

# Carboxylato Complexes of the Platinum Group Metals

## A REVIEW OF RECENT DEVELOPMENTS

By Alan Dobson and Stephen D. Robinson

Department of Chemistry, King's College, London

*The recent rapid growth of interest in the carboxylato complexes of the platinum group metals has led to many significant advances. This article describes some of the more important chemical, structural and catalytic properties displayed by this class of compound.*

Oxygen donors are generally regarded as class 'a' ligands and, except in certain high oxidation-state oxy species, do not feature particularly extensively in the coordination chemistry of the platinum group metals. However, a small number of oxygen donor ligands have gained considerable importance in platinum metal chemistry, and carboxylate anions are the most common and versatile of these. Platinum metal carboxylato complexes are of relatively recent origin (1), most of our present knowledge having been gained within the past decade. Progress has been helped by X-ray diffraction techniques and magnetic studies, and has been encouraged by the promise of novel structural features and important catalytic applications. Surprisingly transition-metal carboxylates have rarely been reviewed (2, 3), and platinum-metal carboxylates in particular have not previously been surveyed. The carboxylate anions (general form  $\text{RCO}_2^-$ ) are versatile ligands capable of existing as counter anions or coordinating to the metal in unidentate, chelate or bridging modes. Their geometry is particularly suited to the last of these functions, and has permitted the isolation of bi- and trinuclear complexes often containing platinum metals in unusual oxidation states (i.e.  $\text{Ru}^{\text{I}}$ ,  $\text{Os}^{\text{I}}$ ,  $\text{Rh}^{\text{II}}$ , and  $\text{Pd}^{\text{I}}$ ). The versatility of carboxylate ligands is greatly enhanced by

the extensive variety of available groups, R; these include hydrogen, simple alkyl or aryl radicals, their perfluoro analogues and numerous more complex entities. The last-mentioned group includes polybasic carboxylic acids (particularly oxalic), amino acids and sequestering agents (i.e., EDTA). This review concentrates on those complexes containing simple carboxylate anions  $\text{RCO}_2^-$  (R=H, alkyl, aryl, perfluoro alkyl, etc.).

