Secondary to Normal Alkyl Group Rearrangements in Octahedral Iridium(III) Complexes. 1. Monoalkyl Derivatives

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sec-Alkyliridium(III) complexes IrYI-*sec*-R(CO)L_2 (Y = Cl, I; L = PMe_3, PMe_2Ph) formed by oxidative addition of *sec*-alkyl iodides to IrY(CO)L_2 rearrange cleanly by a first-order process to the *n*-alkyl isomers on dissolution in dichloromethane containing protic solvents. The order of efficacy of these solvents in promoting alkyl group rearrangement is CF_3CO_2H >> CH_3OH >> C_2H_5OH > CH_3CO_2H ≈ $CH_3CH_2CH_2OH$ > $(CH_3)_2CHOH$, while in the more strongly coordinating medium THF the order is H_2O >> CH_3OH. These orders correlate with the anion-solvating ability of the solvents and, together with the observed retardation by added iodide ion, suggest that the rate-determining step in the rearrangement is dissociation of iodide ion trans to the *sec*-alkyl group. Rapid, reversible β-hydride elimination in the resulting cation and stereospecific return of iodide ion trans to the resulting *n*-alkyl group complete the process. The rearrangement is promoted by increasing bulk, both of the alkyl group, up to a certain limit, and of the tertiary phosphine (PMe_2Ph > PMe_3). Treatment of IrClI{$CH(CH_3)_2$}(CO)(PMe_2Ph)$_2$ (**2c**) with $AgBF_4$ in acetonitrile induces immediate alkyl group rearrangement to give the *n*-propyliridium(III) salt [IrCl($CH_2CH_2CH_3$)(CO)(NCMe)(PMe_2Ph)$_2$]BF_4 (**6**). Studies of analogous CD_2CH_3 compounds suggest that they, and presumably other *n*-alkyliridium(III) complexes, undergo reversible β-hydride elimination more slowly than the *sec*-alkyl complexes. The deuterium labels in the isobutyl-d_2 complex IrClI{$CD_2CH(CH_3)_2$}(CO)(PMe_3)$_2$ (**1e'**) scramble over all the alkyl carbon atoms when the compound is heated in CD_2Cl_2/CD_3OD, indicating that a *tert*-butyliridium(III) species is accessible. Surprisingly, the complexes IrClI{$CH_2CH(CH_3)CH_2CH_3$}(CO)(PMe_3)$_2$ (**1h**) and IrClI{$CH_2CH_2CH(CH_3)_2$}(CO)(PMe_3)$_2$ (**1i**) do not interconvert under the same conditions, implying that a *tert*-pentyliridium(III) species cannot be formed. The results are compared with alkyl group rearrangements that occur in other transition-metal systems, especially those promoted by dissocation of triphenylphosphine in (η-C_5H_5)FeR(CO)(PPh_3).

Introduction

The equilibrium between a hydrido metal olefin complex and a metal alkyl is one of the key processes in many reactions that are homogeneously catalyzed by transition-metal compounds.[1] Addition of a transition-metal hydride to an unsymmetrically substituted olefin can give rise to isomeric alkyls the relative amounts of which depend on the electronic and steric properties of the ancillary ligands. The ability to control the direction of addition is important for several industrial processes. For example, replacement of CO by a tertiary phosphine in both cobalt- and rhodium-catalyzed hydroformylation favors formation of the desirable straight chain aldehyde relative to the unwanted branched isomer.[2,3] It is not clear whether it is the good σ-donor ability of the tertiary phosphine relative to that of CO which influences the polarity of the M–H bonds, and hence the direction of addition, or whether the greater bulk of the tertiary phosphine destabilizes the secondary alkyl intermediate. Also, the proportions of hexenes, methylpentenes, and 2,3-dimethylbutenes formed in the nickel-catalyzed dimerization of propene can be controlled in a remarkably sensitive manner by various tertiary phosphines, which affect the direction of addition of Ni–H and Ni–C bonds to propene.[4] In this system, the steric bulk of the phosphine ligand seems to play a dominant role. However, electronic factors have been suggested to account for the observation that, in the nickel(II)-catalyzed coupling of isopropylmagnesium chloride with chlorobenzene, complexes containing arylphosphines give predominantly isopropylbenzene, whereas complexes containing alkylphosphines give mainly *n*-propylbenzene as a result of alkyl group isomerization.[5]

During an investigation of the oxidative addition of acyl chlorides RCOCl to iridium(I) complexes $IrCl(PPh_3)_3$ (L = PPh_3, $PMePh_2$) to give alkyliridium(III) complexes $IrCl_2R(CO)L_2$,[6,7] it was found that isomeric straight chain and α-branched acyl chlorides gave the same *n*-alkyl complex, e.g., both $CH_3CH_2CH_2COCl$ and $(CH_3)_2CHCOCl$ added to $IrCl(PPh_3)_3$ to give $IrCl_2(CH_2CH_2CH_3)(CO)(PPh_3)_2$. It was proposed that addition of the α-branched acyl chloride gave an undetected *sec*-alkyliridium(III) complex, which then isomerized to the stable *n*-alkyl compound by rapid, reversible β-elimination, and, further, that the vacant site necessary for the latter process could be created by reversible dissociation of triphenylphosphine; this would allow formation of an intermediate $IrHCl_2(CO)(PPh_3)$(olefin). Several alkyl rearrangements of this type have been observed. The *sec*-butyl group in (η-C_5H_5)Fe{$CH(CH_3)CH_2CH_3$}(CO)(PPh_3) isomerizes to a *n*-butyl group when the compound is heated for 4 h at 63 °C in xylene.[8] The *tert*-butyl group in *trans*-$AuMe_2$(*t*-Bu)(PPh_3) isomerizes to an isobutyl group, even at room temperature, when the compound is dissolved in 1,2-dimethoxyethane.[9] In both cases, the rearrangement is believed to be triggered by dissociation of triphenylphosphine. Treatment of $PtClEt(PPh_3)_2$ with isopropyllithium is reported to give an approximately 1:1 mixture of $PtEt(i\text{-}Pr)(PPh_3)_2$ and $PtEt(n\text{-}Pr)(PPh_3)_2$.[10] The for-

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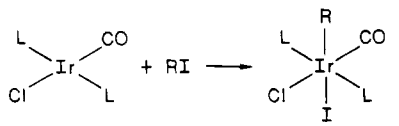
mer isomerizes slowly to the latter in CD_2Cl_2 at room temperature, but in this case added triphenylphosphine does not affect the rate of isomerization. The *sec*-alkyl hydrido complex $(\eta\text{-}C_5Me_5)IrH\{CHMe(n\text{-}Pr)\}(PMe_3)$ formed by reaction of *n*-pentane with $(\eta\text{-}C_5Me_5)IrH_2(PMe_3)$ under irradiation isomerizes to the corresponding *n*-alkyl at 110 °C.[11] Since PMe_3 dissociation is probably very slow, this isomerization may occur by reductive elimination and readdition of the alkane rather than by reversible β-elimination.

It was of obvious interest to prepare octahedral *sec*-alkyliridium(III) complexes containing tertiary phosphines to see whether they would rearrange to the *n*-alkyl isomers and, if so, by what mechanism. Part of this work has appeared in a preliminary form.[12]

Preparative and Spectroscopic Results. Both *sec*- and *n*-alkyl iodides (RI) undergo oxidative addition to *trans*-$IrCl(CO)L_2$ (L = PMe_3, PMe_2Ph) in benzene at room temperature to give colorless or pale yellow, octahedrally coordinated alkyliridium(III) complexes in high yield (eq 1). The ethyl, *n*-propyl, and isopropyl complexes (**1a–c**)



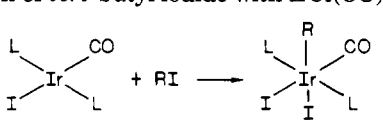
(1)

L = PMe_3; R = CH_2CH_3 (**1a**), $CH_2CH_2CH_3$ (**1b**), $CH(CH_3)_2$ (**1c**), $CH_2CH_2CH_2CH_3$ (**1d**), $CH_2CH(CH_3)_2$ (**1e**), $CH(CH_3)CH_2CH_3$ (**1f**), $CH_2C(CH_3)_3$ (**1g**), $CH_2CH(CH_3)CH_2CH_3$ (**1h**), $CH_2CH_2CH(CH_3)_2$ (**1i**), $CH(CH_2CH_3)_2$ (**1j**), $CH_2(CH_2)_6CH_3$ (**1k**), $CH(CH_3)[CH_2]_5CH_3$ (**1l**), *c*-C_6H_{11} (**1m**)

L = PMe_2Ph; R = CH_2CH_3 (**2a**), $CH_2CH_2CH_3$ (**2b**), $CH(CH_3)_2$ (**2c**), $CH_2CH_2CH_2CH_3$ (**2d**), $CH_2CH(CH_3)_2$ (**2e**), $CH(CH_3)CH_2CH_3$ (**2f**), $CH_2[CH_2]_6CH_3$ (**2k**)

L = PEt_3; R = CH_2CH_3 (**4a**), $CH_2CH_2CH_3$ (**4b**)

have been made previously.[13-15] Neither *n*-propyl nor isopropyl bromide add to $IrCl(CO)(PMe_3)_2$ under similar conditions, and although isopropyl bromide and *sec*-butyl bromide react with $IrCl(CO)(PMe_3)_2$ in refluxing benzene in the presence of the free radical initiator azobis(isobutyronitrile) (AIBN), the resulting mixture of iridium(III) complexes could not be separated or completely identified. Isopropyl iodide and *n*-propyl iodide react with $IrI(CO)(PMe_2Ph)_2$ to give the expected adducts **3b** and **3c** (eq 2). Reaction of *tert*-butyl iodide with $IrCl(CO)(PMe_3)_2$



(2)

L = PMe_2Ph; R = $CH_2CH_2CH_3$ (**3b**), $CH(CH_3)_2$ (**3c**)

failed to give a *tert*-butyliridium(III) complex, and only the diiodo compound $IrClI_2(CO)(PMe_3)_2$ could be isolated.

