CHEMISTRY OF BRIDGED CARBOXYLATE RUTHENIUM COMPLEXES. CRYSTAL STRUCTURES OF [Ru(PhCOO)(CO)$_2$(PhCOOH)]$_2$, [Ru(4-FC$_6$H$_4$COO)$_2$(CO)$_5$(H$_2$O)]$_2$ · 0.5 C$_6$H$_6$, AND [Ru$_2$(s-BuCO$_2$)$_2$(CO)$_4$(s-BuCO$_2$H)]$_2$

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Summary

Aliphatic and aromatic carboxylic acids react with Ru$_3$(CO)$_{12}$ to give bridging carboxylate complexes containing the structural core unit [Ru(μ_3-RCOO)(CO)$_2$]$_2$. The presence of an excess of acid results in side ligation of two carboxylic acid molecules, which are also hydrogen-bonded to the bridging carboxylate ligand; this structure was confirmed by X-ray crystallography. Most of the complexes readily form mono-aquato compounds one of which was investigated by X-ray crystallography. In the case of 2-methylbutyric acid a Ru tetramer complex, in which two core units are bound by two Ru–O–Ru bridges, was isolated; we suggest that this structural element constitutes the back-bone of the ruthenium carboxylate polymers that were obtained under the appropriate reaction conditions from most of the acids. The initial product of the reaction between Ru$_3$(CO)$_{12}$ and a carboxylic acid is [Ru(RCOO)(CO)$_3$]$_2$, which then reacts further. Its reactivity varies on going from straight chain to α-carbon branched chain aliphatic acids and to aromatic acids. Spectral and chemical evidence suggests an associative type mechanism for displacement of CO by other ligands in the primary product. The distribution and rates of formation of the products depend on the nature of the carboxylate ligand and the molar ratio of dodecacarbonyltriruthenium to acid and on whether the reaction is carried out in an open or a closed vessel.

Introduction

Our interest in the chemistry of dodecacarbonyltriruthenium(0) and carboxylic acids was prompted by the recent finding [1] of the catalytic addition reaction of carboxylic acids to alkynes (eq. 1).

$$RCOOH + R'C\equiv CR' \xrightarrow{Ru_3(CO)_{12}} RCOO(R')C=CHR' + RCOO(H)C=CR'_2 \qquad (1)$$
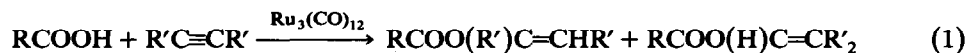
The products are E and Z vinyl esters accompanied by variable quantities of a rearranged vinyl ester isomer (eq. 1). A variety of alkynes and carboxylic acids were found to be reactive. Obviously, the understanding of this reaction calls for the study of the reaction of dodecacarbonyltriruthenium with carboxylic acids, and this is the subject of the present report.

The first extensive investigation of this reaction was carried out by Lewis et al. [2], who studied the behavior of formic, acetic, propionic and decanoic acids. Reactions of each of the above acids with $Ru_3(CO)_{12}$ yielded insoluble polymers, which were assigned the molecular formula $[Ru(RCOO)(CO)_2]_n$. The two infrared bands at ca. 1550 and 1400 cm^{-1} were assigned, respectively, to the asymmetric and symmetric carboxylate stretching vibration modes and were used to support a bridging μ_3-dihapto carboxylate structure. The bonding in the polymer and the mode of polymerization were not discussed. Under CO pressure the polymers yielded unstable dimers $[Ru(RCOO)(CO)_3]_2$, for which structure I was proposed [2]. With various ligands (L) both the polymers and the dimers were transformed into Ia.

(I)   (Ia)
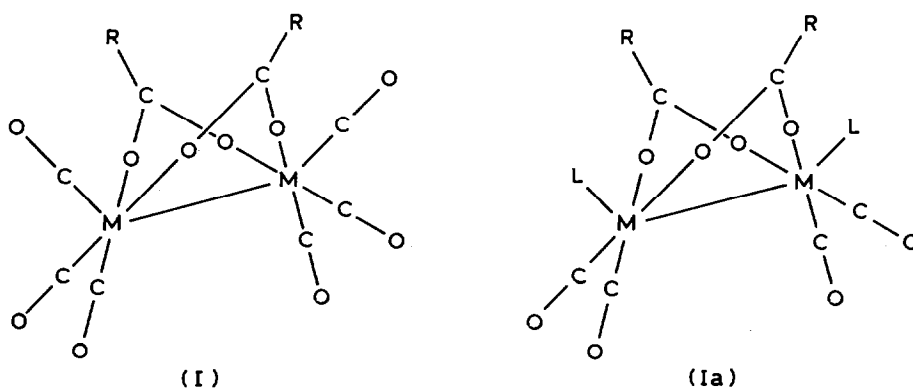
(M = Ru ; L = phosphines , amines , arsines)

Subsequently Schumann et al. prepared a series of dimers of type Ia by the direct reaction of $Ru_3(CO)_{12}$, carboxylic acids and phosphines [3,4]. An X-ray diffraction study of a butyric acid complex revealed the structure of di-(μ_3-butyrato)-bis[di-carbonyl(tri-t-butylphosphine)ruthenium(I)] [3], and the confirmation of this type of structure (Ia) validated Lewis' earlier structural proposal for the dimer I [2]. By hydrogenation of acetic acid with $H_4Ru_4(CO)_8(PBu_3)_4$, Bianchi et al. [5] obtained the complex $[Ru(MeCOO)(CO)_2(PBu_3)]_2$. Later, the same group prepared a variety of ruthenium acetato phosphine complexes by treating the acetato polymer with variable quantities of phosphines [6,7]. Recently Piacenti et al. [8] found that the chirality of the carboxylate ligand does not affect the stereochemical course of olefin hydrogenation. In our hands similar hydrogenation led to the formation of mono-nuclear phosphine complexes.

In an interesting variant of the reaction between dodecacarbonyltriruthenium and propionic acid, the latter was replaced by ethylene and water in THF [9]. the product was a bridging propionato complex, which must have resulted from a Reppe type hydroformylation in which the ruthenium complex served as a CO source.

Thus hitherto, in the absence of ligands, only polymers have been isolated from the reaction of $Ru_3(CO)_{12}$ and aliphatic carboxylic acids. Dimers of type I were reported [2] to decompose spontaneously to polymers with loss of CO.

Our work indicates that under the surface of this rather simple chemistry lies a rich system of reactions which involves generation of new transient and stable complexes, some having novel molecular structures. A clue to this comes from reaction 1, which generates the acetato insoluble polymer with acetic acid but gives a homogeneous solution with benzoic acid. The formation of vinyl esters (eq. 1) proceeds normally with both acids [1]. Furthermore, when reaction 1 is carried out with the acetato polymer, but in the presence of benzoic acid (and an alkyne), the expected vinyl benzoates were obtained but again no polymer formation could be detected. Obviously, aromatic acids, which were not examined previously, must differ from aliphatic acids in their reactions with dodecacarbonyltriruthenium. Furthermore, in contrast to the reported identical behavior of straight chain aliphatic acids [2], branching at the α-carbon of the acid markedly affects the nature of the products and the reactivity toward $Ru_3(CO)_{12}$.

A series of acids were investigated and iso-structural complexes are grouped and discussed under five separate types. Structural aspects will be discussed first, then the chemical behaviour of the system.

Structures

Type I: [Ru(RCOO)(CO)₃]₂

Complexes of this type were generated by all the acids examined in this study. Their stabilities depend on the nature of the carboxylic acid (vide infra), but, they are the most chemically reactive complexes of the present series, and no attempts were made to purify them for elemental analysis. Their structures were assigned by analogy to bis[(μ₃-acetato)(tricarbonyl)Ru] (I), isolated and identified by Lewis et al. [2]. The infrared spectra of type I complexes are characterized by four strong CO stretching bands above 2000 cm^{-1}. The band at 2100 cm^{-1} (or 2080 cm^{-1}) serves as a useful indicator for the presence of type I complexes in reaction mixtures. It is important to note that the locations of these bands are practically constant throughout the present series, and are not affected by change in the carboxylate ligand (Table 1). The relatively high frequencies imply weak Ru–CO bonds.

Type II: [Ru₂(RCOO)₂(CO)₅L]

Type II refers to unsymmetrially ligated ruthenium carboxylato dimer complexes. The most common ones are the mono-aquato complexes (L = H₂O) which were isolated as solids (Table 1). They are not the initial products of the reaction between $Ru_3(CO)_{12}$ and carboxylic acids, but are obtained during work-up of the reaction mixtures; it is, in fact, difficult to avoid their formation (vide infra). They are quite stable compounds and were recovered unchanged after column chromatography (silica).