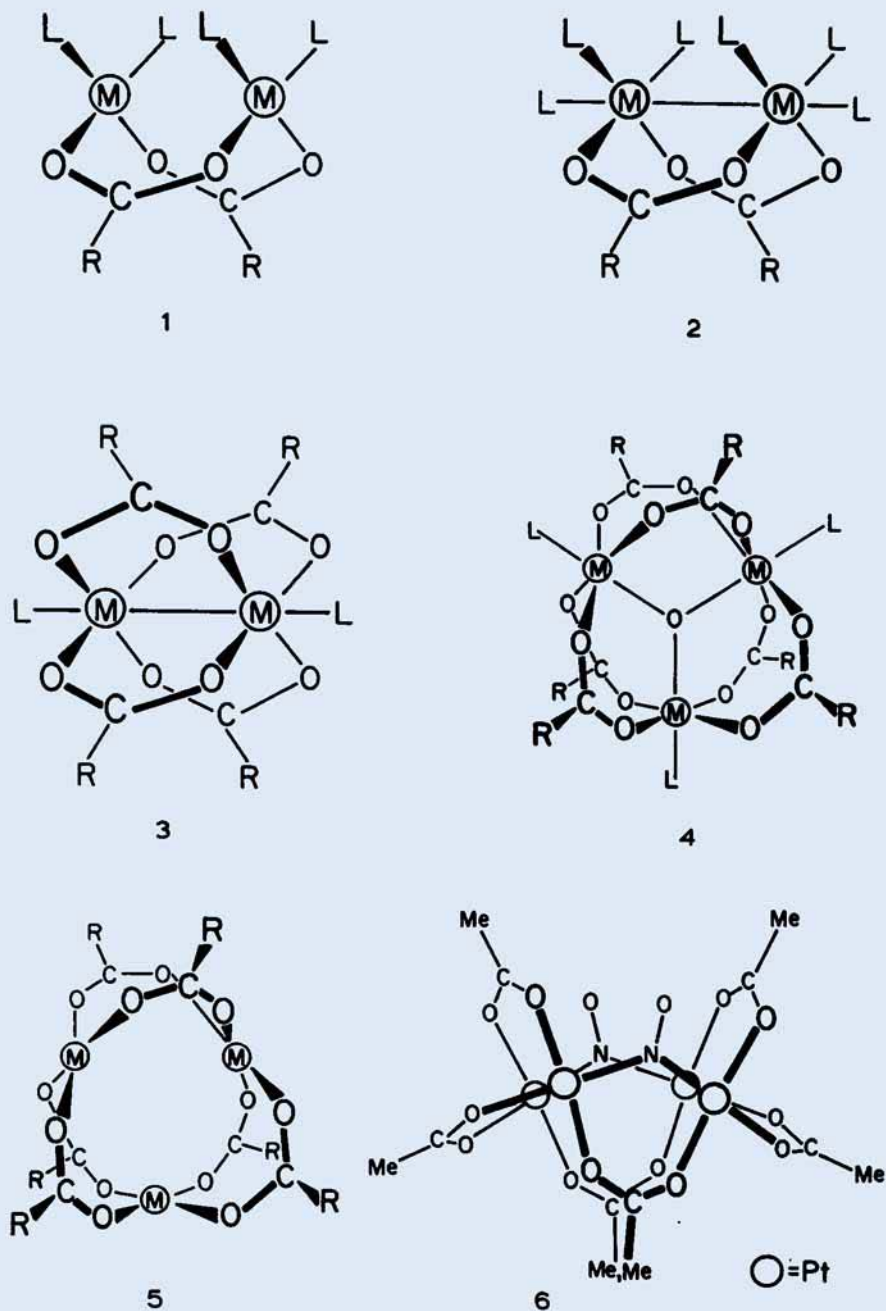
### Syntheses

General methods employed in the synthesis of platinum metal carboxylato complexes, based on the use of carboxylic acids and their alkali metal, silver or thallium salts have been surveyed in two recent papers (4, 5). More novel preparative procedures include insertion of carbon dioxide into metal-hydrogen (6) or metal-carbon bonds (7), reaction of vinyl or alkyl carboxylates with metal hydrides (8) and oxidative-addition of acid anhydrides,  $(\text{RCO}_2)_2\text{O}$ , with iridium(I) and platinum(0) complexes (9). Details of syntheses appropriate for individual complexes, including the many polynuclear species, can be obtained from the references given in later sections of this review. The carboxylato complexes are usually crystalline, air-stable species and frequently display good solubility in common organic solvents.