The triethylphosphine complex $IrCl(CO)(PEt_3)_2$ reacts with ethyl iodide and with *n*-propyl iodide to give alkyliridium(III) complexes $IrClIR(CO)(PEt_3)_2$ (R = Et (**4a**), *n*-Pr (**4b**)) but does not react with isopropyl iodide or with neopentyl iodide, presumably as a consequence of steric hindrance by the more bulky tertiary phosphine. There is no reaction between $IrCl(CO)(PMePh_2)_2$ and either ethyl iodide or isopropyl iodide at room temperature.

The IR spectra of all the alkyliridium(III) complexes show one ν(CO) band in the region 2010–2050 cm^{-1} in solution, and, in the solid state, there is one ν(IrCl) band in the region 300–320 cm^{-1} typical of Cl trans to CO in octahedral iridium(III) complexes (see supplementary material).[16,17] The ^1H NMR spectra of the trimethylphosphine complexes (**1a–m**) show one triplet for the P–Me resonance ($^2J_{PH} + {}^4J_{PH}$ = 8 Hz) which reduces to a singlet on ^{31}P decoupling (Table I). In the case of the corresponding dimethylphenylphosphine complexes, there are two such triplets, since there is no plane of symmetry along the P–Ir–P axis.[18] The $^{31}P\{^1H\}$ NMR spectra of all the complexes show the expected singlet, that for the *sec*-alkyl compounds being 1–3 ppm more shielded than that for the *n*-alkyl compounds (Table I).

The alkyl group resonances in the ^1H NMR spectra of the PMe_3 complexes are unexceptional. In the alkyl chain IrC(1)–C(2)–C(3)–C(4) of the PMe_2Ph complexes, the chemical shifts of the protons on C(2), C(3), and C(4) are ca. 0.5–1.0 ppm more shielded than those of the corresponding PMe_3 complexes and of the corresponding alkyliridium(III) complexes $[IrRCl_2(CO)_2]_2$ that do not contain tertiary phosphines.[6] This effect has been noted previously, particularly for the protons on C(3) and C(4), in the case of the *n*-alkyl triphenylphosphine complexes $IrCl_2R(CO)(PPh_3)_2$,[6] and is attributed to anisotropic shielding by the aromatic rings of the mutually trans arylphosphine ligands.

Alkyl Group Isomerization. (1) Preliminary Observations. When isopropyl iodide is added to $IrCl(CO)(PMe_2Ph)_2$ in nonprotic solvents such as benzene, tetrahydrofuran, acetonitrile, or acetone, the expected isopropyliridium(III) complex **2c** is the main product, but in protic solvents such as methanol, ethanol, or *n*-propanol, the final product is mainly the *n*-propyliridium(III) complex **2b**, **2c** being absent. In methanol, both oxidative addition and alkyl rearrangement are rapid, and again **2b** is the main product. In contrast, if the addition is carried out in ethanol and the product is isolated after 1–3 min, only **2c** is observed. When a solution of **2c** in ethanol is allowed to stand for 6 h at room temperature, it rearranges quantitatively to **2b**, as shown by ^1H and ^{31}P NMR spectroscopy. The oxidative addition and alkyl rearrangement are, therefore, independent processes. Moreover, a freshly prepared solution of **2c** in CD_2Cl_2 is indefinitely stable to rearrangement at room temperature, but on addition of a few drops of methanol-d_4 **2b** begins to form; isomerization is complete after 24 h, as shown by ^1H NMR spectroscopy. All the *sec*-alkyl complexes listed in eq 1 rearrange to the corresponding *n*-alkyls in the presence of protic solvents. Of the dipolar aprotic solvents tested, only dimethyl sulfoxide appeared to be effective, but we have not established whether this is due to the presence of water in this solvent.

Alkyl rearrangement can also be induced thermally in nonpolar solvents, but it is accompanied by halide scrambling. Thus, when **2c** is heated in benzene at 45 °C for 20 h, a mixture of products, including **2b**, **3b**, and $IrCl_2(n\text{-}C_3H_7)(CO)(PMe_2Ph)_2$, is formed. Halide scrambling occurs more rapidly when isopropyl iodide adds to $IrCl(CO)(PMe_2Ph)_2$ in neat methanol at room temperature, the products being **2b** (74%), **3b** (11%), and $IrCl_2(n\text{-}C_3H_7)(CO)(PMe_2Ph)_2$ (15%), as estimated by ^{31}P NMR spectroscopy. Deeming and Shaw[17] have reported halide

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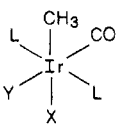
Table I. ^1H and $^{31}P\{^1H\}$ NMR Data for Alkyliridium(III) Complexes IrYIR(CO)L_2[a]

alkyl group (R)	δ(IrR)	δ(PCH$_3$)[b]	δ(P)
	Y = Cl; L = PMe_3		
CH_2CH_3 (**1a**)	1.80–1.60 (m, CH_2CH_3), 1.42 (t, J_{HH} = 7 Hz, CH_2CH_3)	1.82	−40.1
$CH_2CH_2CH_3$ (**1b**)	1.90–1.60 (m, $CH_2CH_2CH_3$), 0.96 (t, J_{HH} = 7 Hz, CH_2CH_3)	1.82	−40.6
$CH(CH_3)_2$ (**1c**)	2.92 (sp, J_{HH} = 7 Hz, $CH(CH_3)_2$), 1.37 (d, J_{HH} = 7 Hz, $CH(CH_3)_2$)	1.86	−41.6
$CH_2CH_2CH_2CH_3$ (**1d**)	1.80–1.20 (m, $CH_2CH_2CH_2CH_3$), 0.92 (t, J_{HH} = 6 Hz, CH_2CH_3)	1.81	−40.5
$CH_2CH(CH_3)_2$ (**1e**)	1.90–1.50 (m, CH_2CH), 1.80 (m, CH_2CH), 1.00 (d, J_{HH} = 6 Hz, $CH(CH_3)_2$)	1.80	−40.8
$CH(CH_3)CH_2CH_3$ (**1f**)	2.67 (m, CH), 1.80–1.60 (m, CH_2), 1.35 (d, J_{HH} = 7 Hz, $CH(CH_3)$), 0.92 (t, J_{HH} = 7 Hz, CH_2CH_3)	1.86	−41.7
$CH_2C(CH_3)_3$ (**1g**)	2.15 (t, J_{PH} = 7 Hz, CH_2), 1.60 (s, $C(CH_3)_3$)	1.88	−42.2
$CH_2CH(CH_3)CH_2CH_3$ (**1h**)	2.00–0.90 (m, $CH_2CH(CH_3)CH_2CH_3$), 0.96 (d, J_{HH} = 5 Hz, CH_2CHCH_3), 0.94 (m, CH_2CH_3)	1.80	−40.8
$CH_2CH_2CH(CH_3)_2$ (**1i**)	1.70–1.30 (m, CH_2CH_2CH), 0.82 (m, CH_2CH_2CH), 0.82 (d, J_{HH} = 6 Hz, $CH(CH_3)_2$)	1.70	−41.0
$CH(CH_2CH_3)_2$ (**1j**)	2.49 (m, CH), 1.80–1.60 (m, CH_2), 0.97 (t, J_{HH} = 7 Hz, CH_3)	1.88	−41.2
$CH_2[CH_2]_6CH_3$ (**1k**)	1.20 (m, CH_2), 0.81 (t, J_{HH} = 7 Hz, CH_2CH_3)	1.73	−40.9
$CH(CH_3)[CH_2]_5CH_3$ (**1l**)	2.70 (m, CH), 1.40–0.80 (m, $[CH_2]_5CH_3$), 1.37 (d, $CHCH_3$)	1.86	−41.6
c-C_6H_{11} (**1m**)	2.80 (m, CH), 2.00–1.20 (m, CH_2)	1.87	−42.9
	Y = Cl; L = PMe_2Ph		
CH_2CH_3 (**2a**)	1.23 (sx, J_{HH} = 7 Hz, J_{PH} = 7 Hz, CH_2CH_3), 0.80 (t, J_{HH} = 7 Hz, CH_2CH_3)	2.32, 2.10	−32.7
$CH_2CH_2CH_3$ (**2b**)	1.00 (m, $CH_2CH_2CH_3$), 0.14 (t, J_{HH} = 7 Hz, CH_2CH_3)	2.29, 2.12	−32.1
$CH(CH_3)_2$ (**2c**)	2.14 (sp, J_{HH} = 7 Hz, $CH(CH_3)_2$), 0.82 (d, J_{HH} = 7 Hz, $CH(CH_3)_2$)	2.30, 2.13	−35.1
$CH_2CH_2CH_2CH_3$ (**2d**)	0.86 (m, $CH_2CH_2CH_2CH_3$), 0.27 (m, $CH_2CH_2CH_2CH_3$)	2.22, 2.06	−32.7
$CH_2CH(CH_3)_2$ (**2e**)	1.39 (d, J_{HH} = 7 Hz, CH_2CH), 1.02 (m, CH_2CH), 0.25 (d, J_{HH} = 7 Hz, $CH(CH_3)_2$)	2.30, 2.12	−34.2
$CH(CH_3)CH_2CH_3$ (**2f**)	1.30–0.88 (m, CH, CH_2), 0.71 (d, J_{HH} = 7 Hz, $CHCH_3$), 0.18 (t, J_{HH} = 7 Hz, CH_2CH_3)	2.26, 2.08	−35.1
$CH_2[CH_2]_6CH_3$ (**2k**)	1.20–0.20 (m)	2.22, 2.04	−32.5
	Y = I; L = PMe_2Ph		
$CH_2CH_2CH_3$ (**3b**	nm	nm	−46.2
$CH(CH_3)_2$ (**3c**)	nm	nm	−48.7