This previously unknown type of complexes required structural characterization. The p-fluorobenzoate complex (11) was subjected to X-ray diffraction study (Fig. 1) [10]. It was found to have no internal symmetry. Each of the hexa-coordinated Ru atom forms a distorted octahedron, with angles of 171.3 and 159.8° for the C(4)–Ru(1)–Ru(18) and Ru(1)–Ru(18)–O(21) arrays, respectively (Table 6). The

TABLE 1

SPECTRAL DATA OF COMPOUNDS 1–27

Type	Compound	IR (ν in cm^{-1})		NMR (δ in ppm, J in Hz, area)[c]
		ν(CO)	ν(acid)	
Benzoic acid				
I	[Ru(PhCOO)(CO)$_3$]$_2$ (1)[a]	2110s,2080vs, 2038vs,2000vs	1600s,1555s. 1415vsbr	
II	[Ru$_2$(PhCOO)$_2$(CO)$_5$H$_2$O] (2)[b]	2095s,2035vs, 1998s,1950vsbr	3420br,3230br, 1600s,1555vs, 1410vsbr	7.42 (t, J 7.5, 3H), 7.98 (dd, J 7.5, 1.5, 2H)
III	[Ru(PhCOO)(CO)$_2$PhCO$_2$H]$_2$ (3)[b]	2050vs,1995s, 1950vsbr	3200–2700, 1660vs,1600s, 1555vs,1400vsbr	7.36 (t, J 7.74, 2H), 7.50 (t, J 7.74, 1H), 7.88 (d, J 7.74, 2H), 7.53 (t, J 7.37, 2H), 7.68 (t, J 7.37, 1H), 8.20 (d, J 7.37, 2H)[d]
	[Ru(PhCOO)(CO)$_2$PPh$_3$]$_2$ (4)[b]	2020vs,1978m, 1950vsbr, 1920w	1595m,1550m, 1485w	7.03 (t, J 7.3, 2H), 7.12 (dd, J 7.3, 1.3, 2H), 7.28 (t, J 7.3, 1H), 7.42 (m, 9H), 7.69 (m, 6H)[d]
	[Ru(PhCOO)(CO)$_2$NMe$_3$]$_2$ (5)[b]	2020vs,1960s, 1940vsbr,1910w	1600m,1560m-s, 1410vsbr	2.77 (s, 9H), 7.38 (m, 3H), 7.9 (dd, J 7.6, 2, 2H)
	[Ru(PhCOO)(CO)$_2$](H$_2$O)$_2$ (6)[b]	2035vs,1990s, 1950vsbr	3550br,3400br 1590m,1530sbr, 1405vsbr	7.36 (m, 3H), 8.03 (dd, J 7.28, 1.8, 2H)
	[Ru(PhCOO)(CO)$_2$MeOCMe$_3$]$_2$ (7)[b]	2030vs,1980s, 1950vsbr,1920sh, 1900sh	1595m,1550s, 1408vsbr	1.18 (s, 9H), 3.21 (s, 3H), 7.31 (t, J 7.3, 2H), 7.41 (t, J 7.3, 1H), 7.96 (d, J 7.3, 2H)[d,f]

IV	[Ru₂(PhCOO)₂(CO)₄Me₂CO)₂]₂ (8) [b]	2035vs,1982s, 1955vsbr	1675s,1605s, 1595s,1550vsbr, 1410vsbr	2.15 (s, 6H), 7.40 (t, J 7.6, 6H), 8 (dd, J 7.6, 1.6, 4H) [e]
V	[Ru(PhCOO)(CO)₂]ₙ (9) [b]	2050vs,2010s, 1990vs,1975vs	1608w,1590w, 1550sh,1540vs, 1523sh,1405vs	
4-Fluoro-benzoic acid				
I	[Ru(p-FC₆H₄COO)(CO)₃]₂ (10) [a]	2100s,2080vs, 2030vs,200vs	1600s,1550s, 1405vs	
II	[Ru₂(p-FC₆H₄COO)₂(CO)₅H₂O]·0.5C₆H₆] (11) [b]	2095vs, 2035vs, 200vsbr, 1940vs	3580br, 3320br 1600vs, 1545vs, 1405vsbr	7.02 (t, (dd), J 8.5, 4H), 7.99 (dd, J 8.5, 5.6, 4H), 7.36 (s, 3H)
III	[Ru(p-FC₆H₄COO)(CO)₂ p-FC₆H₄COOH]₂ (12) [a]	2040vs, 1990m-s, 1960vsbr	3580–2700, 1670m-s,1605s, 1565s,1420vs	7.02 (t(dd), J 7.5, 1H), 7.93 (dd, J 7.5, 6.1, 1H), 7.2 (t(dd), J 8.3, 1H), 8.2 (dd, J 8.3, 5.4, 1H)
	[Ru(p-FC₆H₄COO)(CO)₂Ph₃P]₂ (13) [b]	2025vs,1985m-s, 1955vsbr	1595m,1555m, 1405vsbr	6.66 (t, J 8.6, 2H), 7.04 (dd, J 8.6, 5.7, 2H), 7.42 (m, 9H), 7.65 (m, 6H) [d]
V	[Ru(p-FC₆H₄COO)(CO)₂]ₙ (14) [b]	2040vs,2010s, 1982vsbr,1960sh	1600vs,1535vsbr, 1510vs,1415vs, 1395vs	

TABLE 1 (Continued)

Type	Compound	IR (ν in cm^{-1})		NMR (δ in ppm, J in Hz, area) [c]
		ν(CO)	ν(acid)	
Anisic acid				
I	[Ru(p-MeOC$_6$H$_4$COO)(CO)$_3$]$_2$ (**15**) [a]	2110s,2080vs, 2038vs,2005vs	1608s,1595s, 1548s,1405vsbr	
II	[Ru$_2$(p-MeOC$_6$H$_4$COO)$_2$(CO)$_5$H$_2$O]·0.75C$_7$H$_8$ (**16**) [b]	2080vs,2035vs, 2000vsbr,1930s	3560br,3400br, 1590vs,1540s, 1400vsbr	3.80 (s, 24H), 6.81 (d, J 8.8, 16H) 7.92 (d, J 8.8, 16H), 2.36 (s, 9H) 7.20 (s, 15H)
III	[Ru(p-MeOC$_6$H$_4$COO)(CO)$_2$-p-MeOC$_6$H$_4$COOH]$_2$·0.75C$_7$H$_8$ (**17**) [b]	2040vs,1992s, 1960vsbr	3600–2800,1660s, 1605s,1530s, 1390vsbr	3.79 (s, 24H), 6.81 (d, J 8.5, 16H), 7.82 (d, J 8.5, 16H), 3.91 (s, 24H), 6.97 (d, J 8.9, 6H), 8.12 (d, J 8.9, 16H) 2.36 (s, 9H), 7.21 (s, 15H)
	[Ru(p-MeOC$_6$H$_4$COO)(CO)$_2$MeOCMe$_3$]$_2$ (**18**) [b]	2025vs,1980vs, 1942vsbr,1920w-m	1610m,1592m, 1540s,1410vsbr	1.18 (s, 9H), 3.20 (s, 3H), 3.80 (s, 3H), 6.79 (d, J 8.82, 2H) 7.90 (d, J 8.82, 2H) [f]
	[Ru(p-MeOC$_6$H$_4$COO)(CO)$_2$Ph$_3$P]$_2$ (**19**) [a]	2025vs,1983m, 1953vs,1923w	1612sh,1600s, 1550s,1510w, 1490m,1440w, 1402sbr	3.74 (s, 3H), 6.51 (d, J 8.8, 2H), 7.07 (d, J 8.8, 2H), 7.41 (m, 9H), 7.68 (m, 6H) [d]
V	[Ru(p-MeOC$_6$H$_4$COO)(CO)$_2$]$_n$ (**20**) [b]	2040vs,2005m, 1975mbr,1960vsbr	1605m,1590m, 1545sh,1530mbr, 1515sh,1395vsbr	
Pivalic acid				
II	[Ru$_2$(Me$_3$CCOO)$_2$(CO)$_5$H$_2$O] (**21**) [a]	2100s,2040vs, 2000vs,1940s	1560s,1490s, 1380m	1.13 (s)
III	[Ru(Me$_3$CCOO)(CO)$_2$Me$_3$CCOOH]$_2$ (**22**) [b]	2040vs,1990vs, 1955vsbr, 1930m(sh)	3600–2800, 2975w-m,2940w, 1675vs,1550s, 1490s,1415s	1.13 (s, 1H), 1.25 (s, 1H)

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s-Butyric acid

I	[Ru(s-C$_4$H$_9$COO)(CO)$_3$]$_2$ (**23**) [h]	2110m,2080vs, 2040vs,2005vs	1558mbr, 1410mbr	
	[Ru(s-C$_4$H$_9$COO)(CO)$_2$Ph$_3$P] (**24**) [a]	2020vs,1980s, 1950vs,1920w-m	1560s,1485w, 1470w,1425mbr	0.81 (t, J 7.2, 3H), 0.88 (d, J 7.2, 3H), 1.03 (hep, J 7.2, 1H), 1.16 (hep, J 7.2, 1H), 1.98 (sex, J 7.2, 1H), 7.38 (brd, J 6.7, 9H), 7.56 (brt, J 2.4, 6H) [d]
IV	[Ru$_2$(s-C$_4$H$_9$COO)$_2$(CO)$_4$ s-C$_4$H$_9$COOH]$_2$ (**25**) [b]	2045vs,1990vs, 1960vsbr,1930m	3700–2800, 2990m,2970m, 2945w,1670s, 1560vs,1470m, 1415s	0.87 (t, J 7, 6H), 1.04 (d, J 7, 6H), 0.91 (t, J 7, 3H), 1.12 (d, J 7, 3H), 1.41 (m), 1.61 (m, 6H), 2.33 (m, 3H) [g]
V	[Ru(s-C$_4$H$_9$COO)CO)$_2$]$_n$ (**26**) [b]	2040vs,2000vs, 1995vsbr, 1965vsbr	1550vsbr,1470m, 1415vs	
Tuloic aicd				
III	[Ru(4-MeC$_6$H$_4$COO)(CO)(4-MeC$_6$H$_4$COOH)]$_2$ (**27**) [a]	2040vs,1995s 1960vsbr	1655s,1605s, 1550s,1400sbr	2.34 (s, 3H), 7.14 (d, J 8, 2H), 7.77 (d, J 8, 2H), 2.46 (s, 3H), 7.30 (d, J 8.15, 2H), 8.06 (d, J 8.15, 2H)

[a] In CH$_2$Cl$_2$. [b] In KBr. [c] Deuteriochloroform except where alternative solvent indicated, 90 MHz. [d] 360 MHz. [e] CD$_3$OD. [f] CDCl$_3$ + traces of (CD$_3$)$_2$CO. [g] (CD$_3$)$_2$CO, 360 MHz. [h] In Cyclohexane.

