,[31] $(CH_3)_3CAu(CH_3)_2(PPh_3)$,[32] and $CH_3CH_2CH_2Fe(\eta^5\text{-}C_5H_5)(CO)(PPh_3)$[33a] are known to be preceded by dissociation of triphenylphosphine, a more reasonable formulation for the intermediate would be $IrHCl_2(CO)(olefin)(PPh_3)$. Under our reaction conditions, the rearranged *n*-alkyl can still be isolated even in the presence of an excess of triphenylphosphine, but attempts to obtain rate data have not been successful.

Steric congestion in the intermediate could be relieved either by return of hydrogen to olefin to give the *n*-alkyl or by loss of olefin and hydrogen chloride to give $IrCl(CO)(PPh_3)_2$. The fact that the latter is generally formed in higher yields from the reaction of $IrCl(PPh_3)_3$ with α-branched acyl chlorides than with straight-chain acyl chlorides suggests that the olefin hydride is generated very readily by β-elimination from the initially formed *sec*-alkyl. It should be noted that steric hindrance does not prevent formation of the *sec*-alkyl, which can be isolated provided that β-elimination is suppressed; e.g., $C_6H_5CH(CF_3)IrCl_2(CO)(PPh_3)_2$ formed from $IrCl(N_2)(PPh_3)_2$ and $C_6H_5CH(CF_3)COCl$.[9]

The source of the $IrHCl_2(PPh_3)_3$ which appears as a by-product from the reactions of α-branched acyl halides with $IrCl(PPh_3)_3$ is uncertain. It may arise in part from the reaction of $IrCl(PPh_3)_3$ with traces of hydrogen chloride present initially in the acyl chlorides, or, more likely, with hydrogen chloride lost from the transient olefin hydride intermediate.

Reversible β-hydrogen migration might be expected to occur in the oxidative additions of acyl halides to $RhCl(PPh_3)_3$, or in the decarbonylation of acyl halides catalyzed by $RhCl(PPh_3)_3$, $RhCl(CO)(PPh_3)_2$, and $IrCl(CO)(PPh_3)_2$. The evidence in the literature indicates that it may occur, but that in most cases irreversible β-elimination leading to loss of olefin and HCl seems to take precedence. Thus, on heating with hexamethyldisiloxane (to remove HCl) the *threo*-acyl $PhCHDCHDCORhCl_2(PPh_3)_2$, formed from *threo*-PhCHDCHDCOCl and $RhCl(PPh_3)_3$, forms all possible styrenes containing zero, one, and two deuterium atoms in the vinyl group.[10] This result is consistent with a sequence of reversible β-eliminations of hydrogen or deuterium in an intermediate alkyl *threo*-$PhCHDCHDRhCl_2(CO)(PPh_3)_2$. The analogous alkyliridium(III) complex can be isolated and decomposes similarly.[10] On the other hand, decarbonylation of $C_6D_5CD_2CH_2COCl$ catalyzed by $IrCl(CO)(PPh_3)_2$ gives only DCl, although the accompanying styrene has undergone partial H/D scrambling between the olefinic carbon atoms.[5] *erythro*- and *threo*-2,3-diphenylbutanoyl complexes $PhCH(CH_3)CH(Ph)CORhCl_2(PPh_3)_2$ are reported[8,9] to decompose to give 90% *trans*- and 90% *cis*-α-methylstilbene, respectively. Such stereospecificity is apparently inconsistent with reversible β-eliminations in a rhodium(III) alkyl, and the authors suggest either that the acyl undergoes a concerted cis elimination or that the alkyl is formed with retention of configuration and then undergoes irreversible cis β-hydride elimination. As noted elsewhere,[10] the species $PhCH_2C(Ph)(CH_3)RhCl_2(CO)(PPh_3)_2$ which might be generated in a reversible β-elimination following Scheme II would be severely sterically congested. Loss of olefin from the olefin hydride intermediate might then be preferred over return of hydrogen to the coordinated olefin, or alternatively, insertion might always generate the starting alkyl. Both possibilities would account for the observed stereospecificity.

