# Complexes of the Platinum Metals. Part II.[1] Carboxylato(triphenylphosphine) Derivatives of Ruthenium, Osmium, Rhodium, and Iridium

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Many hydrido- and low oxidation state triphenylphosphine complexes of ruthenium, osmium, rhodium, and iridium are shown to yield carboxylato-derivatives on reaction with carboxylic acids $R{\cdot}CO_2H$ (R = alkyl or aryl) in organic solvents. These reactions provide convenient syntheses for an extensive range of new and previously reported series of carboxylato-complexes including $RuH(OCOR)(PPh_3)_3$, $RuCl(OCOR)(CO)(PPh_3)_2$, $RuH(OCOR)(CO)(PPh_3)_2$, $Ru(OCOR)_2(CO)(PPh_3)_2$, $Ru(OCOR)_2(CO)_2(PPh_3)_2$, $OsH(OCOR)(PPh_3)_3$, $Rh(OCOR)(PPh_3)_3$, $Rh(OCOR)(CO)(PPh_3)_2$, $[Rh(Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2)_2][OCOR]$, $Rh(OCOR)_2(NO)(PPh_3)_2$, $IrH_2(OCOR)(PPh_3)_3$, and $Ir(OCOR)_3(PPh_3)_2$. A single-step synthesis of the complexes $RuH(OCOR)(PPh_3)_3$ from hydrated ruthenium trichloride is also described. The carboxylato-derivatives are characterised by i.r. and $^1H$ n.m.r. spectroscopy.

CARBOXYLIC ACIDS and their platinum-metal derivatives feature extensively in homogeneous catalysis systems;[2-8] moreover the ligand characteristics of carboxylate anions, and the structural features of many platinum-metal carboxylate complexes are of considerable theoretical interest. Therefore, as part of a more extensive study of methods for the synthesis of platinum-metal tertiary phosphine complexes, we have developed a convenient general route to a substantial class of platinum-metal complexes containing carboxylate and triphenylphosphine ligands. Complexes of this type have previously been synthesised in small numbers by a variety of routes; these include addition of triphenylphosphine to metal carboxylates,[3,9-13] reaction of platinum-metal halide–triphenylphosphine complexes with alkali-metal[4] or silver carboxylates,[14-16] and the oxidative addition of carboxylic acids to $d^8$ or $d^{10}$ transition-metal ions. The last technique, which has recently been employed to prepare the carboxylato-derivatives $Ru(OCOR)_2(CO)_2(PPh_3)_2$,[17,18] $Ru_2(OCOR)_2(CO)_4(PPh_3)_2$,[18] $Os(OCOH)_2(CO)_2(PPh_3)_2$,[19] $RhHCl(OCOR)(PPh_3)_2$,[20] $IrHCl(OCOR)(CO)(PPh_3)_2$,[14,21] $IrH(OCOCF_3)_2(CO)(PPh_3)_2$,[14] $IrHCl(OCOR)(PPh_3)_2$,[21] and $PtH(OCOCF_3)(PPh_3)_2$,[22] is similar to that employed in the present work.

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We now find[23] that most hydrido- and/or low oxidation state triphenylphosphine derivatives containing $d^6$, $d^8$, or $d^{10}$ platinum-metal ions react cleanly with carboxylic acids, under relatively mild conditions, to afford an extensive variety of new carboxylato-complexes. In addition the technique provides improved syntheses for some previously known carboxylato-derivatives. Some precursors, particularly carbonyl hydride complexes of osmium, do not react with alkyl or aryl carboxylic acids under the conditions employed in this work, but do react with perfluorocarboxylic acids in boiling benzene to afford perfluorocarboxylato-derivatives.

*Mode of Co-ordination of Carboxylate Ligands: Infrared Data.*—Many of the complexes prepared in this work tend to dissociate in solution, particularly in the presence of oxygen, and meaningful molecular weight data are frequently difficult to obtain. However the measurements made strongly support the assignment of monomeric structures in all cases, and thus exclude the presence of bridging carboxylate ligands in solution at least. The alternative modes of co-ordination, unidentate and bidentate (chelate), were distinguished by i.r. spectroscopy; salts containing carboxylate anions were identified and characterised by i.r. and conductivity measurements. I.r.-active vibrations $\nu(OCO)$ associated with carboxylate ligands, $RCO_2^-$, give rise to bands in the region 1300—1700 cm$^{-1}$; those attributed to $\nu(OCO)_{sym}$ are frequently obscured by bands arising from other organic ligands (in the present instance $PPh_3$) and for this reason are sometimes difficult to detect. In the present work some assignments are tentative and several conflict with previously published data (see Tables). Values of $\nu(OCO)_{asym}$ and $\nu(OCO)_{sym}$ for uni- and bi-dentate carboxylate ligands, $RCO_2^-$, are dependent upon the electronic nature of the group R, the properties of the central metal ion, and possibly the identity of the *trans*-ligands present.[24] It is therefore difficult to give meaningful characteristic frequency ranges for bands associated with OCO stretching modes of carboxylate ligands.

The characteristic frequency ranges given in Table 1 were determined empirically from data provided by the present work, and cannot be expected to form a rigorous basis for future assignments. However it is encouraging to note that they are consistent with recently reported data for a substantial range of uni- and bi-dentate carboxylate derivatives of the platinum metals.[2,4,11,15,16,21]

TABLE 1

Characteristic frequency ranges for unidentate and bidentate carboxylate ligands, $RCO_2$

| R | | $\nu(OCO)_{asym}$ | $\nu(OCO)_{sym}$ | $\Delta\nu$ |
|---|---|---|---|---|
| Fluoroalkyl | | | | |
| | chelate | 1610—1660 | 1430—1440 | 175—215 |
| | unidentate | 1650—1710 | 1390—1440 | 240—310 |
| Alkyl/aryl | | | | |
| | chelate | 1490—1540 | 1400—1470 | 40—120 |
| | unidentate | 1580—1650 | 1310—1390 | 210—270 |

The values of $\nu(OCO)_{asym}$ and $[\nu(OCO)_{asym} - \nu(OCO)_{sym}]$ afford the most sensitive indication of the mode of carboxylate co-ordination. Bidentate carboxylates have values of $\nu(OCO)_{asym}$ and $\nu(OCO)_{sym}$ close to those found in the corresponding free ion whereas unidentate carboxylates have $\nu(OCO)_{asym}$ at substantially higher frequencies and thus give larger values of $[\nu(OCO)_{asym} - \nu(OCO)_{sym}]$.[24] Our assignments of uni- and bi-dentate carboxylates are based on these criteria. Participation in hydrogen bonding by the unco-ordinated oxygen atom of a unidentate carboxylate ligand leads to partial equalisation of the OCO bond orders, and a resultant decrease in the value of $\nu(OCO)_{asym}$. This behaviour has recently been reported for a number of unidentate carboxylate complexes including $Pd(OCOMe)_2(Et_2NH)_2$[13] and $Ni(OCOMe)_2(H_2O)_4$[25] and, in the present work, is observed to occur with the acetic acid adducts $Rh(OCOMe)(CO)(PPh_3)_2,0{\cdot}5MeCO_2H$ and $IrH_2(OCOMe)(PPh_3)_3,MeCO_2H$.