## Structure

The versatility of carboxylate ligands is amply demonstrated by the variety of structures observed for their platinum metal complexes. Salts containing  $(\text{RCO}_2^-)$  or H-bonded  $(\text{RCO}_2\text{HO}_2\text{CR}^-)$  counter anions are frequently found, particularly when R is a perfluoro alkyl or similar electron withdrawing group (10, 11, 12). Simple mononuclear complexes containing carboxylate anions bound in unidentate fashion, as in  $[\text{Rh}(\text{OCOMe})(\text{PPh}_3)_3]$  (13) and  $[\text{Rh}(\text{OCOPh})(\text{PPh}_3)_3]$  (7), or as chelate ligands in, for example,  $[\text{RuH}(\text{OCOMe})(\text{PPh}_3)_3]$  (14), frequently feature long metal-oxygen linkages. These are particularly pronounced when located *trans* to good  $\sigma$ -donor ligands, and further demonstrate the rather weak ligand character of carboxylate anions. The common occurrence of polynuclear carboxylato complexes reflects the good bridging geometry of carboxylate anions. Di-, tri- and occasional tetranuclear platinum-metal clusters with metal-metal interactions ranging from zero to formal triple bonds have been characterised by magnetic, spectroscopic and, in particular, X-ray diffraction studies (15). Some important structural types are illustrated in Figures 1 to 6. Binuclear carboxylato-bridged structures, Fig. 1, have been established by X-ray diffraction studies for  $[\text{Pd}_2(\text{OCOMe})_2(\text{n}^3-\text{C}_3\text{H}_5)_2]$  (16) and  $[\text{Pd}_2(\text{OCOMe})_2(2\text{-methylallyl-3-norbornyl})_2]$  (17). Relatively short Pd-Pd distances in these structures (2.94 and 2.96 Å respectively) have led to speculation concerning possible metal-metal interactions, but may simply reflect the steric constraints of the bridging ligands (16, 17). Similar 'folded' structures have been proposed for a range of binuclear complexes including the species  $[\text{M}_2(\text{OCOR})_2\text{X}_2(\text{EMe}_2\text{Ph})_2]$  ( $\text{M}=\text{Pd}, \text{Pt}; \text{X}=\text{Cl}, \text{Br}, \text{I}; \text{E}=\text{P}, \text{As}$ ) (18),  $[\text{M}_2(\text{OCOR})_2(\text{alkenyl-OCOR})_2]$  ( $\text{M}=\text{Pd}, \text{Pt}$ ) (19, 20),  $[\text{Pd}_2(\text{OCOR})_4\text{L}_2]$  ( $\text{L}=\text{PPh}_3, \text{AsPh}_3, \text{Me}_2\text{CO}$ ) (21),  $[\text{Rh}_2(\text{OCOR})_2(\text{C}_8\text{H}_{12})_2]$  (22),  $[\text{Rh}_2(\text{OCOR})_2(\text{CO})_4]$  (23) and  $[\text{Rh}_2(\text{OCOR})_2(\text{CO})_2(\text{PPh}_3)_2]$  (24). The diamagnetic

ruthenium(I) species  $[\text{Ru}_2(\text{OCOMe})_2(\text{CO})_4(\text{py})_2]$  (25) and the related osmium(I) complex  $[\text{Os}_2(\text{OCOMe})_2(\text{CO})_6]$  (26) have been shown to possess binuclear, metal-metal bonded, acetate-bridged structures of the type shown as Fig. 2. Metal-metal distances are 2.678 Å (Ru-Ru) and 2.731 Å (Os-Os) respectively. Similar structures have been postulated for other ruthenium(I) and osmium(I) complexes of stoichiometry  $[\text{M}_2(\text{OCOR})_2(\text{CO})_4(\text{L})_2]$  ( $\text{L}=\text{CO}, \text{py}, \text{amine}, \text{MeCN}, \text{PR}_3, \text{AsR}_3$ ) (27, 28, 29, 30) and probably exist in the binuclear palladium(I) complex  $[\text{Pd}_2(\text{OCOMe})_2(\text{C}_6\text{H}_8)(0.5\text{MeCOOH})]$  (31). Quadruple-bridged binuclear structures, Fig. 3, with metal-metal interactions ranging from weak antiferromagnetic spin-spin coupling to strong multiple bonds, occur frequently in transition metal chemistry and have aroused much interest (15). Established examples involving platinum group metals include the rhodium(II) species  $[\text{Rh}_2(\text{OCOH})_4(\text{H}_2\text{O})]$  (32),  $[\text{Rh}_2(\text{OCOMe})_4(\text{H}_2\text{O})_2]$  (33, 34) and  $[\text{Rh}_2(\text{OCOMe})_4(\text{PPh}_3)_2]$  (35), and the ruthenium cation  $[\text{Ru}_2(\text{OCOPr}^n)_4]^+$  in  $[\text{Ru}_2(\text{OCOPr}^n)_4\text{Cl}]$  (36). The revised rhodium-rhodium bond length (2.3855 instead of 2.45 Å) for  $[\text{Rh}_2(\text{OCOMe})_4(\text{H}_2\text{O})_2]$  is the shortest known, and indicates the presence of a full triple bond, thus confirming the most recent theoretical predictions (34). A very short ruthenium-ruthenium bond length (2.281 Å) and a two-fold crystallographic axis are reported for the  $[\text{Ru}_2(\text{OCOPr}^n)_4]^+$  ion; the latter is indicative of equivalent metal ions and, by implication, a non-integral oxidation state (+2.5) for the ruthenium (36). This conclusion is supported by magnetic data (see below). Species previously formulated as  $[\text{Ru}_2(\text{OCOR})_4]$  and  $[\text{Ru}_2(\text{OCOR})_4\text{L}_2]$  have now been recognised as oxygen-centred trinuclear species  $[\text{Ru}_3\text{O}(\text{OCOR})_6(\text{H}_2\text{O})_2(\text{OH})]$  and  $[\text{Ru}_3\text{O}(\text{OCOR})_6\text{L}_3]$  respectively ( $\text{L}=\text{py}, \text{PPh}_3$ , etc.) (37). However, one-electron electrolytic reduction of  $[\text{Ru}_2(\text{OCOR})_4\text{Cl}]$  is reported to yield authentic  $[\text{Ru}_2(\text{OCOR})_4]$  ( $\text{R}=\text{Me}, \text{Pr}^n$ ) in a non-crystalline form



