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Reactions of Carboxylic Acid Anhydrides with Nucleophilic Iridium(I) and Platinum(0) Complexes[1]

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Carboxylic acid anhydrides undergo oxidative addition reactions with iridium(I) complexes and platinum(0) complexes. Acyclic anhydrides, $RC(O)OC(O)R$ ($R = CH_3, CF_3, C_2F_5$), react with complexes of the type *trans*-$[IrX(CO)L_2]$ ($X = Cl, Br$; $L = P(C_6H_5)_3, PCH_3(C_6H_5)_2$) to give octahedral complexes $[IrX[C(O)R][O_2CR](CO)L_2]$. The acyl and carboxylato groups are trans in the product. Reaction of the iridium(I) complexes with perfluorosuccinic anhydride results in insertion of the metal into the five-membered ring forming complexes $\{IrCl[C(O)CF_2CF_2CO_2](CO)L_2\}$ with a chelate ring attached *via* an acyl and a carboxylato end. Platinum(0) complexes, $Pt[P(C_6H_5)_3]_2C_2H_4$ or $Pt[P(C_6H_5)_3]_3$, react to form analogous complexes of the type *trans*-$\{PtL_2[C(O)R][O_2CR]\}$ and *cis*-$\{PtL_2[C(O)CF_2CF_2CO_2]\}$. The complex *trans*-$\{IrCl(N_2)[P(C_6H_5)_3]_2\}$ reacts with the anhydrides to give iridium(III) complexes $\{IrCl[C(O)R][O_2CR][P(C_6H_5)_3]_2\}$ having a bidentate carboxyl group. These undergo migration reactions, forming alkylcarbonyl complexes $\{IrCl(R)(O_2CR)(CO)L_2\}$. Perfluoroglutaric anhydride reacts with the dinitrogen complex to give an orange product which may contain a seven-membered chelate ring. The product could not be recrystallized but may be $\{IrCl[C(O)(CF_2)_3CO_2][P(C_6H_5)_3]_2\}$. In refluxing benzene this undergoes a ring contraction reaction to give $\{IrCl(CO)[CF_2CF_2CF_2CO_2][P(C_6H_5)_3]_2\}$. In order to facilitate spectral assignments, the complexes $[IrClI(CF_3)(CO)L_2]$, $\{IrCl_2[C(O)CF_3](CO)L_2\}$, and $\{IrCl_2[C(O)CF_3]L_2\}$ were prepared by the oxidative addition of trifluoromethyl iodide or trifluoroacetyl chloride to *trans*-$[IrCl(CO)L_2]$ and *trans*-$[IrCl(N_2)L_2]$ ($L = P(C_6H_5)_2$). The five-coordinated complex $\{IrCl_2[C(O)CF_3]L_2\}$ undergoes a migration reaction to give $\{IrCl_2(CF_3)(CO)L_2\}$.

Introduction

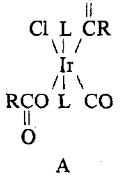
Formation of acyl complexes *via* the oxidative addition of acyl chlorides to d^8 and d^{10} metal complexes is well known (see ref 3 and references therein). The corresponding reaction of carboxylic acid anhydrides has not been reported to yield characterizable products though it has been suggested to be involved in the cobalt carbonyl, $Co_2(CO)_8$, catalyzed CO exchange in anhydrides[4] and in the reaction of anhydrides with isocyanates which is accelerated in the presence of $Co_2(CO)_8$.[5] Oxidative addition reactions of carbon–oxygen bonds have not been observed in other systems. Available information indicates the C–O bond is less reactive than carbon-halogen or -pseudohalogen bonds. For example, chloroformate esters, $Cl\text{-}C(O)OR$,[6] and the α-halo ester, $CH_3\text{-}CHBrC(O)OC_2H_5$,[7] react with iridium(I) complexes at the carbon–halogen bond. Syntheses of carboxylato complexes of the platinum metals and means of elucidating their mode of coordination have been described in recent papers.[8,9] We wish to report the results of our investigation of the reactivity of a variety of carboxylic acid anhydrides with iridium(I) and platinum(0) complexes.

A new method of preparing ethylenebis(triphenylphosphine)platinum(0) *via* the borohydride reduction of carbonatobis(triphenylphosphine)platinum(II) has been developed. This is a useful preparation since the carbonato complex is readily purified and stored. The currently used preparation of the ethylene complex starts with the dioxygen complex $\{Pt[P(C_6H_5)_3]_2O_2\}$ which has a variable shelf life.[10]

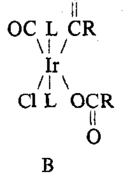
Results and Discussion

The possible isomers that may be obtained in the oxidative addition of a species X-Y to square-planar iridium(I) complexes of the type *trans*-$[IrClCOL_2]$ (L = tertiary phosphine) have been discussed by Collman and Sears.[11] The relative position of the two phosphine ligands in the six-coordinated adducts $[IrClXY(CO)L_2]$ can be inferred from the nmr spectrum when L is methyldiphenylphosphine. The methyl resonance appears as a triplet when the phosphines are trans and as a doublet when they are cis.[12] The octahedral complexes containing methyldiphenylphosphine prepared in this study all showed a triplet for the methyl resonance. For the complexes in which L = triphenylphosphine, a trans orientation of the phosphines may be inferred by analogy with the behavior of the methyldiphenylphosphine complexes. In addition, it has been suggested that the relative intensity of two weak ir bands at *ca.* 1570 and 1585 cm^{-1} is dependent on the relative position of the phosphine ligands. In trans complexes the lower energy band is most intense.[13] In all complexes prepared in this study the low-energy band is the most intense of the two, consistent with trans phosphine ligands.