*Ruthenium Carboxylate Complexes.*—$RuH(OCOR)(PPh_3)_3$. These hydrido(carboxylato)-derivatives of ruthenium(II) have previously been prepared by prolonged reaction of $RuCl_2(PPh_3)_3$ with sodium carboxylate and molecular hydrogen or sodium hypophosphite in boiling methanol, and have been found to act as powerful catalysts for the hydrogenation of terminal olefins.[2] We now find that these complexes can be prepared from $RuH_2(PPh_3)_4$ or, more conveniently, from $RuCl_3,3H_2O$ in rapid efficient single-step syntheses. Preparation from $RuH_2(PPh_3)_4$ involves reaction of this precursor with the appropriate carboxylic acid in boiling 2-methoxyethanol; synthesis from ruthenium trichloride is achieved by rapid successive addition of this reagent, the carboxylic acid, and potassium hydroxide to a solution of triphenylphosphine in vigorously boiling ethanol. Both syntheses afford the required product as microcrystalline precipitates. The spectroscopic data for the hydrido-complexes $RuH(OCOR)(PPh_3)_3$ are essentially in agreement with those previously reported[2] and are compatible with the distorted octahedral structure (I) found by *X*-ray crystallography[26] for the acetato-derivative, $RuH(OCOMe)(PPh_3)_3$.

$RuCl(OCOR)(CO)(PPh_3)_2$. The hydrido-complex, $RuHCl(CO)(PMe_2Ph)_3$, has been shown[27] to react with carboxylic acids in cold ether suspension to yield unidentate carboxylate derivatives $RuCl(OCOR)(CO)(PMe_2Ph)_3$ [stereochemistry (II)]. We now find that the analogous triphenylphosphine complex $RuHCl(CO)(PPh_3)_3$ will undergo a similar reaction with carboxylic acids; however the more vigorous conditions necessary to induce attack on this very insoluble precursor lead

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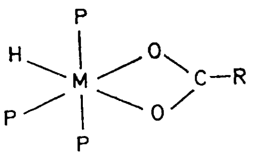
to the formation of chelate carboxylate derivatives, RuCl(OCOR)(CO)$(PPh_3)_2$. These pale yellow, air-stable complexes are monomeric in benzene and show no evidence of appreciable ligand dissociation. Their i.r. spectra contain bands attributable to chelate carboxylate ligands, and a band at *ca.* 1950 cm$^{-1}$ assigned to ν(CO). The latter result suggests the presence of carbonyl *trans* to chloride or carboxylate but there is insufficient spectroscopic evidence to distinguish between two possible structures (III) and (IV).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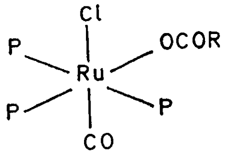
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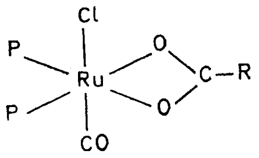
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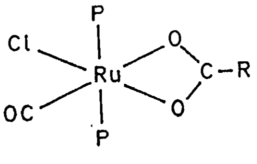
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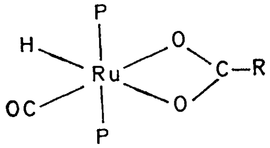
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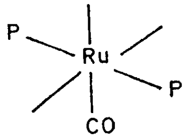
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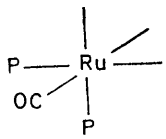
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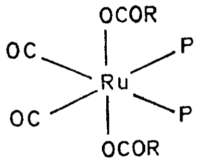
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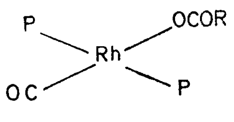
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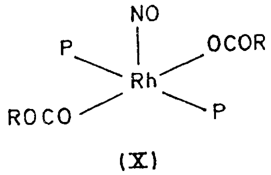
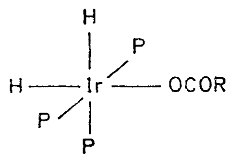

(X)


(XI)

RuH(OCOR)(CO)$(PPh_3)_2$. The dihydrido-complex $RuH_2(CO)(PPh_3)_3$ reacted with weak carboxylic acids ($pK_a > ca.$ 4·2) in boiling 2-methoxyethanol to form hydrido(carboxylato)-derivatives RuH(OCOR)(CO)$(PPh_3)_2$. In each instance a molecule of triphenylphosphine is displaced to accommodate the chelate carboxylate ligand. These white crystalline complexes are air-sensitive; they decompose slowly in the solid state and more rapidly when dissolved in chlorinated solvents. Their i.r. spectra contain bands at *ca.* 2000 and 1925 cm$^{-1}$ attributable to ν(RuH) and ν(CO) respectively, together with bands indicative of chelate carboxylate ligands. The stereochemistry (V) can be assigned unambiguously to these complexes on the evidence of their high-field n.m.r. spectra [triplet *ca.* τ 26; *J*(PH) *ca.* 20 Hz].

$Ru(OCOR)_2(CO)(PPh_3)_2$. Carboxylic acids with $pK_a < ca.$ 4·2 ($RCO_2H$; $R = p\text{-}C_6H_4Cl, p\text{-}C_6H_4{\cdot}NO_2$) react with $RuH_2(CO)(PPh_3)_3$ in boiling 2-methoxyethanol to form dicarboxylato-derivatives $Ru(OCOR)_2(CO)(PPh_3)_2$. The dicarboxylates all show a ν(CO) band at *ca.* 1960 cm$^{-1}$ together with bands attributable to uni- and bi-dentate carboxylate ligands. On the basis of this evidence stereochemistry (VI) is postulated; structure (VII) is a less-favoured alternative (the two carboxylate ligands share the three ' vacant ' co-ordination sites).

$Ru(OCOR)_2(CO)_2(PPh_3)_2$. Members of this series have previously been prepared by reaction of $Ru(CO)_3(PPh_3)_2$ with carboxylic acids in benzene, and by treatment of the carboxylates RuH(OCOR)$(PPh_3)_3$ with carbon monoxide.[2] We have now used the reaction of $Ru(CO)_3(PPh_3)_2$ with carboxylic acids in boiling 2-methoxyethanol to confirm and extend this series of complexes. The products are white or pale yellow, air-stable crystalline solids; their i.r. spectra show bands at *ca.* 2050 and 1980 cm$^{-1}$ attributable to *cis*-carbonyl ligands, together with bands characteristic of unidentate carboxylate groups. In agreement with previous workers we assign stereochemistry (VIII) to these complexes.[18]

*Osmium Carboxylate Complexes.*—OsH(OCOR)$(PPh_3)_3$. These hitherto unknown osmium analogues of Wilkinson's selective hydrogenation catalysts RuH(OCOR)$(PPh_3)_3$ were prepared by reaction of the tetrahydride $OsH_4(PPh_3)_3$ with alkyl carboxylic acids in boiling 2-methoxyethanol. Aryl carboxylic acids also reacted with this osmium precursor but pure complexes could not be isolated from the product mixture.