Fig. 1. Molecular structure of $[Ru_2(4\text{-}F\text{-}C_6H_4CO_2)_2(CO)_5H_2O]$ (11). The crossed circles represnt oxygen atoms.
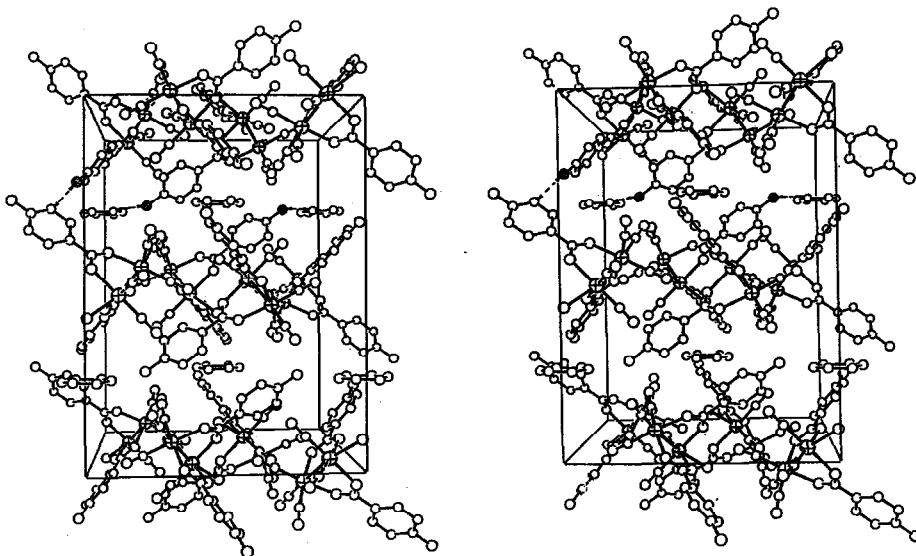
Fig. 2. Stereoview of the molecular packing in the crystal structure of $[Ru_2(4\text{-}F\text{-}C_6H_4CO_2)_2(CO)_5H_2O]$ (11). Specific C–H $\cdots$ F intermolecular interactions are marked by arrows and shaded F atoms.

four basal atoms are practically eclipsed. The Ru–Ru bond distance of 2.649 Å completes an eighteen-electron configuration for each metal atom, which accounts for its diamagnetic properties. The three Ru(1)–CO bonds are longer than those of the adjacent Ru(18)–CO bonds. This can be rationalized in terms of the more extensive electron back-donation Ru(18) → CO, arising from the presence of the non-π-acid water ligand. Accordingly, type II complexes exhibit infrared stretching bands ranging from 2095 to 1950 cm^{-1}, due mainly to Ru(1) and Ru(18) carbonyls, respectively. The particularly long Ru(1)–C(4) bond implies an enhanced reactivity of this carbonyl.

The crystal packing diagram (Fig. 2) reveals a densely packed layered molecular arrangement with channels ca. 10 Å wide between the layers which contain benzene molecules. Three structural details are of interest.

(a) A distance of 2.77 Å is observed between the oxygen atoms of the water and carboxylate ligands of two neighboring molecules. This H-bonding gives rise to ν(OH) at 3320 cm^{-1} in addition to a free ν(OH) at 3580 cm^{-1}. All the aquato complexes exhibit two infrared bands in the above regions.

(b) A distance of 2.69 Å is observed between a F atom and an aromatic C atom *ortho* to a fluorine atom in a different molecule. Such a close contact indicates intermolecular F ⋯ H bonding. Interestingly this interaction takes place between molecules of adjacent layers (Fig. 2), thus forming the crystal channels that include benzene molecules.

(c) There is a distance of 2.74 Å between a F atom and one C atom of a guest benzene molecule, again implying intermolecular F ⋯ H bonding.

Other complexes of type II (L = carboxylic acids, pyridine) are described in the experimental section.

Type III: [Ru(RCOO)(CO)₂(RCOOH)]₂

Complexes having ruthenium to acid ratio of 1/2 were encountered for all of the acids. Most of them could be isolated and purified by column chromatography (silica). Their infrared spectra exhibit two distinct bands associated with carboxylic

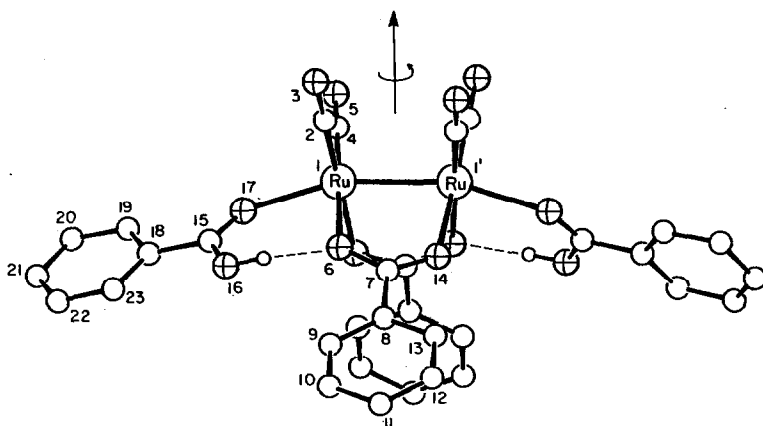Fig. 3. Molecular structure of [Ru(PhCO$_2$)(CO)$_2$PhCO$_2$H]$_2$ (3) (the crossed circles represent oxygen atoms). Geometric parameters of the OH(16) ⋯ O(6) hydrogen bond are as follows: O(16) ⋯ O(6) 2.605(7) Å, H(16) ⋯ O(6) = 1.75 Å, and O(16) ⋯ H ⋯ O(6) 158°.

acids: (a) a broad absorption envelope in the range 2700–3200 cm^{-1} (ν(O–H)); (b) a band in the range of 1660–1670 cm^{-1} (ν(C=O)). The latter is clearly out of the range of the asymmetric carboxylate vibration band (1550–1560 cm^{-1}). Moreover, the NMR spectra of type III complexes exhibit two sets of signals, with intensity ratio of 1/1, associated with the alkyl (or aryl) groups of the carboxylic acid and the carboxylate ligands. It was difficult to reconcile the presence of both carboxylate and carboxylic acids ligands in the same molecule, and an X-ray diffraction study of 3 was undertaken (Fig. 3) [11].

The X-ray picture confirms the presence of two μ_3-benzoate bridges. The benzoic acid is coordinated to the metal via the carbonyl oxygen (η^1) while its acidic H atom is bound to an oxygen atom of the benzoate bridge with O(16)–O(6) distance of 2.57 Å (Fig. 3, Table 6). In the solid state the acidic H atom, which was clearly located from a difference map, is unsymmetrically disposed with respect to the two oxygen atoms. Three basic coordination modes of carboxylic acids (carboxylate) are recognized in transition metal chemistry namely, monodentate, chelating bidentate, and bridging carboxylate [12]. Monohapto coordination of carboxylic acid through its carbonyl oxygen atom, such as in 3, is rare. It has been proposed earlier [13] for Rh(MeCOO)(CO)(PPh$_3$)$_2$ · 0.5MeCOOH and observed very recently by Cotton et al. [14] (X-ray) in Rh$_2$(MeCOO)$_2$[Ph$_2$P(C$_6$H$_4$)]$_2$ · 2MeCOOH. Presumably, the weak π-donor-ability of a carboxyl group usually precludes such coordination, which in the present case is strenghtened by the hydrogen bonding. The distance between the carboxyl oxygen and Ru atoms, 2.265 Å, is only slightly longer than the

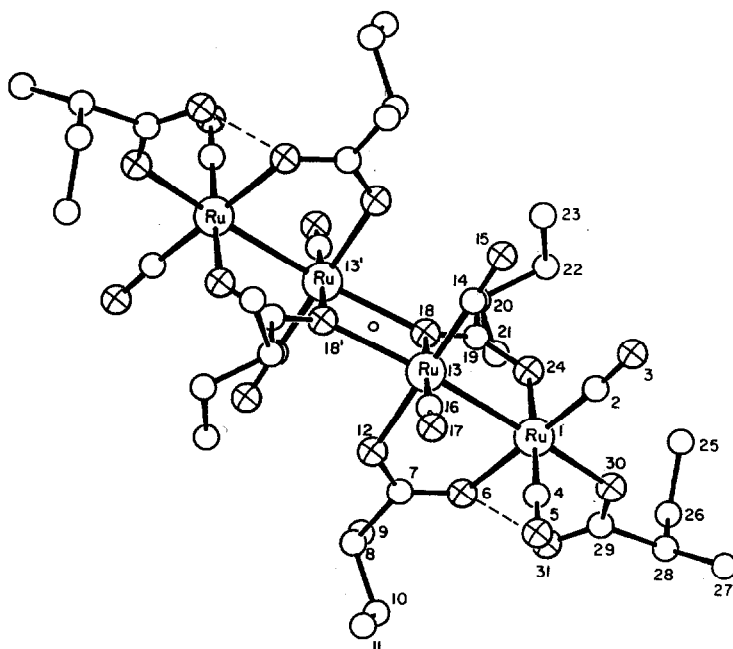Fig. 4. Molecular structure of [Ru$_2$(s-C$_4$H$_9$CO$_2$)$_2$(CO)$_4$(s-C$_4$H$_9$CO$_2$H]$_2$ (25) (the crossed circles represent oxygen atoms). The distance O(6) · · · O(31) of 2.57(1) Å relates to the H-bond interaction (the acidic H atom could not be located).

average carboxylate Ru–O distance of 2.13 Å (Table 6), implying relatively strong coordination of the former. Thus, it appears that 3 retains its carboxylic acid ligands in solution and even upon column chromatography.

To accommodate the carboxylic acid-carboxylate H-bonding (Fig. 3), the two Ru octahedra (Fig. 3) are distorted in opposite directions (Ru–Ru–O(17) angle of 162.8°), conferring C_2 molecular symmetry.

