other atoms which had not been unambiguously located in the first map.

Isotropic refinement for four cycles converged at $R_F = 0.082$ and $R_{wF} = 0.089$. Continued refinement, with anisotropic thermal motion allowed for all atoms, and subdividing the atoms among three matrices, converged after seven cycles with $R_F = 0.050$, $R_{wF} = 0.048$, and a goodness of fit of 2.43. A difference-Fourier map calculated after the fifth anisotropic cycle had revealed all hydrogen atoms except those on the methyl groups and three others. Peak heights ranged from 0.2 to 0.7 e·Å^{-3}. Those hydrogen atoms whose positions could be calculated, except those on the methylene chloride, were located 0.98 Å from either carbon atom and included in the structure factor calculations of the last two cycles of refinement. They were assigned isotropic thermal parameters equal to the final isotropic values of the carbons to which they were attached. A final difference-Fourier map was featureless.

The refined atomic positions and thermal parameters are listed in Table VI.

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Registry No. **1**, 74466-65-2; **2**, 41612-45-7; **3**, 41612-46-8; **4**, 40964-31-6; **5**, 74482-42-1; **6**, 74482-43-2; **7**, 74482-45-4; [Ir(1,5-cyclooctadiene)Cl]$_2$, 12112-67-3.

Supplementary Material Available: Tables of observed and calculated structure amplitudes (16 pages). Ordering information is given on any current masthead page.

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Oxidative Addition of Acyl Chlorides to Diphenylmethylphosphine Complexes of Iridium(I). Formation of Five-Coordinate Acyliridium(III) and Six-Coordinate Alkyliridium(III) Complexes Containing Cis Phosphine Ligands

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Acyl chlorides RCOCl react either with IrCl(PMePh$_2$)$_3$ or with a solution containing the cyclooctene complex [IrCl(C$_8$H$_{14}$)$_2$]$_2$ and diphenylmethylphosphine in a 1:4 mole ratio to give six-coordinate alkyliridium(III) complexes containing mutually cis PMePh$_2$ groups, *cis*-IrCl$_2$R(CO)(PMePh$_2$)$_2$ (R = CH$_3$ (**1a**), C$_2$H$_5$ (**1b**), *n*-C$_3$H$_7$ (**1c**)). In solution **1b** and **1c** equilibrate rapidly (<1 min) with five-coordinate acyliridium(III) complexes IrCl$_2$(COR)(PMePh$_2$)$_2$ (R = C$_2$H$_5$ (**2b**), *n*-C$_3$H$_7$ (**2c**)) which also have cis PMePh$_2$ ligands and are probably square pyramidal with apical acyl groups. The equilibrium constants for the acyl–alkyl equilibrium in chloroform at 32 °C are 3.3 (**2b** ⇌ **1b**) and 4.2 (**2c** ⇌ **1c**). At ambient temperature in chloroform/methanol **1a–c** isomerize by a first-order process to complexes containing mutually trans PMePh$_2$ ligands, *trans*-IrCl$_2$R(CO)(PMePh$_2$)$_2$ (**3a–c**: R = CH$_3$, C$_2$H$_5$, *n*-C$_3$H$_7$), the rates being in the order R = C$_2$H$_5$ ≈ *n*-C$_3$H$_7$ > CH$_3$. Isomerization is suggested to proceed by rapid rearrangement of intermediate five-coordinate alkyliridium(III) cations [IrClR(CO)(PMePh$_2$)$_2$]$^+$ formed by rate-determining loss of Cl$^-$ from **1a–c**. Complexes **1b** and **1c** also isomerize to **3b** and **3c** on heating in benzene, but **1a** is stable under these conditions. In contrast with **1b** and **1c**, solutions of **1a** and of **3a–c** do not contain spectroscopically detectable amounts of iridium(III) acyls. The *n*-propyl complex **3c** is the final product isolated from reaction of 2-methylpropanoyl chloride (CH$_3$)$_2$CHCOCl with [IrCl(C$_8$H$_{14}$)$_2$]$_2$ + 4PMePh$_2$ and presumably is formed by isomerization of an undetected intermediate isopropyliridium(III) complex. ^{1}H and ^{31}P NMR data are reported, and the fact that the alkyl group proton resonances of **3a–c** are consistently to higher field than those of **1a–c** is attributed to diamagnetic shielding by phenyl rings of the mutually trans PMePh$_2$ ligands. Oxidative addition of acyl chlorides to IrCl(PMePh$_2$)$_3$ is compared with literature reports of similar additions to RhCl(PPh$_3$)$_3$, IrCl(N$_2$)(PPh$_3$)$_2$, and IrCl(PPh$_3$)$_3$.