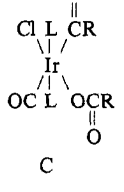
Three isomers, A, B, and C, remain possible. These can be



A



B



C

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(2) Undergraduate research participants.

(3) (a) M. Kubota and D. M. Blake, *J. Amer. Chem. Soc.*, 93, 1368 (1971); (b) M. Kubota, D. M. Blake, and S. A. Smith, *Inorg. Chem.*, 10, 1430 (1971).

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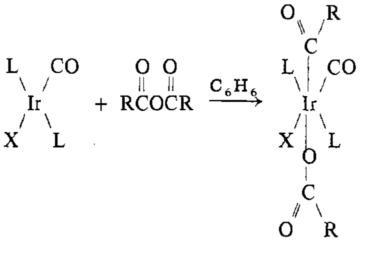
distinguished by the sensitivity of the iridium-chlorine stretching frequency to the nature of the ligand trans to chlorine and the fact that carbon monoxide trans to an acyl group is quite labile.[3a] Hence, isomer C readily loses CO in solution. The limits for ν(Ir-Cl) are approximately as follows: 300-315 cm^{-1}, Cl trans to carbon monoxide;[11] 240-260 cm^{-1}, Cl trans to an acyl or alkyl group;[3a] 320-330 cm^{-1}, Cl trans to a carboxylato ligand.[14] The relevant infrared data for the complexes prepared in this study are given in Table I.

Square-planar iridium(I) complexes react with acyclic anhydrides as shown in reaction 1 to give complexes of type I.



(1)

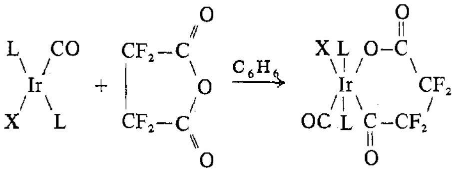
Ia, L = P(C$_6$H$_5$)$_3$, X = Cl, R = CF$_3$
b, L = P(C$_6$H$_5$)$_3$, X = Br, R = CF$_3$
c, L = P(C$_6$H$_5$)$_3$, X = Cl, R = C$_2$F$_5$
d, L = PCH$_3$(C$_6$H$_5$)$_2$, X = Cl, R = CF$_3$
e, L = PCH$_3$(C$_6$H$_5$)$_2$, X = Cl, R = CH$_3$

The ^{1}H nmr spectrum of compounds Id and Ie show triplets at τ 7.72 and 7.60, respectively, for the *P*-CH$_3$. In addition, compound Ie shows singlets at τ 8.85 for the acetyl group and at τ 8.40 for the acetate group. The iridium-chlorine stretching frequency for the compounds containing the perfluoro ligands are in the range 315-325 cm^{-1}. This is higher than usually observed for Cl trans to CO. Since compounds Ia-Ie do not lose CO in solution and the phosphines are trans, they must correspond to isomer A and the addition of the anhydride is trans.

The adducts of trifluoroacetic anhydride, Ia and Ib, exhibit one strong band in the ν(C=O) region of the infrared spectra (Ia, 1678 cm^{-1}; Ib, 1678 cm^{-1}). The positions of ν(C=O) for the acyl group and ν_A(CO$_2$) for the carboxyl group are too close to be resolved. That the trifluoroacetyl and trifluoroacetate groups are present is shown by the presence of two sharp medium-intensity bands between 800 and 900 cm^{-1}. This region of the infrared spectrum has been assigned by other workers to ν(C-C) for the trifluoroacetate ion.[15] The carboxylate ligand, CF$_3$CO$_2$, has ν(C-C) at *ca.* 845-850 cm^{-1} and the acyl ligand, CF$_3$CO, has ν(C-C) at *ca.* 877-890 cm^{-1}. These have been identified in compounds containing only the trifluoroacetate or trifluoroacyl groups (see Table I).

In compounds Ic, Id, and Ie two bands are present in the 1600-1710-cm^{-1} region. In each case the lower energy band is assigned to ν_A(CO$_2$) for the carboxyl group and the higher energy band to ν(C-O) for the acyl group. The observed differences between the frequencies for the asymmetric and symmetric vibrational modes of the carboxyl groups, $\nu_A - \nu_S$, are 250 cm^{-1} for compound Ic, 240 cm^{-1} for Id, and 292 cm^{-1} for Ie. These better agree with the limits suggested by Robinson[9] for unidentate perfluoroalkyl carboxylates, 240-310 cm^{-1}, and for unidentate alkyl carboxylates, 210-270 cm^{-1}, than would values obtained by assigning the higher energy band to ν_A(CO$_2$).

Perfluorosuccinic anhydride undergoes oxidative addition (eq 2) with ring opening producing chelate complexes, II.



