

polyamide column in hexane, and a yellow band was eluted from the column with hexane. An additional 100 ml of eluent was collected. Rotary evaporation of the eluent to 50 ml gave white crystalline needles of 1-[Mn(CO)₅]-2-CH₂-1,2-(σ-B₁₀C₂H₁₀), mp 85–87°. A total of 1.30 g (3.68 mmol, 57%) was collected. Rotary evaporation to dryness gave 0.30 g of a mixture of the product and Mn₂(CO)₁₀. This was discarded. The white crystals were sublimed and recrystallized from hexane. Analytical data and the infrared,

¹H nmr, ¹¹B nmr, and electronic spectra are presented in Tables I–V.

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Acyl, Alkyl, and Aryl Complexes of Iridium from Acid Chlorides

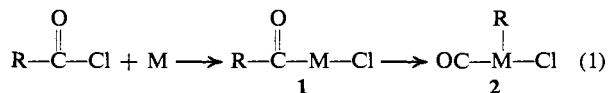
Mitsuru Kubota* and Daniel M. Blake

Contribution from the Department of Chemistry, Harvey Mudd College, Claremont, California 91711. Received July 28, 1970

Abstract: Acyl chlorides react with *trans*-chlorobis(triphenylphosphine)dinitrogeniridium(I) to form alkyl and aryl iridium complexes, [P(C₆H₅)₃]₂Cl₂(CO)IrR, where R is CH₃, C₂H₅, C₆H₅CH₂, C₆H₅, C₆F₅, etc. These reactions proceed *via* molecular rearrangement of intermediate acyl–iridium complexes. Various aspects of the acyl–alkyl (aryl) rearrangement, including stereochemical and solvent effects, have been investigated. New acyl complexes, L₂Cl₂(CO)IrC(O)R, where L is triphenylphosphine, methyl-diphenylphosphine, tri-*p*-tolylphosphine, or triphenylarsine, are described and their proclivity to decarbonylation has been investigated. Carbonylation of [P(C₆H₅)₃]₂-Cl₂(CO)IrCH₃ is rapid in dichloromethane–methanol solution, but the reaction is negligible in benzene solution.

Information on the role of metal atoms in the facilitation of interaction of attached reactant groups is relevant to the elucidation of mechanisms of reactions which are homogeneously catalyzed by complexes of transition metals. Proposals for the mechanism of decarbonylation of acid chlorides catalyzed by rhodium complexes, for example, have been advanced following the isolation of intermediate acyl and alkyl complexes.^{1,2} The interaction of alkyl or aryl groups with carbon monoxide or the rearrangement of acyl groups at a metal site has been extensively studied in the context of CO insertion into metal–alkyl bonds or migration of alkyl to CO attached to a metal atom.³

Oxidative addition reactions of carboxylic acid chlorides with complexes of metals with d⁸ or d¹⁰ electronic configuration lead to formation of acyl–metal complexes **1** (M represents a metal atom with its appro-



prate ligands).^{1,2,4–19} σ-Alkyl or aryl carbonyl–metal

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complexes **2** may be obtained by molecular rearrangement of the acyl complex **1** presumably by migration of R to the metal atom. Five-coordinated acyl complexes, [(C₆H₅)₃P]₂Cl₂RhC(O)R, where R is cyclohexyl or CH₃-(CH₂)_x (x = 1, 4, 5, 14) are obtained in the reaction of acyl halides RC(O)Cl with chlorotris(triphenylphosphine)rhodium(I).^{1,16} Acetyl and benzoyl chloride, on the other hand, react^{15,16} with chlorotris(triphenylphosphine)rhodium(I) to give the six-coordinated methyl and phenyl carbonyl complexes, [(C₆H₅)₃P]₂-Cl₂(CO)Rh–R. Six-coordinated acetyl–rhodium complexes, [C₆H₅(CH₃)P]₂Cl₂(CO)RhC(O)CH₃ and [C₆H₅-(C₂H₅)₂P]₂Cl₂(CO)RhC(O)CH₃, have also been reported.^{14,18} Other five- and six-coordinated acyl complexes of rhodium have also been isolated by Blum and coworkers.²

The tendency for migration of R, given as C₆H₅ > CH₃ > C₂H₅, has been related to the stability of C–Rh(III) bonds and the promotional energy for the Rh(I)-to-Rh(III) process.^{12,16} From the greater tendency of iridium(I) complexes to undergo oxidation,¹⁹ and from the known stabilities of iridium–alkyl or –aryl complexes,¹⁶ it might be expected that acyl–iridium complexes may be readily converted to the corresponding alkyl or aryl complexes. This expectation has not as yet been demonstrated.