Introduction

The oxidative addition of acyl chlorides RCOCl to RhCl(PPh$_3$)$_3$ has been widely studied in view of its potential application to the decarbonylation of acyl halides catalyzed by rhodium(I) and iridium(I) complexes.[1-10] The first product is a five-coordinate acylrhodium(III) complex, RhCl$_2$(COR)(PPh$_3$)$_2$, which undergoes alkyl group migration to give a six-coordinate rhodium(III) complex, RhCl$_2$R(CO)(PPh$_3$)$_2$. Finally, reductive elimination of alkyl or aryl halide, or of alkene and HCl, gives the rhodium(I) carbonyl complex RhCl(CO)(PPh$_3$)$_2$. A recent ^{1}H and ^{31}P NMR study of the reaction of acetyl chloride with RhCl(PPh$_3$)$_3$ has shown[10] that

Scheme I

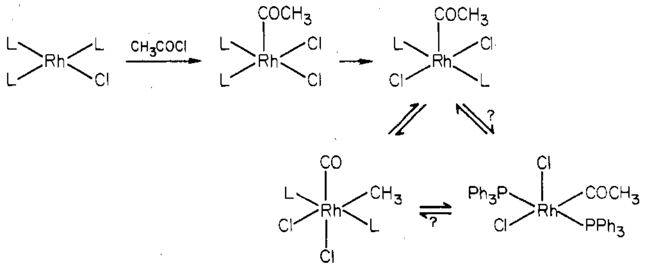

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Table I. Analytical and IR Data for Alkyliridium(III) Complexes[a]

	% C		% H		% Cl		ν(CO)		
complex	calcd	found	calcd	found	calcd	found	Nujol	CH_2Cl_2	ν(IrCl), cm^{-1}
cis-$IrCl_2(CH_3)(CO)(PMePh_2)_2$[b] (1a)	47.6	47.9	4.1	4.1	10.0	9.8	2020	2040	310, 280
cis-$IrCl_2(C_2H_5)(CO)(PMePh_2)_2$[c] (1b)	48.3	48.4	4.3	4.2	9.8	9.6	2020	2030, 1670 (C=O)	310, 280
cis-$IrCl_2(n\text{-}C_3H_7)(CO)(PMePh_2)_2$[d] (1c)	49.05	49.1	4.5	4.6	9.65	9.6	2015	2030, 1675 (C=O)	305, 275
trans-$IrCl_2(CH_3)(CO)(PMePh_2)_2$ (3a)	47.6	47.8	4.1	4.5	10.0	9.8	2020[e]	nm	300, 250[f]
trans-$IrCl_2(C_2H_5)(CO)(PMePh_2)_2$ (3b)	48.3	48.0	4.3	4.3			2020	nm	307, 251
trans-$IrCl_2(n\text{-}C_3H_7)(CO)(PMePh_2)_2$ (3c)	49.05	49.0	4.5	4.5			2020	nm	300, 250

[a] nm = not measured. [b] Mol wt: calcd 707; found (CH_2Cl_2) 719. [c] Mol wt: calcd 721; found (CH_2Cl_2) 692. [d] Mol wt: calcd 735; found (CH_2Cl_2) 736. [e] Literature value[16] 2020 cm^{-1} (KBr). [f] Literature values[16] 305, 257 cm^{-1} (C_6H_6).

Table II. ^1H and $^{31}P\{^1H\}$ NMR Data for Alkyliridium(III) Complexes *cis*- and *trans*-$IrCl_2R(CO)(PMePh_2)_2$ (1a–c and 3a–c) and Acyliridium(III) Complexes **2b** and **2c**[a,b]

	δ(P–CH_3)	δ(IrR) and δ(IrCOR)	δ_P
1a	1.72 (d, $^2J_{PH}$ = 12 Hz), 2.15 (d, $^2J_{PH}$ = 10 Hz)	1.09 (dd, $IrCH_3$, $^3J_{PH}$ = 4, 7 Hz)	−24.9 (d), −14.5 (d, $^2J_{PP}$ = 9 Hz)
1b[c]	1.82 (d, $^2J_{PH}$ = 11 Hz), 2.11 (d, $^2J_{PH}$ = 10 Hz)	0.92 (dt, $IrCH_2CH_3$, $^3J_{HH}$ = 7.5 Hz, J_{PH} = 10 Hz), 2.22 (m, $IrCH_2CH_3$)	−24.3 (d), −14.5 (d, $^2J_{PP}$ = 6 Hz)
1c	1.82 (d, $^2J_{PH}$ = 11 Hz), 2.12 (d, $^2J_{PH}$ = 9 Hz)	0.53 (m, $IrCH_2CH_2CH_3$, ~1.6 (m, $IrCH_2CH_2CH_3$), ~2.3 (m, $IrCH_2CH_2CH_3$)	−29.4 (d), −15.05 (d, $^2J_{PP}$ = 6 Hz)
2b[d]	1.52 (d, $^2J_{PH}$ = 11 Hz)	1.08 (t, $COCH_2CH_3$), 3.51 (q, $COCH_2CH_3$, $^3J_{HH}$ = 7 Hz)	−11.0 (s)
2c	1.55 (d, $^2J_{PH}$ = 10 Hz)	0.94 (t, $COCH_2CH_2CH_3$, $^3J_{HH}$ = 7 Hz), ~1.6 (m, $COCH_2CH_2CH_3$), 3.50 (t, $COCH_2CH_2CH_3$, $^3J_{HH}$ = 7 Hz)	−11.6 (s)
3a[e]	2.39 (t, "J_{PH}" = 10 Hz)	0.36 (t, $IrCH_3$, $^3J_{PH}$ = 5 Hz)	−13.5 (s)
3b	2.39 (t, "J_{PH}" = 10 Hz)	0.73 (t, $IrCH_2CH_3$, $^3J_{HH}$ = 7 Hz), 1.27 (m, $IrCH_2CH_3$)	−13.7 (s)
3c	2.34 (t, "J_{PH}" = 8 Hz)	0.10 (m, $IrCH_2CH_2CH_3$), 0.92 (m, $IrCH_2CH_2CH_3$)	−12.2 (s)