*Figs. 1 to 6 Some of the polynuclear structures encountered in platinum metal carboxylate chemistry. Details of the illustrated complexes are given on pages 57 and 59*

(38, 39). The oxygen-centred, trinuclear 'basic' carboxylate structure, commonly found in transition-metal chemistry, has recently been established for a range of ruthenium (37, 40), rhodium (42) and iridium (42) complexes. An X-ray diffraction study has confirmed an oxygen-centred trinuclear structure, of the type shown in Fig. 4, for  $[\text{Ru}_3\text{O}(\text{OCOMe})_6(\text{PPh}_3)_3]$  (37, 43). In the absence of any direct metal-metal interactions (Ru-Ru distances about 3.3 Å), the diamagnetism of the complex and the non-integral oxidation state ( $+2\frac{2}{3}$ ) for ruthenium are rationalised in terms of a qualitative MO treatment of the  $\text{Ru}_3\text{O}\text{P}_3$   $\pi$ -electron system (43). Redox and substitution reactions (see below) lead to other products containing the  $[\text{M}_3\text{O}(\text{OCOR})_6]$  moiety. Further evidence for the delocalisation of electrons over the  $\text{Ru}_3\text{O}$  cluster is supplied by ESCA data for the species  $[\text{Ru}_3\text{O}(\text{OCOMe})_6(\text{py})_3]^{n+}$  ( $n=0-2$ ) (44).

The trinuclear structure, Fig. 5, devoid of metal-metal bonding, has been established for  $[\text{Pd}_3(\text{OCOMe})_6(0.5\text{H}_2\text{O})]$  (45) and a ligated version of this structure possibly exists in the trinuclear ruthenium complexes  $[\text{Ru}_3(\text{OCOR})_6\text{L}_3]$  ( $\text{L}=\text{H}_2\text{O}, \text{MeOH}, \text{py}$ ), (40). A similar trinuclear structure has been reported for tris( $\mu$ -acetato- $\mu$ -acetoximato palladium)0.5-benzene (46). The "platinum(II) acetate" obtained by reducing platinum(IV) in acetic acid/nitric acid contains a variety of nitrogenous complexes including the species  $[\text{Pt}_4(\text{OCOMe})_6(\text{NO})_2]$  for which the tetranuclear structure shown in Fig. 6, with bridging acetate and nitrosyl ligands, has been established (47). An alternative synthesis (48) leads to authentic platinum(II) acetate but the structure of this product has not been determined.

To date, tetranuclear platinum metal complexes, analogous to the cobalt species  $[\text{Co}_4\text{O}(\text{OCOR})_4]$ , have not been reported. Structural studies on carboxylate complexes including oxalate, amino acid and EDTA derivatives of the platinum group metals are comprehensively listed in an annual publication (49).