Acyl chlorides react with complexes L₂Ir(CO)X (L = PCH₃(C₆H₅)₂,⁴ P(CH₃)₂C₆H₅,⁶ P(C₂H₅)₃,⁵ or P(C₂H₅)₂C₆H₅)⁵ to give the six-coordinated acyl complexes L₂XCl(CO)IrC(O)R. The decarbonylation of an acyl–iridium complex under forcing conditions has been reported only in one instance;⁵ namely, the thermal decomposition of [P(C₆H₅)(C₂H₅)₂]₂Br₂(CO)IrC(O)CH₃ at 200–210° gave the six-coordinated methyl–iridium complex

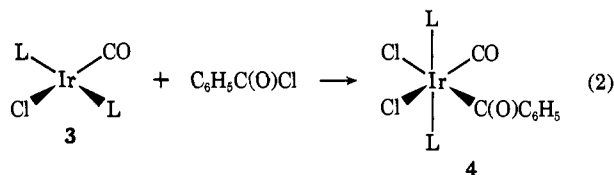
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$[\text{P}(\text{C}_6\text{H}_5)(\text{C}_2\text{H}_5)_2]_2\text{Br}_2(\text{CO})\text{IrCH}_3$. The cyclopropyl acyl complex $[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{Cl}_2(\text{CO})\text{Ir}(\text{OCC}_6\text{H}_5)$ could not be decarbonylated to give the desired cyclopropyl-iridium complex.⁷ Alkyl migrations upon the addition of triorganophosphines to dicarbonyl-iridium(III) complexes have been reported by Shaw and Singleton.²⁰

Investigations of a variety of new acyl complexes have been conducted in order to elucidate factors which may be of significance in the conversion of acyl-iridium complexes **1** to alkyl- or aryl-iridium complexes **2**. Facile (ambient temperature) alkyl and aryl group migrations to the metal atom which have been observed in this study provide new insights on the acyl to alkyl or aryl carbonyl molecular rearrangement.

Results and Discussion

Acylation of Iridium(I)-Carbonyl Complexes. Oxidative-addition reactions of *trans*-chlorobis(triphenylphosphine)carbonyliridium(I) (**3**) have been extensively investigated,¹⁹ but reports on its reactions with acyl halides appear to be limited to its reaction with cyclopropanecarboxylic acid chloride.⁷ When Vaska's compound, **3**, was stirred in benzoyl chloride for 4 days, there was no evidence for reaction. With the more basic¹⁹ iridium complexes **3a**, **3b**, and **3c**, the acylated products **4a**, **4b**, and **4c**, characterized by acyl bands in the 1570–1622-cm⁻¹ region were obtained. The acyl



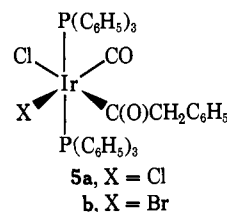
a, L = As(C₆H₅)₃; b, L = P(*p*-tolyl)₃; c, L = P(CH₃)(C₆H₅)₂

products **4** have $\nu(\text{CO})$ at 2040 cm⁻¹ compared to $\nu(\text{CO})$ at 1950 cm⁻¹ for the four-coordinated complexes **3**. This increase in CO frequency is diagnostic of the decreased back-bonding to CO due to the oxidation. That the arrangement of L in **4c** is *trans* is indicated by a nmr triplet at τ 7.54, $J(\text{PCH}_3) = 9.1$ cps, for the methyl protons of the methyl-diphenylphosphine.^{4,6} This *trans* orientation of triorganophosphine has been observed in most iridium(III) complexes which are formed in oxidative-addition reactions of bis(triorganophosphine)iridium(I) complexes.^{4,6,19} The disposition of Cl atoms on Ir is readily determined by far-infrared data. Numerous studies indicate that the Ir-Cl stretching frequencies are dependent on the ligand *trans* to the Cl atom.^{4,6} For example, compounds with Cl *trans* to Cl show absorption in the 315–335-cm⁻¹ region; Cl *trans* to CO, in the 297–315-cm⁻¹ region; Cl *trans* to triorganophosphine, in the 270–290-cm⁻¹ region; and Cl *trans* to CH₃, in the 255–270-cm⁻¹ region. We find, in concurrence with the results of Deeming and Shaw,⁶ that compounds with Cl *trans* to acyl groups show absorption in the 215–247-cm⁻¹ region. Each of the compounds **4a**, **4b**, and **4c** has two bands in the far-ir region, one in the 296–305-cm⁻¹ region due to Cl *trans* to CO, and one in the 222–246-cm⁻¹ region due to Cl *trans* to the benzoyl group. The structure proposed for **4** is thus as shown, with Cl atoms *cis* and P or As atoms *trans*. Other structures such as those with Cl *trans* to Cl or Cl *trans* to triorganophosphine or arsine can be

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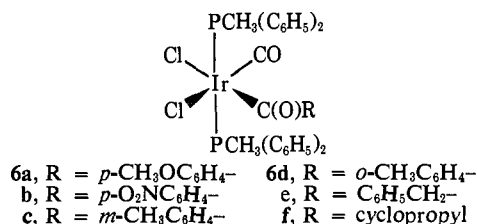
excluded because of absence of bands in the 320–330- and 270–290-cm⁻¹ regions, respectively.

While benzoyl chloride does not readily react with *trans*-[(C₆H₅)₃P]₂(CO)IrX, phenylacetyl chloride gave the acyl products **5a** and **5b**. The structure depicted for



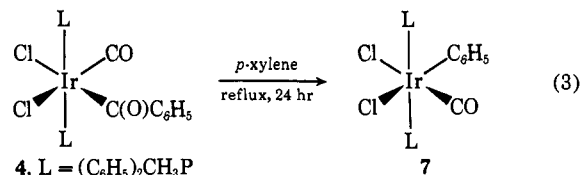
5a is based on the far-ir data: 305 cm⁻¹ (Cl *trans* to CO) and 231 cm⁻¹ (Cl *trans* to phenylacetyl). Phenylacetyl chloride and *trans*-bromobis(triphenylphosphine)-carbonyliridium(I) in benzene solution gave product **5b**, which has $\nu(\text{Ir}-\text{Cl})$ at 230 cm⁻¹, indicating that Cl is *trans* to the phenylacetyl group. The stereochemistry of the oxidative addition of the acyl chloride is thus *trans*. The report of Collman and Sears⁴ of mixtures of *cis* and *trans* products for the oxidative addition of acetyl chloride and bromide to the carbonyl **3c** and its bromo analog may be due to substitution reactions in the presence of an ionizing solvent.²¹