[a] ^1H spectra measured in $CDCl_3$ at 34 °C with internal $(CH_3)_4Si$; ^{31}P spectra measured in $CHCl_3$ at 32 °C. Chemical shifts (δ_P) are in ppm relative to external 85% H_3PO_4, positive to high frequency. [b] "J_{PH}" = $^2J_{PH}$ + $^4J_{PH}$ (separation between outer lines of 1:2:1 triplet). [c] In CD_2Cl_2, δ 1.89, 2.11 (PCH_3), 0.86 ($IrCH_2CH_3$), 2.18 ($IrCH_2CH_3$). [d] In CD_2Cl_2, δ 1.47 (PCH_3), 1.02 ($COCH_2CH_3$), 3.37 ($COCH_2CH_3$). [e] ^1H NMR[16] δ 2.49 (PCH_3), 0.36 ($IrCH_3$). Referance 16 gives the separation between the central and outer lines of the PCH_3 triplet as 10 Hz; we believe this should be 5 Hz.

two isomeric square-pyramidal acetylrhodium(III) species are formed sequentially, both having an apical acetyl group (Scheme I). Isomerization to the six-coordinate methylrhodium(III) complex may involve a third acetyl isomer in which chlorine occupies the apical site.

Oxidative addition of acyl chlorides to the iridium(I) complexes $IrCl(N_2)(PPh_3)_2$ or $IrCl(PPh_3)_3$ gives stable octahedral alkyliridium(III) complexes $IrCl_2R(CO)(PPh_3)_2$ which do not readily eliminate RCl.[9,11-14] The intermediate five-coordinate acyliridium(III) complexes isomerize fairly rapidly to the six-coordinate alkyls, and only when R is a benzyl or fluoromethyl group can they be isolated as crystalline solids.[12,13] The alkyliridium(III) complex $IrCl_2R(CO)(PPh_3)_2$ obtained by addition of an α-branched acyl halide to $IrCl(PPh_3)_3$ contains a rearranged *n*-alkyl group; e.g., $(CH_3)_2CHCOCl$ gives $IrCl_2(CH_2CH_2CH_3)(CO)(PPh_3)_2$.[14] Presumably the initially formed *sec*-alkyl undergoes β elimination to form an olefin hydride, and readdition takes place preferentially at the substituted carbon atom to give the *n*-alkyl. We[14] suggested that steric hindrance by the phenyl rings of the mutually trans triphenylphosphine ligands might favor the formation of the less bulky *n*-alkyl isomer.

It was of interest to see whether similar isomerizations would occur in complexes containing smaller and more basic phosphines than triphenylphosphine and whether intermediates could be identified. Since methyl resonances in the ^1H NMR spectra of methylphosphine complexes of the later transition elements often provide stereochemical information,[15,16] we chose to study the reaction of $IrCl(PMePh_2)_3$ with acyl halides.

Experimental Section

IR spectra were measured on Nujol mulls or dichloromethane solutions with use of CsI windows on PE 457 or 225 instruments calibrated against polystyrene. ^1H NMR spectra were measured at 100 MHz on a Varian HA-100 spectrometer. ^1H NMR kinetic measurements were performed at 34 °C on a 60-MHz JEOL PMX-60 instrument. $^{31}P\{^1H\}$ FT NMR spectra were measured at 24.28 MHz on a Bruker 322S instrument.

Microanalyses were carried out in the Microanalytical Unit of this university by Dr. Joyce Fildes, Miss Brenda Stevenson, and their associates. Molecular weights were measured at 25 °C on ca. 0.02 M solutions in dichloromethane by using a Knauer vapor pressure osmometer. Analytical and spectroscopic data are in Tables I and II.

Starting Materials. Benzene was dried by refluxing over calcium hydride. It was then distilled and stored over sodium wire. Other solvents were dried by standard procedures and stored over sodium wire or molecular sieves as appropriate. Acid chlorides were obtained commercially and were freed from HCl by distillation and pumping at −78 °C before use. Owing to its air sensitivity the complex $IrCl(PMePh_2)_3$ was prepared in situ by treatment of $[IrCl(C_8H_{14})_2]_2$[17] with diphenylmethylphosphine (6 mol/mol of dimer) in benzene. It could be isolated as an orange-red solid by evaporation to dryness, washing with *n*-hexane, and drying in vacuo. All reactions were carried out under dry nitrogen although the isolated acyl- and alkyliridium(III) complexes are air stable as solids and in solution.