The complexes OsH(OCOR)$(PPh_3)_3$ are yellow crystalline solids and are similar to their ruthenium analogues in that they slowly darken on exposure to air and rapidly decompose in solution. The i.r. spectra of the new complexes showed a band at *ca.* 2120 cm$^{-1}$ attributable to ν(OsH) together with bands characteristic of chelate carboxylate ligands. The high-field $^1H$ n.m.r. spectra comprise a quartet at *ca.* τ 32 (relative intensity 1) indicative of a single hydride ligand coupling with three apparently equivalent *cis*-phosphorus ligands; similar n.m.r. patterns have been established for the analogous ruthenium carboxylates.[2] *X*-Ray powder photographs of the ruthenium and osmium acetates MH(OCOMe)-

$(PPh_3)_3$ show them to be isomorphous. A distorted octahedral stereochemistry (I), similar to that established for the ruthenium acetate by *X*-ray crystallography,[26] is therefore suggested for the osmium carboxylates $OsH(OCOR)(PPh_3)_3$.

The precursors $OsH_2(CO)_2(PPh_3)_2$, $OsH_2(CO)(PPh_3)_3$, and $OsHCl(CO)(PPh_3)_3$ all react with perfluorocarboxylic acids in boiling benzene to give perfluorocarboxylate derivatives; the synthesis and investigation of these products will be discussed in a future paper. In contrast all attempts to induce reaction between the osmium carbonyl hydride precursors and weaker, non-fluorinated carboxylic acids were unsuccessful.

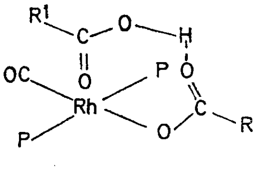
*Rhodium Carboxylate Complexes*.—$Rh(OCOR)(PPh_3)_3$. Complexes of this general stoicheiometry have recently been prepared by reaction of the dirhodium cation '$Rh_2^{4+}$' with triphenylphosphine and lithium carboxylates in methanol, and shown to act as catalysts in the homogeneous hydrogenation of olefins.[4] A bis(triphenylphosphine) derivative $Rh(OCOCF_3)(PPh_3)_2$ has also been obtained by reaction of $RhCl(PPh_3)_3$ with trifluoroacetic acid.[20]

We now find that the complexes of general formula $Rh(OCOR)(PPh_3)_3$ are formed on treating $RhH(PPh_3)_4$ with carboxylic acids in boiling ethanol, and deposit rapidly from the reaction solution as orange microcrystalline solids. The mother liquors from these reactions occasionally afforded small amounts of more soluble products which showed i.r. bands attributable to bidentate carboxylate ligands and were formulated as bis(triphenylphosphine) complexes, $Rh(OCOR)(PPh_3)_2$.

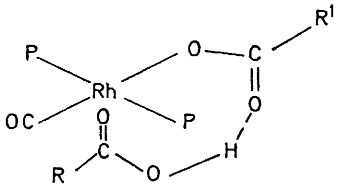
Molecular weight measurements taken for the complexes $Rh(OCOR)(PPh_3)_3$ by use of degassed benzene solutions gave values considerably below those required for monomer formulation. However other workers have recently reported substantial lowering of experimentally determined molecular weights, for these and related rhodium complexes, brought about by traces of dissolved oxygen.[4] It is highly probable that our low molecular weights similarly reflect the presence of residual traces of oxygen in the benzene solutions studied. The i.r. spectra indicate the presence of unidentate carboxylate ligands in each complex; accordingly we formulate these products as four-co-ordinate square-planar derivatives of rhodium(I), in agreement with a previous assignment.

$Rh(OCOR)(CO)(PPh_3)_2$. The rhodium(I) carbonyl derivatives of general formula $Rh(OCOR)(CO)(PPh_3)_2$ are conveniently prepared by reaction of $RhH(CO)(PPh_3)_3$ with carboxylic acids in boiling ethanol. These syntheses compare favourably with recently reported alternative routes involving carbonylation of the complexes $Rh(OCOR)(PPh_3)_3$ [4] or reaction of $[Rh(OCOR)(CO)_2]_2$ with excess of triphenylphosphine.[9] The new complexes are pale yellow air-stable crystalline solids, which show ν(CO) bands at *ca.* 1980 $cm^{-1}$. We formulate these products as four-co-ordinate, square-planar rhodium(I) derivatives (IX) containing unidentate carboxylate ligands, on the basis of assignments for $\nu_{asym}(OCO)$ and $\nu_{sym}(OCO)$ at *ca.* 1580—1620 and 1350—1415 $cm^{-1}$ respectively. Mitchell *et al.*[4] also formulate these complexes as four-co-ordinate species with unidentate carboxylate ligands on the basis of similar i.r. assignments, and this conclusion is supported by more recent work.[28] In contrast Csontos *et al.* make a different i.r. assignment [$\nu_{sym}(OCO) = 1470\ cm^{-1}$] for the acetate and interpret their observations in terms of a five-co-ordinate structure containing bidentate acetate ligands.[9] However the latter conclusion is probably incorrect since triphenylphosphine gives rise to a strong absorption at *ca.* 1470 $cm^{-1}$.

The acetate derivative, prepared from $RhH(CO)(PPh_3)_3$ in the presence of excess of acetic acid, crystallises as an adduct $Rh(OCOMe)(CO)(PPh_3)_2,0{\cdot}5MeCO_2H$ which on recrystallisation from dichloromethane–methanol loses acetic acid to give the unsolvated complex. The presence of hydrogen-bonded acetic acid in the adduct was established by i.r. spectroscopy. The i.r. spectrum showed a band at 1710 $cm^{-1}$ attributable to ν(CO) for the free acetic acid, and a shift of *ca.* 60 $cm^{-1}$ for the $\nu_{asym}(OCO)$ frequency of the co-ordinated acetate ion, the latter being characteristic of hydrogen bonding. The n.m.r. spectrum of the unsolvated acetate showed a single methyl resonance ($\tau$ 9·24; relative intensity 3) whereas that of the adduct showed a single methyl resonance ($\tau$ 8·65; relative intensity 4·5) midway between the values recorded for co-ordinated acetate ($\tau$ 9·24) and free acetic acid ($\tau$ 7·90). We believe that the apparent equivalence of acetate and acetic acid methyl groups in the n.m.r. spectrum of the adduct is attributable to a very labile exchange equilibrium, possibly of the form (XII) $\rightleftharpoons$ (XIII). However, attempts to confirm this by low-temperature $^1H$ n.m.r. studies were only partially successful; at the lowest accessible temperature (213 K) the combined methyl signal was extensively broadened but had not reached the decoalescence point. This broadening may simply reflect the increased viscosity of the solution at lower temperatures.