In order to investigate the propensity of acyl complexes to decarbonylation, reactions of the carbonyl **3c** with various acid chlorides were carried out to obtain



the acyl complexes **6a**–**6f**. Evidence for the *cis*-chloro structure is again available from the far-infrared spectra as shown in Table I ($\nu(\text{IrCl})$, 298–309 cm⁻¹, Cl *trans* to CO; 215–247 cm⁻¹, Cl *trans* to acyl). Differential scanning calorimetric thermograms indicated that no transitions occurred prior to melting, when compounds **6a**–**6f** were heated, but the melting transitions were accompanied by additional endothermic processes. Upon melting, all the acyl complexes **6a**–**6f** gave indication of gas evolution. As the melting points of the acyl complexes depend primarily on their lattice energies, the proclivity for decarbonylation in the solid state as a function of R cannot be readily ascertained.

Attempts to decarbonylate the aryl carbonyl complex **4c** by refluxing it in benzene-methanol solution or acetone containing sodium perchlorate were unsuccessful. The acyl carbonyl complex **4c** was decarbonylated in refluxing *p*-xylene as shown in eq 3. The *cis* geometry of the two Cl atoms in the decarbonylated product **7**



is indicated by the far-ir: 316 cm⁻¹ (Cl *trans* to CO), 240 cm⁻¹ (Cl *trans* to C₆H₅). By analogy with results of a recent study of the decarbonylation of an acyl car-

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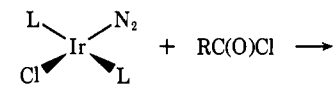
Table I. Analytical and Spectral Data for Acyl-Iridium Complexes

		Analytical data ^a			Mp, ^g °C	Ir frequencies, cm ⁻¹		
		C, %	H, %	Cl, %		$\nu(\text{CO})^b$	$\nu(>\text{C}=\text{O})^c$	$\nu(\text{Ir}-\text{Cl})^d$
4a	$[(\text{As}(\text{C}_6\text{H}_5)_2)_2\text{Cl}_2(\text{CO})\text{IrC}(\text{O})\text{C}_6\text{H}_5]$	52.4 (52.5)	3.50 (2.82)	7.03 (7.31)	174	2042	1622, 1596	305 (sh), 246
4b	$[\text{P}(\text{p}-\text{CH}_3\text{C}_6\text{H}_4)_2]_2\text{Cl}_2(\text{CO})\text{IrC}(\text{O})\text{C}_6\text{H}_5$	59.8 (59.7)	4.71 (4.64)	7.06 (7.13)	177	2073, 2043	1595, 1582, 1569	296, 238
4c	$[\text{PCH}_3(\text{C}_6\text{H}_5)_2]_2\text{Cl}_2(\text{OC})\text{IrC}(\text{O})\text{C}_6\text{H}_5$	51.3 (51.4)	3.92 (3.92)		187	2036	1654	299, 222
5a	$[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{Cl}_2(\text{CO})\text{IrC}(\text{O})\text{CH}_2\text{C}_6\text{H}_5$	57.8 (58.5)	4.09 (4.19)		177	2052	1638	305, 231
5b	$[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{ClBr}(\text{CO})\text{IrC}(\text{O})\text{CH}_2\text{C}_6\text{H}_5^e$	57.9 (57.5)	4.10 (4.06)	10.9' (11.5)	160	2071, 2046 (sh)	1633	230
6a	$[\text{PCH}_3(\text{C}_6\text{H}_5)_2]_2\text{Cl}_2(\text{CO})\text{IrC}(\text{O})\text{p}-\text{CH}_3\text{OC}_6\text{H}_4$	50.9 (51.1)	3.91 (3.67)		176	2035	1604	306 (m), 246 (m)
6b	$[\text{PCH}_3(\text{C}_6\text{H}_5)_2]_2\text{Cl}_2(\text{CO})\text{IrC}(\text{O})\text{p}-\text{O}_2\text{NC}_6\text{H}_4$	48.5 (48.8)	3.59 (3.71)		200	2049	1598	308, 247
6c	$[\text{PCH}_3(\text{C}_6\text{H}_5)_2]_2\text{Cl}_2(\text{CO})\text{IrC}(\text{O})\text{m}-\text{CH}_3\text{C}_6\text{H}_4$	51.8 (51.8)	4.10 (3.71)		187	2037	1653	298, 215
6d	$[\text{PCH}_3(\text{C}_6\text{H}_5)_2]_2\text{Cl}_2(\text{CO})\text{IrC}(\text{O})\text{o}-\text{CH}_3\text{C}_6\text{H}_4$	51.8 (52.1)	4.10 (4.15)		182	2044, 2026	1656, 1649, 1631	305, 225
6e	$[\text{PCH}_3(\text{C}_6\text{H}_5)_2]_2\text{Cl}_2(\text{CO})\text{IrC}(\text{O})\text{CH}_2\text{C}_6\text{H}_5$	55.4 (56.7)	4.42 (4.59)		78	2054	1632	304, 231
6f	$[\text{PCH}_3(\text{C}_6\text{H}_5)_2]_2\text{Cl}_2(\text{CO})\text{IrC}(\text{O})\text{C}_3\text{H}_5^e$	49.0 (49.1)	4.11 (4.13)		178	2057	1602	309, 236
7	$[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]_2\text{Cl}_2(\text{CO})\text{IrC}_6\text{H}_5^e$	55.3 (54.6)	4.41 (4.38)	8.37 (9.26)	201	2030		316, 240
9a	$[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{Cl}_2\text{IrC}(\text{O})\text{CH}_2\text{C}_6\text{H}_5$	58.2 (58.4)	4.22 (4.21)	7.81 (7.74)	138-148		1672	316 (m)
12	$[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{Cl}_2(\text{CO})\text{IrC}(\text{O})\text{CH}_2\text{C}_6\text{H}_5$					2045	1638	318, 301
13	$[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]_2\text{Cl}_2\text{IrC}(\text{O})\text{CH}_2\text{C}_6\text{H}_5$	48.2 (48.3)	5.06 (5.12)	8.90 (8.90)	139-145		1651	305
16	$[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{Cl}_2(\text{CO})\text{IrC}(\text{O})\text{CH}_3$	54.5 (54.4)	3.88 (4.03)		238-241	2040	1620	302, 294, 232