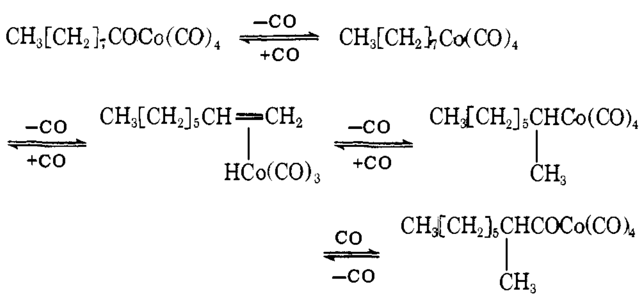
It seems reasonable to suggest that in type II complexes the olefin hydride intermediate is six-coordinate $IrHCl_2(CO)_2(olefin)$, which could be generated by cleaving the chlorine bridge in II to provide a vacant coordination site for β-elimination to occur. The absence of triphenylphosphine in this system means that steric effects are likely to be less important than in type I complexes; hence the almost equal preference for *n*- and isopropyl complexes. The limited data available indicate that, with longer alkyl chains, *n*-alkyl is favored over *sec*-alkyl, perhaps as a consequence of increasing steric crowding in the latter.

Although *tert*- to iso- and *sec*- to *n*-alkyl isomerizations are well known for boron[39] and aluminum,[39,40] the only reported example of which we are aware in a transition metal complex is the spontaneous *tert*- to isobutylgold(III) isomerization mentioned above.[32] The addition of $ZrHCl(\eta^5\text{-}C_5H_5)_2$ to internal olefins to give exclusively *n*-alkylzirconium complexes $RZrCl(\eta^5\text{-}C_5H_5)_2$ may also proceed via transient *sec*-alkyls, although these have not been isolated.[41] In the transition metal series, the evidence for reversibility of β-elimination has come mainly from studies of exchange reactions of metal hydrides or deuterides with olefins,[36,42–44] and from studies of the thermal decomposition of labeled alkyls.[31,33–35] However, there are many instances in which an equilibrium between transient *n*- and *sec*-alkyls accounts for observed products, e.g., isomerization of acyl carbonyls of cobalt[45–48] and iron[49] (Scheme

Table III. Analytical Data for New Alkyliridium(III) Complexes $[RIrCl_2(CO)_2]_2$ and Derived Acyls $RCOIrCl_2(CO)L_2$ (L = PPh_3 or $PMePh_2$)

	% C		% H		% Cl	
	Calcd	Found	Calcd	Found	Calcd	Found
$[n\text{-}C_3H_7IrCl_2(CO)_2]_2$	16.6	16.7	1.95	1.8	19.6	19.4
$[n\text{-}C_4H_9IrCl_2(CO)_2]_2$	19.15	19.4	2.4	2.6	18.9	18.65
$[C_6H_5CH_2CH_2IrCl_2(CO)_2]_2$	28.3	27.85	2.1	2.2	16.7	16.5
$[C_6H_5CHCH_3IrCl_2(CO)_2]_2$	28.3	28.4	2.1	2.3	16.7	16.6
$n\text{-}C_3H_7COIrCl_2(CO)(PMePh_2)_2$	48.8	49.1	4.4	4.4	9.3	9.1
$n\text{-}C_3H_7COIrCl_2(CO)(PPh_3)_2$	55.5	55.8	4.2	4.3	7.9	7.7
$i\text{-}C_3H_7COIrCl_2(CO)(PPh_3)_2$	55.5	55.7	4.2	4.5	7.9	7.8
$n\text{-}C_5H_{11}COIrCl_2(CO)(PPh_3)_2$	56.4	57.0	4.5	4.7	7.75	7.6