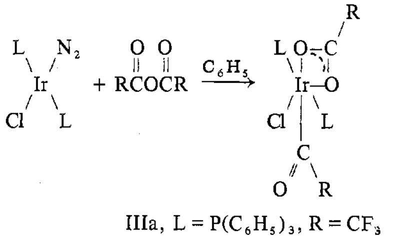
(2)

IIa, X = Cl, L = P(C$_6$H$_5$)$_3$
b, X = Br, L = P(C$_6$H$_5$)$_3$
c, X = Cl, L = PCH$_3$(C$_6$H$_5$)$_2$

Again the phosphines remain trans in the products (for compound IIc: τ(CH$_3$) 7.75, triplet). The product is stereospecifically that with the carboxyl end of the chelate ring trans to carbon monoxide since the compounds show no tendency to lose CO in solution. The position of ν(Ir-Cl) for the compounds, 274-265 cm^{-1}, is higher in energy than that observed in other acyliridium(III) complexes.[3a] In these complexes the band near 1715 cm^{-1} is assigned to ν(C=O) for the acyl end of the chelate and the band near 1670 cm^{-1} to the asymmetric stretch for the carboxyl end. There are two bands in the ν(C-C) region at *ca.* 878 and 808-815 cm^{-1}.

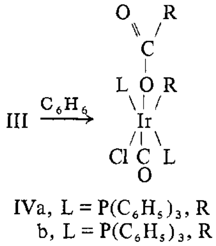
Perfluoroglutaric anhydride reacts with Vaska's complex but the product, which would contain a seven-membered chelate ring, had a tendency to give an insoluble, sticky solid and was not characterized. Succinic anhydride does not react to a detectable extent with *trans*-{IrCl(CO)[PCH$_3$(C$_6$H$_5$)$_2$]$_2$} within a period of 7 days at 75° in benzene.

The dinitrogen-iridium(I) complex *trans*-{IrCl(N$_2$)[P(C$_6$H$_5$)$_3$]$_2$} reacts with anhydrides to yield golden yellow complexes, III, having bidentate carboxyl groups (reaction 3). The migration of the perfluoro groups requires prolonged reflux; hence it is possible to recrystallize complexes IIIa and IIIb. Migration of the methyl group proceeds at a rate comparable to that of the reaction of acetic anhydride with the dinitrogen complex so only the methylacetato complex, IVa, was isolated. The presence of IIIc was indicated by the orange color of the reaction mixture.



(3)

IIIa, L = P(C$_6$H$_5$)$_3$, R = CF$_3$
b, L = P(C$_6$H$_5$)$_3$, R = C$_2$F$_5$
c, L = P(C$_6$H$_5$)$_3$, R = CH$_3$ (not isolated)



(4)

IVa, L = P(C$_6$H$_5$)$_3$, R = CH$_3$
b, L = P(C$_6$H$_5$)$_3$, R = CF$_3$

The acyl-carboxylato complexes, IIIa and IIIb, show a split band in the 1670-1695-cm^{-1} region which is assigned to ν(C=O) for the acyl ligand and bands at 1605 and 1602 cm^{-1}, respectively, which are assigned to the asymmetric

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(14) S. A. Smith, D. M. Blake, and M. Kubota, *Inorg. Chem.*, 11, 660 (1972).

(15) (a) M. B. Dines, *Inorg. Chem.*, 11, 2949 (1972); (b) M. J. Baillie, D. H. Brown, K. C. Moss, and D. W. A. Sharp, *J. Chem. Soc. A*, 3310 (1968).

Table I. Infrared Data (cm^{-1})[a]

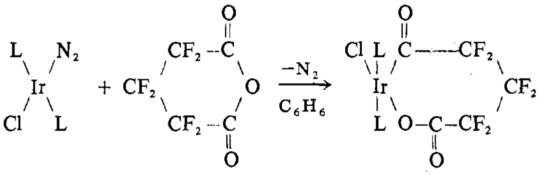
No.	Compd[e]	$\nu(C{\equiv}O)$	$\nu(-C(=O)R)$	$\nu_A(R-CO_2)$	$\nu_S(R-CO_2)$	$\nu(C-C)$	$\nu(Ir-Cl)$
Ia	$IrCl[O_2CCF_3][C(O)CF_3](CO)L_2$	2070	1678	*b*	*c*	886, 848	325
Ib	$IrBr[O_2CCF_3][C(O)CF_3](CO)L_2$	2065	1678	*b*	*c*	885, 847	
Ic	$IrCl[O_2CC_2F_5][C(O)C_2F_5](CO)L_2$	2080	1710 sh	1690	1440	800	315
Id	$IrCl[O_2CCF_3][C(O)CF_3](CO)L'_2$	2070	1685	1660	1418	*c*, 850	318
Ie	$IrCl[O_2CCH_3][C(O)CH_3](CO)L'_2$	2058	1625	1610	1318		307
IIa	$IrCl[C(O)CF_2CF_2CO_2](CO)L_2$	2062	1718	1670	1365	880, 815	265
IIb	$IrBr[C(O)CF_2CF_2CO_2](CO)L_2$	2062	1715	1668	1365	878, 808	
IIc	$IrCl[C(O)CF_2CF_2CO_2](CO)L'_2$	2075	1715	1668	1370	875, 808	274
IIIa	$IrCl(O_2CCF_3)[C(O)CF_3]L_2$		1692, 1672	1605, 1610	*c*	880, 870, 780	327
IIIb	$IrCl(O_2CC_2F_5)[C(O)C_2F_5]L_2$		1696, 1675	1602	1335	842, 802	324
IVa	$IrCl(O_2CCH_3)(CH_3)(CO)L_2$	2038		1650	1368		248
IVb	$IrCl(O_2CCF_3)(CF_3)(CO)L_2$	2060		1688, 1660 sh	1410	890, 845	310
V	$IrCl[C(O)CF_2CF_2CF_2CO_2]L_2$		1680 br	1780 br	*c*		
VI	$IrCl[O_2CCF_2CF_2CF_2](CO)L_2$	2050		1705	1360	882, 810	288
VIIIa	$Pt(O_2CCF_3)[C(O)CF_3]L_2$		1680	1660	1415	890, 840	
VIIIb	$Pt[C(O)CF_2CF_2CO_2]L_2$		1705	1685	*c*	855, 800	
IX	$IrCl_2[C(O)CF_3](CO)L_2$	2053	1689			877	313, 252
X	$IrCl_2[C(O)CF_3]L_2$		1665			888	335
XI	$IrCl_2CF_3(CO)L_2$	2078					321, 273
XII	$IrClICF_3(CO)L_2$	2080					308, 262
	$IrHCl(O_2CCF_3)(CO)L_2$[d]	2034		1685		845	308, 262