XII



XIII

$\{Rh[Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2]_2\}\{OCOR\}$. The rhodium(I) complexes $Rh(OCOR)(CO)(PPh_3)_2$ on treatment with two moles of bis(diphenylphosphino)ethane in cold benzene evolve one mole of carbon monoxide and afford the ionic derivatives $\{Rh[Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2]_2\}\{OCOR\}$ as pale yellow crystalline precipitates. Molar conductivities of 90—120 $ohm^{-1}\ cm^2\ mol^{-1}$ recorded for $10^{-3}$M-solutions

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[28] D. F. Steele and T. A. Stephenson, *J.C.S. Dalton*, 1972, 2161.

in acetonitrile confirm these complexes as 1 : 1 electrolytes. I.r. bands at 1590—1610 and 1350 $cm^{-1}$ are in accordance with the presence of carboxylate anions. Four-co-ordinate rhodium(I) will only form weak additional bonds to hard ligands such as carboxylates, and this factor, together with possible steric hindrance arising from the bulky phosphine ligands, is apparently sufficient to prevent appreciable carboxylate co-ordination in these complexes. However, molecular weight measurements taken in benzene solution suggest a high degree of ion-pair formation in non-polar solvents.

$Rh(OCOR)_2(NO)(PPh_3)_2$. Nitrosyltris(triphenylphosphine)rhodium reacts with carboxylic acids in boiling acetone to afford the dicarboxylato(nitrosyl) complexes $Rh(OCOR)_2(NO)(PPh_3)_2$ as green air-stable crystalline solids. These new complexes are the hitherto unknown carboxylate analogues of the well-established nitrosyl halide complexes $RhX_2(NO)(PPh_3)_2$ [29] and, like the latter, show $\nu$(NO) bands in their i.r. spectra at *ca.* 1610—1670 $cm^{-1}$. We tentatively assign, but are unable to prove, stereochemistry (X) for the new complexes.

*Iridium Carboxylate Complexes.*—$IrH_2(OCOR)(PPh_3)_3$. The reactions of acetic acid and some dibasic carboxylic acids with ' $IrH_3(PPh_3)_3$ ' have been briefly reported and the products characterised as the carboxylato-dihydrides $IrH_2(OCOR)(PPh_3)_3$ of indeterminate stereochemistry.[30] The trihydride ' $IrH_3(PPh_3)_3$ ' dissolved in the presence of acetic acid has been reported to act as a homogeneous catalyst for the hydrogenation of aldehydes and olefins, and isolation of a mixture of acetato-hydride complexes from this solution has been claimed.[6]

We now find that *mer*- and *fac*-$IrH_3(PPh_3)_3$ react with carboxylic acids in boiling 2-methoxyethanol to give identical series of products $IrH_2(OCOR)(PPh_3)_3$ in good yield. High-field n.m.r. spectra of these products (Table 3) confirm their stoicheiometry and indicate that in each case a single stereoisomer (XI) is formed. The acetate $Ir(OCOMe)H_2(PPh_3)_3$, unlike the higher homologues, was always deposited as a solvate. The product precipitated directly from the boiling 2-methoxyethanol as an acetic acid solvate $IrH_2(OCOMe)(PPh_3)_3,MeCO_2H$ which, on recrystallisation from dichloromethane–methanol, gave a methanol adduct $IrH_2(OCOMe)(PPh_3)_3$,-MeOH. The acetic acid solvate is characterised by an i.r. band at 1730 $cm^{-1}$ due to $\nu$(CO) for the acetic acid and a lowering of the asymmetric stretching frequency for co-ordinated acetate by *ca.* 42 $cm^{-1}$; this frequency shift is in accord with the presence of acetate–acetic acid hydrogen bonding interactions. The n.m.r. spectrum of the acetic acid adduct shows two methyl resonances of equal intensity, attributable to acetate ligand ($\tau$ 8·28) and acetic acid ($\tau$ 8·12). The presence of two discrete methyl resonances indicates that a dynamic exchange process of the type suggested for the rhodium(I) acetate, Rh-$(OCOMe)(CO)(PPh_3)_2,0{\cdot}5MeCO_2H$, is not occurring in the iridium(III) derivative. The methanol adduct $IrH_2(OCOMe)(PPh_3)_3$,MeOH is characterised by a broad i.r. hydroxyl band at 3300 $cm^{-1}$ and an extra methyl resonance ($\tau$ 6·70, relative intensity 3) in the $^1H$ n.m.r. spectrum, but does not show any appreciable lowering of the asymmetric stretching vibration $\nu_{asym}$(OCO). *mer*- and *fac*-$IrH_3(PPh_3)_3$ react with acetic acid neat or in boiling ethanol or 2-methoxyethanol to yield samples of $IrH_2(OCOMe)(PPh_3)_3$ which differ only in the nature and degree of solvation. All attempts to obtain di- or triacetates from these reactions were unsuccessful. We were thus unable to substantiate a previous report [6] that the reaction of ' $IrH_3(PPh_3)_3$ ' with acetic acid afforded a mixture of hydridic complexes.

*Reaction of* $IrH(CO)(PPh_3)_3$ *with Carboxylic Acids.*—The reactions of $IrH(CO)(PPh_3)_3$ with alkyl [20] and perfluoroalkyl [20,31] carboxylic acids have recently been described by several authors. The present investigation confirms and extends the previously reported work. With perfluorocarboxylic acids ($R_FCO_2H$) the final product observed is the hydride $IrH(OCOR_F)_2(CO)$-$(PPh_3)_2$, whereas the non-fluorinated acids give tricarboxylate complexes $Ir(OCOR)_3(PPh_3)_2$. The latter products are pale yellow, air-stable crystalline solids and their i.r. spectra indicate the presence of uni- and bidentate carboxylate ligands. They are soluble in dichloromethane but sparingly soluble in other organic solvents.

## EXPERIMENTAL

Triphenylphosphine complexes of the platinum metals were prepared as previously described. Carboxylic acids were used as purchased. Reactions were performed under nitrogen.

N.m.r. spectra were recorded on Varian HA 100 and Bruker HFX 90 spectrometers. I.r. spectra were taken on Perkin-Elmer 457 and 621 grating spectrometers for samples mulled in Nujol. M.p.s were measured in air (Kofler hot stage) or in a sealed capillary under nitrogen (Buchi m.p. apparatus). Results are in Tables 2 and 3.

*Ruthenium Complexes.*—*Hydridoacetatotris(triphenylphosphine)ruthenium*(II), $RuH(OCOMe)(PPh_3)_3$. *Method* (a). Acetic acid (0·5 ml) was added to a boiling suspension of dihydridotetrakis(triphenylphosphine)ruthenium (0·38 g) in ethanol (10 ml). The mixture was heated under reflux for 4 min, during which the solution cleared and precipitation commenced. After cooling the precipitate was filtered off, washed with methanol, water, and then methanol and dried *in vacuo* as yellow *crystals* (0·20 g, 63%).

*Method* (b). Ruthenium trichloride trihydrate (0·13 g) in warm ethanol (10 ml), acetic acid (0·5 ml), and potassium hydroxide (0·2 g) in warm ethanol (5 ml) were added successively to a boiling solution of triphenylphosphine (0·78 g) in ethanol (10 ml) and the mixture heated under reflux for 10 min. After cooling, the precipitate was washed successively with small volumes of acetone, water and methanol and dried *in vacuo* as yellow crystals (0·38 g, 80%).