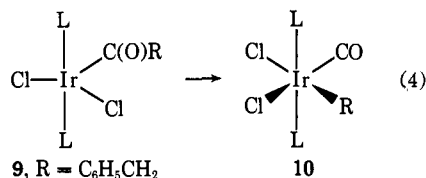
^a Found values in parentheses. ^b In Nujol. $\nu(\text{Ir}-\text{CO})$ bands are usually split in the solid state, but are singlets in CHCl_3 solution; intensity very strong. ^c Intensity strong or very strong. ^d Weak intensity unless indicated m (medium). ^e Benzene solvate. ^f Total halogen. ^g The compounds decompose at these temperatures.

bonyl complex of iron,²² it is likely that the CO which is lost is that which is attached to the metal atom. A reasonable route to the *cis*-dichloro product would be the rearrangement whereby the phenyl group migrates to a site *cis* to the CO on which it was previously bonded. Migration of methyl group to a *cis* position has been demonstrated in the thermal decarbonylation of $\text{Mn}(\text{C}(\text{O})\text{CH}_3)(\text{CO})_4(\text{C}_6\text{H}_5)_3\text{P}$.²³

Acylation of *trans*-Chlorobis(triphenylphosphine)dinitrogeniridium(I). The course of reactions of acyl chlorides with the dinitrogen complex²⁴ **8** in chloroform solution was followed by observing spectral changes in the infrared. The consumption of the dinitrogen complex **8** could be observed by the decay of the $\nu(\text{IrNN})$ band at 2100 cm^{-1} . The presence of the acyl intermediate **9** was indicated by absorption in the 1660-



8, L = $(\text{C}_6\text{H}_5)_3\text{P}$



(22) J. J. Alexander and A. Wojcicki, *J. Organometal. Chem.*, **15**, 253 (1968).

(23) R. J. Mawby, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, **86**, 5043 (1964).

(24) J. P. Collman, M. Kubota, F. D. Vastine, J. Y. Sun, and J. W. Kang, *ibid.*, **90**, 5430 (1968).

cm^{-1} region: e.g., for R = ethyl, 1663; R = $\text{CH}_3-(\text{CH}_2)_{10}$, 1665; R = cyclopropyl, 1648; R = cyclobutyl, 1660; R = vinyl, 1660; R = benzyl, 1665 cm^{-1} . The 1660- cm^{-1} peak was short lived for some complexes and it was not possible to observe acyl peaks for complexes with R = CH_3 , C_6F_5 , or C_6H_5 . Concomitant with the decay of the 1660- cm^{-1} band was the increasing intensity of the 2034- cm^{-1} band characteristic of the carbonyl complex **10**. Analytical and spectral data and melting points for a variety of alkyl and aryl carbonyl complexes **10** which have been isolated and characterized are given in Table II. The *cis* orientation of the chloro ligands in **10a-g** as depicted is again supported by the far-ir spectral data: Cl *trans* to CO, 300-307 cm^{-1} ; Cl *trans* to R, 242-262 cm^{-1} .

The aryl carbonyl complexes **10h** and **10i** with R = C_6F_5 and $\text{p}-\text{O}_2\text{NC}_6\text{H}_4$ differ from the other complexes **10a-g** in two respects. First, **10h** and **10i** have $\nu(\text{CO})$ at 2060 and 2090 cm^{-1} compared to 2020-2048 cm^{-1} for the others. Secondly, **10h** and **10i** have strong bands at 330 and 325 cm^{-1} , respectively, which indicate that the Cl atoms are *trans* to each other. The presence of other very weak bands in the far-ir indicates the presence of small amounts of the *cis* complexes. Thus, it is proposed that C_6F_5 and $\text{p}-\text{O}_2\text{NC}_6\text{H}_4$ are *trans* to CO in **10h** and **10i**. The greater π -acceptor power of C_6F_5 and $\text{p}-\text{O}_2\text{NC}_6\text{H}_4$ compared to the Cl ligand may account for the higher CO frequencies observed in **10h** and **10i**.