[a] Nujol mull. [b] $\nu_A(R-CO_2)$ and $\nu(-C(=O)R$ coincide. [c] Obscured by phosphine bands. [d] H. Singer and G. Wilkinson, *J. Chem. Soc. A*, 2516 (1968). [e] $L = P(C_6H_5)_3$ and $L' = PCH_3(C_6H_5)_2$.

stretching frequency of the carboxyl group. This is characteristic of a bidentate carboxylato ligand.[9,14] The iridium-chlorine stretch is near 325 cm^{-1} which is characteristic of Cl trans to the oxygen of a carboxyl group.[14]

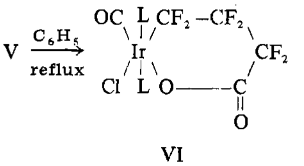
Compound IVa, obtained *via* a migration reaction, shows $\nu(C{\equiv}O)$ at 2038 cm^{-1} and bands at 1650 and 1368 cm^{-1} due to the asymmetric and symmetric carboxyl stretching frequencies. The band at 248 cm^{-1} indicates chlorine is trans to the methyl group. A satisfactory elemental analysis of IVb could not be obtained; however the presence of a strong, carbonyl stretching frequency at 2060 cm^{-1} shows that the migration reaction takes place.

Reaction 5 ($L = P(C_6H_5)_3$) of perfluoroglutaric anhydride with the dinitrogen complex gave an orange product which presumably has a seven-membered chelate ring. Attempts to recrystallize this product gave oils. The crude product shows two broad infrared bands between 1650 and 1800 cm^{-1}. A characterizable adduct of perfluorosuccinic anhydride could not be obtained. The orange color is characteristic of other five-coordinate iridium-acyl complexes.[3] Reactions of V were carried out using the crude material. It undergoes a migration reaction leading to ring contraction in refluxing benzene (reaction 6) giving a complex containing a chelate attached *via* a carboxyl end and an iridium-carbon σ bond. The ir spectrum of the compound has a band at 2050 cm^{-1} assigned to $\nu(C{\equiv}O)$, bands characteristic of the monodentate carboxyl group at 1650 and 1368 cm^{-1}, and the iridium chlorine stretch at 288 cm^{-1}. The latter band is at a higher frequency than usually observed for Cl trans to a σ-bonded carbon.



V

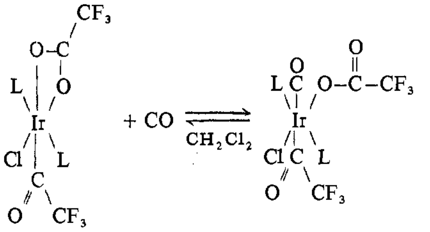
(5)



VI

(6)

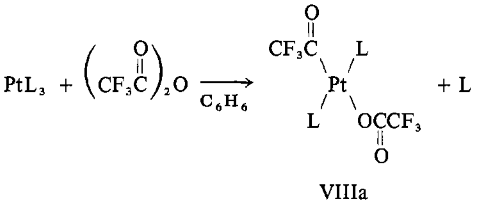
Complexes III and V reversibly add carbon monoxide in solution (see eq 7). The carbonyl group occupies the position trans to the acyl group to give colorless six-coordinate complexes. The CO adducts have a strong band at 2070-2090 cm^{-1} which is assigned to $\nu(C{\equiv}O)$. Other infrared data for these adducts are shown in Table II. The reaction is readily reversed by purging the solution with dinitrogen. Due to the lability of the carbonyl adducts they were characterized in solution but not isolated. The lability of a carbon monoxide trans to an acyl group has previously been observed.[3a]



IIIa VII

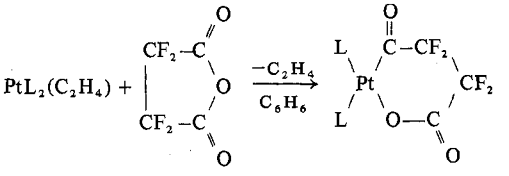
(7)

Tris(triphenylphosphine)platinum(0), PtL_3, and ethylenebis(triphenylphosphine)platinum(0), $PtL_2(C_2H_4)$, also undergo oxidative addition reactions with perfluorocarboxylic acid anhydrides (eq 8 and 9, $L = P(C_6H_5)_3$). The ir spectrum of the trifluoroacetic anhydride adduct VIIIa has a band at 1680



VIIIa

(8)



VIIIb

(9)