The following were similarly prepared by method (b): *hydridopropionatotris(triphenylphosphine)ruthenium*(II) as yellow crystals (71%); *hydridobenzoatotris(triphenylphos-*

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[29] S. D. Robinson and M. F. Uttley, *J. Chem. Soc.* (*A*), 1971, 1254.

[30] M. Angoletta and A. Araneo, *Gazzetta*, 1963, **93**, 1343.

[31] P. C. Kong and D. M. Roundhill, *Inorg. Chem.*, 1972, **11**, 1437.

TABLE 2

M.p.s and analyses

| Complex | R | M.p./°C | C (%) | H (%) | P (%) | X (%) | *M* |
|---|---|---|---|---|---|---|---|
| $RuH(OCOR)(PPh_3)_3$ | Me [a] | 222—223 | 70·8(70·95) | 5·2(5·2) | 9·5(9·8) | | |
| | Me | | 70·65(70·95) | 5·1(5·2) | | | |
| | Et | 230—231 | 71·05(71·15) | 5·5(5·35) | 9·6(9·65) | | |
| | Ph | 217—220 | 72·25(72·55) | 5·05(5·1) | 9·05(9·2) | | |
| | $o$-$MeC_6H_4$ | 219—221 | 72·45(72·7) | 5·15(5·2) | 9·1(9·1) | | |
| | $p$-$MeC_6H_4$ | 222—223 | 72·75(72·7) | 5·15(5·2) | 8·7(9·1) | | |
| | $p$-$MeO{\cdot}C_6H_4$ | 220—221 | 70·85(71·6) | 4·85(5·15) | | | |
| | $p$-$ClC_6H_4$ | 223—224 | 70·4(70·15) | 4·9(4·8) | 9·15(8·9) | | |
| | $p$-$NO_2{\cdot}C_6H_4$ | 196—198 | 69·45(69·45) | 5·0(4·8) | | 1·25(1·35)N | |
| $RuCl(OCOR)(CO)(PPh_3)_2$ | Me | 242—243 | 63·3(62·6) | 4·7(4·45) | | | |
| | Et | 244—245 | 63·7(63·05) | 5·0(4·65) | | | |
| | Ph | 257—260 | 65·3(65·2) | 4·65(4·35) | 7·95(7·65) | 4·85(4·4) Cl | |
| | $o$-$MeC_6H_4$ | 238—241 | 65·3(65·55) | 4·6(4·55) | | | 796(823) |
| | $p$-$MeO{\cdot}C_6H_4$ | 250—253 | 64·4(64·3) | 4·7(4·45) | | | |
| | $p$-$ClC_6H_4$ | 258—260 | 62·65(62·55) | 4·0(4·05) | | | 873(843) |
| | $p$-$NO_2{\cdot}C_6H_4$ | 255—259 | 62·2(61·8) | 4·2(4·0) | | 1·4(1·65)N | 781(853) |
| $RuH(OCOR)(CO)(PPh_3)_2$ | Me | 181—183 | 65·4(65·6) | 5·0(4·8) | 9·65(8·7) | | |
| | Et | 180—181 | 65·5(66·0) | 5·1(5·0) | 8·55(8·5) | | |
| | $p$-$MeC_6H_4$ | 202—204 | 68·25(68·45) | 5·1(4·85) | | | 727(789) |
| | $p$-$MeO{\cdot}C_6H_4$ | 199—200 | 66·3(67·05) | 4·55(4·75) | | | |
| $Ru(OCOR)_2(CO)(PPh_3)_2$ | $p$-$ClC_6H_4$ | 198—202 | 62·9(63·5) | 4·05(3·95) | | 7·05(7·35) Cl | |
| | $p$-$NO_2{\cdot}C_6H_4$ | 147—149 | 62·5(62·1) | 4·4(3·8) | | 2·55(2·85) N | |
| $Ru(OCOR)_2(CO)_2(PPh_3)_2$ | Me | 214—216 | 63·2(63·05) | 4·25(4·55) | | | |
| | $p$-$ClC_6H_4$ | 228—238 | 62·7(62·9) | 3·75(3·85) | | | |
| | $p$-$NO_2{\cdot}C_6H_4$ | 245—248 | 61·0(60·65) | 3·85(3·85) | | 2·65(2·85) N | 1074(1013) |
| $OsH(OCOR)(PPh_3)_3$ | Me | 221—222 | 64·45(64·8) | 5·5(4·7) | 9·7(8·95) | | |
| | Et | 222—228 | 64·9(65·0) | 5·05(5·05) | 8·7(8·8) | | |
| $Rh(OCOR)(PPh_3)_3$ | Me | 208—209 | 70·75(70·9) | 5·0(5·1) | | | |
| | Et | 208—211 | 70·8(71·1) | 5·0(5·2) | 9·4(9·65) | | |
| | $p$-$ClC_6H_4$ | 193—195 | 69·7(70·1) | 4·8(4·75) | | 3·8(3·4) Cl | 500(1044) |
| | $p$-$NO_2{\cdot}C_6H_4$ | 183—185 | 68·35(69·4) | 4·4(4·7) | | 1·6(1·35) N | |
| $Rh(OCOR)(CO)(PPh_3)_2$ | Me | | 65·25(65·55) | 4·7(4·65) | | | |
| | Me [b] | | 64·95(64·5) | 5·2(4·75) | 8·35(8·3) | | 786(745) |
| | Et | 150—152 | 65·4(65·95) | 4·95(4·85) | 8·6(8·5) | | |
| | $p$-$MeC_6H_4$ | 172—174 | 68·0(68·35) | 5·0(4·7) | | | 619(790) |
| | $p$-$MeO{\cdot}C_6H_4$ | 176—178 | 66·8(67·0) | 4·8(4·6) | | | |
| | $p$-$ClC_6H_4$ | 177—178 | 65·05(65·15) | 4·2(4·25) | | 4·65(4·35) Cl | |
| | $p$-$NO_2{\cdot}C_6H_4$ | 210—211 | 64·4(64·3) | 3·95(4·15) | | 1·5(1·7) N | 736(821) |
| $Rh(OCOR)_2(NO)(PPh_3)_2$ | Me | 202—203 | 62·3(61·95) | 4·85(4·7) | | 1·6(1·8) N | |
| | Et | 205—207 | 63·45(62·8) | 5·0(5·0) | | 1·65(1·75) N | 663(803) |
| | $p$-$MeC_6H_4$ | 210—211 | 67·6(67·3) | 5·0(4·9) | | 1·35(1·4) N | |
| | $p$-$ClC_6H_4$ | 214 | 62·2(62·0) | 4·0(3·95) | | 1·35(1·45) N | |
| | $p$-$NO_2{\cdot}C_6H_4$ | 215—216 | 61·1(60·7) | 4·0(3·85) | | 4·0(4·25) N | |
| $Rh(Ph_2PCH_2CH_2PPh_2)_2OCOR$ | Me | | 67·8(67·65) | 5·6(5·35) | 12·5(12·9) | | |
| | $p$-$ClC_6H_4$ | 197—200 | 67·1(67·15) | 5·1(4·95) | | 3·4(3·3) Cl | |
| | $p$-$NO_2{\cdot}C_6H_4$ | 213—217 | 66·7(66·5) | 5·0(4·9) | | 1·2(1·3) N | 1015(1065) |
| $IrH_2(OCOR)(PPh_3)_3$ | Me [c] | | 63·5(63·45) | 5·2(4·95) | | | |
| | Me [d] | 150—152 | 63·5(63·85) | 4·25(5·05) | | | |
| | $p$-$MeC_6H_4$ | 170—172 | 66·15(66·7) | 5·1(4·9) | | | |
| | $p$-$ClC_6H_4$ | 151—153 | 65·0(64·55) | 4·35(4·55) | | 3·35(3·15) Cl | |
| | $p$-$NO_2{\cdot}C_6H_4$ | 164—167 | 64·25(64·0) | 4·65(4·5) | | 1·1(1·2) N | |
| $Ir(OCOR)_3(PPh_3)_2$ | Me | 224—229 | 56·9(56·4) | 4·3(4·3) | 7·15(6·95) | | |
| | Ph [e] | 186—187 | 58·4(58·2) | 4·15(4·0) | | | |
| | $p$-$MeC_6H_4$ [e] | 183—185 | 58·9(59·1) | 4·25(4·35) | | | |
| | $p$-$ClC_6H_4$ | 220—223 | 58·4(57·9) | 4·0(3·6) | | 8·7(9·0) Cl | |