The alkyl and aryl carbonyl complexes in Table II may also be regarded as the products expected from the oxidative-addition reactions of alkyl or aryl chlo-

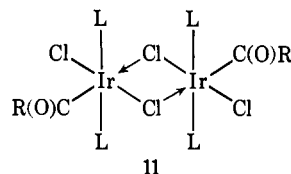
Table II. Analytical and Spectral Data for Dichloro(alkyl or aryl)bis((triphenylphosphine)carbonyl)iridium(III), $[P(C_6H_5)_3]_2Cl_2(CO)Ir-R$

	R	Analytical data ^a			Mp, °C ^g	Ir ^b frequencies, cm ⁻¹	
		C, %	H, %	Cl, %		$\nu(CO)^c$	$\nu(Ir-Cl)^d$
10a	C ₆ H ₅ CH ₂	58.2 (59.0)	4.22 (4.34)	7.81 (7.72)	200	2048	302, 249
10b	<i>m</i> -CH ₃ C ₆ H ₄ ^e	58.3 (60.2)	4.11 (4.33)	7.82 (7.00)	183	2047	307, 264, 240 (vw)
10c	C ₆ H ₅	57.8 (57.1)	3.95 (3.97)	7.94 (9.56)	276	2046	305, 260
10d	CH ₃ (CH ₂) ₁₀	59.3 (58.3)	5.50 (5.37)	7.30 (8.88)	168	2020	300, 248
10e	CH ₃	55.0 (55.1)	4.01 (3.89)	8.54 (9.29)	247	2050, 2026	302, 291, 242
10f	<i>p</i> -CH ₃ OC ₆ H ₄	57.3 (55.8)	4.04 (4.09)		276	2044	300, 261
10g	C ₂ H ₅ ^f	52.5 (52.5)	3.96 (3.98)	13.7 (13.2)	210	2035	302, 244, 229
10h	<i>p</i> -O ₂ NC ₆ H ₄	55.1 (55.0)	3.66 (3.71)	1.49 ^h (1.70)	211	2060	330, 314 (vw), 254 (vw), 230 (vw)
10i	C ₆ F ₅	52.6 (53.2)	3.08 (3.34)	7.22 (7.32)	160–164	2091	325, 305 (vw), 250 (vw)

^a Found values in parentheses. ^b In Nujol. ^c Very intense. ^d Weak. ^e Benzene solvate. ^f Recrystallized from chloroform; contains 0.5 CHCl₃. ^g Begins to decompose at this temperature. ^h Analysis for nitrogen.

rides and *trans*-chlorobis(triphenylphosphine)carbonyl-iridium(I). However, these oxidative-addition reactions are exceedingly slow and have not been observed thus far.

An example of intermediate **9** which was isolated and characterized is the orange compound **9a** which results from the reaction of phenylacetyl chloride with the dinitrogen complex **8**. The acyl moiety in **9a** is indicated by absorption at 1672 cm⁻¹, which differs significantly from the acyl frequencies (1570–1650 cm⁻¹) in the acyl complexes **4**, **5**, and **6**, which have a chloro ligand *trans* to the acyl group. Only a single Ir–Cl stretching frequency at 316 cm⁻¹ was observed for **9a**, whereas at least two Ir–Cl frequencies would be expected for chloro-bridged oligomers such as **11**. The low Ir–Cl frequencies for Cl *trans* to acyl (data in Table I) indicate that the acyl group exerts a stronger trans-labilizing influence²⁵ than the hydrido or methido ligands. Accordingly, the tendency for dimerization of the five-coordinated complexes **9** through chloro bridge bonds to a coordination position *trans* to the acyl group is expected to be low. Like the five-coordinated rhodium complexes analogous to **9** which have been found



to be monomeric,¹ the five-coordinated acyl complex **9a** was shown to be monomeric in benzene solution.

The structure of the five-coordinated low-spin d⁶ complex **9a** is probably square pyramidal with the strongest *trans*-directing ligand, in this case, the acyl group occupying the apex, and the triphenylphosphine ligands occupying *trans* positions. A similar structure has been shown for a five-coordinated rhodium(III) complex.²⁶ Warming the acyl compound **9a** in benzene solution or in the solid state led to its conversion to the

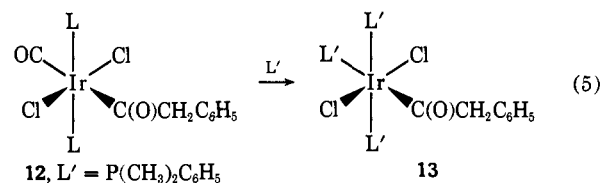
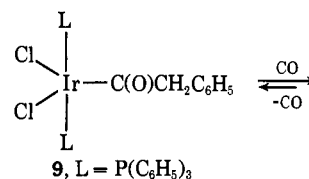
(25) M. J. Church and M. J. Mays, *J. Chem. Soc. A*, 3074 (1968).