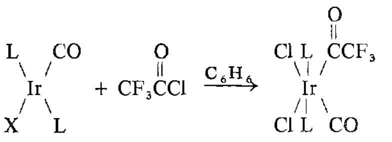
Table II. Carbon Monoxide Addition Products of Coordinatively Unsaturated Acyl Complexes

	$\nu(C{\equiv}O)$	ν-(-C-(=O)R)	ν_A(R-CO$_2$)
trans-$[IrCl[O_2CCF_3][C(O)CF_3](CO)L_2]$	2090 vs	1695	1668
trans-$[IrCl[C(O)(CF_2)_3CO_2](CO)L_2]$	2080 vs	1690	1650
trans-$[IrCl_2[C(O)CF_3](CO)L_2]$	2070 vs	1658	

cm^{-1} which is assigned to ν(C=O) for the acyl group and asymmetric and symmetric stretching frequencies of the carboxylato group at 1660 and 1415 cm^{-1}, respectively. A trans configuration is assigned based on the relative intensities of the 1570- and 1585-cm^{-1} bands in the infrared spectrum of VIIIa. The platinum(0)-ethylene complex reacts cleanly with perfluorosuccinic anhydride to give the chelate complex VIIIb, which must have the phosphines cis. Reaction of tris(triphenylphosphine)platinum(0) with perfluorosuccinic anhydride was complicated by the reaction of the excess phosphine ligand with the anhydride. For the same reason, satisfactory products were not obtained starting with tetrakis(methyldiphenylphosphine)platinum(0).

The acetylene complex $\{Pt[P(C_6H_5)_3]_2[C_6H_5CCC_6H_5]\}$ reacts with trifluoroacetic anhydride to give compound VIIIa. The only other product of the reaction that was detected was diphenylacetylene. The analogous hexafluorobutyne complex did not react at room temperature. The trifluoroacetic anhydride adduct VIIIa was not decarbonylated after refluxing for 24 hr in toluene.

Trifluoroacetyl chloride adds to *trans*-$\{IrCl(CO)[P(C_6H_5)_3]_2\}$ as shown in reaction 10 (L = $P(C_6H_5)_3$) to give compound IX.

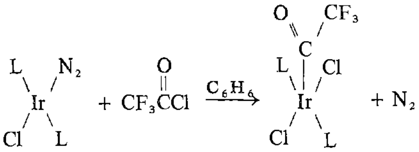


IX

(10)

The ir spectrum of this compound has $\nu(C{\equiv}O)$ at 2053 cm^{-1}, ν(C=O) for the acyl group at 1689 cm^{-1}, and ν(C-C) for the acyl group at 877 cm^{-1}.

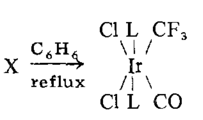
The dinitrogen complex reacts (eq 11) with trifluoroacetyl chloride to give a red five-coordinated acyl complex, X. The ir spectrum has a band due to ν(C=O) at 1665 cm^{-1} and a single band at 335 cm^{-1} assigned to ν(Ir-Cl).



X

(11)

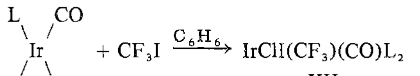
As has been previously reported for five-coordinated iridium(III)-acyl complexes[3] compound X undergoes a migration reaction in refluxing benzene to give a six-coordinated carbonyl complex, XI (eq 12). The ir spectrum of XI has a band at 2078 cm^{-1} assigned to $\nu(C{\equiv}O)$ and bands at 321 and 273 cm^{-1} attributable to the stretching frequencies of chlorine trans to CO and CF$_3$, respectively.



XI

(12)

An analog of compound XI can be obtained by the addition of trifluoromethyl iodide to Vaska's complex, reaction 13 (L = $P(C_6H_5)_3$). The ir spectrum of complex XII has a single carbonyl stretching frequency at 2080 cm^{-1} which is indicative of the presence of only one isomer but there are bands at 308 and 262 cm^{-1}, in the ν(Ir-Cl) region. If the addition is trans, as has been found for methyl halides,[11] then ν(Ir-Cl) would correspond to the 308-cm^{-1} band, characteristic of Cl trans to carbon monoxide.



XII

(13)

Conclusions

The C-O bond in perfluorocarboxylic acid anhydrides is readily cleaved by nucleophilic transition metal complexes. The stereochemistry of the oxidative addition reaction with acyclic anhydrides is trans. Thus compounds corresponding to isomer A are obtained starting with *trans*-$[IrX(CO)L_2]$. The possibility of an initial formation of a cis adduct (isomer B) followed by isomerization to the trans form (isomer A) cannot be ruled out by our data. Isomerization in methyl halide adducts of *trans*-$\{IrX(CO)[P(C_6H_5)_2CH_3]_2\}$ has been observed to occur upon prolonged reflux in a polar solvent. It does seem unlikely that the mild conditions employed in the formation of the anhydride adducts would result in isomerization of a kinetically controlled product even if it were the least stable isomer. Therefore, it is likely that isomer A is the result of the initial oxidative addition step and not of a subsequent isomerization. It is interesting to note the high stereospecificity of the addition of acyclic anhydrides. Pearson has suggested that isomers having hard ligands trans to soft ligands should be the most stable.[16] Due to the similarity in hardness of chloride and trifluoroacetate, one would predict isomers A and B should be of about equal stability. With cyclic anhydrides oxidative addition corresponds to insertion of the metal into the ring to give a chelated ligand having a carboxylato and an acyl end attached to the metal in cis positions. The anhydrides are a noteworthy case in which both cis and trans oxidative addition can be observed for compounds of the same type. Compounds of the same type have always been found to add stereospecifically cis or trans.[17] Where mixtures of types have been found, they were probably due to secondary reactions.[18] Compounds having carbon monoxide trans to the acyl ligand, isomer C, can be obtained by the addition of carbon monoxide to complexes containing a bidentate carboxylato group, $[IrCl(O_2CR)[C(O)R]L_2]$, or to five-coordinate acyl complexes, $[IrCl_2[C(O)R]L_2]$. Isomer C is the least stable isomer since the carbon monoxide is labilized by the acyl group and is readily lost.