## Spectroscopic and Magnetic Studies

Infra-red spectral data, in particular the parameters  $\nu(\text{OCO})_{\text{asym}}$ ,  $\nu(\text{OCO})_{\text{sym}}$  and  $[\nu(\text{OCO})_{\text{asym}} - \nu(\text{OCO})_{\text{sym}}]$ , have been extensively employed in the assignment of carboxylate ligand bonding modes. Bidentate carboxylate ligands have values of  $\nu(\text{OCO})_{\text{asym}}$  and  $\nu(\text{OCO})_{\text{sym}}$  rather similar to those found for the corresponding free carboxylate anions, whereas unidentate carboxylate ligands have  $\nu(\text{OCO})_{\text{asym}}$  at substantially higher frequencies and thus display larger values of  $[\nu(\text{OCO})_{\text{asym}} - \nu(\text{OCO})_{\text{sym}}]$  (21, 50, 51). However, in several instances the situation is complicated by the occurrence of hydrogen-bonding between the non-coordinated oxygen atom of a unidentate carboxylate ligand and a solvate molecule leading to a reduction of  $\nu(\text{OCO})_{\text{asym}}$  (50). Moreover, the infra-red frequencies  $\nu(\text{OCO})_{\text{asym}}$  and  $\nu(\text{OCO})_{\text{sym}}$  are highly sensitive to the structure of the carboxylate group, the nature of the accompanying ligands and the identity of the central metal ion. In consequence considerable caution must be exercised in any attempt to deduce carboxylate bonding modes on the basis of infra-red data alone. Far infra-red and Raman data have been reported for the rhodium(II) complexes  $[\text{Rh}_2(\text{OCOR})_4]$  and  $[\text{Rh}_2(\text{OCOR})_4\text{L}_2]$  ( $\text{R}=\text{Me}, \text{Et}$ ;  $\text{L}=\text{H}_2\text{O}, \text{MeOH}, \text{Me}_2\text{SO}, \text{PPh}_3$ ); Raman active vibrations in the range 288 to 351  $\text{cm}^{-1}$  are attributed to rhodium-rhodium triple-bond stretching, infra-red bands at about 320 to 440  $\text{cm}^{-1}$  are assigned to  $\nu(\text{Rh}-\text{O})$  (52).

Very little work has been reported on the n.m.r. spectra of carboxylate ligands. However, variable-temperature n.m.r. has been used to demonstrate the rapid exchange of uni- and bi-dentate carboxylate ligands in the complexes  $[\text{M}(\text{OCOR})_2(\text{CO})(\text{PPh}_3)_2]$  ( $\text{M}=\text{Ru}, \text{Os}$ ;  $\text{R}=\text{Me}, \text{CF}_3$ ) (4, 5), and to study the dynamic stereo-chemistry of the dimeric palladium(II) and platinum(II) species  $[\text{Pd}_2(\text{OCOR})_2(\text{n}^3\text{-allyl})_2]$  and  $[\text{M}_2(\text{OCOR})_2\text{X}_2(\text{PMe}_2\text{Ph})_2]$  ( $\text{X}=\text{halide}$  or  $\text{OCOR}$ ) (18, 53).