Preparations. (1) *ab*-Bis(diphenylmethylphosphino)-*c*-carbonyl-*de*-dichloro-*f*-alkyliridium(III) Complexes, *cis*-$IrCl_2R(CO)(PMePh_2)_2$ (1a–c), from Straight-Chain Acyl Chlorides RCOCl (R = CH_3, C_2H_5, *n*-C_3H_7). (i) Diphenylmethylphosphine (0.447 g, 2.23 mmol) was added dropwise by syringe to a solution of $[IrCl(C_8H_{14})_2]_2$ (0.5 g, 0.56 mmol) in benzene (ca. 10–12 mL). The resulting deep orange solution was stirred for 10 min and treated with the appropriate acyl chloride (ca. 0.15 mL) from a syringe. The deep orange-red solution was heated under reflux for ca. 1–5 min and was cooled to room

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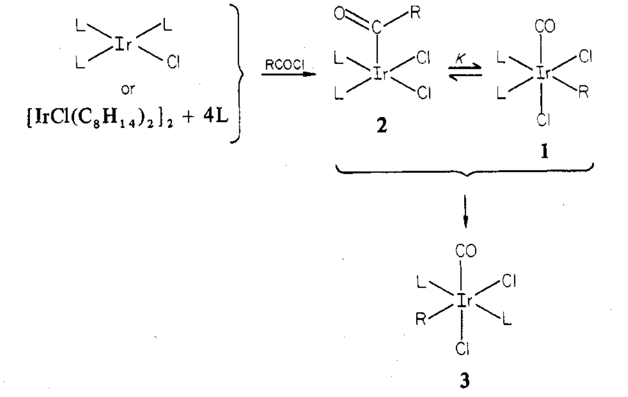
Scheme II



L = PMePh$_2$; R = CH$_3$ (a), C$_2$H$_5$ (b), *n*-C$_3$H$_7$ (c)

temperature as soon as the color became pale yellow. The solution, which occasionally began to deposit crystals at this stage, was concentrated in vacuo to ca. 5 mL and the container wall scratched to induce crystallization. The process was completed by addition of *n*-hexane (30 mL). The resulting pale yellow to colorless microcrystals were filtered, washed with *n*-hexane in three 5-mL portions, and dried in vacuo. Typical yields were as follows: R = CH$_3$ (**1a**), 0.7 g (89%); R = C$_2$H$_5$ (**1b**), 0.68 g (84%); R = *n*-C$_3$H$_7$ (**1c**), 0.7 g (85%). Complexes **1b** and **1c** were always contaminated with small amounts of the trans isomers **3b** and **3c**.

(ii) A solution of IrCl(PMePh$_2$)$_3$ (0.3 g, 0.36 mmol) in benzene (5 mL) was treated with acetyl chloride (0.5 mL). The dark red solution rapidly became colorless and was stirred for 10 min at room temperature. The colorless solid which precipitated on addition of *n*-pentane (30 mL) was collected and recrystallized from dichloromethane/*n*-pentane to give 0.19 g (73%) of *cis*-IrCl$_2$(CH$_3$)(CO)(PMePh$_2$)$_2$ (**1a**).

(2) *af*-Bis(diphenylmethylphosphino)-*b*-carbonyl-*cd*-dichloro-*e*-alkyliridium(III) Complexes, *trans*-IrCl$_2$R(CO)(PMePh$_2$)$_2$ (3a–c), from Straight-Chain Acyl Halides RCOCl (R = CH$_3$, C$_2$H$_5$, *n*-C$_3$H$_7$). (i) Complexes **3b** and **3c** were prepared following the procedure given under section 1(i) except that the reaction mixtures were heated under reflux for ca. 3 h. The resulting white crystalline products were recrystallized from dichloromethane/*n*-hexane to give **3b** and **3c** in ca. 70–80% yield.

(ii) Complex **3c** was also prepared in 70% yield from IrCl(PMePh$_2$)$_3$ and propanoyl chloride as under section 1(ii), the mixture being maintained at 60 °C for 4 h.

(iii) Complexes **1b** and **1c** (0.1 g) were dissolved in a mixture of dichloromethane (2 mL) and methanol (1 mL). Over a 12-h period some of the trans isomers **3b** and **3c** crystallized, and the process was completed by addition of *n*-hexane. Yields of **3b** and **3c** were almost quantitative.

(iv) Complex **1a** (0.1 g) was dissolved in dichloromethane/methanol as above, and LiClO$_4$ (ca. 10 mg) was added. After 12 h *trans*-IrCl$_2$(CH$_3$)(CO)(PMePh$_2$)$_3$ (**3a**) was isolated quantitatively.

(3) Preparation of *trans*-IrCl$_2$(*n*-C$_3$H$_7$)(CO)(PMePh$_2$)$_2$ (3c) from 2-Methylpropanoyl Chloride. The reaction was carried out as in section 1(i) except that the mixture was stirred at 60 °C overnight. The yield of **3c** was 75%.