The adducts of acid anhydrides may be analogs of intermediates in homogeneously catalyzed reactions in which anhydrides undergo CO exchange[4] or decarbonylation[19] or in reactions in which anhydrides are formed from β-lactones.[20] This speculation is supported by the fact that those

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Table III. Analytical Data

	% C		% H		% Cl		
	Calcd	Found	Calcd	Found	Calcd	Found	Mp, °C
$IrCl(O_2CCF_3)[C(O)CF_3][P(C_6H_5)_3]_2$	53.1	52.17	3.49	3.58	5.95	6.35	175–178
$IrCl(O_2CC_2F_5)[C(O)C_2F_5][P(C_6H_5)_3]_2$	50.55	50.21	3.18	3.23	3.11	3.13	171–172
$IrCl_2(CF_3)(CO)[P(C_6H_5)_3]_2$	51.59	51.85	3.41	3.82	8.01	7.26	269–271
$IrCl(O_2CCF_3)(CF_3)(CO)[P(C_6H_5)_3]_2$	49.92	46.86	3.13	3.34			215–225
$IrCl[O_2CC_3F_6](CO)[P(C_6H_5)_3]_2 \cdot C_6H_6$	53.63	51.61	3.45	3.48	3.37	3.19	230–232
$IrCl(O_2CCH_3)(CH_3)(CO)[P(C_6H_5)_3]_2$	56.23	56.29	4.25	4.28	4.15	5.07	229–231
$IrClI(CF_3)(CO)[P(C_6H_5)_3]_2$	46.75	47.31	3.09	3.24	3.67	4.30	256–257
$Pt(O_2CCF_3)[C(O)CF_3][P(C_6H_5)_3]_2$	51.68	51.57	3.23	3.09			216–218
$Pt[C(O)CF_2CF_2CO_2][P(C_6H_5)_3]_2$	53.87	53.72	3.39	3.45			216–219
$IrCl[C(O)CF_3][P(C_6H_5)_3]_2$	51.59	51.96	3.41	3.42	8.01	8.56	173
$IrCl_2[C(O)CF_3](CO)[P(C_6H_5)_3]_2$	51.33	51.66	3.31	3.47	7.77	8.32	217–219
$IrCl(O_2CCF_3)[C(O)CF_3](CO)[P(C_6H_5)_3]_2$	49.72	50.95	3.05	3.26	3.58	3.73	210–217
$IrBr(O_2CCF_3)[C(O)CF_3](CO)[P(C_6H_5)_3]_2$	47.59	48.17	2.92	3.08	7.72[a]	7.05[a]	210–212
$IrCl[O_2CCF_3][C(O)CF_3](CO)[PCH_3(C_6H_5)_2]_2$	42.98	43.25	3.02	3.20	4.10	4.00	195–196
$IrCl(O_2CC_2F_3)[C(O)C_2F_5](CO)[P(C_6H_5)_3]_2$	50.36	50.03	3.11	3.15	3.04	3.26	199–201
$IrCl[C(O)C_2F_4CO_2](CO)[P(C_6H_5)_3]_2$	51.72	51.33	3.17	3.22	3.73	4.29	228–235
$IrBr[C(O)C_2F_4CO_2](CO)[P(C_6H_5)_3]_2$	49.40	49.31	3.03	3.66	8.01[a]	6.92[a]	203–205
$IrCl[C(O)C_2F_4CO_2](CO)[PCH_3(C_6H_5)_2]_2$	44.96	45.25	3.16	2.92	4.29	3.52	211–213
$IrCl(O_2CCH_3)[C(O)CH_3](CO)[PCH_3(C_6H_5)_2]_2$	56.23	56.29	4.25	4.28	4.15	5.07	179–180

[a] Br analysis.

adducts which have a readily available coordination site (complexes IIIa, V, and X) undergo migration reactions in which the metal-acyl group is converted to an alkyl-metal-carbonyl complex. Perfluoro groups undergo this reaction at a rate much slower than their hydrocarbon analogs. The migration of the CF_3 group in the coordinatively unsaturated complex $\{IrCl_2[C(O)CF_3][P(C_6H_5)_3]_2\}$ requires prolonged reflux in benzene whereas the CH_3 group in $\{IrCl_2[C(O)CH_3][P(C_6H_5)_3]_2\}$ has been reported to migrate within minutes at room temperature.[3a]