Scheme IV



IV), isomerization of alkyl Grignard reagents in the presence of a α olefin and $TiCl_4$[50] or $NiCl_2$,[51] alkyl group isomerization in the coupling reaction

$$(CH_3)_2CHMgBr + C_6H_5Cl \xrightarrow[-MgBrCl]{Ni^{II}\ complex} C_6H_5CH(CH_3)_2 + C_6H_5CH_2CH_2CH_3 \quad (3)$$

which is catalyzed by nickel(II)-tertiary phosphine complexes,[52,53] and the formation of n-butane in addition to 2-methylpropane in the thermal decomposition of $(CH_3)_2CHAu(CH_3)_2(PPh_3)$.[32] Precise comparison with our results is not possible, but there is a general tendency for the systems containing tertiary phosphines to favor straight-chain products. However, in eq 3, the sterically more demanding phosphines seem to favor isopropylbenzene, whereas methylphosphines favor n-propylbenzene.[53] The exact nature of the catalytic species in this reaction is unknown, but it is unlikely to be six coordinate and is probably four coordinate, so that the equilibrium between n- and sec-alkyls may be controlled in this case more by the electronic than the steric requirements of the tertiary phosphines. The fact that the planar isopropylgold(III) complex $(CH_3)_2CHAu(CH_3)_2(PPh_3)$ does not spontaneously isomerize to the n-propyl complex[32] is in marked contrast to the behavior of isopropyliridium(III) complexes, which further emphasizes the importance of steric control in octahedral systems.

Experimental Section

Measurements. IR spectra were measured as Nujol mulls on KBr windows or as KBr pellets on Perkin-Elmer 457 or 225 instruments calibrated with polystyrene. Far IR spectra (450–200 cm^{-1}) were measured as Nujol mulls between high-density polythene plates or CsI plates on the PE 225. ^1H NMR spectra were measured at 100 MHz on a Varian HA-100 instrument. Microanalyses were carried out in the John Curtin School of Medical Research and in the Research School of Chemistry (Dr. Joyce Fildes and Miss Brenda Stevenson and their associates). Molecular weights were measured at 25 °C in Analar solvents (ca. 0.02 M) using a vapor pressure osmometer (Model 301A, Mechrolab) calibrated with benzil. Melting points (uncorrected) were measured on a Gallenkamp hot-stage apparatus using samples sealed in evacuated capillaries. Analytical and spectroscopic data are in Tables I–III.

Starting Materials. Benzene was dried by heating under reflux over calcium hydride for 24 h, distilling, and storing over sodium wire. Other solvents were dried over sodium wire or molecular sieves as appropriate.

Acid chlorides were obtained commercially except for pentanoyl chloride, hexanoyl chloride, and 3-phenylpropanoyl chloride, which were prepared from the appropriate carboxylic acid and oxalyl chloride.[54] 2-Phenylpropanoyl chloride was prepared from 2-phenylpropionaldehyde,[55] which was converted into the carboxylic acid,[56] and finally into the acid chloride using oxalyl chloride. Di-2-deuteriopropionic acid, $CH_3CD_2CO_2H$, was made from methylmalonic acid and D_2O,[57] and was converted into the acid chloride using phthaloyl chloride.[58] ^1H NMR ($CDCl_3$) δ 1.26 (m, CH_3, 12), 2.94 (q of t, CHD, 1; J_{HH} = 7, J_{HD} = 3 Hz), corresponding to 75% CH_3CD_2COCl, 25% $CH_3CHDCOCl$. The complexes $IrCl(PPh_3)_3$,[16] $[IrCl(C_8H_{14})_2]_2$,[28] and $[IrCl(CO)(C_8H_{14})_2]_2$[28,59] were prepared by literature procedures. All reactions were carried out under dry nitrogen using acid chlorides which had been freshly distilled and pumped in vacuo at −78 °C.

1. Preparation of n-Alkyls $RIrCl_2(CO)(PPh_3)_2$ from n-Acyl Chlorides (RCOCl). (a) A solution of $IrCl(PPh_3)_3$ (0.45 g, 0.45 mmol) in benzene (5 mL) was treated with the straight-chain acid chloride (0.5 mL) and the mixture was heated under reflux for 45 min. n-Hexane (10 mL) was added to the pale yellow solution which was then cooled to −10 °C. The colorless, crystalline solid which precipitated was recrystallized from dichloromethane/ether (R = C_2H_5, C_4H_9, C_5H_{11}, CH_2CH_2Ph), dichloromethane/n-hexane (R = C_3H_7), or benzene/n-pentane (R = C_7H_{15}), washed with ether (2 × 10 mL), and dried in a stream of nitrogen. Yields were generally 75–80%.