The substitution of two CO ligands in type I complexes by two monohapto RCOOH ligands (type III) shifts the infrared CO stretching bands to lower frequencies (Table 1). This must reflect the better π-acidity of a CO ligand relative to RCOOH.

Complex 3 is a C_2 dissymmetric molecule. Two kinds of intramolecular processes must be considered.

(a) Torsion about Ru(1)–O(17) and Ru(1′)–O(17′) will result in site exchange of the hydrogen bonds. From symmetry consideration this degenerate process will lead to internal racemization. Although energetically feasible, such a process will be difficult to detect experimentally.

(b) A second conceivable process is the interchange of the η^2 carboxylate and η^1 carboxylic acid ligands. We have found that this process does not occur either at room temperature or at 100°C. Thus, the two narrow NMR t-butyl signals of 22 (pivalic acid and pivalate ligands) persist also at 100°C in toluene. Upon addition of acid, an intermolecular exchange process does take place, as is described later.

Type IV: [Ru₂(RCOO)₂(CO)₄(RCOOH)]₂

A complex 25 with ruthenium to acid ratio of 2/3 (elemental analysis) was obtained by treating $Ru_3(CO)_{12}$ with 2-methylbutyric acid (Table 1). Infrared spectroscopy revealed a bridging carboxylate structure (1560 and 1470 cm⁻¹) and a coordinated carboxylic acid (1675, 3200–2700 cm⁻¹). Its NMR spectrum showed two s-butyl group signals in the ratio of 1/2. Although the infrared spectrum is indicative of a type III complex, it is incompatible with the elemental analysis and the NMR integral ratio. The structure of 25 was thus established by X-ray crystallography (Fig. 4) [11].

The bridging carboxylate and the monohapto coordinated acid ligands are clearly evident from Fig. 4. The Ru–O–Ru bridge is a new structural element in this series of complexes. The only other known structure containing the Ru–O–Ru bridging element, recently described by Bianchi et al. [6], is that in $Ru_4(CO)_8$-$(MeCOO)_4(PBu_3)_2$, which was obtained by the reaction between $Ru_3(CO)_{12}$, acetic acid, and tributylphosphine. Following our preliminary report of the structure of 25 Bianchi et al. described a complex they formulated as $[Ru_2(CO)_4(s-BuCOO)_2(s-BuCOOH)]_n$ [8], made from optically active 2-methylbutyric acid. The molecular ratio of the carboxylate to carboxylic acid ligands is 2 for all values of n. However for $n = 1$ the resulting complex is coordinatively unsaturated, whereas for $n > 2$ it is "over-coordinated". For $n = 2$ the above complex is identical with 25 [11] and a comparison of the infrared spectra of the two complexes confirms this. A similar bridging element is also found in $[(Me_2SnO_2CCH_2Cl)_2O]_2$ [15].

Formally, 25 may be regarded as a dimer of a type III complex (after the removal of one monohapto acid ligand) that is united by two Ru–O–Ru bridges. The Ru–O bond distance in the bridge is 2.31 Å which, when compared with the average intracore Ru–O bond distance of 2.13 Å, indicates a fairly tight bonding. In keeping

with this, **25** is a stable 72e$^-$ Ru tetramer which can be readily crystallized and chromatographed. The structural parameters of each dimeric Ru unit of **25** (Fig. 4) are very similar to those of **3** (Fig. 3), indicating that there is no structural perturbation upon formation of the tetramer.

Complex **25** is centrosymmetric in the solid state (Fig. 4) and therefore achiral. Nevertheless, it carried six chiral 2-methylbutyric acid molecules. Their relative geometrical disposition must be such that each chiral ligand is reflected through the symmetry point.

An acetone-containing complex (**8**) (Table 1) was obtained by treating **1** or **2** with acetone. It was also assigned a tetrameric molecular formula on the basis of its elemental analysis and the integral ratio (NMR) of the signals from the acetone (**1**) and phenyl groups (**2**). An infrared stretching band at 1675 cm^{-1} (Table 1) was assigned to the coordinated acetone molecules ($\diagup$C=O → Ru). The molecular structure of **8** is probably analogous to that of **25**, with two acetone molecules replacing the monohapto coordinated carboxylic acid molecules.

Type V: [Ru(RCOO)(CO)$_2$]$_n$

Except for pivalic acid, all the acids in the present series, form ruthenium carboxylato polymers. The rate of polymerization and the chemical stabilty of the polymer depend on the specific carboxylate ligand (vide infra). The polymers are orange red powders unsuitable for X-ray crystallography and insoluble in non-ligating solvents.

The X-ray structure of the tetramer **25** provides a logical structural model for the polymeric complexes. The number of CO infrared stretching bands of the tetramer **25** and the polymer **26** are similar. While multiple Ru–O–Ru bridges may constitute the backbone of the polymer, carboxylic acids cap the ends.

A propionato oligomer with a molecular structure similar to that of **25** but capped by two THF molecules was recently described [9]. The basic structure was deduced from infrared and Raman spectral data. The (average) chain length can be best deduced from NMR analysis using the integral ratio of carboxylate to end ligand. Nevertheless, the basic structure of the above propionate oligomer also supports Ru–O–Ru interactions in the molecular framework of polymers.

Chemical reactivity

Our results revealed that the stabilities of the various carboxylato complexes generated by the reaction of dodecacarbonyltriruthenium(0) and carboxylic acids depend on the nature of the incipient carboxylate ligand. The progress of the reaction was monitored by infrared spectroscopy, and the identification of the various components was based on previous knowledge of the infrared spectra of the isolated products. When a complex with a given carboxylate ligand could not be isolated, its presence in the reaction mixture was inferred from the presence of infrared bands similar to those from an iso-structural complex bearing a different carboxylate ligand. Evidently, iso-structural complexes with different carboxylate ligands exhibit practically identical infrared spectra in the CO region (Table 1).

It is important to stress that almost invariably the composition of the mixture at the completion of the reaction differs from that after work-up.

Complexes of type I are the first stable products of the reaction between

$Ru_3(CO)_{12}$ and carboxylic acids (vide infra), and so the stoichiometry of the reaction can be represented as in eq. 2.

$$6RCOOH + 2Ru_3(CO)_{12} \rightarrow 3[Ru(RCOO)(CO)_3]_2 + 3H_2 + 6CO \qquad (2)$$
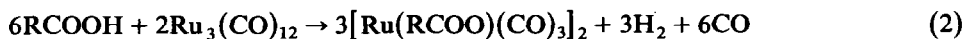
As previously reported [2], $H_4Ru_4(CO)_{12}$ is a by-product of the above reaction, but we find that its formation can be completely suppressed if the reaction is carried out in a closed vessel so that the escape of the generated CO is prevented CO (eq. 2).

Two reaction variables were found to be of importance: (a) the molar ratio of the two reactants, and (b) use of a closed rather than an open reaction system. Generally the use of the stoichiometric molar ratio of $Ru_3(CO)_{12}/RCOOH$ of 1/3 (eq. 2) leads to the predominance of type I complexes if the reac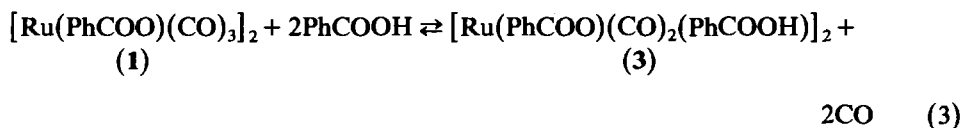tion is carried out in a closed vessel. The use of the above reactant ratio in an open reaction system leads to the formation of other types of complexes as well as I.
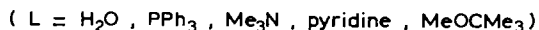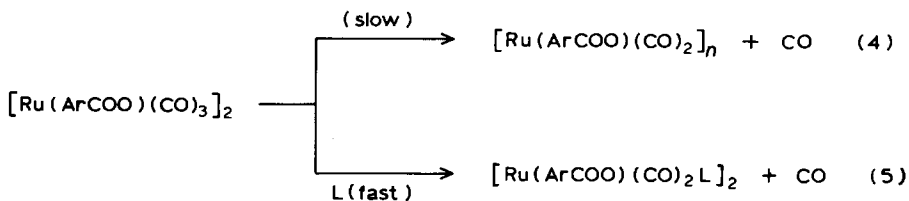
When an excess of benzoic acid (in toluene) was used in a closed system the infrared spectrum of the mixture at the end of the reaction indicated the presence of 1 and free benzoic acid. However, when the CO pressure was released, 1 (in the presence of the excess acid) was slowly transformed into 3 at room temperature. Correspondingly, 3 in solution reverts to 1 when subjected to CO pressure. Thus under the conditions of reaction 2 an equilibrium exists (eq. 3), and is shifted to the left in a closed vessel.

$$[Ru(PhCOO)(CO)_3]_2 + 2PhCOOH \rightleftharpoons [Ru(PhCOO)(CO)_2(PhCOOH)]_2 +$$
$$\qquad (1) \qquad\qquad\qquad\qquad\qquad (3)$$

$$2CO \qquad (3)$$

Complex 1 was obtained in good purity in the solid state (yellow powder) only by fusion of $Ru_3(CO)_{12}$ and PhCOOH at 145°C in a closed vessel. Attempts to crystallize or chromatograph 1 gave various mixtures of 1, 2 and 3 but no polymer. On the other hand complexes of type I at room temperature readily exchange two CO groups with ligands (L) such as phoshines, tertiary amines, or ether to give symmetrical complexes of the type $[Ru(RCOO)(CO)_2L]_2$ (Table 1).

Use of a stoichiometric ratio of $Ru_3(CO)_{12}$ and benzoic acid in refluxing toluene (CO escape) leads initially to the formation of 1 (IR), and it is only after 48 h that precipitation of the benzoato polymer (9) occurs. This behavior contrasts with that of the straight chain aliphatic acid complexes of type I. It was found that all type I aromatic as well as α-branched chain aliphatic carboxylate complexes do not show a pronounced tendency toward polymerization. Thus, under the above conditions the acetato polymer is formed from $[Ru(MeCOO)(CO)_3]_2$ immediately and quantitatively. This observation must have a bearing on the mechanism of CO exchange and therefore merits discussion.