[a] ^1H NMR spectra at 29 °C in CD_2Cl_2 containing $(CH_3)_4Si$ as internal reference; $^{31}P\{^1H\}$ NMR spectra at 35 °C in CH_2Cl_2, chemical shifts referenced to external 85% H_3PO_4, positive to high frequency. [b] "Virtual" triplet, $^2J_{PH} + {}^4J_{PH}$ = 8 Hz.

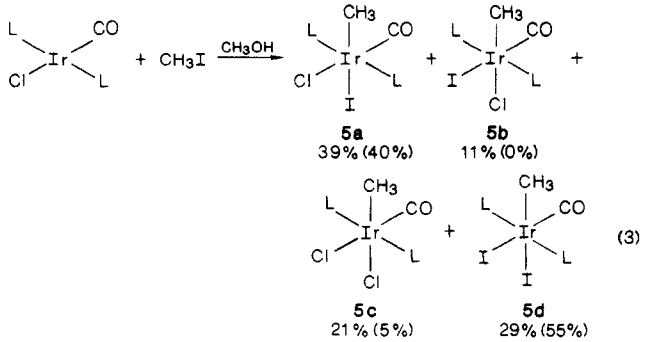
Table II. NMR (^1H and ^{31}P) Spectroscopic Data for Adducts Resulting from Reaction IrY(CO)L_2 + CH_3X



	Y	X	δ(IrCH_3)[a]	δ(P)[b]
5c	Cl	Cl	0.42	−25.7
5a	Cl	I	0.53	−32.3
5d	I	I	0.85	−47.9
5b	I	Cl	0.70	−39.1

[a] In CD_2Cl_2; all resonances were triplets ($^3J_{PH}$ = 5 Hz). [b] In CH_2Cl_2, ppm from external 85% H_3PO_4, positive to high frequency.

scrambling in the corresponding addition of methyl iodide to IrCl(CO)$(PMe_2Ph)_2$ in methanol (eq 3), the products being identified by their Ir–CH_3 resonances. We have reexamined this reaction by ^{31}P NMR spectroscopy and find that all four possible products **5a–d** arising from halide scrambling are formed (eq 3). The individual complexes



(3)

L = PMe_2Ph; figures in brackets are those reported in ref. 17

were made independently for this identification by trans oxidative addition of the appropriate methyl halide to IrX(CO)$(PMe_2Ph)_2$ (X = Cl, I); their IrCH_3 and ^{31}P NMR chemical shifts are given in Table II. It is well-known that alkyliridium(III) complexes containing two different halide groups can isomerize in methanol[19] or, more slowly, in benzene[20] and that they undergo halide exchange with an excess of alkyl halide.[14]

Since halide scrambling is almost absent (ca. 5%) when **2c** is allowed to isomerize to **2b** in dichloromethane–methanol at room temperature, these conditions have been chosen for kinetic studies.

(2) Kinetic Studies. Although ^1H NMR spectroscopy can be used to monitor the alkyl isomerization qualitatively, it is not suitable for study of the kinetics because the resonances for the various isomers overlap. For this purpose, we have taken advantage of the 1–3 ppm difference in the ^{31}P chemical shifts of the isomers (Table I). The $^{31}P\{^1H\}$ NMR spectra as a function of time of a solution of IrClI$\{CH(CH_3)_2\}(CO)(PMe_3)_2$ (**1c**) in dichloromethane–methanol (4:1 v/v) at 30 °C are presented in Figure 1. The resonance due to **1c** gradually disappears and is replaced by that of the *n*-propyl isomer **1b**. The rearrangement goes to completion over a period of 4 h, no other signals being observed, and gives a good first-order rate plot, as shown in Figure 2, the rate constant being (6.9 ± 0.5) × 10^{-5} s^{-1} at 30 °C. Within experimental error, the same rate constant is found for the isomerization of the complex IrClI$\{CH(CD_3)_2\}(CO)(PMe_3)_2$ to IrClI$(CD_2CHDCD_3)(CO)(PMe_3)_2$.

As shown in Table III, the first-order rate constants for the isomerization of IrClI$\{CH(CH_3)_2\}(CO)(PMe_3)_2$ (**1c**) and of IrClI$\{CH(CH_3)_2\}(CO)(PMe_2Ph)_2$ (**2c**) to the corresponding *n*-propyl compounds **1b** and **2b**, respectively, in dichloromethane–methanol increase as the proportion of methanol increases. The PMe_2Ph compound **2c** isomerizes

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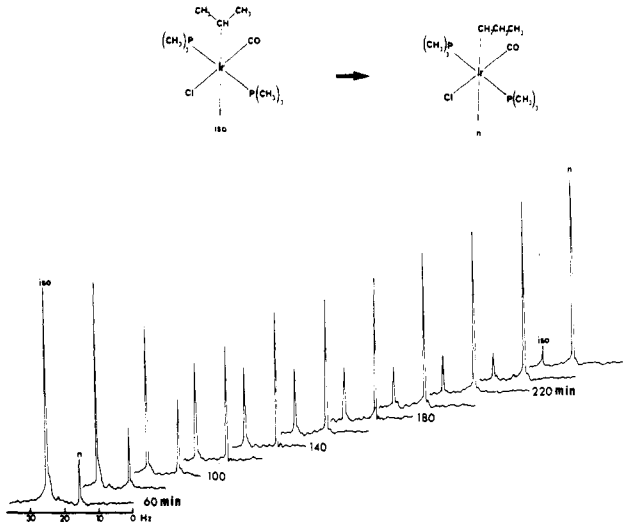


Figure 1. $^{31}P\{^1H\}$ NMR spectra of $IrClI\{CH(CH_3)_2\}(CO)(PMe_3)_2$ (**1c**) in CH_2Cl_2–CH_3OH (4:1 v/v) at 30 °C, showing rearrangement to $IrClI(CH_2CH_2CH_3)(CO)(PMe_3)_2$ (**1b**).

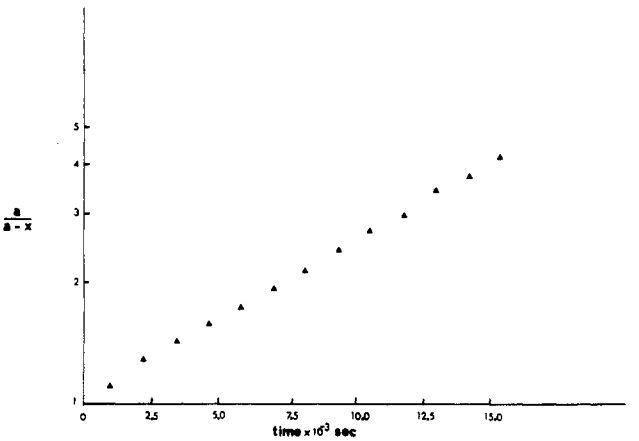


Figure 2. Plot of ln $[a/(a - x)]$ vs. time for rearrangement of $IrClI\{CH(CH_3)_2\}(CO)(PMe_3)_2$ (**1c**) to $IrClI\{CH_2CH_2CH_3\}(CO)(PMe_3)_2$ (**1b**) in CH_2Cl_2–CH_3OH (4:1 v/v) at 30 °C.

Table III. First-Order Rate Constants (k) and Half-Lives ($t_{1/2}$) for Isomerization of $IrClI\{CH(CH_3)_2\}(CO)L_2$ [L = PMe_3 (1c**), PMe_2Ph (**2c**)] to $IrClI(CH_2CH_2CH_3)(CO)L_2$ [L = PMe_3 (**1b**), PMe_2Ph (**2b**)] in Dichloromethane–Methanol Mixtures at 32 °C**

ratio CH_2Cl_2–CH_3OH		10^5 k, s^{-1}		$t_{1/2}$ min	
vol.	mol	L = PMe_3	L = PMe_2Ph	L = PMe_3	L = PMe_2Ph
2:1	1:0.79	32 ± 3	*a*	36	*a*
4:1	1:0.40	9 ± 1	78 ± 8	128	15
9:1	1:0.32	5 ± 0.5	13 ± 1	231	89

[a] Too fast to monitor by NMR spectroscopy.

considerably faster than its PMe_3 analogue **2b**.