(26) P. G. H. Troughton and A. C. Skapski, *Chem. Commun.*, 575 (1968).

cis-dichloro carbonyl complex **10a**, characterized by $\nu(CO)$ at 2048 cm⁻¹, $\nu(Ir-Cl)$ at 302 (Cl *trans* to CO) and 249 cm⁻¹ (Cl *trans* to benzyl). In forming the alkyl (aryl) complexes **10a–g** from **9**, the migration of the R group thus proceeds from CO to a *cis* site. The origin of the apparent migration of C₆F₅ and *p*-O₂-NC₆H₄ from CO to a site *trans* to the CO remains to be explored; however, one possible path might be the migration of these species as carbanions to a site *trans* to the CO.²⁷

In solutions containing a large excess of acyl chloride such that the dinitrogen complex **8** was rapidly converted to the acyl complex **9**, the decay of the 1660-cm⁻¹ band could be monitored to obtain the rates of spontaneous migration of R to the iridium atom. Preliminary studies indicate that the rates of migration decrease: C₆F₅, CH₃ ≫ vinyl > ethyl > CH₃(CH₂)₁₀ > benzyl. The reaction is first order with respect to the five-coordinated complex **9**. Investigations of the kinetics of the migration reactions will be described elsewhere.

The five-coordinated acyl complex **9a** reacts reversibly with carbon monoxide to give **12**, which could not be

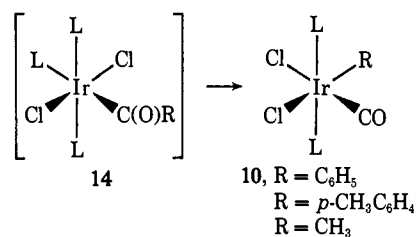
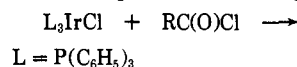


isolated as a pure compound (samples always contained some **9a**), but is characterized by $\nu(CO)$ at 2045, acyl $\nu(CO)$ at 1638, and $\nu(Ir-Cl)$ at 318 cm⁻¹ (Cl *trans* to Cl). The stereodirection of nucleophilic addition of CO to

(27) D. M. Blake and M. Kubota, *J. Amer. Chem. Soc.*, **92**, 2578 (1970).

the five-coordinated complex **9a** to a position trans to the ligand with the strongest trans-labilizing influence is in accord with our earlier proposal.²⁷ The *trans*-dichloro complex **12** is an isomer of the *cis*-dichloro complex **5a**. The reaction of a mixture of **9a** and **12** and dimethylphenylphosphine proceeded with complete substitution of triphenylphosphine to give **13**. The proposed structure depicted for **13** is supported by a methyl nmr triplet at τ 8.40, $J(\text{P-H}) = 8.8$ cps (indicating two phosphines in *trans* positions⁶), and a doublet at τ 8.78, $J(\text{P-H}) = 8.6$ cps (indicating phosphines in *cis* positions). A strong singlet band at 305 cm^{-1} in the far-ir spectrum of **13** indicates that the Cl atoms are in *trans* positions.

Acylation of Chlorotris(triphenylphosphine)iridium(I).^{24,28} The reaction of acyl halides with $[\text{P}(\text{C}_6\text{H}_5)_3]_3\text{IrCl}$ in benzene solution gave the same products as were obtained in the reactions with the dinitrogen complex **8**. The spontaneous migration of R with loss of tri-



phenylphosphine should be contrasted to the more difficult migration of R with loss of carbon monoxide as in reaction 3. This difference may be due to the stronger Ir-CO bond compared to the Ir-L bond, or it may be due to the formation of an intermediate depicted as **14**, in which a triphenylphosphine ligand is labilized by the strongly *trans*-labilizing acyl group.

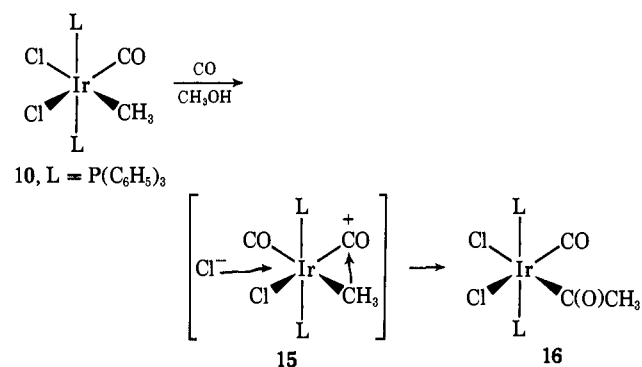
Carbonylation of Methyl-Iridium Complex 10e. Facile methyl migration in rhodium-carbonyl complexes is exemplified by the formation of acetyl complexes when methyl iodide is added to rhodium-carbonyl complexes.^{12,29} Where $[\text{P}(n\text{-butyl})_3]_2\text{IrCl}(\text{CO})\text{RhCH}_3$ was readily carbonylated to form an acetyl complex, the related iridium complex $[\text{P}(\text{C}_6\text{H}_5)_3]_3\text{IrCl}(\text{CO})\text{IrCH}_3$ could not be carbonylated.³⁰ Similarly, treatment of $[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{Br}_2(\text{CO})\text{IrCH}_3$ (**10j**) in dichloromethane-ethanol solution with carbon monoxide at 20 psi for 12 hr gave no indication of conversion of the methyl ligand to the acetyl ligand. On the other hand, similar treatment of $[\text{P}(\text{C}_6\text{H}_5)_3]_3\text{Cl}_2(\text{CO})\text{IrCH}_3$ (**10e**) in dichloromethane-methanol with carbon monoxide at 20 psi for 12 hr led to carbonylation and formation of the acetyl complex **16**. The acetyl moiety in **16** is indicated by a strong band at 1640 cm^{-1} , and the Ir^{III}-CO frequency is at 2060 cm^{-1} . Far-ir bands at 232 (Cl *trans* to acetyl) and $302\text{--}294\text{ cm}^{-1}$ (Cl *trans* to CO)⁶ indicate that carbonylation of the *cis*-dichloro methyl complex **10e** leads to the *cis*-dichloro acetyl complex **16**. Of singular significance is the observation that similar treatment of **10e** in benzene solution with carbon monoxide at 20 psi for 19 hr does not lead to carbonylation. The presence of an ionizing solvent, methanol, thus promotes carbonylation, and a reasonable way to

(28) M. A. Bennett and D. L. Milner, *J. Amer. Chem. Soc.*, **91**, 6983 (1969).