Experimental Section

Preparations of the iridium complexes were as reported previously.[3a] The complexes $Pt[P(C_6H_5)_3]_3$,[21] $Pt[P(C_6H_5)_3]_2(C_6H_5C{\equiv}CC_6H_5)$,[22] $Pt[P(C_6H_5)_3]_2(CF_3C{\equiv}CCF_3)$,[22] and $Pt[P(C_6H_5)_3]_2CO_3 \cdot C_6H_6$[23] were prepared by methods in the literature. The perfluorocarboxylic acid anhydrides were purchased from PCR Inc. The anhydrides were purified by distillation from calcium hydride to remove acid impurities and stored *in vacuo* in containers with Teflon stopcocks. Acetic anhydride was treated similarly. Benzoic and succinic anhydrides were sublimed *in vacuo*. Solvents were dried and stored *in vacuo*. All manipulations of the volatile anhydrides in the preparation of reaction mixtures were done using standard vacuum techniques. Subsequent work-up of the products was carried out open to the atmosphere as the products are not sensitive to air or moisture. Infrared spectra were recorded on a Perkin-Elmer Model 621 spectrometer. Proton nmr spectra were recorded in a Varian T-60 spectrometer. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn. Infrared data are presented in Tables I and II and the analytical data are in Table III.

General Procedure for the Reaction of Perfluorocarboxylic Acid Anhydrides with *trans*-$[IrX(CO)L_2]$ ($X = Cl, Br, L = P(C_6H_5)_3, P(C_6H_5)_2CH_3$). The anhydride, 0.2 ml, and 4–5 ml of benzene were distilled onto 0.5 g of the complex at 77°K. Upon warming to room temperature the mixture rapidly turned colorless. In those cases in which the product did not precipitate directly from the mixture, the volatile components were removed *in vacuo* and the residue was washed from the flask with ether to give the colorless adduct in 80–90% yield. Complexes in which L is methyldiphenylphosphine were generally treated this way, while those in which L is triphenylphosphine generally precipitated directly from the reaction mixture. The complexes are readily recrystallized from hot benzene by addition of *n*-hexane to produce cloudiness and then by allowing the mixture to stand at room temperature.

Reaction of Perfluoro Anhydrides with *trans*-$\{IrCl(N_2)[P(C_6H_5)_3]_2\}$. The anhydride, 0.2 ml, was condensed onto 0.5 g of the dinitrogen complex and 5 ml of benzene at 77°K. Upon warming to room temperature, vigorous evolution of nitrogen occurred. The volatile components were removed *in vacuo* and the remaining solid was washed from the flask with ether. Crude yields are 80–100%. The golden yellow to orange products were recrystallized from benzene-*n*-hexane.

Reaction of *trans*-$\{IrCl(CO)[PCH_3(C_6H_5)_2]_2\}$ with Benzoic and Succinic Anhydrides. The iridium(I) complex, 0.25 g, and benzoic anhydride, 0.5 g, were sealed in a tube with 5 ml of benzene. The mixture was stirred at 75° for 1 week. Only unreacted starting materials were detected. A similar result was obtained with succinic anhydride.

$\{IrCl(OC(O)CH_3)[C(O)CH_3](CO)[PCH_3(C_6H_5)_2]_2\}$. Acetic anhydride, 3 ml, was condensed onto 0.25 g of *trans*-chlorocarbonylbis(methyldiphenylphosphine)iridium(I) and the tube was sealed. The mixture was stirred at 60° for 1 week and then allowed to cool. Filtration gave 0.15 g of colorless product. This was recrystallized from benzene-*n*-hexane.

$\{IrCl(CH_3)[OC(O)CH_3](CO)[P(C_6H_5)_3]\}_2$. The iridium-dinitrogen complex, 0.4 g, was stirred *in vacuo* with 1 ml of acetic anhydride and 5 ml of benzene. The liquid phase gradually turned orange indicating the formation of a five-coordinate acyl complex. Concurrent with this was the precipitation of the white product. After 2 days at room temperature the mixture was nearly colorless; yield is 0.3 g.

Reaction of Iridium(I) Complexes with Trifluoroacetyl Chloride. Vaska's complex, 0.5 g, in 5 ml of benzene was exposed to gaseous trifluoroacetyl chloride (500 Torr) on a vacuum line. Within 5 min a heavy white precipitate of $IrCl_2[C(O)CF_3](CO)[P(C_6H_5)_3]_2$ formed. Reaction with the dinitrogen complex gave an orange solid $IrCl_2[C(O)CF_3][P(C_6H_5)_3]_2$. Yields were nearly quantitative in each case. The complexes were recrystallized from benzene-*n*-hexane.

$\{IrClI(CF_3)CO[P(C_6H_5)_3]_2\}$. A suspension of *trans*-$\{IrClCO[P(C_6H_5)_3]_2\}$ in 5 ml of benzene was saturated with trifluoromethyl iodide and left to stir for 2 days in a "pop bottle" with a rubber cap. Filtration gave a cream-colored product; 57% yield. This was recrystallized from benzene-*n*-hexane.

Migration Reactions of Coordinatively Unsaturated Acyl Complexes. The acyl-carboxylato complex $IrCl[C(O)CF_3][O_2CCF_3][P(C_6H_5)_3]_2$, 0.2 g, was stirred in 5 ml of benzene at 75° in a "pop bottle" under nitrogen for 25 hr. After filtration to remove some suspended solid, the liquid phase was evaporated to a thick oil. This was triturated with ether. The resulting solid was recrystallized from benzene-*n*-hexane; yield 30%.

The complexes $\{IrCl[C(O)CF_2CF_2CF_2CO_2][P(C_6H_5)_3]_2\}$ and $IrCl_2[C(O)CF_3][P(C_6H_5)_3]_2$ were treated similarly to give the carbonyl complexes $IrCl(CO)[CF_2CF_2CF_2CO_2][P(C_6H_5)_3]_2$ (50% yield) and $IrCl_2(CO)(CF_3)[P(C_6H_5)_3]_2$ (60% yield).