The efficacy of various protic solvents in promoting the *sec*- to *n*-alkyl rearrangement has been examined by monitoring the rate of disappearance of **2c** in a mixture of dichloromethane and the solvent. The observed first-order rate constants are shown in Table IV; they decrease in the order CF_3CO_2H >> CH_3OH >> C_2H_5OH > CH_3CO_2H ≈ $CH_3CH_2CH_2OH$ > $(CH_3)_2CHOH$. Only small quantities of trifluoroacetic acid (10 μL in 2 mL of dichloromethane) are required to induce isomerization. The position of water in this series cannot be established directly because of the poor miscibility of water with dichloromethane. If dichloromethane–methanol is replaced by tetrahydrofuran–methanol, isomerization occurs only very slowly, but addition of water to a THF solution of **2c** induces a rapid first-order isomerization, as shown in Table IV; thus the ordering is H_2O >> CH_3OH. As shown in Table V, the first-order rate constants for the isomerization of *sec*-alkyls $IrClIR(CO)(PMe_3)_2$ in dichloromethane–methanol (4:1 v/v) at 32 °C are in the order R = $CH(CH_3)_2$ (**1c**) < $CH(CH_3)CH_2CH_3$ (**1f**) < $CH(CH_2CH_3)_2$ (**1j**) ≈ $CH(CH_3)[CH_2]_5CH_3$ (**1l**), indicating that an increase in the size of the alkyl group accelerates the isomerization up to a limit, after which further increase has little effect. In dichloromethane–methanol (4:1 v/v), complex **2c**, which has Cl trans to CO, isomerizes more rapidly than complex **3c**, in which I is trans to CO (Table V).

Table IV. First-Order Rate Constants (k) and Half-Lives ($t_{1/2}$) for Isomerization of $IrClI\{CH(CH_3)_2\}(CO)(PMe_2Ph)_2$ (2c**) to $IrClI(CH_2CH_2CH_3)(CO)(PMe_2Ph)_2$ (**2b**) in Dichloromethane–Solvent and Tetrahydrofuran–Solvent Mixtures (1:0.40 Mole Ratio) at 32 °C**

solv mixture	10^5 k, s^{-1}	$t_{1/2}$, min
CH_2Cl_2–CF_3CO_2H	*a*	*a*
CH_2Cl_2–CH_3OH	78 ± 8	15
CH_2Cl_2–C_2H_5OH	9 ± 1	128
CH_2Cl_2–CH_3CO_2H	6 ± 0.5	193
CH_2Cl_2–$CH_3CH_2CH_2OH$	6 ± 0.5	193
CH_2Cl_2–$(CH_3)_2CHOH$	3 ± 0.3	385
THF–H_2O	7 ± 1	165
THF–CH_3OH	<0.3	

[a] Too fast to monitor by NMR spectroscopy.

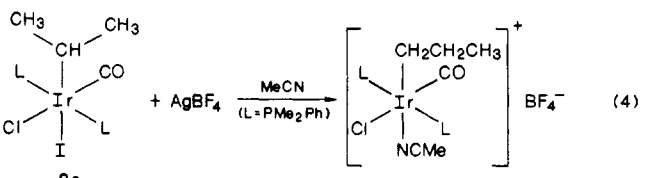
Table V. First-Order Rate Constants and Half-Lives for Isomerization of IrYI-*sec*-R(CO)L_2 to IrYI-*n*-R(CO)L_2 in Dichloromethane–Methanol Mixtures[a] at 32 °C

Y	L	R	10^5k, s^{-1}	$t_{1/2}$, min
Cl	PMe_3	$CH(CH_3)_2$ (**1c**)	9 ± 1	128
Cl	PMe_3	$CH(CH_3)CH_2CH_3$ (**1f**)	14 ± 2	83
Cl	PMe_3	$CH(CH_2CH_3)_2$ (**1j**)	25 ± 2	46
Cl	PMe_3	$CH(CH_3)[CH_2]_5CH_3$ (**1l**)	25 ± 2	46
Cl[b]	PMe_2Ph	$CH(CH_3)_2$ (**2c**)	13 ± 1	89
I[b]	PMe_2Ph	$CH(CH_3)_2$ (**4c**)	5 ± 0.5	231

[a] 4:1 v/v (mol ratio 1:0.40), except where stated. [b] 9:1 v/v (mol ratio 1:0.32).

As discussed in detail below, the solvent effect on the rate of alkyl rearrangement is consistent with an initial, reversible rate-determining loss of iodide ion from the alkyliridium(III) complex. In agreement, addition of iodide ion causes a marked decrease in the rate of rearrangement. Thus the half-life for the rearrangement of $IrClI\{CH(CH_3)_2\}(CO)(PMe_2Ph)_2$ (**2c**) in dichloromethane–methanol (4:1 v/v) is 15 min at 32 °C, but this is increased to 128 min in the presence of 16 mol % of sodium iodide. Unfortunately, simple first-order behavior is not observed under these conditions and the poor solubility of NaI in the solvent mixture allows little variation in the iodide ion concentration. This could obviously be increased by the use of $Bu_4N^+I^-$ or of crown ethers, but these techniques have not been investigated.

Although dipolar aprotic solvents do not promote the *sec*- to *n*-alkyl rearrangement, addition of 1 equiv of $AgBF_4$ to a solution of the isopropyl complex **2b** in acetonitrile gives immediately the *n*-propyliridium(III) cation **6** (eq 4).

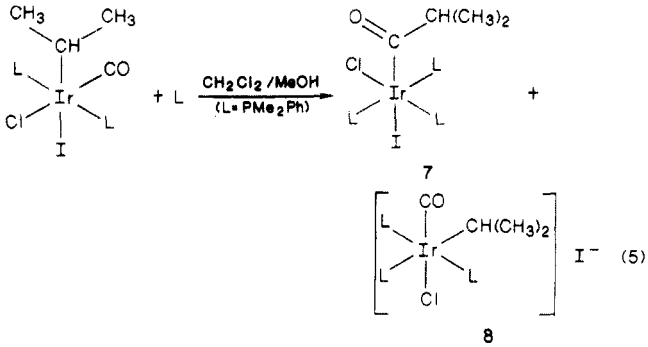


2c 6 (4)

The ^1H NMR spectrum of **6** shows typical *n*-propyl reso-

nances at δ 0.57 (t, J_{HH} = 6 Hz, $IrCH_2CH_2CH_3$) and 0.76–1.18 (m, $IrCH_2CH_2CH_3$). The IR spectrum of the isolated solid shows a ν(CO) band at 2050 cm^{-1}, a ν(CN) band at 2300 cm^{-1}, and a ν(IrCl) band at 316 cm^{-1} characteristic of Cl trans to CO in octahedral iridium(III) complexes.[16,17]

An attempt to study the effect of added tertiary phosphine on the rate of alkyl group isomerization was not successful. Although dimethylphenylphosphine does not react with **2c** in benzene, addition of 1 equiv of PMe_2Ph to **2c** in CH_2Cl_2–MeOH (4:1 v/v) gives mainly the acyl complex **7**, together with two other minor products; one of these is probably the cationic isopropyliridium(III) complex **8** (eq 5). The IR spectrum of the solid isolated



from this reaction shows an acyl ν(C=O) band at 1600 cm^{-1} both in the solid state and in dichloromethane solution; in the latter, there is also a terminal ν(CO) band at 2030 cm^{-1}. The ^1H NMR spectrum in CD_2Cl_2 is complex, but resonances due to **7** can be identified. The P–Me resonances appear as two triplets ($^2J_{PH} + {}^4J_{PH}$ = 8 Hz) at δ 2.06 and 2.02 due to the trans PMe_2Ph ligands and a doublet ($^2J_{PH}$ = 10 Hz) at δ 1.59 due to the unique PMe_2Ph ligand, and there are isopropyl group signals at δ 0.50 (d, J_{HH} = 7 Hz) and 3.45 (m). A close analogue of **7**, $IrCl_2(COCHMe_2)(CO)(PMe_2Ph)_2$, has been made by addition of 2-methylpropanoyl chloride to $IrCl(PMe_2Ph)_3$, and it shows similar spectroscopic properties to those of **7**.[21]

(3) Deuterium-Labeling Experiments. In order to examine the ability of alkyl groups in iridium(III) complexes to undergo reversible β-elimination, the behavior of some deuterium-labeled derivatives has been studied. Dissolution of the ethyl-*1,1-d*$_2$ complex $IrClI(CD_2CH_3)(CO)(PMe_2Ph)_2$ (**2a′**) in dichloromethane–methanol (1:1 v/v) at room temperature causes no detectable scrambling of the deuterium between the two carbon atoms, as shown by ^1H NMR spectroscopy. Thus the *n*-alkyl complexes do not undergo rapid, reversible β-elimination under conditions which induce *sec*- to *n*-alkyl rearrangement. Scrambling does occur, however, when the solution is heated at 80 °C for 2 h, as shown in Figure 3; some decomposition (ca. 10%) is evident from the presence of an additional pair of P–Me triplets in the ^1H NMR spectrum. Dissolution of **2a′** in CD_2Cl_2–CF_3CO_2H (10:1 v/v) at 30 °C induces immediate deuterium scrambling, suggesting that CF_3CO_2H promotes alkyl rearrangement and β-hydride migration by a common mechanism. This mechanism does not involve protonation of the alkyliridium(III) bond since addition of CF_3CO_2D to $IrClI(CH_2CH_3)(CO)(PMe_2Ph)_2$ (**2a**) causes no incorporation of deuterium into the ethyl group, as shown by ^1H NMR spectroscopy. Addition of $AgBF_4$ to **2a′** in CD_3CN gives the cationic species $[IrCl(CD_2CH_3)(CO)(CD_3CN)(PMe_2Ph)_2]^+$, and this shows evidence of deuterium scrambling only after 16 h at 30 °C.