Kinetics. The ^{1}H NMR spectra of solutions of complexes **1a–c** (0.23 M) in a mixture of CDCl$_3$ (0.4 mL) and CD$_3$OD (0.2 mL) were studied as a function of time at 34 °C. Integration established that the growth in the PCH$_3$ triplet of **3a–c** corresponded with the decrease in the PCH$_3$ doublets of **1a** or of **1b–c**/**2b–c**. Good first-order rate plots of log ($A - A_\infty$) vs. t were obtained, the values of $t_{1/2}$ estimated by a full-matrix least-squares fit of the data being 7.7 (1) and 10.4 (4) min, respectively, for **1b** and **1c**, and ca. 1 month for **1a**. (The estimated standard deviations in parentheses refer to the last significant figure, and, since they do not take full account of errors in NMR integration, the quoted $t_{1/2}$ values are probably only accurate to within 10%.) The $t_{1/2}$ value for the isomerization of a 0.23 M solution of **1c** in a mixture of CDCl$_3$ (0.58 mL) and CD$_3$OD (0.2 mL) was 23.1 (4) min, while in the absence of methanol, $t_{1/2}$ for the isomerization of 0.23 M solutions of complexes in CDCl$_3$ (0.5 mL) was respectively >1 month (**1a**) and ca. 1 week (**1b**, **1c**). The half-life for isomerization of a 0.23 M solution of **1c** in CDCl$_3$ (0.4 mL) and CD$_3$OD (0.2 mL) containing LiClO$_4$ (50 mg) was only 1.5 (1) min; replacement of LiClO$_4$ by LiCl (20 mg) increased the value to 24.6 (1) min.

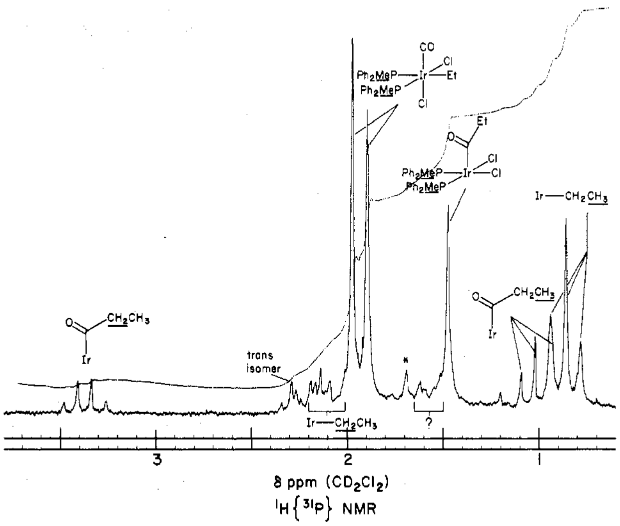


Figure 1. ^{1}H{^{31}P} NMR spectrum at 32 °C of an equilibrium mixture of *cis*-IrCl$_2$(C$_2$H$_5$)(CO)(PMePh$_2$)$_2$ (**1b**) and *cis*-IrCl$_2$(COC$_2$H$_5$)(PMePh$_2$)$_2$ (**2b**).

Preparative and Spectroscopic Results

The main features of the chemistry are summarized in Scheme II. Under mild conditions acyl chlorides RCOCl (R = CH$_3$, C$_2$H$_5$, *n*-C$_3$H$_7$) react with IrCl(PMePh$_2$)$_3$, or with a solution containing [IrCl(C$_8$H$_{14}$)$_2$]$_2$ (1 mol) and diphenylmethylphosphine (4 mol), to give colorless or pale yellow, six-coordinate iridium(III) alkyls IrCl$_2$R(CO)(PMePh$_2$)$_2$ (**1a–c**) in which the phosphine ligands are mutually cis. Their ^{1}H NMR spectra (Table II) exhibit a pair of doublet P–CH$_3$ resonances and the methyl compound **1a** shows a doublet of doublets (J = 4, 7 Hz) for the Ir–CH$_3$ resonances owing to coupling with the ^{31}P nuclei of phosphines cis and trans, respectively, to the methyl group. The solid-state IR spectra have strong bands at ca. 310 and ca. 280 cm^{-1} assignable to ν(IrCl) trans to CO and PMePh$_2$, respectively,[18] and a strong ν(CO) band at ca. 2020 cm^{-1}. In dichloromethane, the IR spectra of the ethyl and *n*-propyl complexes, **1b** and **1c**, show an additional intense band at ca. 1670 cm^{-1} which is assigned to ν(C=O) of isomeric five-coordinate acyliridium(III) complexes IrCl$_2$(COR)(PMePh$_2$)$_2$ (R = C$_2$H$_5$ (**2b**), *n*-C$_3$H$_7$ (**2c**)); the methyl complex **1a** shows no acyl band, either in solution or in the solid state. The ^{31}P{^{1}H} NMR spectra of **1b** and **1c** show a singlet resonance due to the equivalent phosphines of the acyls **2b** and **2c** in addition to a pair of doublets arising from the weakly coupled ^{31}P nuclei of the inequivalent phosphine ligands of **1b** and **1c** ($^2J_{PP}$ = 6–10 Hz). The ^{1}H NMR spectra of **1b** and **1c** contain many overlapping resonances, but with the aid of homonuclear and ^{31}P decoupling most of these can be satisfactorily assigned to an equilibrium mixture of alkyl and acyl. Figure 1 the ^{1}H{^{31}P} NMR spectra and assignments for the equilibrium mixture of ethyl and propionyl complexes **1b** **2b** at room temperature. As expected, there are two singlets at δ 1.82 and 2.11 due to the inequivalent P–CH$_3$ groups of **1b** and a singlet at δ 1.47 arising from the equivalent P–CH$_3$ groups of **2b**; in the undecoupled spectrum the signal at δ 1.47 is a doublet, showing that the phosphine ligands in the acyl **2b** are mutually cis. The quartet due to the CH$_2$ group of the propionyl coomplex **2b** appears at δ 3.7 in CD$_2$Cl$_2$ and is well downfield of the remaining overlapping resonances, the positions and appearance of which are unex-