$\{Pt[C(O)CF_2CF_2CO_2][P(C_6H_5)_3]_2\}$. The ethylene complex, 0.5 g, was cooled to 77°K and 0.12 ml of perfluorosuccinic anhydride and 5 ml benzene were added, *in vacuo*. Upon warming to room temperature, a gas was evolved and a light yellow precipitate of the product formed in 40% yield. This was recrystallized from benzene-*n*-hexane.

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$\{Pt[C(O)CF_3](O_2CCF_3)[P(C_6H_5)_3]\}_2$. Tris(triphenylphosphine)platinum(0), 0.81 g, 0.5 ml of trifluoroacetic anhydride, and 10 ml of benzene were mixed *in vacuo*. After 2 hr at room temperature, the colorless mixture was evaporated to dryness and the colorless product washed with ether; 85% yield. The product was recrystallized from benzene–*n*-hexane.

$[Pt[P(C_6H_5)_3]_2(C_2H_4)]$. A continuous flow of ethylene was maintained through a suspension of carbonatobis(triphenylphosphine)platinum(II), 1.5 g, in 40 ml of ethanol at 25°. In a period of 20 min 18 ml of 0.1 *M* $NaBH_4$ in ethanol solution was added. The resulting white suspension was stirred for an additional 2 hr under ethylene at 25°. Filtration gave 1.33 g of product, 100% yield, whose infrared spectrum, melting point, and reactivity were the same as those of an authentic sample.[20] The product was washed with ethanol, water, and ethanol and then dried *in vacuo*. If sufficient reaction time is not allowed, some of the carbonato complex will remain. This results in a product which is not completely soluble in benzene.

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Trimeric (Alkoxy)(alkylimino)methylgold(I) Compounds, $[(RO)(R'N{=})CAu]_3$

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The title compounds are stable, not cluster-type molecules, having an enneaatomic and probably planar cycle. They are prepared by action of potassium hydroxide in an alcohol on a mixture of an isocyanide and a gold(I) complex, such as Me_2SAuCl or Ph_3PAuCl; alternatively they are obtained by deprotonation of a carbene complex, $[(RO)(R'NH)C]AuCl$, which is re-formed when the trimer is treated with hydrochloric acid.

The reaction of aromatic isocyanides in alcoholic potassium hydroxide with phosphine complexes of metals such as platinum,[1,2] palladium,[3] or gold[1,4] yields compounds containing the -C(OR)=NR′ group, *e.g.*

$$(Ph_3P)AuCl + ROH + KOH + Ar{-}NC = (Ph_3P)AuC(OR){=}NAr + KCl + H_2O$$

$$(Ph_3P)_2PtCl_2 + 2ROH + 2KOH + 3Ar{-}NC = Ph_3P + 2KCl + 2H_2O + (Ph_3P)(Ar{-}NC)Pt[C(OR){=}NAr]_2$$

While extending the reaction to other isocyanides, we obtained a new phosphine-free compound, *i.e.*,[5] $[Au{-}C(OMe){=}NC_6H_{11}]_3$. This is a discrete coordination polymer and is likely to be one of the few polynuclear gold compounds not containing a cluster of metal atoms.[6] Here we describe a general synthesis of complexes having the formula $[Au{-}C(OR){=}NR']_3$, where R′ is an aliphatic, cycloaliphatic, alkylaromatic, or aromatic group. The similar, less stable silver(I) derivatives have been briefly described recently.[7]

Experimental Section

$(Me_2S)AuCl$,[8] $(RNC)AuCl$,[9] and $(Ph_3P)AuCl$[10] were prepared according to published methods. Evaporation was always carried out under reduced pressure. All the analytical samples were dried to constant weight under vacuum (*ca.* 0.1 Torr). All the reactions were carried out at room temperature.

Reaction 1. This was carried out as described elsewhere.[5]

Reaction 2: (Methoxy)(*N-p*-tolylimino)methylgold(I) Trimer (V). To a stirred suspension of $(Me_2S)AuCl$ (2.59 g, 8.7 mmol) in methanol (30 ml) *p*-tolyl isocyanide (1.13 ml, 8.7 mmol) and, later, potassium hydroxide (0.50 g, 8.7 mmol) in methanol (50 ml) were added. After 0.5 hr the solution was evaporated to dryness, and the residue was extracted with chloroform. On concentration the extract afforded a precipitate, which was crystallized from chloroform–ether to afford the analytical sample. When compound I was prepared, the extraction was carried out with hot CH_2Cl_2 in place of $CHCl_3$. When compound VII was prepared, the methanol suspension was filtered, and the precipitate was stirred under water overnight, filtered again, washed with acetone, with ether, and then with hot $CHCl_3$ until the washings were colorless. While the other compounds gave colorless crystals, VII is a brownish powder.

Reaction 3: [(Methoxy)(methylimino)carbene]chlorogold(I) (X). To a stirred suspension of compound I (426.8 mg) in methanol (20 ml) aqueous hydrochloric acid (1 ml) in the same solvent (9 ml) was added. After 2 hr the solution was concentrated to a small volume to afford a precipitate; this was dissolved in CH_2Cl_2, the solution was concentrated, and the analytical sample was obtained after addition of ether.

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