(21) Bennett, M. A.; Jeffery, J. C.; Robertson, G. B. *Inorg. Chem.* **1981**, *20*, 323.

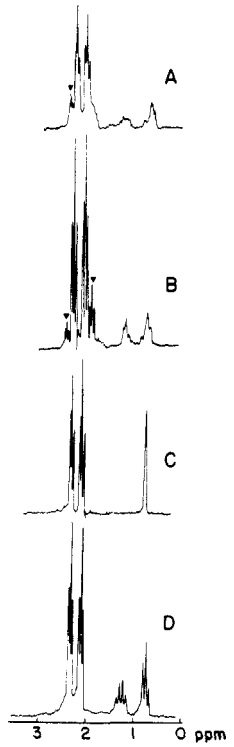
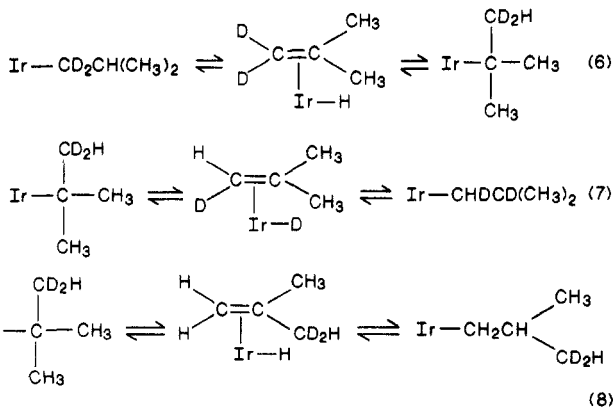


Figure 3. ^1H NMR spectra showing scrambling of deuterium label in $IrClI(CD_2CH_3)(CO)(PMe_2Ph)_2$ (**2a′**): ▼, peaks due to unidentified side products; A, CD_2Cl_2–CF_3CO_2H (10:1, v/v), 25 °C, 2 h; B, CD_2Cl_2–CD_3OD (1:1, v/v), 80 °C, 28 h; C, CD_2Cl_2, 25 °C; D, $IrClI(CH_2CH_3)(CO)(PMe_2Ph)_2$ (**2a**) in CD_2Cl_2.

These results, taken together, indicate that reversible β-hydride migration does occur in *n*-alkyliridium(III) complexes, but the process is considerably slower than in the *sec*-alkyliridium(III) analogues.

To determine whether alkyl group rearrangement can proceed through a tertiary carbon-bonded intermediate, the isobutyl-*1,1-d*$_2$ complex $IrClI\{CD_2CH(CH_3)_2\}(CO)(PMe_3)_2$ (**1e′**) has been prepared. Scrambling of the deuterium label over all the alkyl carbon atoms in this complex would implicate a *tert*-butyliridium(III) intermediate in a series of reversible β-eliminations (eq 6–8). When a



solution of **1e′** in CD_2Cl_2–CD_3OD (1:1 v/v) is heated at 80 °C over a period of 9 h, a broad singlet grows in between the lines of the isobutyl methyl doublet at δ 1.00 in the ^1H NMR spectrum (Figure 4); the new singlet is assigned to the methyl group of the Ir–$CHDCD(CH_3)_2$ complex. Concomitantly, the total intensity of the singlet and doublet methyl resonances relative to the internal hexamethyldisiloxane standard decreases with time. The ^2H-{^1H} NMR spectrum of a freshly prepared solution of **1e′** in methanol shows a single resonance at δ 1.67, but after being heated at 80 °C for 24 h there are two additional

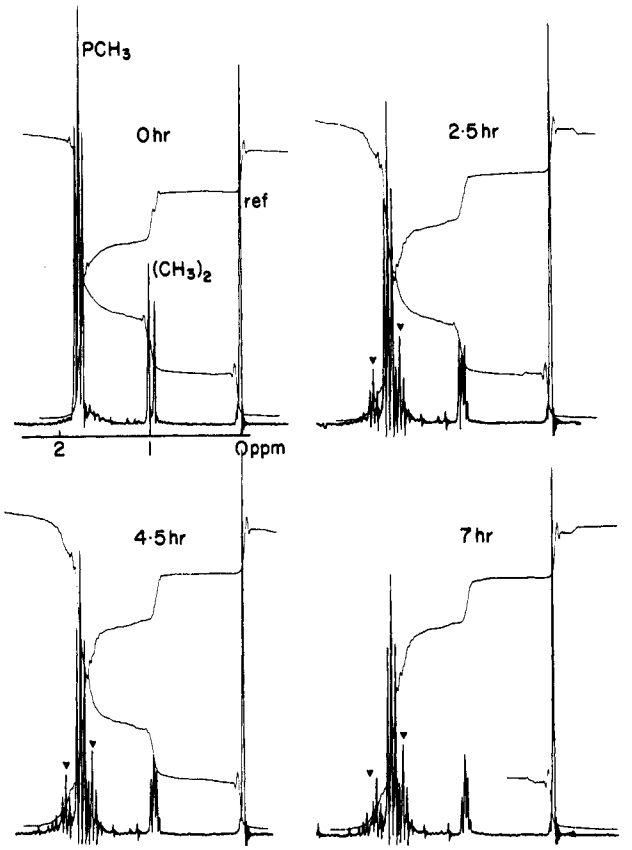
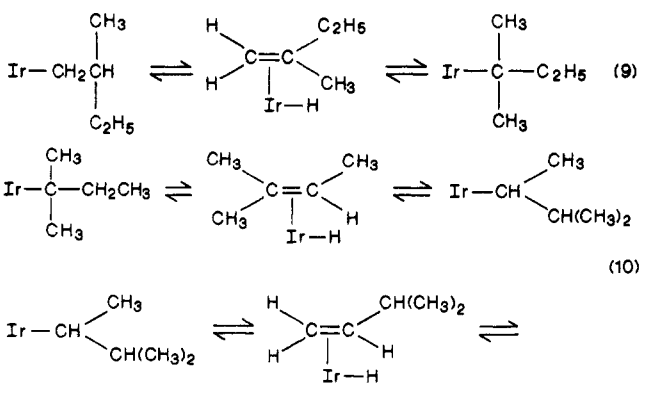


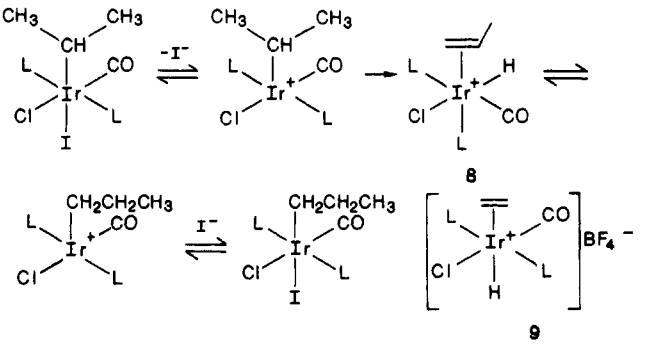
Figure 4. ^1H NMR spectra showing scrambling of deuterium label in $IrClI\{(CD_2CH(CH_3)_2\}(CO)(PMe_3)_2$ (**1e'**) on heating in CH_2Cl_2–CD_3OD (1:1 v/v) (reference is hexamethyldisiloxane): ▼, peaks due to unidentified side products.

resonances of comparable intensity at δ 1.43 and 0.79, corresponding to the three different environments expected for the deuterium atoms from eq 6–8. These observations are, therefore, consistent with the occurrence of deuterium scrambling over all the alkyl carbon atoms.

In the light of this result, it is surprising that the ^1H and ^{13}C NMR spectra of the isomers $IrClI\{CH_2CH(CH_3)CH_2CH_3\}(CO)(PMe_3)_2$ (**1h**) and $IrClI\{CH_2CH_2CH(CH_3)_2\}(CO)(PMe_3)_2$ (**1i**) remain essentially unchanged, except for some irreversible decomposition, when either compound is heated in CD_2Cl_2–CD_3OD at 80 °C for 24 h. A solution of $IrClI\{CD_2CH(CH_3)CH_2CH_3\}(CO)(PMe_3)_2$ in methanol shows a single ^2H resonance at δ 1.68, and this remains after the solution is heated at 80 °C for 24 h, although there are two additional broad, low intensity resonances at δ ca. 1.1 and 0.85 indicative of minor scrambling of the label. In principle, **1h** and **1i** should be interconvertible by reversible β-eliminations via a tertiary alkyliridium(III) intermediate (eq 9–11). It is not clear



Scheme I



whether this intermediate is too sterically hindered to be formed, thus blocking the rearrangement, or whether β-hydride migration occurs preferentially from the methyl group rather than from the methylene group of the intermediate.