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Table III. Chemical Shift Differences $\delta_{cis} - \delta_{trans}$ between Corresponding Protons in the Alkyl Chains Ir–C(1)–C(2)–C(3) of **1a–c** and **3a–c**

R	C(1)	C(2)	C(3)
CH_3	0.73		
CH_2CH_3	0.95	0.19	
$CH_2CH_2CH_3$	~1.3	~0.7	0.4

ceptional. The ^1H NMR spectrum of the methyl complex **1a** shows no resonance assignable to CH_3CO of $IrCl_2(COCH_3)(PMePh_2)_2$ (**2a**), in agreement with IR and ^{31}P NMR evidence that this species is not present in detectable amounts at equilibrium. Since the molecular weights of the equilibrium mixtures **1b**/**2b** and **1c**/**2c** agree well with those calculated for monomers, we can rule out dimeric, chloro-bridged structures for the acyliridium(III) complexes. They are probably square pyramidal with the acyl group in the apical position, as found in the X-ray studies of the rhodium(III) complexes $RhCl_2(COCH_2CH_2Ph)(PPh_3)_2$,[10] $[Ph_4As][RhI(COC_2H_5)(mnt)(PPh_3)]$ (mnt = maleonitriledithiolate),[19] $RhCl_2(COC_6H_5)(Ph_2PCH_2CH_2CH_2PPh_2)$,[20] and $[RhCl(COCH_3)(PMe_2Ph)_3]PF_6$,[21] but in contrast with the first listed complex our iridium(III) acyls have mutually cis phosphine ligands. The equilibrium constants K for **2b** ⇌ **1b** at 32 °C are 3.2 (CD_2Cl_2, determined by ^1H NMR spectroscopy) and 3.3 ($CHCl_3$, determined by $^{31}P\{^1H\}$ NMR spectroscopy); the corresponding values for **2c** ⇌ **1c** are 4.5 (CD_2Cl_2) and 4.2 ($CHCl_3$). In both cases equilibrium is established within the time taken to mix and monitor the solutions (ca. 1 min). A preliminary study of **2b** ⇌ **1b** in $CDCl_3$ over the temperature range +32 to −40 °C shows that K is relatively insensitive to temperature, with $\Delta H = 0.3 \pm 0.6$ kcal/mol and $\Delta S = 3.2 \pm 0.7$ cal/(mol deg). The signals remain sharp in this temperature range, showing that equilibrium is slow on the NMR time scale.

Solutions of **1b** and **1c** isomerize at room temperature, or more rapidly on heating, to give colorless complexes **3b** and **3c** in which the phosphine ligands are mutually trans. In contrast, the methyl complex **1a** shows little evidence for isomerization even after 1 h in refluxing benzene or dichloromethane, but the process goes to completion over 12 h at room temperature in dichloromethane/methanol containing lithium perchlorate to give quantitatively *trans*-$IrCl_2(CH_3)(CO)(PMePh_2)_2$ (**3a**) identical with the product of oxidative addition of methyl chloride to $IrCl(CO)(PMePh_2)_2$.[16] The far-IR spectra of **3a–c** show bands at ca. 305–310 and ca. 250 cm^{-1} arising from ν(IrCl) trans to CO and the alkyl group, respectively,[18] and the ^1H NMR spectra show the expected 1:2:1 triplet resonance for the P–CH_3 groups. In the methyl complex **3a** the Ir–CH_3 resonance is a triplet owing to coupling with the equivalent ^{31}P nuclei ($^3J_{PH} = 7$ Hz). ^1H and ^{31}P NMR spectra give no evidence for the presence of acyliridium(III) complexes in equilibrium with **3a–c**.