The stable product before polymerization is a type I complex, which in the polymerization reaction loses CO (eq. 4). In this sense the polymerization reaction is similar to the ligand exchange reaction which is also accompanied by the loss of CO (eq. 5). Complexes 2, 3 and 4–8 (Table 1), as well as other complexes previously reported [2,3], could be readily obtained by such a reaction. However while the aromatic type I complexes polymerize very slowly, they exchange their ligands (eq. 5) very rapidly. Since both reactions require elimination of CO, this step cannot be

$$[\text{Ru(ArCOO)(CO)}_3]_2 \begin{cases} \xrightarrow{\text{(slow)}} [\text{Ru(ArCOO)(CO)}_2]_n + \text{CO} \quad (4) \\ \\ \xrightarrow{\text{L(fast)}} [\text{Ru(ArCOO)(CO)}_2\text{L}]_2 + \text{CO} \quad (5) \end{cases}$$

$$(\ \text{L} = \text{H}_2\text{O}\ ,\ \text{PPh}_3\ ,\ \text{Me}_3\text{N}\ ,\ \text{pyridine}\ ,\ \text{MeOCMe}_3\ )$$

the rate-limiting in both reactions. The experimental results support an associative type mechanism [16] for substitution of CO by other ligands in type I complexes (eq. 5). Thus, the rate of disappearance of **1** is proportional to the ligand concentration (pyridine, benzoic acid). Infrared data also support this conclusion (vide infra). No intermediate was observed, but it can be assumed that the carboxylate ligand serves as an electron acceptor in an associative substitution process. With phosphines and **1**, the reaction is instantaneous at ambient and at sub-zero temperatures.

The rates of substitution of CO by carboxylic acids in type I complexes to give type III complexes are substantially slower than with ligands such as phosphines and amines. It is unlikely that a carboxylic acid would behave as a nucleophile toward the metal atom in an S_N2-type reaction (associative pathway). Although a dissociative mechanism may be invoked, it would be inconsistent with the (qualitative) observation that the rate of the reaction of **1** and PhCOOH (eq. 5; L = benzoic acid) depends on the acid concentration. The final product of this reaction is **3**; an unsymmetrical mono-substituted complex of type II was observed as a transient intermediate. Thus, addition of benzoic acid to a toluene solution of **1** induces a slow concurrent development of two sets of infrared bands ν(CO) at 2100, 2040, 2005, 1940 cm^{-1} and 2045, 1998, 1968 cm^{-1}. The first set is assigned to the unsymmetrical complex $\text{Ru}_2(\text{PhCOO})_2(\text{CO})_5(\text{PhCOOH})$ which is characterized by the highest (2100 cm^{-1}) and lowest (1940 cm^{-1}) frequency bands. The second set is assigned to the symmetrically substituted **3** (Table 1). As the reaction proceeds further the first set of bands disappears while the second set intensifies, leading eventually to the spectrum of **3**.

An associative type mechanism for substitution of CO by a carboxylic acid is proposed in Scheme 1. Protonation of the carboxylate ligand by the added acid may, in a limiting representation, open up the carboxylate bridge or alternatively induce electron shift from Ru to carboxylate. On either description this would amount to labilization of the Ru–CO bonds [17], thus inducing a fast substitution reaction of CO by the oxygen atom of the incoming acid (Scheme 1). Protonation of the carboxylate ligand is consistent with the presence of the hydrogen-bonded acid in the product (Fig. 3). It may also lead to an intermolecular exchange of the carboxylate ligand with added acid (vide infra).

The relative polymerization rates for the aliphatic acid complexes follow the order: acetic > 2-methylbutyric > pivalic acid. (In fact no polymer was obtained with pivalic acid.) This order must have its origin in steric effect associated with the alkyl part of the carboxylate ligand. The fact that such a kinetic effect is observed strongly supports an associative mechanism for the polymerization reaction. This

Type I + RCO$_2$H $\longrightarrow$ [structure, M = Ru] $\xrightarrow{-CO}$ Ru$_2$(RCO$_2$)$_2$(CO)$_5$RCO$_2$H

(M = Ru)
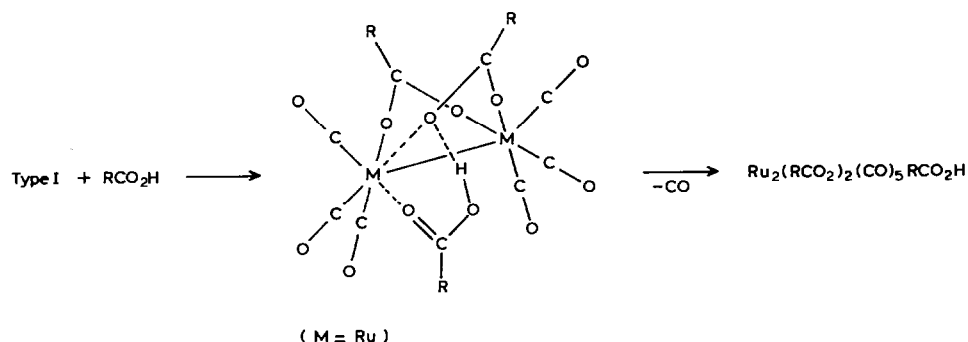
SCHEME 1

steric effect could also be responsible for the lower polymerization rates of the aromatic carboxylato complexes. Since polymerization of type I complexes occurs under conditions where CO could escape, and since with complexes which polymerize slowly no decomposition products but only polymers were formed, it seems that the steric effect is of kinetic origin.

If the associative type polymerization mechanism is assumed, a high electron density on the carboxylate ligand involved in the Ru–O–Ru bridge formation would raise the polymerization rate. From basicity consideration and from infrared data (vide infra), aliphatic carboxylate ligands must carry a higher electron density than the aromatic ones. This also may account for the observed higher rate of polymerization of the aliphatic than of the aromatic carboxylic acid complexes. Both steric and electronic structural factors must be considered.

Several features in the infrared spectral data (Table 1) support aspects of the above arguments.

(1). The CO stretching frequencies of the aliphatic and aromatic complexes of type I, which differ markedly in their polymerization rates, are practically identical. This indicates similar ground state Ru–CO bond strengths, and is incompatible with a dissociative mechanism of CO substitution in the polymerizations

(2). Symmetrical dimers of the type [Ru(PhCOO)(CO)$_2$L]$_2$ (L = H$_2$O, PPh$_3$, NMe$_3$ and PhCOOH) all exhibit CO stretching bands at frequencies lower than those from the benzoato polymer (8). This implies that the above ligands form stronger Ru coordination bonds than the oxygen atom of the benzoate ligand in the polymer, and provides a thermodynamic explanation of the fact that polymers depolymerize in the presence of the above ligands. It also supports our previous kinetic interpretation of the slow polymerization vs. fast ligand exchange reactions.

(3). The asymmetric stretching vibration of the acetate ligand in [Ru(MeCOO)(CO)$_3$]$_2$ is at 1567 [2] vs. 1555 cm^{-1} in [Ru(PhCOO)(CO)$_3$]$_2$. Similar relationships are found on comparing other aliphatic and aromatic pairs (Table 1). We take this to indicate a more extensive charge delocalization in the aromatic carboxylate ligands, thus a diminishing p character of the oxygen atom involved in polymerization. This supports our previous interpretation of the slower polymerization rates of the aromatic carboxylato complexes.

It is possible to bring about intermolecular exchange of the carboxylate ligands. Thus benzoate dimer (2) was quantitatively converted to the acetato polymer by

heating it with acetic acid (eq. 6). Other examples are illustrated in eqs. 7 and 8. Since the pivalate polymer can not be formed, the reaction stops with the formation of **22**.

$$Ru_2(PhCOO)_2(CO)_5H_2O + MeCOOH \rightarrow [Ru(MeCOO)(CO)_2]_n + PhCOOH \quad (6)$$
$$\textbf{(2)}$$

$$[Ru(4\text{-}MeOC_6H_4COO)(CO)_2(4\text{-}MeOC_6H_4COOH)]_2 + Me_3CCOOH \quad (7)$$
$$\textbf{(17)} \qquad \downarrow$$

$$[Ru(Me_3CCOO)(CO)_2(Me_3\overset{\cdot}{C}COOH)]_2$$
$$\textbf{(22)} \qquad \uparrow$$

$$[Ru(n\text{-}C_9H_{19}COO)(CO)_2]_n + Me_3CCOOH \quad (8)$$
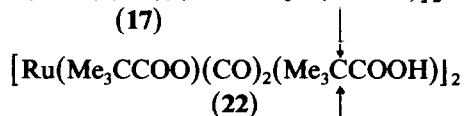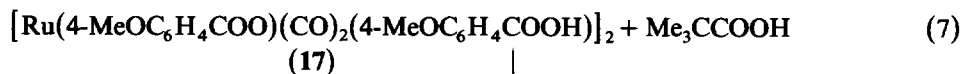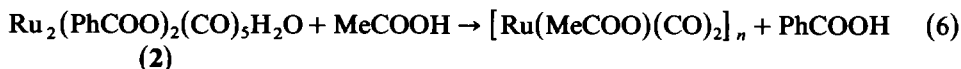
A partial exchange takes place when **3** is treated with a limited quantity of pivalic acid at room temperature. The mixed acid complex was detected by NMR, since the signals of bound and free pivalic acid show different chemical shifts.

The above transformations imply that in a reaction system consisting of $Ru_3(CO)_{12}$ and carboxylic acid, complexes of types I, III, IV and V can exist in equilibrium (Scheme 2).