Discussion

The rate-determining step in the mechanism proposed for the *sec*- to *n*-alkyl rearrangement in the iridium(III) complexes is believed to be reversible loss of iodide ion trans to the alkyl group. This creates a vacant site that allows a series of reversible β-hydride migrations to occur. Reentry of iodide ion trans to the rearranged alkyl group then completes the process. This sequence is shown for the case of the isopropyl complexes (L = PMe_3, PMe_2Ph) in Scheme I. The driving force for the process is probably the high trans influence of the *sec*-alkyl group combined with the tendency of iridium(III) to reach its favored coordination number of six in the hydrido olefin intermediate **8**. Since the hydride ligand must be cis to the olefin for migration to occur, one of the other ligands must move as well. In the corresponding alkyl rearrangement of bis(alkyl)iridium(III) complexes, there is evidence for an intermediate containing cis phosphine ligands,[22] and we suggest the same to be true in the present case, as shown in Scheme I. The rearrangement in the coordination sphere is remarkably stereospecific, since iodide ion returns almost exclusively to the site from which it leaves, at least in protic media at room temperature.

The cis hydrido olefin intermediate **8** could not be detected and presumably is short-lived. The fact that the closely related hydrido olefin complex **9** can be isolated[23] must be a consequence of the trans dispositions both of the coordinated hydride and olefin and of the tertiary phosphine ligands.

The evidence in favor of reversible loss of I^- as the initial rate-determining step is as follows: (1) The rate of alkyl group isomerization is reduced significantly by addition of sodium iodide. (2) Removal of iodide ion by $AgBF_4$ causes immediate alkyl group isomerization. (3) The effect of solvents on the first-order rate constants correlates with their ability to solvate anions and suggests that solvents act to promote dissociation of I^-. (4) The absence of a detectable kinetic isotope effect for the deuterated isopropyl group $CH(CD_3)_2$ suggests that β-hydride migration is not the rate-determining step. A value of 2.28 ± 0.20 has been found for β-hydride elimination from alkyliridium(I) complexes.[24]

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Heterolysis of the iridium(III)–iodine bond could be facilitated either by a strong donor solvent which preferentially solvates the cation or by a strong acceptor solvent which preferentially solvates the anion. Clearly, alkyl rearrangement will be favored in the second case, where the vacant coordination site is maintained, rather than in the first case, where the solvent tends to occupy the site needed for the olefin produced by β-elimination. Several scales of solvent acceptor and solvent donor properties have been proposed.[25,26] We find that the logarithms of the rates of rearrangement in various solvents in admixture with dichloromethane correlate reasonably with both the Dimroth–Reichardt E_T and the Taft α parameters,[27] both of which are believed to reflect the hydrogen bond-forming ability of protic solvents. There is only a fair correlation between the isomerization rate and either the acceptor number or the Grunwald–Winstein Y value of the solvents, and the rate does not correlate at all with either the dielectric constant or with the donor number (a measure of solvent nucleophilicity). Thus electrophilic solvation of the displaced iodide ion by hydrogen bonding with the protic solvent seems to be the major factor in determining the solvent effect on the rate of alkyl rearrangement. The same order of effectiveness of alcoholic solvents, viz., $CH_3OH > C_2H_5OH > CH_3CH_2CH_2OH > (CH_3)_2CHOH$ has also been observed in the isomerization of *cis*- to *trans*-$PtCl(m\text{-}CH_3C_6H_4)(PEt_3)_2$, where the rate-determining step is thought to be dissociation of Cl^-.[28,29] The rate of cis to trans isomerization of phosphine ligands in $IrCl_2R(CO)(PMePh_2)_2$ complexes dissolved in dichloromethane is also increased by addition of methanol and retarded by added LiCl.[7]

The fact that isomerization of **2c** to **2b** in THF/CH_3OH is much slower than in CH_2Cl_2–CH_3OH may be due either to coordination of THF to the five-coordinate iridium(III) cation formed by loss of I^- (see above) or to the donor ability of THF, which could reduce the hydrogen-bonding ability, and hence the anion-solvating ability, of the protic cosolvent.

The exclusive formation of $IrCl_2(n\text{-alkyl})(CO)(PPh_3)_2$ from the reaction of α-branched acyl chlorides with $IrCl(PPh_3)_3$ was ascribed originally to an unfavorable steric interaction between the *sec*-alkyl group and the phenyl rings of the PPh_3 ligands in the putative intermediate $IrCl_2(sec\text{-alkyl})(CO)(PPh_3)_2$.[6] The present work shows that, in the similar system $IrClIR(CO)L_2$, *n*-alkyls are always thermodynamically more stable than *sec*-alkyls, even for the smallest tertiary phosphine L(PMe_3). Yoneda and Blake[15] have estimated the enthalpy change for the isomerization of **1c** to **1b** as -5 ± 29 kJ/mol and, in general, the mean bond dissociation enthalpies of *sec*-alkyls of both the main-group and transition elements are somewhat lower than those of the corresponding *n*-alkyls.[30,31] The balance is obviously fine, because the sterically less hindered, phosphine-free complex $[IrCl_2(C_3H_7)(CO)_2]_2$ reaches a thermodynamic equilibrium state of 2:3 for the isopropyl to the *n*-propyl compound.[6]

As noted above, the final compounds $IrClI(n\text{-alkyl})(CO)L_2$ still undergo reversible β-hydride migration, presumably as a consequence of reversible dissociation of I^-, but the process is slower than for the *sec*-alkyls. The *sec*- to *n*-alkyl rearrangement is promoted by increasing bulk of both the alkyl group and the tertiary phosphine, but we do not know whether this rate enhancement is due to faster displacement of I^-, faster β-hydride migration, or some other factor.

It is of interest to compare the rearrangements reported here with those in the $(\eta\text{-}C_5H_5)FeR(CO)(PPh_3)$ series, which are promoted by thermal dissociation of PPh_3.[8] Deuterium labeling studies on the iron system have shown that reversible β-hydride migration in the *n*-alkyls is occurring under the same conditions as those required for the *sec*- to *n*-alkyl rearrangement, whereas in the iridium system, the first process requires more forcing conditions than the second. A *tert*-butyl intermediate, $M\text{–}C(CH_3)_3$, appears in both systems, as shown by scrambling of the deuterium label in the appropriate isobutyl-d_2 complexes, but a *tert*-pentyl intermediate, $M\text{–}C(CH_3)_2(CH_2CH_3)$, is accessible only in the iron system. Thus, a 5.7:1 mixture of $(\eta\text{-}C_5H_5)Fe\{CH_2CH_2CH(CH_3)_2\}(CO)(PPh_3)$ and $(\eta\text{-}C_5H_5)Fe\{CH_2CH(CH_3)(CH_2CH_3)\}(CO)(PPh_3)$ is obtained when either component is heated at 64 °C for 4 h,[8] whereas the corresponding iridium alkyls do not interconvert. The formation of tertiary carbon intermediates has been excluded both in the addition of internal alkenes to $(\eta\text{-}C_5H_5)_2ZrHCl$ to give *n*-alkylzirconium complexes $(\eta\text{-}C_5H_5)_2ZrRCl$ as the sole products[32] and in the thermal decomposition of isomeric acylmanganese pentacarbonyls.[33]

Experimental Section

Measurements. The following instruments were used: Varian HA100 (^1H NMR at 100 MHz), Bruker 322S (^{31}P NMR at 24.3 MHz), Bruker HX270 (^2H NMR at 41.45 MHz), Perkin-Elmer PE457 or 225 (IR spectra in the range 4000–200 cm^{-1} on CsI windows, calibrated against polystyrene). Microanalyses were carried out in the laboratories of the John Curtin School of Medical Research and in this School by Dr. Joyce Fildes and Miss Brenda Stevenson and their associates. Molecular weights were measured at 25 °C on ca. 0.02 M solutions in dichloromethane by means of a Knauer vapor pressure osmometer. Melting points (uncorrected) were measured on a Gallenkamp hot stage apparatus.

Starting Materials. Benzene and toluene were distilled from sodium benzophenone ketyl under nitrogen, dichloromethane and methanol were distilled from respectively calcium hydride and magnesium methoxide. Isobutyl, neopentyl, 2-methylbutyl, 3-methylbutyl, 1-ethylpropyl, and 1-methylheptyl iodides were prepared from the appropriate alcohol and triphenyl phosphite–methyl iodide.[34] These, and the other alkyl iodides obtained commercially, were purified by distillation under nitrogen or in vacuo before use. 2-Methyl-1-propanol-*1,1*-d_2 was prepared by $LiAlD_4$ reduction of 2-methylpropanoic acid and was converted into isobutyl iodide-*1,1*-d_2, $(CH_3)_2CHCD_2I$, by means of HI.[35] Similarly, 2-propanol-*1,1,1,3,3,3*-d_6 was prepared from acetone-d_6 and $LiAlH_4$[34] and was converted into isopropyl-*1,1,1,3,3,3*-d_6 iodide by use of HI. Ethyl-*1,1*-d_2 iodide and triethylphosphine were obtained commercially; diphenylmethylphosphine,[36] dimethylphenylphosphine,[36] and trimethylphosphine[37] were made by literature procedures. The iridium(I) complexes $IrCl(CO)L_2$ (L = PMe_3,[38] PMe_2Ph,[39] $PMePh_2$,[39] or PEt_3[39]) and $IrI(CO)$-

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$(PMe_2Ph)_2$[40] were prepared from chloroiridic acid (Johnson-Matthey) by literature methods.