(b) A red solution containing $[IrCl(C_8H_{14})_2]_2$ (0.30 g, 0.33 mmol) and triphenylphosphine (0.37 g, 1.35 mmol) in benzene (3 mL) was stirred for 1 h. Propanoyl chloride (0.35 mL) was added by syringe and the mixture was heated under reflux for 40 min giving a pale yellow solution. Workup as under (a) and recrystallization from dichloromethane/ether gave $C_2H_5IrCl_2(CO)(PPh_3)_2$ (0.45 g, 80%).

(c) A solution prepared as under (b) from $[IrCl(C_8H_{14})_2]_2$ (0.23 g, 0.26 mmol) and triphenylphosphine (0.28 g, 1.07 mmol) in benzene (3 mL) was heated under reflux with CH_3CD_2COCl (0.4 mL) for 1 h. The usual workup gave $C_2H_3D_2IrCl_2(CO)(PPh_3)_2$ (0.30 g, 68%): ^1H NMR ($CDCl_3$) δ 0.77 (s with fine structure, CH_3, CH_2D, CHD_2), 1.56 (br m, CHD, CH_2), intensity ratio 5:1.

The product isolated after a 4.5-h reaction time had a similar ^1H NMR spectrum, but the intensity ratio was now 2.5:1.

2. Preparation of n-Alkyls $RIrCl_2(CO)(PPh_3)_2$ from α-Branched Acyl Chlorides. (a) A solution of $IrCl(PPh_3)_3$ (0.8 g, 0.79 mmol) in benzene (10 mL) was treated with 2-phenylpropanoyl chloride, $PhCH(CH_3)COCl$ (1 mL), and the mixture was heated under reflux for 20 min. Solvent was removed at 25 °C (15 mm) leaving a yellow oil which solidified on addition of ether. The yellow solid (0.2 g) was washed thoroughly with ether and after recrystallization from chloroform/ether gave lemon-yellow crystals of $IrCl(CO)(PPh_3)_2$ (0.16 g, 32%). Evaporation of the ether extracts gave a pale yellow oil which was redissolved in the minimum volume of dichloromethane. Dropwise addition of 40–60 °C petroleum ether caused colorless crystals to form. These were filtered off, washed with n-pentane, and dried in a stream of nitrogen to give $PhCH_2CH_2IrCl_2(CO)(PPh_3)_2$ (0.29 g, 40%). Slow evaporation of the filtrate gave white crystals of $IrHCl_2(PPh_3)_3$ (0.2 g, 42%).

(b) Reaction of $IrCl(PPh_3)_3$ (0.45 g, 0.45 mmol) in benzene (5 mL) with 2-methylpropanoyl chloride, $(CH_3)_2CHCOCl$ (0.5 mL), as under 1(a) gave colorless crystals of $CH_3CH_2CH_2IrCl_2(CO)(PPh_3)_2$ (0.2

g, 55%) as the main product, together with ca. 30% of $IrHCl_2(PPh_3)_3$.

Similarly, reaction of $IrCl(PPh_3)_3$ with 2-methylbutanoyl chloride and 2-ethylbutanoyl chloride gave respectively the *n*-butyl and *n*-pentyl complexes $RIrCl_2(CO)(PPh_3)_2$ (R = n-C_4H_9, n-C_5H_{11}) in ca. 40–50% yield.

(**c**) Treatment of a solution containing $[IrCl(C_8H_{14})_2]_2$ (0.34 g, 0.38 mmol) and triphenylphosphine (0.42 g, 1.60 mmol) with 2-ethylbutanoyl chloride, $(CH_3CH_2)_2CHCOCl$ (0.5 mL), as under 1(b) gave n-$C_5H_{11}IrCl_2(CO)(PPh_3)_2$ (0.47 g, 70%).