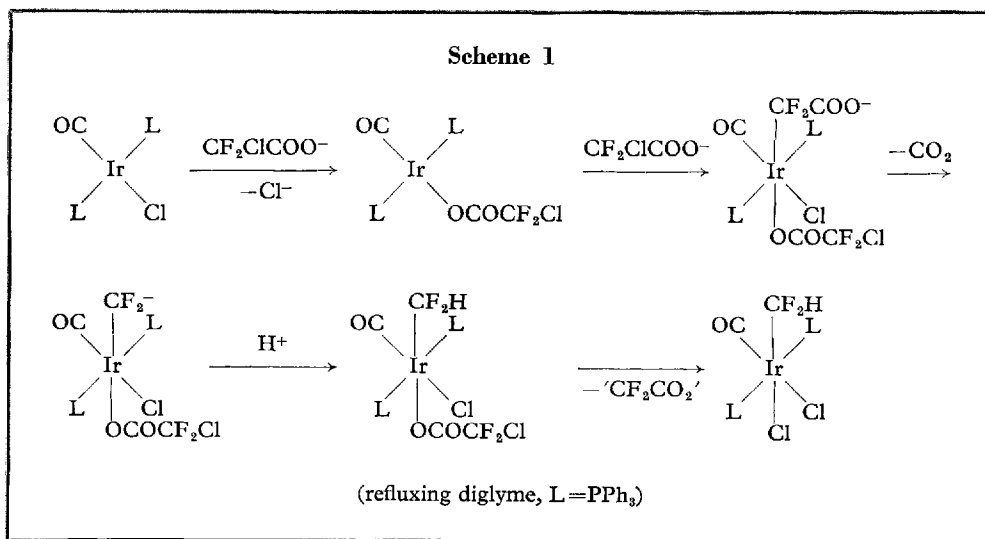
Electronic spectra have been recorded and interpreted for the binuclear species  $[\text{Rh}_2(\text{OCOR})_4\text{L}_2]$  (54),  $[\text{Rh}_2(\text{OCOMe})_4(\text{H}_2\text{O})_2]^+$  (38) and  $[\text{Ru}_2(\text{OCOMe})_4\text{Cl}]$  (36, 38), and the trinuclear products  $[\text{M}_3\text{O}(\text{OCOR})_6\text{L}_3]\text{X}$  ( $\text{M}=\text{Rh}, \text{Ir}, \text{Ru}$ ) (40, 41, 42).

Use of ESCA data in the study of the trinuclear systems has been noted above. Detailed magnetic susceptibility and e.p.r. spectra measurements for  $[\text{Ru}_2(\text{OCOBu}^n)_4\text{Cl}]$  indicate a quartet ground state and support the symmetrical structure deduced from crystallographic data (39). Magnetic data have also been reported for the trinuclear species  $[\text{M}_3\text{O}(\text{OCOMe})_6\text{L}_3]\text{X}$  (40, 42).

## Reactivity

Interesting and important results have been achieved in this highly promising area; however, studies are fragmented and much remains to be done. Known reactions encompass ligand substitution, ligand fragmentation and redox processes. The excellent leaving characteristics of carboxylate anions in general and perfluorocarboxylate anions in particular are reflected in a range of substitution and/or reductive elimination reactions. Thus  $[\text{RuH}(\text{OCOMe})(\text{PPh}_3)_3]$ ,  $[\text{Ru}_3\text{O}(\text{OCOMe})_6(\text{H}_2\text{O})_3][\text{OCOMe}]$  and  $[\text{Rh}_2(\text{OCOMe})_4]$ , the last in the presence of