(29) I. C. Douek and G. Wilkinson, *J. Chem. Soc. A*, 2604 (1969).

(30) R. F. Heck, *J. Amer. Chem. Soc.*, **86**, 2796 (1964).

account for the reaction would be the substitution³¹ of the chloro ligand *trans* to the strong *trans*-labilizing methido ligand by carbon monoxide, as shown in the proposed intermediate **15**. Migration of the methyl group onto the *cis*-carbon monoxide as shown in **15**,



followed by nucleophilic attack of the chloride ion at a position *trans*²⁷ to the acetyl group, can lead to the formation of the acetyl complex **16**.

Summary and Conclusions

Benzoyl chloride does not react with *trans*- $[\text{P}(\text{C}_6\text{H}_5)_3]_2(\text{CO})\text{IrCl}$ at room temperature, but it reacts with the more basic complexes, *trans*- $\text{L}_2(\text{CO})\text{IrCl}$ ($\text{L} =$ triphenylarsine, tri-*p*-tolylphosphine, and methylphenylphosphine). The stereochemistry of the oxidative addition of acyl chloride to planar iridium(I) is *trans*. Decarbonylation of the *cis*-dichlorobenzoyl-iridium complex (**4c**) gives the *cis*-dichlorophenyl carbonyl complex **7**, presumably by a phenyl migration to a *cis* coordination position vacated by the expelled CO. Acyl chlorides react with *trans*-chlorobis(triphenylphosphine)dinitrogeniridium(I) (**8**) to form five-coordinated acyl intermediates, one of which has been isolated and characterized in this study. The stabilities of these five-coordinated acyl intermediates with respect to rearrangement to six-coordinated alkyl (aryl) carbonyl complexes are related to the strength of the iridium(III)-alkyl (aryl) bonds. Kinetic studies in progress should provide significant information on the details of the acyl-alkyl (aryl) rearrangement. Migration of alkyl (aryl) groups in these five-coordinated acyl intermediates is facile because of the existing coordination site left vacant by the loss of the nitrogen molecule. Migration of the alkyl or aryl group from CO to the iridium atom proceeds usually to a position *cis* to the CO. Migration of C_6H_5 and $p\text{-O}_2\text{NC}_6\text{H}_4$ apparently proceeds to a site *trans* to the CO. Carbonylation of *cis*-dichloromethylbis(triphenylphosphine)carbonyl-iridium(III) gives the corresponding *cis*-dichloroacetyl complex **16**. Since the carbonylation proceeds in methanol-dichloromethane solution, but not in benzene solution, the reaction is thought to proceed by substitution of chloride ion by carbon monoxide, followed by migration of methyl to an adjacent CO.

Experimental Section

The complexes $\text{Ir}(\text{CO})\text{Cl}_2$ ($\text{L} = \text{P}(\text{C}_6\text{H}_5)_3$, $\text{PCH}_2(\text{C}_6\text{H}_5)_2$, $\text{P}(p\text{-C}_6\text{H}_4\text{CH}_3)_3$, $\text{As}(\text{C}_6\text{H}_5)_3$, $\text{IrCl}[\text{P}(\text{C}_6\text{H}_5)_3]_3$, and $\text{IrCl}(\text{N}_2)[\text{P}(\text{C}_6\text{H}_5)_3]_2$) were prepared by methods previously described.^{4-6,21,24} Acyl chlorides were either reagent grade samples or were prepared by reaction of thionyl chloride and the corresponding carboxylic acid. Where appropriate, the acyl chlorides were redistilled or sublimed

(31) M. J. Church and M. J. Mays, *Chem. Commun.*, 435 (1968).

in vacuo. All acyl chlorides were stored and handled in a Vacuum Atmospheres drybox. Benzene and other solvents were redistilled and stored over molecular sieves. All reactions of the acyl halides were carried out in the drybox. Infrared spectra were recorded on a Perkin-Elmer Model 621 spectrophotometer. Proton nmr spectra were obtained on a Varian A60 spectrometer. Molecular weights were determined on a Mechrolab osmometer. Melting points were obtained using a Mel-Temp apparatus and are uncorrected. A Perkin-Elmer DSC-1B differential scanning calorimeter was used to study the thermal behavior of some of the acyl complexes. Elemental analyses were performed by Dr. F. Pascher, Bonn, Germany, and Chemalytics, Inc., Tempe, Ariz.

***cis*-Dichloro(benzoyl)carbonylbis(triphenylarsine)iridium(III) (4a) and the Corresponding Tri-*p*-tolylphosphine Complex 4b.** A suspension of 300 mg of *trans*-chlorocarbonylbis(triphenylarsine)iridium(I) in 2 ml of benzoyl chloride was stirred for 48 hr. Filtration gave a nearly quantitative yield of colorless iridium(III) product which was recrystallized from benzene-*n*-hexane. Compound 4b was obtained in the same manner.