All operations involving iridium(I) complexes and tertiary phosphines were carried out under nitrogen with use of standard Schlenk techniques. Analyses, melting points, molecular weights, and IR data are included in the supplementary material. Proton and ^{31}P NMR data are given in Table I.

Alkylbis(trimethylphosphine)carbonylchloroiodoiridium(III) Complexes, $IrClIR(CO)(PMe_3)_2$ (1a–m). A solution of $IrCl(CO)(PMe_3)_2$ (0.10 g, 0.25 mmol) in benzene (5 mL) was treated with the appropriate alkyl iodide (0.5 mL). The initially yellow solution turned colorless over a period of 2–60 min, depending on the alkyl iodide. Evaporation of volatile material in vacuo and trituration of the residue with hexane gave the product as a white solid in 80–95% yield. Samples for analysis were recrystallized from dichloromethane–hexane.

Alkylbis(dimethylphenylphosphine)carbonylchloroiodoiridium(III) Complexes, $IrClIR(CO)(PMe_2Ph)_2$ (2a–f). These were prepared as described above from $IrCl(CO)(PMe_2Ph)_2$ (0.10 g, 0.19 mmol) in benzene (5 mL) and the alkyl iodide (0.15 mL). The colorless products were obtained in 80–90% yield and were recrystallized for analysis from dichloromethane–hexane.

Treatment of $IrI(CO)(PMe_2Ph)_2$ with *n*-propyl iodide or isopropyl iodide similarly gave the complexes $IrI_2R(CO)(PMe_2Ph)_2$ [R = $CH_2CH_2CH_3$ (**3b**), $CH(CH_3)_2$ (**3c**)], respectively.

Bis(triethylphosphine)carbonylchloroethyliodoiridium(III), $IrClI(C_2H_5)(CO)(PEt_3)_2$ (4a). A solution of $IrCl(CO)(PEt_3)_2$ (0.10 g, 0.20 mmol) in benzene (5 mL) was treated with ethyl iodide (0.15 mL, 1.4 mmol). The initially yellow solution turned colorless after 1 h. Workup as described above gave the product as a white solid (0.1 g, 77%), which could be recrystallized from dichloromethane–hexane: mp 96–97 °C; IR (Nujol) 2010 (CO), 305 cm^{-1} (IrCl); $^1H\{^{31}P\}$ NMR (CD_2Cl_2) δ 1.17 (t, PCH_2CH_3), 1.42 (t, J_{HH} = 7 Hz, $IrCH_2CH_3$), 1.97 (q, J_{HH} = 7 Hz, $IrCH_2CH_3$), 2.20 (m, PCH_2CH_3); $^{31}P\{^1H\}$ NMR (CH_2Cl_2) δ −21.4 (s).

The complex $IrClI(CH_2CH_2CH_3)(CO)(PEt_3)_2$ (**4b**) was prepared similarly from $IrCl(CO)(PEt_3)_2$ and *n*-propyl iodide but could only be obtained as a dark oil: IR (CH_2Cl_2) 2020 cm^{-1} (CO); $^{31}P\{^1H\}$ NMR (CH_2Cl_2) δ −21.3 (s).

Attempted addition of isopropyl iodide or neopentyl iodide to $IrCl(CO)(PEt_3)_2$ gave only starting material.

Reaction of Methyl Iodide with $IrCl(CO)(PMe_2Ph)_2$. A solution of $IrCl(CO)(PMe_2Ph)_2$ (0.10 g, 0.19 mmol) in methanol (5 mL) was treated with methyl iodide (0.15 mL). The initially yellow solution rapidly became colorless. Evaporation of solvents and trituration of the residue with hexane gave a white solid (0.10 g). This contained **5a** (39%), **5b** (11%), **5c** (21%), and **5d** (29%) (eq 3), as shown by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy.

The individual components were synthesized independently by reaction of methyl chloride over 4 days with $IrCl(CO)(PMe_2Ph)_2$ (**5c**) and with $IrI(CO)(PMe_2Ph)_2$ (**5b**), both in benzene, and by reaction of methyl iodide over ca. 1 h with $IrCl(CO)(PMe_2Ph)_2$ (**5a**) and with $IrI(CO)(PMe_2Ph)_2$ (**5d**), both in benzene. Their characteristic NMR data are summarized in Table II.

Reaction of Isopropyl Iodide with $IrCl(CO)(PMe_2Ph)_2$ in Methanol. Carried out as described above, this reaction gave a white solid. The $^{31}P\{^1H\}$ NMR spectrum in CH_2Cl_2 showed singlets at δ −46.5, −32.7, and −25.3 due respectively to $IrI_2(CH_2CH_2CH_3)(CO)(PMe_2Ph)_2$ (**3b**) (11%), $IrClI(CH_2CH_2CH_3)(CO)(PMe_2Ph)_2$ (**1b**) (74%), and $IrCl_2(CH_2CH_2CH_3)(CO)(PMe_2Ph)_2$ (15%). The peak due to the last species was assigned on the basis of the similarity of its chemical shift to that of its methyl chloride analogue (see above).

(Acetonitrile)bis(dimethylphenylphosphine)carbonylchloro-*n*-propyliridium(III) Tetrafluoroborate, $[IrCl(CH_2CH_2CH_3)(CO)(CH_3CN)(PMe_2Ph)_2]BF_4$ (6). A solution of $IrClI\{CH(CH_3)_2\}(CO)(PMe_2Ph)_2$ (**2c**) (0.10 g, 0.14 mmol) in acetonitrile (1 mL) was placed in a Schlenk tube wrapped in aluminum foil, and $AgBF_4$ (0.03 g, 0.16 mmol) was added. A yellow precipitate formed immediately. After the mixture had been stirred for 0.5 h, solvent was removed in vacuo and the residue was extracted with three 5-mL portions of dichloromethane. The extracts were filtered through Celite and evaporated to dryness. The resulting pale yellow solid was recrystallized from dichloromethane–hexane to give **6** as a colorless solid (0.08 g, 80%): IR (Nujol) 2285 (CN), 2040, 2030 (CO), 316 cm^{-1} (IrCl); IR (CH_2Cl_2) 2300 (CN), 2050 cm^{-1} (CO). ^1H NMR (CD_2Cl_2) δ 1.98, 1.95 (each t, $^2J_{PH}$ + $^4J_{PH}$ = 8 Hz, PCH_3), 1.18–0.76 (m, $IrCH_2CH_2CH_3$), 0.57 (t, J_{HH} = 6 Hz, $IrCH_2CH_2CH_3$). Anal. Calcd for $C_{22}H_{32}BClF_4IrNOP_2$: C, 37.6; H, 4.6; N, 2.0; P, 8.8. Found: C, 37.6; H, 4.7; N, 1.8; P, 9.0.

Reaction of $IrClI\{CH(CH_3)_2\}(CO)(PMe_2Ph)_2$ (2c) with Dimethylphenylphosphine. A solution of **2c** (0.10 g, 0.14 mmol) in dichloromethane (0.6 mL) and methanol (0.2 mL) was treated with PMe_2Ph (0.019 g, 0.14 mmol), and the mixture was stirred for 0.5 h. Solvents were removed in vacuo, and the residue was triturated with hexane to give an off-white solid (0.08 g), consisting mainly of $IrClI\{COCH(CH_3)_2\}(PMe_2Ph)_3$ (**7**): IR (Nujol) 1600 cm^{-1} (C=O); IR (CH_2Cl_2) 2030 (C≡O), 1600 cm^{-1} (C=O); ^1H NMR (CD_2Cl_2) δ 3.45 (m, $COCH(CH_3)_2$), 2.06, 2.02 (each t, $^2J_{PH}$ + $^4J_{PH}$ = 8 Hz, PCH_3), 1.59 (d, $^2J_{PH}$ = 10 Hz, PCH_3), 0.50 (d, J_{HH} = 7 Hz, $COCH(CH_3)_2$).

Deuterium Scrambling Experiments. A solution of the appropriate alkyliridium(III) complex [$IrClI(CD_2CH_3)(CO)(PMe_2Ph)_2$ (**2a′**) or $IrClI\{CD_2CH(CH_3)_2\}(CO)(PMe_3)_2$ (**1e′**)] in CD_2Cl_2 (0.3 mL) and CD_3OD (0.3 mL) was filtered through Celite into a 5-mm NMR tube fitted with a pressure seal and was heated at 80 °C for ca. 30 h. In the case of **2a′**, the singlet at δ 0.79 due to $IrCD_2CH_3$ was replaced by a pair of multiplets at ca. δ 0.8 and 1.3. The changes in the case of **1e′** have been described in the text.

A solution of **1e′** in methanol (2 mL) was heated at 80 °C for 24 h in a sealed tube. Solvent was removed in vacuo, the residue was taken up in CH_2Cl_2, and the ^2H NMR spectrum of the solution was recorded (see text).