acid, react with carbon monoxide under mild conditions to yield  $[\text{Ru}(\text{CO})_3(\text{PPh}_3)_2]$  (55),  $[\text{Ru}_3(\text{CO})_{12}]$  (56) and  $[\text{Rh}_6(\text{CO})_{16}]$  (56) respectively. The complexes  $[\text{Rh}_2(\text{OCOMe})_4]$ ,  $[\text{Ru}_3\text{O}(\text{OCOMe})_6(\text{H}_2\text{O})_3][\text{OCOMe}]$  and  $[\text{Ru}_2(\text{OCOMe})_4\text{Cl}]$  react with strong non-coordinating acids (such as  $\text{HBF}_4$ ) in hydroxylic media to afford air-sensitive solutions containing cationic species of high catalytic activity (41, 57, 58). The green solution formed in the rhodium system is now thought to contain the aquated cations  $[\text{Rh}_2(\text{OCOMe})_3]^+$  and  $[\text{Rh}_2(\text{OCOMe})_2]^{2+}$  rather than the species  $[\text{Rh}_2\text{aq}]^{4+}$  (38). Reaction of  $[\text{RuH}(\text{OCOMe})(\text{PPh}_3)_3]$  with fluoroboric acid in hot methanol affords the novel  $\pi$ -arene complex  $[\text{RuH}(\eta^6\text{-C}_6\text{H}_5\text{PPh}_2)(\text{PPh}_3)_2][\text{BF}_4]$  (59). The unusual versatility of carboxylato complexes in synthesis is dramatically illustrated by formation of the metal-metal bonded, acetylene-bridged, palladium(I) complex  $[(\eta^5\text{-C}_5\text{Ph}_5)\text{Pd}(\text{PhC}\equiv\text{CPh})\text{Pd}(\eta^5\text{-C}_5\text{Ph}_5)]$  (Pd-Pd 2.639 Å) from  $[\text{Pd}_3(\text{OCOMe})_6]$  and diphenylacetylene in methanol (60). The species  $[\text{M}_3\text{O}(\text{OCOMe})_6(\text{L})_3]\text{X}$  ( $\text{M}=\text{Ru}, \text{Rh}, \text{Ir}$ ;  $\text{L}=\text{H}_2\text{O}, \text{MeOH}$ ) frequently undergo substitution of the ligands L, with retention of the trinuclear cluster (40, 41, 42, 61). The trinuclear ruthenium complexes  $[\text{Ru}_3\text{O}(\text{OCOR})_6\text{L}_3]$  are unique in



their ability to undergo reversible loss of the central oxygen atom (40, 42). The scope for work on the reactivity of bound carboxylate ligands is illustrated (62) by the reaction of sodium chlorodifluoroacetate with Vaska's compound in refluxing diglyme (Scheme 1).

The redox behaviour of the complex cations  $[M_3O(OCOMe)_6L_3]^+$  ( $M = Ru, Rh, Ir; L = py, H_2O$ ) has been studied electrochemically, and redox products obtained using chemical and electrical methods (Scheme 2) (40, 42, 61). Other electrochemical studies include reduction of  $[Ru_2(OCOMe)_4Cl]$  to  $[Ru_2(OCOMe)_4]$  and oxidation of  $[Rh_2(OCOMe)_4]$  to  $[Rh_2(OCOMe)_4]^+$  (38).

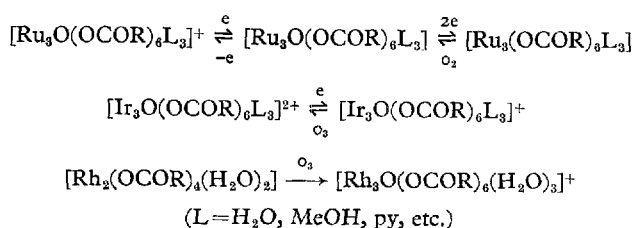
### Fixation of Carbon Dioxide

Current work on the fixation of carbon dioxide by transition metals has yielded several examples of  $CO_2$  'insertion' into platinum metal-hydrogen or carbon bonds. Products are either carboxylato derivatives  $[L_xMOCOR]$  ( $R = H, aryl$ ) or metal-carboxylic acids  $[L_xMCO_2H]$ . Thus carbon dioxide reacts with  $[RuH_2(PPh_3)_4]$  to yield  $[RuH(OCOH)(PPh_3)_3]$  (63) and with  $[RhPh(PPh_3)_3]$  to form  $[Rh(OCOPh)(PPh_3)_3]$  (7). The ruthenium complex has the expected formate structure in the solid state but shows some characteristics of a  $CO_2$  complex  $[RuH_2(CO_2)(PPh_3)_3]$  in solution (64). The reverse reaction, elimination of carbon dioxide from a formate or metalcarboxylic acid, probably occurs in the iridium (65) and platinum catalysed (66) decomposition of formic acid, and in the catalytic transfer of dihydrogen from formic acid to olefins by platinum metal salts (67). Work in this field has recently been reviewed (68).