In the alkyl chain Ir–C(1)–C(2)–C(3)–C(4) of the complexes *trans*-$IrCl_2R(CO)(PPh_3)_2$, the chemical shifts of the protons on C(3) and C(4) are ca. 0.4 ppm to higher field than expected, an effect which we attributed to shielding by aromatic rings of the trans triphenylphosphine ligands.[14] The chemical shifts of the alkyl protons of **3a–c** are similar to those of the analogous triphenylphosphine complexes, and all are to higher field than those of the corresponding protons of the cis isomers **1a–c**, especially in the case of the protons on C(1) (Table III). Since molecular models indicate that in **1a–c** the alkyl protons are not constrained to lie within the shielding zones of the cis phosphine ligands, we suggest that all the alkyl chain protons in the trans isomers **3a–c** (and their triphenylphosphine analogues) are subject to the aromatic shielding effect. A similar conclusion can be reached by comparing the ^1H NMR spectra of *trans*-$IrCl_2R(CO)L_2$ (L = PPh_3, $PMePh_2$) with those of $[IrCl_2R(CO)_2]_2$.[14,17]

Reaction of either *n*-butanoyl chloride, *n*-C_3H_7COCl, or 2-methylpropanoyl chloride, $(CH_3)_2CHCOCl$, with $IrCl(PMePh_2)_3$ in hot benzene gives the same *n*-propyl complex **3c**. In the case of $(CH_3)_2CHCOCl$ intermediate isopropyl- and (2-methylpropanoyl)iridium(III) complexes similar to **1a–c** and **2a–c** may be formed, but attempts to isolate or detect them gave inconclusive results.

Discussion

The first step in the reaction of acyl chlorides RCOCl with $IrCl(PMePh_2)_3$, or with $[IrCl(C_8H_{14})_2]_2 + 4PMePh_2$, is undoubtedly formation of the five-coordinate acyliridium(III) complexes **2** containing cis phosphines (Scheme II); in this respect there is a marked similarity to the corresponding reaction with $RhCl(PPh_3)_3$ (Scheme I).[10] Whereas the iridium(III) acyls rapidly equilibrate with octahedral iridium(III) alkyls **2** containing cis phosphines, the rhodium(III) acyls undergo cis–trans isomerization. These differences probably reflect the greater steric bulk of PPh_3 relative to $PMePh_2$ and the greater tendency of rhodium(III) relative to iridium(III) to form five-coordinate in preference to six-coordinate complexes. Five-coordinate iridium(III) acyls, $IrCl_2(COR)(PPh_3)_2$, have been isolated from the reaction of variously substituted phenylacetyl chlorides and fluorine-substituted acetyl chlorides with $IrCl(N_2)(PPh_3)_2$.[12,13] Far-IR spectra indicate that these complexes contain mutually trans chlorines, at least in the solid state. Thus, if the acyl groups occupy the apical site of a square-pyramidal structure, the PPh_3 ligands must also be mutually trans. These trans acyls isomerize relatively slowly but completely to the corresponding alkyls *trans*-$IrCl_2R(CO)(PPh_3)_2$, whereas the *cis*-$IrCl_2(COR)(PMePh_2)_2$ complexes **2** isomerize rapidly (<1 min) to give an equilibrium mixture of acyl **2** and alkyl **1**, with the latter predominating (70–80% at equilibrium in the case of R = C_2H_5, *n*-C_3H_7; ca. 100% in the case of R = CH_3). In view of the different alkyl groups employed in the two series, one cannot speculate on the reasons for these differences, and more detailed studies with a wider range of acyl chlorides should be informative, especially in respect of recent theoretical predictions concerning the effects of ligand substitution on the rate of methyl migration from metal to CO in octahedral manganese(I) carbonyl complexes.[22] The trend in the position of equilibrium between **1** and **2** as R varies is in accord with theoretical predictions for $RMn(CO)_5$[22] and with that reported[10] for the equilibrium *trans*-$RhCl_2(COR)(PPh_3)_2$ ⇌ *trans*-$RhCl_2R(CO)(PPh_3)_2$. The greater ease of migration with increasing chain length of R in $RMn(CO)_5$ has been traced[22] to decreasing M–R bond strengths and decreasing electronegativity of R. In the present case, steric effects may also be significant, since the octahedral ethyl and *n*-propyl complexes **1b** and **1c** are more crowded than either their methyl analogue **1a** or the corresponding acyls **2b** and **2c**. The fact that we find no evidence for spectroscopically detectable amounts of *trans*-$IrCl_2(COR)(PMePh_2)_2$ in equilibrium with *trans*-$IrCl_2R(CO)(PMePh_2)_2$ also suggests that steric effects are important and is apparently inconsistent with the prediction[22] that phosphine substitution in the migration plane should slow down methyl migration. Further comment is

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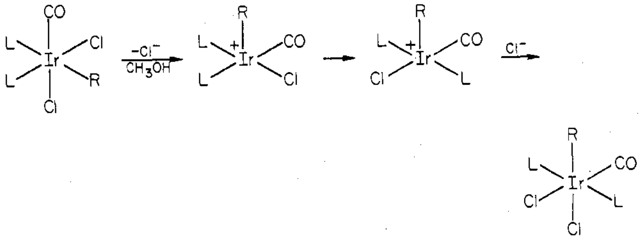
Scheme III



unjustified until the appropriate rate data are available.