[a] Prepared from $RuCl_3$, aq. directly. [b] Solvated with $MeCO_2H$ (0·5 mole). [c] Solvated with $MeCO_2H$ (1 mole). [d] Solvated with MeOH (1 mole). [e] Solvated with $CH_2Cl_2$ (1·5 mole). [f] Calculated figures in parentheses.

TABLE 3

I.r. and n.m.r. spectra

| Complex | R | $\nu$(MH) | $\nu$(CO) | $\nu_A$(OCO) | $\nu_B$(OCO) | $\Delta\nu$ | $\tau$(MH) | $J$(PH) | $J$(HH′) |
|---|---|---|---|---|---|---|---|---|---|
| RuH(OCOR)(PPh$_3$)$_3$ | Me | 2016 | | 1526 | 1449 | 77 | 28·6 | 27·0(q) | |
| | Et | 2020 | | 1519 | 1462 | 57 | 28·75 | 26·5(q) | |
| | Ph | 1986 | | 1518 | 1421 | 97 | | | |
| | *o*-MeC$_6$H$_4$ | 2004 | | 1514 | 1403 | 111 | | | |
| | | 1992 | | | | | | | |
| | *p*-MeC$_6$H$_4$ | 1979 | | 1503 | 1418 | 85 | 28·7 | 27·0(q) | |
| | *p*-MeO·C$_6$H$_4$ | 1981 | | 1502 | 1419 | 83 | 28·6 | 27·0(q) | |
| | *p*-ClC$_6$H$_4$ | 2018 | | 1518 | 1417 | 101 | | | |
| | | 1950 | | | | | | | |
| | *p*-NO$_2$·C$_6$H$_4$ | 2028 | | 1541 | 1422 | 119 | 28·7 | 27·0(q) | |
| RuCl(OCOR)(CO)(PPh$_3$)$_2$ | Me | | 1941 | 1507 | 1465 | 42 | | | |
| | Et | | 1943 | 1510 | 1470 | 40 | | | |
| | Ph | | 1935 | 1506 | 1446 | 60 | | | |
| | *o*-MeC$_6$H$_4$ | | 1929 | 1502 | 1413 | 89 | | | |
| | *p*-MeO·C$_6$H$_4$ | | 1950 | 1491 | 1439 | 52 | | | |
| | | | 1929 | | | | | | |
| | *p*-ClC$_6$H$_4$ | | 1962 | 1491 | 1439 | 52 | | | |
| | | | 1921 | | | | | | |
| | *p*-NO$_2$·C$_6$H$_4$ | | 1946 | 1528 | 1441 | 87 | | | |
| RuH(OCOR)(CO)(PPh$_3$)$_2$ | Me | 2000 | 1928 | 1528 | 1455 | 73 | 26·45 [a] | 20·0(t) | |
| | Et | 1994 | 1923 | 1526 | 1443 | 83 | 26·3 [a] | 20·0(t) | |
| | *p*-MeC$_6$H$_4$ | 2026 | 1929 | 1496 | 1428 | 68 | 26·3 [a] | 20·0(t) | |
| | *p*-MeO·C$_6$H$_4$ | 2008 | 1922 | 1493 | 1427 | 66 | 26·3 [a] | 20·0(t) | |
| | | 2026 | 1935 | | | | | | |
| | Ph | 2003 | 1924 | 1514 | 1425 | 89 | 26·35 [a] | 20·0(t) | |
| | | 1988 | | | | | | | |
| Ru(OCOR)$_2$(CO)(PPh$_3$)$_2$ | *p*-ClC$_6$H$_4$ | | 1965 | 1632 | 1326 | 306 | | | |
| | | | | 1503 | 1438 | 65 | | | |
| | *p*-NO$_2$·C$_6$H$_4$ | | 1966 | 1643 | 1328 | 315 | | | |
| | | | | 1534 | 1439 | 95 | | | |
| Ru(OCOR)$_2$(CO)$_2$(PPh$_3$)$_2$ | Me | | 2044 | 1613 | 1315 | 289 | | | |
| | | | 1973 | 1596 | | | | | |
| | *p*-ClC$_6$H$_4$ | | 2054 | 1613 | 1341 | 272 | | | |
| | | | 1982 | | | | | | |
| | *p*-NO$_2$·C$_6$H$_4$ | | 2066 | 1622 | 1340 | 271 | | | |
| | | | 1994 | 1600 | | | | | |
| OsH(OCOR)(PPh$_3$)$_3$ | Me | 2119 | | 1526 | 1457 | 69 | 32·45 | 21·0(q) | |
| | Et | 2124 | | 1518 | 1444 | 74 | 32·4 | 21·0(q) | |
| Rh(OCOR)(PPh$_3$)$_3$ | Me | | | 1598 | 1373 | 225 | | | |
| | Et | | | 1597 | 1379 | 218 | | | |
| | *p*-ClC$_6$H$_4$ | | | 1600 | 1350 | 250 | | | |
| | *p*-NO$_2$·C$_6$H$_4$ | | | 1580 | 1371 | 209 | | | |
| Rh(OCOR)(CO)(PPh$_3$)$_2$ | Me | | 1970 | 1604 | 1376 | 228 | | | |
| | Me [b] | | 1954 | 1543 | 1327 | 216 | | | |
| | Et | | 1976 | 1601 | 1382 | 219 | | | |
| | *p*-MeC$_6$H$_4$ | | 1963 | 1615 | 1354 | 261 | | | |
| | *p*-MeO·C$_6$H$_4$ | | 1962 | 1609 | 1359 | 250 | | | |
| | *p*-ClC$_6$H$_4$ | | 1962 | 1614 | 1357 | 257 | | | |
| | *p*-NO$_2$·C$_6$H$_4$ | | 1968 | 1610 | 1361 | 234 | | | |
| | | | | 1580 | | | | | |
| Rh(OCOR)$_2$(NO)(PPh$_3$)$_2$ | Me | | 1614 | 1600 | 1362 | 238 | | | |
| | Et | | 1639 | 1607 | 1376 | 231 | | | |
| | *p*-MeC$_6$H$_4$ | | 1624 | 1618 | 1348 | 270 | | | |
| | *p*-ClC$_6$H$_4$ | | 1627 | 1614 | 1344 | 270 | | | |
| | *p*-NO$_2$·C$_6$H$_4$ | | 1632 | 1601 | 1332 | 269 | | | |
| Rh[Ph$_2$P·CH$_2$·CH$_2$·PPh$_2$]$_2$OCOR | *p*-ClC$_6$H$_4$ | | | 1614 | 1354 | 260 | | | |
| | *p*-NO$_2$·C$_6$H$_4$ | | | 1624 | | | | | |
| | | | | 1590 | | | | | |
| IrH$_2$(OCOR)(PPh$_3$)$_3$ | Me [c] | 2198 | | 1553 | 1378 | 175 | 33·60 | | |
| | | 2157 | | | | | 21·1 | | |
| | Me [d] | 2195 | | 1595 | 1375 | 220 | | | |
| | | 2150 | | | | | | | |
| | *p*-MeC$_6$H$_4$ | 2178 | | 1598 | 1354 | 244 | 33·60 | Not resolved | 6 |
| | | | | | | | 20·52 | 139(d) 20(t) | |
| | *p*-ClC$_6$H$_4$ | 2192 | | 1603 | 1351 | 252 | 33·75 | 8(d) 20(t) | 6 |
| | | | | | | | 20·62 | 139(d) 20(t) | |
| | *p*-NO$_2$·C$_6$H$_4$ | 2176 | | 1619 | 1324 | 281 | 33·90 | 8(d) 20(t) | 5 |
| | | | | 1590 | | | 20·61 | 137(d) 20(t) | |
| Ir(OCOR)$_3$(PPh$_3$)$_2$ | Me | | | 1641 | 1360 | | | | |
| | | | | 1543 | | | | | |
| | Ph [e] | | | 1642 | 1331 | | | | |
| | | | | 1523 | 1414 | | | | |
| | *p*-MeC$_6$H$_4$ [e] | | | 1638 | 1344 | | | | |
| | | | | 1533 | 1414 | | | | |
| | *p*-ClC$_6$H$_4$ | | | 1639 | 1338 | | | | |
| | | | | 1521 | 1420 | | | | |