### Catalytic Activity

Carboxylato complexes possess a combination of moderate stability and high

Scheme 2



ability which renders them particularly promising as homogeneous catalysts. Studies in this field have centred on palladium carboxylates, however increasing attention is now being given to carboxylates of the remaining five platinum metals, particularly rhodium and ruthenium.

Palladous acetate trimer has found use in the commercial synthesis of vinyl acetate from ethylene and acetic acid (69). Other reactions, too numerous to list fully, catalysed by palladium(II) acetate include oxidative coupling of arenes (70), oxidative arylation of olefins (71, 72), acetoxylation of aromatics (73, 74) and the oxidation of hexenes, cyclohexene and cyclohexadienes (75, 76). In the course of these last reactions the novel palladium(I) complex  $[Pd_2(OCOMe)_2(C_6H_8)(0.5 MeCOOH)]$  (77) and the polynuclear species  $[Pd_2(OCOMe)_2(C_6H_8)_2]$  and  $[Pd_3(OCOMe)_4(C_6H_8)_2]$  (75) were isolated. Equilibria between palladous acetate,  $[Pd_3(OCOMe)_6]$ , and sodium acetate in acetic acid involve the species  $Na_2[Pd_2(OCOMe)_6]$  and  $Na_2[Pd(OCOMe)_4]$  (78). Addition of an olefin (ol) leads to formation of  $Na[Pd_2(OCOMe)_5(ol)]$  and  $Na[Pd(OCOMe)_3(ol)]$  but not  $[Pd_2(OCOMe)_4(ol)_2]$  (79). The catalytic activity of palladium carboxylates has been discussed at length in recent books (80, 81) and review articles (82, 83). Several new catalytic reactions involving ruthenium and rhodium carboxylates have recently been reported. Thus selective hydrogenation of 1-alkynes to 1-alkenes, alkadienes to alkenes, and 1-alkenes to alkanes has recently been observed using  $[Rh(OCOPh)(C_8H_{12})(PPh_3)]$

(84),  $[\text{Ru}(\text{OCOME})_2(\text{PPh}_3)_2]$  or  $[\text{Rh}(\text{OCOME})(\text{PPh}_3)_3]$  (85), and  $[\text{RuH}(\text{OCOR})(\text{PPh}_3)_3]$  (55) respectively. Other hydrogenation catalysts include the complexes  $[\text{Rh}_2(\text{OCOME})_4]$  (86), and  $[\text{Rh}(\text{OCOR})(\text{PPh}_3)_3]$  (87), and the species obtained on treating ruthenium or rhodium carboxylates with strong non-coordinating acids (57, 58, 85). Inter- or intra-molecular hydrogen-transfer from alcohols to olefins and acetylenes are catalysed by  $[\text{Ru}_3\text{O}(\text{OCOME})_6][\text{OCOME}]$  (88) and  $[\text{RuH}(\text{OCOFCF}_3)(\text{CO})(\text{PPh}_3)_2]$  (89) respectively. Dehydrogenation of alcohols to aldehydes or ketones is catalysed by  $[\text{Ru}(\text{OCOFCF}_3)_2(\text{CO})(\text{PPh}_3)_2]$  (90). Other interest-

ing catalytic reactions include the carbonylation of amines in the presence of the ruthenium(I) species  $[\text{Ru}(\text{OCOME})(\text{CO})_2(\text{amine})_2]$  (29, 30) and the hydroformylation of olefins in the presence of the rhodium(I) complexes *trans*- $[\text{Rh}(\text{OCOR})(\text{CO})(\text{PR}_3)_2]$  (24). Very little has been reported on the catalytic activity of platinum, iridium and osmium carboxylates. However, decarbonylation of aldehydes by  $[\text{IrH}_2(\text{OCOME})(\text{PPh}_3)_3]$  and related species has been described (66).

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