The state of equilibrium is controlled by several factors:

(a) The development of CO pressure will usually prevent the reaction proceeding beyond type I complexes. Only in the case of acetic acid was the formation of polymer (V) observed in a closed reaction system.

(b) Excess of acid will push the equilibrium toward type III complexes. Again with acetic acid the polymer is formed in spite of the presence of an excess of acid.

(c) The type of acid is of major importance in determining the state of the above equilibrium. Acetato and most other straight chain aliphatic carboxylato complexes drive the equilibrium toward polymers even in presence of excess acid and CO

$$Ru_3(CO)_{12} + RCOOH \qquad\qquad [Ru(RCOO)(CO)_2RCOOH]_2$$
$$(type\ III\ )$$

$$\big\Downarrow \begin{array}{l} -CO \\ -H_2 \end{array} \qquad\qquad +CO \updownarrow +RCOOH$$

$$[Ru(RCOO)(CO)_3]_2 \quad \underset{CO}{\overset{RCOOH}{\rightleftharpoons}} \quad Ru_2(RCOO)_2(CO)_5RCOOH$$
$$(type\ I\ ) \qquad\qquad\qquad\qquad (type\ II\ )$$

$$+CO \updownarrow -CO$$

$$[Ru(RCOO)(CO)_2]_n(RCOOH)_2$$
$$(type\ IV\ or\ V\ )$$
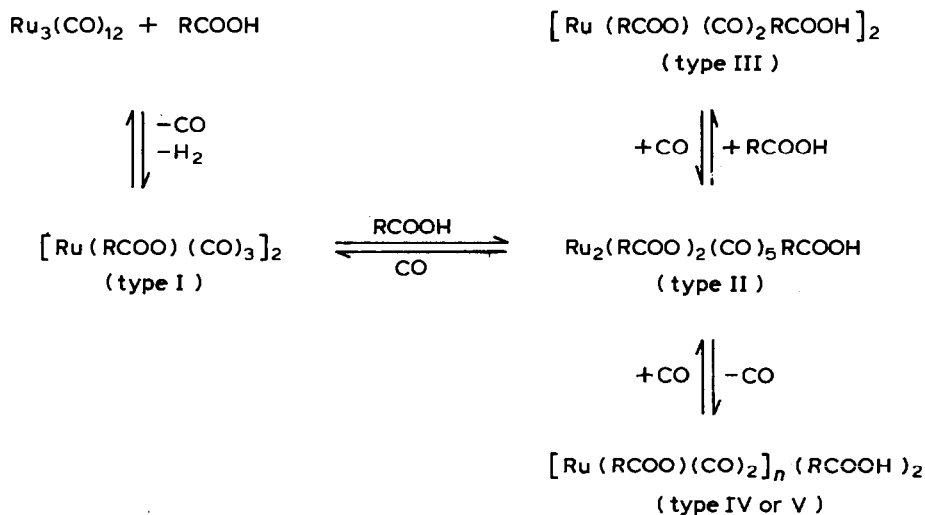
SCHEME 2

pressure. Complexes involving branched chain carboxylate ligands respond to CO pressure and acid concentration. Extreme steric crowding of the α position of the acid hinders the formation of polymers (pivalic acid). Aromatic carboxylic acids also respond to CO pressure and acid concentration, but polymerize only to a very small extent.

In conclusion, recognition of the effects of the variables considered means that it will now be possible to predict the nature of the products and their distribution in a reaction system consisting of dodecacarbonyltriruthenium(0) and carboxylic acids. Furthermore, the results clarify the kinetic behavior and the molecular structure of the variety of complexes generated in the above reaction.

Experimental

Infrared spectra were recorded on a Perkin–Elmer Grating Infrared Spectrophotometer Model 177, and NMR spectra on a Bruker WH-90 and FT-360 MHz spectrometers. ^{1}H and ^{13}C chemical shifts are given in δ(ppm) relative to TMS as internal standard. All the ^{13}C NMR spectra are proton-decoupled. ^{19}F NMR spectra are reported in ppm upfield from $CFCl_3$.

The X-ray diffraction experiments were carried out at ca. 18°C on a CAD4 diffractometer equipped with a graphite monochromator employing Mo-K_α (λ 0.72069 Å) radiation and the $\omega-2\theta$ scan technique. The crystal data are summarized in Table 2. An empirical method was used to correct the intensity data for absorption effects [18]. The crystal structures were solved by a combination of direct methods and Fourier techniques (MULTAN 80), and were refined anisotropically using intensity data above a threshold of $3\sigma(I)$. The aromatic hydrogen atoms were introduced in calculated positions and those of H_2O (in 11) and carboxylic acid (in 3) ligands were located from difference maps. In 25 the s-butyl side chains and the acid ligand were found to be partially disordered; in order to prevent unreasonable distortions of the molecular structure these fragments were included in the least-squares calculations (SHELX 76) with restrained geometries and isotropic thermal parameters only. The anisotropic refinements of 3 and 11 as well as the constrained refinement of 25 (see above) converged smoothly at relatively low R indices (Table 2). The final atomic parameters of 3, 11 and 25 (excluding H's) are given in Tables 3, 4 and 5 respectively.

The observed molecular geometries of the three structures are characterized by a common Ru–Ru–$(CO)_4$–di-μ_3-carboxylato core, but different side ligands. The latter involve molecules of benzoic acid in 3 (Fig 3), and CO and H_2O in 11 (Fig. 1). In 25 the structural data indicate a definite interaction between the bis(μ_3-carboxylato)Ru–Ru entities that are related to each other by inversion through a bridging 2-methylbutyric carboxylate, which results in formation of a centrosymmetric ruthenium tetramer (Fig. 4). At both ends of the tetramer the outer Ru atoms are further coordinated by molecules of 2-methylbutyric acid. The geometric parameters which describe the distorted octahedral coordination around each of the Ru atoms, and which are most relevant to the present discussion, are summarized in Table 6. Evidently, the observed distortions in the octahedral arrangements around ruthenium are primarily due to the different functional and geometric characters of the ligating moieties. They are also somewhat affected, however, by the carbonyl–carbonyl and carboxylate–carboxylate repulsions as well as by the tendency for optimization of

TABLE 2

CRYSTAL DATA AND EXPERIMENTAL DETAILS

Compound	3	11	25
M_r	800.7	677.5	1236.2
Space group	$C2/c$	$Pbcn$	$P\bar{1}$
Z	4	8	1
a (Å)	19.598(12)	15.123(1)	9.988(3)
b (Å)	16.909(3)	15.646(11)	11.006(9)
c (Å)	10.900(6)	20.530(3)	12.916(4)
α (°)	90.0	90.0	107.63(4)
β (°)	118.41(3)	90.0	90.42(3)
γ (°)	90.0	90.0	109.91(4)
V (Å^3)	3176.9	4857.7	1262.6
d_c (g cm^{-3})	1.674	1.853	1.556
μ(Mo-K_α) (cm^{-1})	9.9	12.9	11.6
2θ-limits (°)	54	50	54
Data with $I \geqslant 3\sigma(I)$	2087	2239	3512
R'	0.037	0.045	0.055
R_w	0.049	0.050	0.055 [a]

[a] Unit weights.

the carboxylic acid–carboxylate hydrogen bonds in 3 and 25. The different orientation of the ligand octahedra surrounding adjacent Ru atoms with respect to the Ru–Ru bond is reflected in the torsion angles around this bond (Table 6). In 3, in which there are no hydrogen bonds with the side ligands, the corresponding angular values vary between 9 and 11°. The intramolecular H-bonding requires a larger twist about the Ru–Ru bond, varying within 14–21° in 11 and 13–16° in 25. Other structural parameters obtained for chemically equivalent fragments of the three structures show good internal consistency.

The covalent bond lengths and angles obtained for the remaining parts of the various molecules (excluding the partially disordered side chains in 25) show no unusual features.

Benzoato complexes

$[Ru(PhCOO)(CO)_3]_2$ *(1)*. Although 1 was detected in reaction mixtures in many experiments the solution of the pure complex was best obtained by subjecting 9, as a suspension in cyclohexane, to CO (600 psi) in a glass lined closed reactor at 80°C for 4 h. The IR spectrum of the resulting homogeneous solution revealed the presence of 1 (Table 1). In the solid state 1 was obtained by heating a mixture of dodecacarbonyltriruthenium (337 mg, 0.53 mmol) and benzoic acid (210 mg, 1.72 mmol) for 18 h under N_2 in a closed glass-lined reactor. The orange-yellow powder was identified (IR, Table 1) as 1, slightly contaminated with 2 and 3.