(**d**) A solution containing $[IrCl(C_8H_{14})_2]_2$ (0.36 g, 0.40 mmol) and triphenylphosphine (0.45 g, 1.72 mmol) in benzene (5 mL) was treated with 2-phenylpropanoyl chloride, $PhCH(CH_3)COCl$ (0.4 mL), as under 1(b). Solvent was removed under reduced pressure to give a colorless solid which after recrystallization from dichloromethane/*n*-pentane gave $PhCH_2CH_2IrCl_2(CO)(PPh_3)_2$ (0.39 g, 53%).

3. Reaction of Acyl Chlorides with $[IrCl(CO)(C_8H_{14})_2]_2$. (**a**) To a solution of $[IrCl(CO)(C_8H_{14})_2]_2$ (0.3 g, 0.31 mmol) in boiling benzene (10 mL) was added *n*-butanoyl chloride (0.5 mL). The hot solution was filtered and an equal volume of petroleum ether (100–120 °C) was added. Evaporation under reduced pressure gave 0.18 g (80%) of off-white $[CH_3CH_2CH_2IrCl_2(CO)_2]_2$.

The corresponding isopropyl, *n*-butyl, *sec*-butyl, *n*-pentyl, and 2-phenethyl complexes were prepared similarly using 2-methylpropanoyl chloride, *n*-pentanoyl chloride, 2-ethylpropanoyl chloride, and 3-phenylpropanoyl chloride, respectively. The 2-phenethyl complex was recrystallized from dichloromethane/petroleum ether (40–60 °C).

(**b**) A suspension of $[IrCl(CO)(C_8H_{14})_2]_2$ (0.3 g, 0.31 mmol) in benzene (10 mL) was treated with 2-phenylpropanoyl chloride at room temperature and the mixture was stirred for 3 h. The solution was filtered and the filtrate was evaporated at 25 °C (15 mm) to give a pale yellow oil. Addition of *n*-pentane caused a yellow solid to form which, after recrystallization from dichloromethane/petroleum ether (40–60 °C), gave colorless, crystalline $[PhCH(CH_3)IrCl_2(CO)_2]_2$ in 60% yield.

(**c**) A suspension of $[IrCl(CO)(C_8H_{14})_2]_2$ (0.3 g) in benzene (10 mL) was treated with acetyl chloride (0.5 mL). The mixture was stirred at room temperature until most of the solid had dissolved (ca. 5–6 min). The solution was filtered and an equal volume of petroleum ether (100–120 °C) was added. Removal of solvent at 25°C (15 mm) gave off-white prisms of $[CH_3COIrCl_2(CO)(C_8H_{14})]_2$ which were filtered off and washed with *n*-pentane, yield 0.20 g (50%).

(**d**) Triphenylphosphine (0.4 g, excess) was added to a solution of $[CH_3CH_2CH_2IrCl_2(CO)_2]_2$ (0.2 g, 0.27 mmol) in dichloromethane (5 mL). An equal volume of ether was added and the solution was cooled to 0 °C, whereupon colorless crystals of the product, $CH_3CH_2CH_2COIrCl_2(CO)(PPh_3)_2$, precipitated. These were filtered, washed with ether, and dried in a stream of nitrogen, yield ca. 65%.

Similarly prepared from $[RIrCl_2(CO)_2]_2$ and the appropriate tertiary phosphine were $(CH_3)_2CHCOIrCl_2(CO)(PPh_3)_2$, $CH_3CH_2CH_2COIrCl_2(CO)(PMePh_2)_2$, and $CH_3(CH_2)_4COIrCl_2(CO)(PPh_3)_2$.

(**e**) A suspension of $[IrCl(CO)(C_8H_{14})_2]_2$ (0.30 g, 0.31 mmol) in benzene (10 mL) was heated under reflux with CH_3CD_2COCl (0.5 mL) for 12 min. Workup as under 3(a) gave $[C_2H_3D_2IrCl_2(CO)_2]_2$ in ca. 70% yield: ^1H NMR ($CDCl_3$) δ 1.42 (s, CH_3), 2.76 (br, m, CH_2 + CHD), intensity ratio 12:1, identical with that of the CH_3CD_2COCl used. In the ^1H NMR spectra of products isolated after 4 and 8 h refluxing, respectively, this intensity ratio was 5:1 and 1.5:1, and the methyl resonance showed fine structure attributable to deuterium coupling.

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