Isomerization Kinetics. These were measured in 10-mm NMR tubes on 0.12–0.16 M solutions of the various *sec*-alkyliridium(III) complexes in 1.5 mL of solvent. The solvent mixtures were prepared in volumetric flasks before each run. No particular precautions were taken to exclude air as the complexes are air-stable. The rate of disappearance of the $^{31}P\{^1H\}$ NMR resonance (500-Hz bandwidth) at 35 °C was measured, spectral data being accumulated for 10 min with a subsequent 10-min delay. This sequence was repeated until the resonance of the *sec*-alkyl complex had disappeared. Time intervals were taken from the midpoint of each accumulation period. The sum of the peak heights of the resonances of the *sec*- and *n*-alkyl complexes was proportional to the initial concentration of *sec*-alkyl complex. Plots of $\ln [a/(a - x)]$ against time, where $(a - x)$ is the concentration of *sec*-alkyl complex at a particular time, were linear for at least 3 half-lives, indicating that the isomerization was first-order in *sec*-alkyl complex. Repetition of some rearrangements and calculation of the standard deviations of the rate constants gave values of 10% or less.

For detection of any possible difference in the contributions of T_1 and NOE effects to the intensity of the ^{31}P resonances of the *sec*- and *n*-alkyl isomers, a 1:1 mixture of **2b** and **2c** was subjected to a $(180° - \tau - 90°)$ pulse sequence. No significant difference in the intensities of the ^{31}P resonances of the two isomers was observed.

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Registry No. **1a**, 74511-76-5; **1b**, 75112-08-2; **1c**, 74511-77-6; **1d**, 103191-21-5; **1e**, 103191-22-6; **1f**, 103239-18-5; **1g**, 103191-23-7; **1h**, 103191-24-8; **1i**, 103191-25-9; **1j**, 103239-19-6; **1k**, 103191-26-0; **1l**, 103239-20-9; **1m**, 103191-27-1; **2a**, 103191-28-2; **2b**, 103191-29-3; **2c**, 103239-21-0; **2d**, 103191-30-6; **2e**, 103191-31-7; **2f**, 103191-32-8; **2k**, 103191-33-9; **3b**, 103191-34-0; **3c**, 103191-35-1; **4a**, 103191-36-2; **4b**, 103191-37-3; **5a**, 22606-11-7; **5b**, 103239-22-1; **5c**, 22606-07-1; **5d**, 22606-09-3; **6**, 103191-40-8; **7**, 103191-41-9; $IrCl_2(CH_2CH_2CH_3)(CO)(PMe_2Ph)_2$, 103191-38-4; $IrCl(CO)(PMe_3)_2$, 21209-86-9; $IrCl(CO)(PMe_2Ph)_2$, 21209-82-5; $IrI(CO)(PMe_2Ph)_2$, 21209-87-0; $IrCl(CO)(PEt_3)_2$, 21209-85-8; CH_3CH_2I, 75-03-6; $CH_3CH_2CH_2I$, 107-08-4; $(CH_3)_2CHI$, 75-30-9; $CH_3CH_2CH_2CH_2I$, 542-69-8; $(CH_3)_2CHCH_2I$, 513-38-2; $CH_3CH_2CH(CH_3)I$, 513-48-4; $(CH_3)_3CCH_2I$, 15501-33-4; $CH_3CH_2CH(CH_3)CH_2I$, 616-14-8; $(CH_3)_2CHCH_2CH_2I$, 541-28-6; $(CH_3CH_2)_2CHI$, 1809-05-8; $CH_3[CH_2]_6CH_2I$, 629-27-6; $CH_3[CH_2]_5CH(CH_3)I$, 557-36-8; c-$C_6H_{11}I$,

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626-62-0; CH_3I, 74-88-4; CH_2Cl_2, 75-09-2; CH_3OH, 67-56-1; CF_3CO_2H, 76-05-1; C_2H_5OH, 64-17-5; CH_3CO_2H, 64-19-7; $CH_3CH_2CH_2OH$, 71-23-8; $(CH_3)_2CHOH$, 67-63-0; H_2O, 7732-18-5; PMe_2Ph, 672-66-2; THF, 109-99-9.

Supplementary Material Available: Tables of elemental analyses, melting points, molecular weights, and IR data [ν(CO), ν(IrCl)] (4 pages). Ordering information is given on any current masthead page.

Secondary to Normal Alkyl Group Rearrangements in Octahedral Iridium(III) Complexes. 2. Bis(organo) Derivatives

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Organoiridium(I) complexes $IrR'(CO)(PMe_3)_2$ [R' = Me (1), CH_2SiMe_3 (2), and Ph (3)] have been made by reaction of the appropriate alkyllithium R'Li with $IrCl(CO)(PMe_3)_2$. The methyl derivative 1 oxidatively adds primary or secondary alkyl bromides or iodides RX to give octahedral bis(organo)iridium(III) complexes $IrXMeR(CO)(PMe_3)_2$ [R = $CH_2CH_2CH_3$, $CH(CH_3)_2$, $CH_2CH_2CH_2CH_3$, $CH(CH_3)CH_2CH_3$, $CH_2[CH_2]_3CH_3$, $CH(CH_3)CH_2CH_2CH_3$]. The (trimethylsilyl)methyl (2) and phenyl (3) derivatives oxidatively add primary or secondary alkyl iodides RI, but not bromides, to give similar complexes $IrIR'R(CO)(PMe_3)_2$. In all cases the stereochemistry of oxidative addition is trans and the PMe_3 ligands are mutually trans. The *sec*-alkyl complexes $IrXR'$-*sec*-$R(CO)(PMe_3)_2$ rearrange to the corresponding *n*-alkyl isomers $IrXR'$-*n*-$R(CO)(PMe_3)_2$ in benzene/methanol at room temperature. The rearrangement is quantitative for R' = Me or Ph, but in the case of R' = CH_2SiMe_3 it is accompanied by reductive elimination, giving $IrI(CO)(PMe_3)_2$, olefin (propene or butene from R = $CH(CH_3)_2$ or $CH(CH_3)CH_2CH_3$, respectively), and $(CH_3)_4Si$. The alkyl rearrangement is probably initiated by reversible, methanol-promoted dissociation of halide ion trans to the *sec*-alkyl group. This is followed by rapid, reversible β-hydride elimination and stereospecific return of halide ion trans to the rearranged alkyl group. When R' = Me or CH_2SiMe_3, an intermediate containing cis PMe_3 ligands can be detected as isomerization proceeds, probably *cis*-$IrXR'$-*n*-$R(CO)(PMe_3)_2$; however, it is not established with certainty whether the alkyl group in the intermediate is normal or secondary.

In the preceding paper,[1] we showed that *sec*-alkyliridium(III) complexes IrClI-*sec*-$R(CO)L_2$ (L = PMe_3, PMe_2Ph), formed by oxidative addition of *sec*-alkyl iodides to $IrCl(CO)L_2$, isomerize cleanly to the thermodynamically more stable *n*-alkyl compounds in the presence of protic solvents such as methanol, water, or trifluoroacetic acid. Alkyl- and aryliridium(I) complexes of the type $IrR(CO)L_2$[2,3] should be more electron-rich than $IrCl(CO)L_2$ and could be expected to oxidatively add alkyl halides, provided the σ-bonded group is not too bulky. The addition of hydrogen halides (HX) to $Ir(aryl)(CO)(PPh_3)_2$ to give iridium(III) hydrido aryls $IrHX(aryl)(CO)(PPh_3)_2$ is well-known,[4] but at the start of our work the only example of addition of an alkyl halide was the reaction of methyl iodide with $Ir(C_6F_5)(CO)(PPh_3)_2$ to give $IrIMe(C_6F_5)(CO)(PPh_3)_2$.[5] When this paper was about to be submitted, a report of the preparation of $IrMe(CO)(PPh_3)_2$ and its reaction with methyl iodide to give $IrIMe_2(CO)(PPh_3)_2$ appeared.[6] Related dimethyliridium(III) complexes $IrXMe_2L_3$ (X = Cl, I; L = PMe_2Ph, $AsMe_2Ph$) have been prepared by halogen cleavage of one of the Ir–Me bonds of the trimethyliridium(III) complexes *fac*-$IrMe_3L_3$; the latter are made by reaction of *mer*-$IrCl_3L_3$ with an excess of methylmagnesium chloride.[7] We were interested to see whether a range of bis(alkyl)iridium(III) complexes could be made by the oxidative addition procedure and whether the added alkyl group also would undergo secondary to normal rearrangement. Because $IrCl(CO)(PMe_3)_2$ adds alkyl halides much more readily than does $IrCl(CO)(PPh_3)_2$, we have used as precursors alkyliridium(I) complexes containing trimethylphosphine.

Results

Organoiridium(I) Complexes and Their Reactions with Alkyl Halides. Addition of 1 equiv of methyllithium, [(trimethylsilyl)methyl]lithium, or phenyllithium to $IrCl(CO)(PMe_3)_2$ in toluene at −78 °C gives the corresponding organoiridium(I) complexes $IrR'(CO)(PMe_3)_2$ in yields of 47% (R' = Me, 1), 58% (R' = CH_2SiMe_3, 2), and 86% (R' = Ph, 3), respectively. They are yellow, thermally stable, highly air-sensitive solids which are very soluble in hydrocarbons; they can be recrystallized from hexane. The method of preparation is general, since addition of [(trimethylsilyl)methyl]lithium to $IrCl(CO)L_2$ (L = PPh_3, PMe_2Ph) gives the expected products $Ir(CH_2SiMe_3)(CO)L_2$ which have been identified by their NMR spectra (see Experimental Section).

In the preparation of $IrMe(CO)(PMe_3)_2$ it is important to use just 1 mol of methyllithium/mol of $IrCl(CO)(PMe_3)_2$. Use of 2 mol of methyllithium gives a brown,

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