$[Ru_2(PhCOO)_2(CO)_5H_2O]$ *(2)*. Dodecacarbonyltriruthenium (516 mg, 0.81 mmol) and benzoic acid (310 mg, 2.54 mmol) were heated together at 145°C under nitrogen for 16 h in a glass-lined closed reactor. There was obtained an orange-yellow solid, IR (CH_2Cl_2): 2105s, 2085s, 2040vs, 2000vsbr, 1970sh, 1940sbr cm^{-1}; these bands show the presence of 1, 2 with traces of 3. The solid was taken up in hot cyclohexane and filtered. Evaporation of the filtrate gave almost pure 1 (IR, Table

TABLE 3

ATOMIC COORDINATES AND ISOTROPIC THERMAL PARAMETERS FOR [Ru(Ph-COO)(CO)$_2$(PhCO$_2$H)]$_2$

Atom	x	y	z	U_{eq}/U (Å^2) [a]
Ru(1)	0.0625(1)	0.2799(1)	0.7339(1)	0.0507
C(2)	0.0329(4)	0.3640(3)	0.6147(8)	0.0772
O(3)	0.0151(4)	0.4170(3)	0.5408(7)	0.1247
C(4)	0.1184(4)	0.3504(4)	0.8752(7)	0.0694
O(5)	0.1524(3)	0.3941(3)	0.9604(6)	0.1154
O(6)	−0.0010(2)	0.1946(2)	0.5737(4)	0.0495
C(7)	−0.0638(3)	0.1642(3)	0.5568(5)	0.0450
C(8)	−0.1011(3)	0.1021(3)	0.4474(5)	0.0469
C(9)	−0.0637(3)	0.0667(3)	0.3810(6)	0.0608
C(10)	−0.1005(4)	0.0107(3)	0.2818(6)	0.0712
C(11)	−0.1747(4)	−0.0127(3)	0.2443(6)	0.0711
C(12)	−0.2122(4)	0.0222(4)	0.3079(7)	0.0728
C(13)	−0.1770(3)	0.0787(3)	0.4082(5)	0.0580
O(14)	−0.0957(2)	0.1821(2)	0.6278(4)	0.0519
C(15)	0.1724(3)	0.2009(3)	0.6234(5)	0.0483
O(16)	0.1120(2)	0.1695(3)	0.5162(4)	0.0692
O(17)	0.1669(2)	0.2403(2)	0.7125(4)	0.0556
C(18)	0.2469(3)	0.1831(3)	0.6299(5)	0.0490
C(19)	0.3131(3)	0.2144(4)	0.7364(6)	0.0715
C(20)	0.3837(4)	0.1999(5)	0.7436(8)	0.0991
C(21)	0.3878(4)	0.1511(4)	0.6466(7)	0.0848
C(22)	0.3226(4)	0.1193(4)	0.5408(7)	0.0690
C(23)	0.2514(3)	0.1360(3)	0.5307(6)	0.0569
H(9)	−0.006	0.082	0.410	0.050
H(10)	−0.071	−0.015	0.232	0.050
H(11)	−0.202	−0.057	0.169	0.050
H(12)	−0.269	0.005	0.279	0.050
H(13)	−0.207	0.105	0.455	0.050
H(16)	0.066	0.179	0.512	0.050
H(19)	0.309	0.250	0.811	0.050
H(20)	0.435	0.223	0.827	0.050
H(21)	0.442	0.140	0.654	0.050
H(22)	0.327	0.082	0.468	0.050
H(23)	0.201	0.113	0.447	0.050

[a] U_{eq} is one third of the trace of the orthogonalized U_{ij} tensor.

1). The solid from filtration was chromatographed on silica. Elution with 10% dichloromethane/cyclohexane gave 2, 500 mg (69%). Anal. Found: C, 37.21; H, 2.07. C$_{19}$H$_{12}$O$_{10}$Ru$_2$ calcd.: C, 37.87; H, 1.99%. Elution of the column with dichloromethane gave an orange solid 6, which was crystallized from benzene (36 mg). The IR bands at 3550 and 3400 cm^{-1} disappeared when the solid was dried at 0.1 mbar, and the resulting material gave a good analysis for [(PhCOO)(CO)$_2$Ru]$_n$. Anal. Found: C, 38.81; H, 1.62. C$_9$H$_9$O$_4$Ru calcd.: C, 38.85; H, 1.80%.

[Ru(PhCOO)(CO)$_2$(PhCOOH)]$_2$ (3). A mixture of dodecacarbonyltriruthenium (500 mg, 0.78 mmol), benzoic acid (1.4 g, 11.5 mmol), and toluene (5 ml) was heated for 16 h under nitrogen at 145°C in a closed glass-lined reactor. The IR spectrum of the solid which separated upon cooling was that of 1 (Table 1) containing benzoic acid. Crystallization from toluene/cyclohexane mixture gave orange crystals (450

TABLE 4

ATOMIC COORDINATES AND ISOTROPIC THERMAL PARAMETERS FOR $[Ru_2(4-FC_6H_4COO)_2(CO)_5(H_2O)]\cdot 0.5C_6H_6$

Atom	x	y	z	U_{eq}/U (Å^2) [a]
Ru(1)	0.3064(1)	0.2742(1)	0.0554(0)	0.0341
C(2)	0.1966(7)	0.2912(7)	0.0142(5)	0.0443
O(3)	0.1308(5)	0.3034(6)	−0.0076(4)	0.0706
C(4)	0.2634(7)	0.1809(7)	0.1138(5)	0.0464
O(5)	0.2354(7)	0.1339(6)	0.1481(4)	0.0879
C(6)	0.2797(6)	0.3608(6)	0.1146(5)	0.0351
O(7)	0.2688(5)	0.4125(5)	0.1520(4)	0.0600
O(8)	0.4339(4)	0.2609(4)	0.0970(3)	0.0280
C(9)	0.4923(6)	0.3164(6)	0.0889(4)	0.0268
C(10)	0.5730(6)	0.3101(5)	0.1305(4)	0.0233
C(11)	0.6467(7)	0.3608(6)	0.1183(5)	0.0369
C(12)	0.7215(6)	0.3531(7)	0.1564(5)	0.0404
C(13)	0.7206(6)	0.2955(7)	0.2056(5)	0.0408
F(14)	0.7953(4)	0.2883(4)	0.2429(3)	0.0672
C(15)	0.6492(7)	0.2446(6)	0.2193(5)	0.0420
C(16)	0.5764(6)	0.2496(6)	0.1796(5)	0.0308
O(17)	0.4869(4)	0.3802(4)	0.0508(3)	0.0293
Ru(18)	0.3868(1)	0.3846(0)	−0.0225(0)	0.0295
C(19)	0.3307(7)	0.4781(7)	0.0111(5)	0.0410
O(20)	0.2910(5)	0.5347(5)	0.0293(4)	0.0664
O(21)	0.4972(4)	0.4486(4)	−0.0821(3)	0.0375
C(22)	0.3013(7)	0.3854(7)	−0.0856(5)	0.0412
O(23)	0.2474(6)	0.3904(6)	−0.1239(4)	0.0714
O(24)	0.4453(4)	0.2732(4)	−0.0610(3)	0.0325
C(25)	0.4150(6)	0.1990(6)	−0.0503(5)	0.0296
C(26)	0.4571(6)	0.1288(5)	−0.0873(4)	0.0264
C(27)	0.5148(7)	0.1439(6)	−0.1370(5)	0.0355
C(28)	0.5514(7)	0.0772(7)	−0.1716(5)	0.0481
C(29)	0.5308(7)	−0.0032(7)	−0.1533(6)	0.0522
F(30)	0.5684(5)	−0.0678(4)	−0.1879(4)	0.0890
C(31)	0.4747(8)	−0.0230(7)	−0.1050(6)	0.0574
C(32)	0.4374(7)	0.0447(7)	−0.0714(5)	0.0464
O(33)	0.3525(4)	0.1825(4)	−0.0121(3)	0.0302
C(34)	0.0478(9)	0.1257(8)	0.2500(8)	0.0816
C(35)	0.0877(8)	0.0493(10)	0.2517(7)	0.0785
C(36)	0.0422(8)	−0.0216(8)	0.2492(7)	0.0703
H(11)	0.645	0.407	0.080	0.050
H(12)	0.779	0.392	0.147	0.050
H(15)	0.654	0.201	0.259	0.050
H(16)	0.522	0.209	0.188	0.050
H(21A)	0.553	0.462	−0.098	0.050
H(21B)	0.474	0.500	−0.059	0.050
H(27)	0.532	0.209	−0.149	0.050
H(28)	0.597	0.090	−0.211	0.050
H(31)	0.458	−0.088	−0.093	0.050
H(32)	0.393	0.036	−0.031	0.050
H(34)	0.084	0.183	0.249	0.050
H(35)	0.159	0.045	0.255	0.050
H(36)	0.076	−0.081	0.243	0.050

[a] U_{eq} is one third of the trace of the orthogonalized U_{ij} tensor. Atoms of the lattice-included benzene, located on inversion, are CH(34), CH(35) and CH(36).

TABLE 5

ATOMIC COORDINATES AND ISOTROPIC THERMAL PARAMETERS FOR [Ru$_2$(s-C$_4$H$_9$CO$_2$)$_2$(CO)$_4$(s-C$_4$H$_9$CO$_2$H)]$_2$

Atom	x	y	z	U_{eq}/U (Å^2) ^{a}
Ru(1)	0.5974(1)	0.1437(1)	0.8160(1)	0.0491
C(2)	0.5643(15)	0.3045(14)	0.8605(10)	0.0745
O(3)	0.5409(14)	0.4053(10)	0.8848(9)	0.1154
C(4)	0.4624(13)	0.0839(13)·	0.8995(9)	0.0686
O(5)	0.3728(11)	0.0425(11)	0.9512(8)	0.1009
O(6)	0.6338(8)	−0.0442(7)	0.7627(6)	0.0664
C(7)	0.5537(13)	−0.1461(9)	0.6859(10)	0.0630
C(8)	0.5796(10)	−0.2826(12)	0.6629(9)	0.0976
C(9)	0.7362(12)	−0.2632(21)	0.6400(17)	0.147
C(10)	0.5672(21)	−0.3247(22)	0.7659(12)	0.162
C(11)	0.4098(20)	−0.3572(22)	0.7865(18)	0.161
O(12)	0.4570(8)	−0.1460(6)	0.6244(6)	0.0548
Ru(13)	0.4322(1)	0.0374(1)	0.6276(1)	0.0427
C(14)	0.4202(13)	0.1988(11)	0.6291(9)	0.0641
O(15)	0.4151(13)	0.2998(9)	0.6279(8)	0.1111
C(16)	0.2707(13)	0.0053(13)	0.6928(9)	0.0672
O(17)	0.1663(10)	−0.0107(12)	0.7343(8)	0.1101
O(18)	0.6320(5)	0.0787(6)	0.5580(5)	0.0449
C(19)	0.7453(10)	0.1594(10)	0.6158(9)	0.0598
C(20)	0.8797(8)	0.1983(9)	0.5580(9)	0.1123
C(21)	0.9964(20)	0.1621(23)	0.6119(18)	0.182
C(22)	0.9714(21)	0.3514(11)	0.6070(25)	0.254
C(23)	0.8589(23)	0.4108(22)	0.5786(18)	0.175
O(24)	0.7563(8)	0.2072(8)	0.7186(6)	0.0702
C(25)	−0.1454(28)	0.6185(25) ·	0.0620(21)	0.204
C(26)	−0.1457(21)	0.7271(23)	0.0117(18)	0.170
C(27)	0.0293(29)	0.6869(27)	−0.1489(18)	0.224
C(28)	−0.0068(14)	0.7664(18)	−0.0406(12)	0.140
C(29)	0.1255(11)	0.8438(17)	0.0482(9)	0.0873
O(30)	0.2115(9)	0.7861(9)	0.0573(6)	0.0784
O(31)	0.1338(10)	0.9602(10)	0.1075(8)	0.0950