[a] N.m.r. spectra taken in $CH_2Cl_2$ solution, all other n.m.r. spectra taken in $CDCl_3$ solution. [b] Solvated with $MeCO_2H$ (0·5 mole). [c] Solvated with $MeCO_2H$ (1·0 mole). [d] Solvated with MeOH (1·0 mole). [e] Solvated with $CH_2Cl_2$ (1·5 mole).

*phine)ruthenium*(II) as yellow crystals (70%); *hydrido*-o-*toluatotris(triphenylphosphine)ruthenium*(II) as yellow crystals (33%); *hydrido*-p-*toluatotris(triphenylphosphine)ruthenium*(II) as yellow crystals (70%); *hydrido*-p-*methoxybenzoatotris(triphenylphosphine)ruthenium*(II) as yellow crystals (71%); *hydrido*-p-*chlorobenzoatotris(triphenylphosphine)-ruthenium*(II) as yellow crystals (23%); and *hydrido*-p-*nitrobenzoatotris(triphenylphosphine)ruthenium*(II) as brown crystals (63%).

*Chloroacetato(carbonyl)bis(triphenylphosphine)ruthenium*-(II), $RuCl(OCOMe)(CO)(PPh_3)_2$. Acetic acid (0·5 ml) was added to a boiling suspension of hydridochloro(carbonyl)-tris(triphenylphosphine)ruthenium (0·31 g) in 2-methoxyethanol (5 ml). The mixture was heated under reflux for 10 min, during which the solution cleared and precipitation commenced. Methanol (20 ml) was added and, after cooling, the precipitate was filtered off, washed successively with methanol, water, then methanol, and dried *in vacuo* as *yellow crystals* (72%).

The following were similarly prepared: *chloropropionato-(carbonyl)bis(triphenylphosphine)ruthenium*(II) as yellow crystals (79%); *chlorobenzoate(carbonyl)bis(triphenylphosphine)ruthenium*(II) as yellow crystals (85%); *chloro*-o-*toluato(carbonyl)bis(triphenylphosphine)ruthenium*(II) as yellow crystals (44%); *chloro*-p-*methoxybenzoato(carbonyl)bis(triphenylphosphine)ruthenium*(II) as yellow crystals (57%); *chloro*-p-*chlorobenzoato(carbonyl)bis(triphenylphosphine)ruthenium*(II) as yellow crystals (45%); and *chloro*-p-*nitrobenzoato(carbonyl)bis(triphenylphosphine)-ruthenium*(II) as yellow crystals (63%).

*Hydridoacetato(carbonyl)bis(triphenylphosphine)ruthenium*-(II), $RuH(OCOMe)(CO)(PPh_3)_2$. Acetic acid (0·5 ml) was added to a boiling suspension of dihydrido(carbonyl)tris-(triphenylphosphine)ruthenium (0·31 g) in 2-methoxyethanol (5 ml). The mixture was heated under reflux for 15 min during which the solution cleared. Methanol (20 ml) was added and, after cooling, the precipitate was washed successively with methanol, water, then methanol and dried *in vacuo* as white *crystals* (68%).

The following were similarly prepared: *hydridopropionato(carbonyl)bis(triphenylphosphine)ruthenium*(II) as white crystals (63%); *hydrido*-p-*methoxybenzoato(carbonyl)bis(triphenylphosphine)ruthenium*(II) as white crystals (54%); *hydrido*-p-*toluato(carbonyl)bis(triphenylphosphine)ruthenium*-(II) as white crystals (76%); *bis*-(p-*chlorobenzoato)carbonylbis(triphenylphosphine)ruthenium*(II) as white crystals (81%); and *bis*(p-*nitrobenzoato)carbonylbis(triphenylphosphine)ruthenium*(II) as white crystals (57%).

*Bis(acetato)dicarbonylbis(triphenylphosphine)ruthenium*(II), $Ru(OCOMe)_2(CO)_2(PPh_3)_2$. Acetic acid (1·0 ml) was added to a boiling suspension of tricarbonylbis(triphenylphosphine)ruthenium (0·24 g) in 2-methoxyethanol (5 ml). The mixture was heated under reflux for 15 min and the precipitate, which formed on cooling, was washed successively with methanol, water, then methanol and dried *in vacuo* as pale yellow *crystals* (75%).