The cis → trans isomerizations **1** → **3** are slow relative to the rate of equilibration of **1** and **2** and show clean first-order kinetics. The rates for the ethyl and *n*-propyl complexes **1b** and **1c** are comparable and larger than that of the methyl complex **1a**. In all three cases, isomerization is accelerated by addition of methanol. Thus, for **1b** and **1c**, the half-lives for isomerization are reduced from about 1 week in $CDCl_3$ to 7.7 and 10.4 min, respectively, in 2:1 $CDCl_3/CD_3OD$. For **1c**, the rate of isomerization is increased markedly in the presence of $LiClO_4$ and decreased in the presence of LiCl (see the Experimental Section). These preliminary data are consistent with a mechanism involving rate-determining loss of Cl^- from *cis*-$IrCl_2R(CO)(PMePh_2)_2$ (**1a–c**), rapid rearrangement of the resulting transient five-coordinate alkyliridium(III) cation, and subsequent reentry of Cl^- to give *trans*-$IrCl_2R(CO)(PMePh_2)_2$ (**3a–c**, Scheme III). There is some precedent for cationic species of the type proposed here. Oxidative addition of methyl iodide to $IrCl(CO)(PMe_2Ph)_2$ in benzene is believed to occur via a tight ion pair, $[IrCl(CH_3)(CO)(PMe_2Ph)_2]^+I^-$, but in methanol separation of these ions leads to rapid substitution of chloride by iodide in the iridium(I) complex and thus to a mixture of oxidative addition products.[18] Cationic five-coordinate alkylmetal species are almost certainly formed when rhodium(III) or iridium(III) fluorosulfates or triflates, e.g., $IrClX(CH_3)(CO)(PPh_3)_2$ (X = SO_3F, SO_3CF_3), are dissolved in polar solvents or when they undergo substitution of X by other ligands,[23–25] and in some cases they can be isolated, e.g., $[RhClR(ttp)]PF_6$ [R = CH_3, C_2H_5; ttp = $PhP(CH_2CH_2CH_2PPh_2)_2$].[26]

Finally, the fact that despite the smaller size and greater basicity of $PMePh_2$ relative to PPh_3 addition of $(CH_3)_2CHCOCl$ to $IrCl(PMePh_2)_3$ still gives exclusively the *n*-alkyl shows the latter to be the thermodynamically favored isomer in these systems, regardless of the nature of the substituents on phosphorus. This assertion is supported by the observation[27] that, although closely related *sec*-alkyl complexes containing dimethylphenylphosphine or trimethylphosphine, *trans*-$IrClIR(CO)L_2$ (L = PMe_2Ph, PMe_3; R = various alkyl groups), can be isolated, they undergo complete isomerization to the corresponding *n*-alkyl in methanol- or water-containing solvents.

Registry No. **1a**, 74561-76-5; **1b**, 74524-99-5; **1c**, 74525-00-1; **2b**, 74525-01-2; **2c**, 74525-02-3; **3a**, 19469-17-1; **3b**, 74561-16-3; **3c**, 74561-17-4; $[IrCl(C_8H_{14})_2]_2$, 12246-51-4; $IrCl(PMePh_2)_3$, 63945-96-0; CH_3COCl, 75-36-5; C_2H_5COCl, 79-03-8; *n*-C_3H_7COCl, 141-75-3; 2-methylpropanoyl chloride, 79-30-1.

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Optical Spectra of Hafnium, Tungsten, Rhenium, and Ruthenium Atoms and Other Heavy Transition-Metal Atoms and Small Clusters ($Zr_{1,2}$, $Pd_{1,2}$, $Au_{1,2,3}$) in Noble Gas Matrices

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Codeposition of transition-metal atoms with weakly interacting, low-temperature matrices has led to the isolation and UV–visible spectroscopic identification of a fairly wide range of atomic, diatomic, and sometimes higher cluster species. In this study, the optical spectra (200–700 nm) have been obtained for Hf, W, Re, and Ru atoms isolated in argon matrices at 10–12 K. The observed lines can be satisfactorily correlated with the reported gas-phase atomic transitions of the respective elements. Blue matrix shifts of roughly 800–2800 cm^{-1} are generally in agreement with the predictions of AMCOR methods. The investigation of these four refractory metals essentially completes a study in which combined resistive-evaporation and matrix-isolation techniques have been utilized to investigate or reexamine the atomic spectra of about 80% of the transition elements. The optical spectra of Zr, Pd, and Au atoms cocondensed with noble gas matrices are reinvestigated under a variety of concentration, deposition, and annealing conditions. By use of relaxed isolation methods, new absorptions are observed which can be associated with Zr_2, Pd_2, Au_2, and Au_3. Extended Hückel molecular orbital techniques provide an insight into the electronic and optical properties of some of these heavy-metal molecules. In the case of gold, electronic assignments are discussed in the light of gas-phase optical studies and relativistic molecular quantum mechanical calculations for Au_2 and by comparison with the gas- and matrix-phase data for Ag_2 and Ag_3.

Introduction

Recently there has been an intensification of interest in the organometallic chemistry of the "electron-rich" refractory elements to the left of the periodic table.[1] Concurrent developments in the metal-vapor chemistry of these heavier elements have also been realized, initially to establish reliable methods for generating and handling the vapors and subsequently to elucidate their potential for the synthesis of novel

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