Reactions of Acyl Chlorides with *trans*-Chlorobis(methyldiphenylphosphine)carbonyliridium(I) (3c). The acyl chloride (0.5 ml for liquids or 500 mg for solids) was added to a solution of 250 mg of 3c in 2 ml of benzene and the mixture was stirred for 3-12 hr. The mixture was then poured into 50 ml of boiling hexane to give colorless product (4c, 6a-f) which were recrystallized from *n*-hexane-benzene. The yields of the crude products were 80-98%.

***cis*-Dichloro(phenylacetyl)carbonylbis(triphenylphosphine)iridium(III) (5a) and the Corresponding Bromo-Chloro Complex 5b.** A suspension of *trans*-chlorocarbonylbis(triphenylphosphine)iridium(I) in 1 ml of phenylacetyl chloride was stirred for 2 hr. Filtration gave the colorless product 5a in nearly quantitative yield. In the same manner compound 5b was obtained in 60% yield starting with *trans*-bromocarbonylbis(triphenylphosphine)iridium(I). Both compounds were recrystallized from *n*-hexane-benzene.

Decarbonylation of *cis*-Dichloro(benzoyl)carbonylbis(methyldiphenylphosphine)iridium(III) (4c). The complex (4c) (290 mg) was refluxed in 5 ml of *p*-xylene, under nitrogen, for 24 hr. The mixture was evaporated to dryness and the crude product was recrystallized from benzene-*n*-hexane affording 150 mg of colorless product, *cis*-dichloro(phenyl)carbonylbis(methyldiphenylphosphine)iridium(III) (7).

General Method for Synthesis of Alkyl (Aryl)-Iridium Complexes (10) from *trans*-Chlorobis(triphenylphosphine)dinitrogeniridium(I) (8). The dinitrogeniridium complex 8 was suspended in 2 ml of benzene and 1.5 ml of the acyl chloride RC(O)Cl was added. Immediate gas evolution was noted for reactions of alkyl acid chlorides, but the reactions of aryl acid chloride took considerably longer. The mixture was then stirred for 20-30 hr. Hexane (10-20 ml) was added and the pale yellow to white products were obtained by filtration. The products were recrystallized from *n*-hexane-benzene or dichloromethane-ethanol.

Reaction of Chlorotris(triphenylphosphine)iridium(I) with Acyl Chlorides. Solutions of 250 mg of the complex in 2 ml of benzene

were treated with 1 ml (500 mg of solids) of the acyl halide RCOC1 (R = C₂H₅, CH₃, C₆H₅, *p*-NO₂-C₆H₄, or *p*-CH₃O-C₆H₄) and stirred for 2-5 days. Filtration gave a 25-90% yield of products which were identical with those obtained from reactions of the dinitrogen complex 8.

Dichloro(phenylacetyl)bis(triphenylphosphine)iridium(III) (9a). A suspension of the dinitrogen complex 8 (300 mg) in 3 ml of benzene was treated with 0.5 ml of phenylacetyl chloride. There was immediate gas evolution accompanied by formation of a dark red solution. Within a few minutes an orange precipitate formed which was recovered by filtration. The product (280 mg) was washed with ether. *Anal.* Calcd: mol wt, 907. Found (in benzene): 872. Samples of the solid stored for up to 1 month show only slight decomposition to compound 10a, as evidenced by the appearance of a weak carbonyl band at 2048 cm⁻¹ in the infrared.

***trans*-Dichloro(phenylacetyl)bis(triphenylphosphine)carbonyliridium(III) (12).** Phenylacetyl chloride (0.6 ml) was added to a suspension of 600 mg of the dinitrogen complex 8 in 6 ml of benzene. After stirring for about 2 min, the red mixture was treated with a slow stream of carbon monoxide. Over the period of a few minutes the mixture became pale yellow and a precipitate formed. A very pale orange powder (520 mg) was recovered by filtration. The infrared spectrum showed this to contain the five-coordinated phenylacetyl complex 9a as an impurity. Owing to the facile reversibility of the carbon monoxide addition, it was not possible to isolate the pure six-coordinate complex.

***trans*-Dichloro(phenylacetyl)tris(dimethylphenylphosphine)iridium(III) (13).** Dimethylphenylphosphine (0.2 ml) was added to a suspension of 500 mg of compound 12 in 5 ml of benzene. After stirring for 10 min at room temperature, the yellow solution was evaporated *in vacuo* to a thick oil. The oil was extracted with 25 ml of ether. Slow evaporation of yellow extract gave 250 mg of product as small lemon-yellow crystals.

Carbonylation of Dichloro(methyl)bis(triphenylphosphine)carbonyliridium(III) (10e). A solution of 20 mg of the methyl-iridium complex 10e in 10 ml of dichloromethane and 10 ml of methanol was treated with CO at 20 psi. The solution was vigorously stirred and a white precipitate was formed within 1 hr. After 12 hr, the acetyl product 16 was recovered by filtration. The methyl-iridium complex 10e was similarly treated in benzene solution for 19 hr. The solvent was removed at reduced pressure on a rotary evaporator and the crude product had ir bands at 2051, 2028, and 1732 cm⁻¹. Recrystallization of this crude product in dichloromethane-methanol gave the starting material 10e.

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