*Bis*-(p-*chlorobenzoato)dicarbonylbis(triphenylphosphine)-ruthenium*(II) as white crystals (62%) and *bis*-(p-*nitrobenzoato)dicarbonylbis(triphenylphosphine)ruthenium*(II) as yellow crystals (84%) were similarly prepared.

*Osmium Complexes.—Hydridoacetatotris(triphenylphosphine)osmium*(II), $OsH(OCOMe)(PPh_3)_3$. Acetic acid (0·5 ml) was added to a boiling suspension of tetrahydridotris-(triphenylphosphine)osmium (0·33 g) in 2-methoxyethanol (5 ml). The mixture was heated under reflux for 10 min during which the solution cleared and precipitation commenced. After cooling, the precipitate was filtered off, washed successively with methanol, water, then methanol, and dried *in vacuo* as yellow *crystals* (57%).

*Hydridopropionatotris(triphenylphosphine)osmium*(II) was prepared similarly as yellow crystals (65%).

*Rhodium Complexes.—Acetatotris(triphenylphosphine)rhodium*(I), $Rh(OCOMe)(PPh_3)_3$. Acetic acid (0·5 ml) was added to a boiling suspension of hydridotetrakis(triphenylphosphine)rhodium (0·29 g) in ethanol (10 ml). The mixture was heated under reflux for 15 min during which precipitation occurred. After cooling, the precipitate was filtered off, washed successively with methanol, water, then methanol and dried *in vacuo* as orange *crystals* (55%).

The following were similarly prepared as orange crystals: *propionatotris(triphenylphosphine)rhodium*(I) (56%); p-*chlorobenzoatotris(triphenylphosphine)rhodium*(I), (79%); and p-*nitrobenzoatotris(triphenylphosphine)rhodium*(I) (86%).

*Acetato(carbonyl)bis(triphenylphosphine)rhodium*(I), $Rh(OCOMe)(CO)(PPh_3)_2$. Acetic acid (0·5 ml) was added to a boiling suspension of hydrido(carbonyl)tris(triphenylphosphine)rhodium (0·3 g) in ethanol (10 ml) and the mixture heated under reflux for 15 min. On cooling a precipitate formed. This was filtered off, washed successively with methanol, water, then methanol, and dried *in vacuo* as pale yellow *needles* (86%) of the adduct $Rh(OCOMe)(CO)(PPh_3)_2,\text{-}0{\cdot}5MeCO_2H$. Recrystallisation from dichloromethane–methanol gave the unsolvated product as yellow crystals.

The following were similarly prepared, all as unsolvated yellow crystals: *propionato(carbonyl)bis(triphenylphosphine)-rhodium*(I) (68%), p-*toluato(carbonyl)bis(triphenylphosphine)-rhodium*(I) (70%), p-*methoxybenzoato(carbonyl)bis(triphenylphosphine)rhodium*(I) (70%), p-*chlorobenzoato(carbonyl)bis-(triphenylphosphine)rhodium*(I) (97%), and p-*nitrobenzoato-(carbonyl)bis(triphenylphosphine)rhodium*(I) (97%).

*Bis(acetato)nitrosylbis(triphenylphosphine)rhodium*, $Rh(OCOMe)_2(NO)(PPh_3)_2$. Acetic acid (0·5 ml) was added to a boiling suspension of nitrosyltris(triphenylphosphine)-rhodium (0·2 g) in acetone (10 ml), and the mixture heated under reflux for 20 min. The precipitate which formed on cooling of the reaction solution was washed with methanol and recrystallised from dichloromethane–methanol as green *crystals* (54%).

The following were similarly prepared, all as green crystals: *bis(propionato)nitrosylbis(triphenylphosphine)rhodium* (55%), *bis*-(p-*chlorobenzoato)nitrosylbis(triphenylphosphine)rhodium* (66%), *bis*-(p-*nitrobenzoato)nitrosylbis(triphenylphosphine)rhodium* (93%), and *bis(toluato)nitrosylbis-(triphenylphosphine)rhodium* (45%).

*Bis*-(1,2-*bis[diphenylphosphino]ethane)rhodium*(I) *acetate*, $[Rh(Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2)_2][OCOMe]$. 1,2-Bis(diphenylphosphino)ethane (0·1 g) was added to a suspension of acetato(carbonyl)bis(triphenylphosphine)rhodium (0·1 g) in benzene (3 ml). Rapid evolution of gas occurred and the suspension cleared. Then, after a few seconds, precipitation commenced. After 30 min the precipitate was filtered off, washed with a small volume of benzene, and dried *in vacuo* as orange *crystals* (93%). The following were similarly prepared as yellow crystals: *bis*-[1,2-*bis(diphenylphosphino)ethane]rhodium*(I) p-*chlorobenzoate* (56%) and *bis*-[1,2-*bis(diphenylphosphino)ethane]rhodium*(I) p-*nitrobenzoate* (90%).

*Iridium Complexes.—Dihydrido(acetato)tris(triphenylphosphine)iridium*(III), $IrH_2(OCOMe)(PPh_3)_3$. Acetic acid (0·5 ml) was added to a boiling suspension of *mer*- or *fac*-trihydridotris(triphenylphosphine)iridium (0·2 g) in ethanol (10 ml) and the mixture heated under reflux for 30 min. The solution was concentrated by evaporation under reduced pressure and the precipitate of crude product which formed was filtered off, washed successively with methanol, water, then methanol, and dried *in vacuo* (80%).

Recrystallisation from dichloromethane–methanol gave the methanol adduct $IrH_2(OCOMe)(PPh_3)_3,MeOH$. Recrystallisation from dichloromethane–acetic acid gave the acetic acid adduct $IrH_2(OCOMe)(PPh_3)_3,MeCO_2H$. Both formed colourless crystals.

The following were similarly prepared but not recrystallised: *dihydro*-(p-*toluato*)*tris*(*triphenylphosphine*)*iridium*(III) as colourless crystals (75%); *dihydrido*-(p-*chlorobenzoato*)-*tris*(*triphenylphosphine*)*iridium*(III) as colourless crystals (78%); and *dihydrido*-(p-*nitrobenzoato*)*tris*(*triphenylphosphine*)*iridium*(III) as pale yellow crystals (82%).

*Tris*(*acetato*)*bis*(*triphenylphosphine*)*iridium*(III), $Ir(OCOMe)_3(PPh_3)_2$. Acetic acid (0·5 ml) and hydrido-(carbonyl)tris(triphenylphosphine)iridium (0·2 g) were heated together under reflux in benzene (5 ml) for 40 min. The solution was evaporated under reduced pressure and the residue crystallised from methanol as very pale yellow *crystals* (57%).

The following were similarly prepared: *tris*-(p-*chlorobenzoato*)*bis*(*triphenylphosphine*)*iridium* as yellow crystals (60%); *tris*(*benzoato*)*bis*(*triphenylphosphine*)*iridium*-1·5-*dichloromethane* as white crystals (55%) from dichloromethane–methanol; and *tris*-(p-*toluato*)*bis*(*triphenylphosphine*)*iridium*(III)-1·5-*dichloromethane* as white crystals (55%) from dichloromethane–methanol.

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