^{a} U_{eq} is one third of the trace of the orthogonalized U_{ij} tensor. Atoms C(9)–C(11), C(21)–C(23) and C(25)–C(28) in the partially disordered aliphatic side chains were refined with isotropic temperature factors only.

mg, 48%). Anal. Found: C, 47.70; H, 2.69. C$_{16}$H$_{11}$O$_6$Ru calcd.: C, 48.00; H, 2.75%. ^{13}C NMR (90.56 MHz, CDCl$_3$): 128.38, 128.56, 129.17, 130.34, 131.68, 132.79, 134.11 (aromatic C), 174.03 (COOH), 178.93 (COO), 200.25 (CO). A single crystal of 3 was used for X-ray diffraction analysis (Fig. 2).

Treatment of 3 in cyclohexane with CO (750 psi) at 80°C for 2 h gave a solution containing a mixture of 1 and 3. IR (cyclohexane): 2095s, 2080vs, 2030vs, 2005vs, 1950vs, 1670s, 1595s, 1550s, 1415vsbr cm^{-1}.

[Ru(PhCOO)(CO)$_2$Ph$_3$P]$_2$ (4). The polymer 9 (13 mg) was suspended in diethyl ether (1 ml) containing triphenylphosphine (17 mg). The mixture was refluxed for 1 h, the yellow crystals were filtered off, and washed with diethyl ether to give 4 (16 mg, 63%). Anal. Found: C, 59.71; H, 3.92. C$_{27}$H$_{20}$O$_4$PRu calcd.: C, 60.00; H, 3.70%. Identical material was obtained by treating 2 and 3 with triphenylphosphine in ether and 1 in benzene as described above, and also (in 75–85% yield) by treating

TABLE 6

GEOMETRY OF THE COORDINATION SPHERE OF RUTHENIUM [a]

(a) Bond lengths (Å) and angles (°) within the Ru−Ru−(CO)₄−di-carboxylato core

3		11		25	
Ru(1)−Ru(1')	2.637(2)	Ru(1)−Ru(18)	2.649(2)	Ru(1)−Ru(13)	2.630(2)
Ru(1)−C(2)	1.826(7)	Ru(1)−C(2)	1.883(11)	Ru(1)−C(2)	1.832(16)
Ru(1)−C(4)	1.842(6)	Ru(1)−C(6)	1.864(10)	Ru(1)−C(4)	1.806(12)
		Ru(18)−C(19)	1.826(11)	Ru(13)−C(14)	1.815(14)
		Ru(18)−C(22)	1.831(11)	Ru(13)−C(16)	1.802(13)
Ru(1)−O(6)	2.146(3)	Ru(1)−O(8)	2.119(6)	Ru(1)−O(6)	2.130(8)
Ru(1)−O(14')	2.121(4)	Ru(1)−O(33)	2.113(6)	Ru(1)−O(24)	2.097(8)
		Ru(18)−O(17)	2.136(6)	Ru(13)−O(12)	2.104(8)
		Ru(18)−O(24)	2.109(6)	Ru(13)−O(18)	2.157(6)
C(2)−O(3)	1.144(9)	C(2)−O(3)	1.107(14)	C(2)−O(3)	1.162(21)
C(4)−O(5)	1.123(9)	C(6)−O(7)	1.129(13)	C(4)−O(5)	1.170(16)
		C(19)−O(20)	1.133(13)	C(14)−O(15)	1.135(18)
		C(22)−O(23)	1.134(13)	C(16)−O(17)	1.160(16)
O(6)−C(7)	1.265(7)	O(8)−C(9)	1.249(11)	O(6)−C(7)	1.259(11)
O(14)−C(7)	1.241(8)	O(17)−C(9)	1.271(10)	O(12)−C(7)	1.247(16)
		O(24)−C(25)	1.267(11)	O(18)−C(19)	1.236(10)
		O(33)−C(25)	1.256(11)	O(24)−C(19)	1.260(13)
Ru(1)−C(2)−O(3)	179.3(7)	Ru(1)−C(2)−O(3)	176.6(10)	Ru(1)−C(2)−O(3)	177.5(12)
Ru(1)−C(4)−O(5)	179.2(6)	Ru(1)−C(6)−O(7)	175.7(9)	Ru(1)−C(4)−O(5)	178.2(11)
		Ru(18)−C(19)−O(20)	175.3(9)	Ru(13)−C(14)−O(15)	175.2(11)
		Ru(18)−C(22)−O(23)	176.3(10)	Ru(13)−C(16)−O(17)	177.3(13)
Ru(1)−O(6)−C(7)	122.6(3)	Ru(1)−O(8)−C(9)	121.4(6)	Ru(1)−O(6)−C(7)	122.2(8)
Ru(1')−O(14)−C(7)	123.8(4)	Ru(18)−O(17)−C(9)	120.3(6)	Ru(13)−O(12)−C(7)	121.2(7)
		Ru(18)−O(24)−C(25)	122.7(6)	Ru(13)−O(18)−C(19)	120.4(7)
		Ru(18)−O(33)−C(25)	121.3(6)	Ru(1)−O(24)−C(19)	125.5(8)
O(6)−C(7)−O(14)	123.8(5)	O(8)−C(9)−O(17)	125.6(9)	O(6)−C(7)−O(12)	122.2(8)
		O(24)−C(25)−O(33)	124.7(8)	O(18)−C(19)−O(24)	123.5(10)

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(b) Bond lengths (Å) and angles (°) between Ru and side ligands

Ru(1)–O(17)	2.265(5)	Ru(18)–O(21)	2.299(6)	Ru(1)–O(30)	2.259(8)
		Ru(1)–C(4)	1.999(11)	Ru(13)–O(18')	2.314(6)
O(17)–C(15)	1.222(8)	C(4)–O(5)	1.101(14)	O(30)–C(29)	1.253(21)
C(15)–O(16)	1.316(6)			C(29)–O(31)	1.252(19)
Ru(1)–O(17)–C(15)	131.8(4)	Ru(1)–C(4)–O(5)	174.6(10)	Ru(1)–O(30)–C(29)	129.6(8)
O(17)–C(15)–O(16)	122.9(6)			O(30)–C(29)–O(31)	125.6(12)

(c) Angular disposition of ligating atoms around Ru

C(2)–Ru(1)–C(4)	87.2(3)	C(2)–Ru(1)–C(6)	90.0(4)	C(2)–Ru(1)–C(4)	86.8(6)
O(6)–Ru(1)–O(14')	85.3(1)	O(8)–Ru(1)–O(33)	84.1(2)	O(6)–Ru(1)–O(24)	84.9(3)
C(2)–Ru(1)–O(6)	94.6(2)	C(2)–Ru(1)–O(33)	95.3(4)	C(2)–Ru(1)–O(24)	95.2(5)
C(4)–Ru(1)–O(14')	92.9(2)	C(6)–Ru(1)–O(8)	90.3(3)	C(4)–Ru(1)–O(6)	93.2(5)
Ru(1')–Ru(1)–O(17)	162.8(1)	Ru(18)–Ru(1)–C(4)	171.1(3)	Ru(13)–Ru(1)–O(30)	161.7(2)
		C(19)–Ru(18)–C(22)	86.2(5)	C(14)–Ru(13)–C(16)	88.4(6)
		O(17)–Ru(18)–O(24)	86.6(2)	O(12)–Ru(13)–O(18)	84.9(3)
		C(19)–Ru(18)–O(17)	95.1(4)	C(16)–Ru(13)–O(12)	94.4(5)
		C(22)–Ru(18)–O(24)	92.1(4)	C(14)–Ru(13)–O(18)	92.3(5)
		Ru(1)–Ru(18)–O(21)	159.8(2)	Ru(1)–Ru(13)–O(18')	156.5(2)

(d) Torsion angles (°) around the Ru–Ru bond

C(2)–Ru(1)–Ru(1')–C(4')	10.9(3)	C(2)–Ru(1)–Ru(18)–C(22)	17.6(5)	C(2)–Ru(1)–Ru(13)–C(14)	15.6(6)
		C(6)–Ru(1)–Ru(18)–C(19)	21.0(5)	C(4)–Ru(1)–Ru(13)–C(16)	14.7(6)
O(6)–Ru(1)–Ru(1')–O(14)	9.1(2)	O(8)–Ru(1)–Ru(18)–O(17)	16.6(2)	O(6)–Ru(1)–Ru(13)–O(12)	12.7(3)
		O(24)–Ru(1)–Ru(18)–O(33)	14.0(3)	O(18)–Ru(1)–Ru(13)–O(24)	13.1(3)

[a] Atom numbers are those used in refs. 10 and 11 and Figs. 1, 3 and 4. Primed atoms are related to the corresponding nonprimed atoms by a symmetry of twofold rotation in **3** and inversion in **25**.

equimolar solutions of **1**, **2** and **3** with triphenylphosphine in ether at room temperature.

[Ru(PhCOO)(CO)₂Me₃N]₂ (5). A mixture of dodecacarbonyltriruthenium (67 mg, 0.105 mmol), benzoic acid (0.5 g, 4.13 mmol), and triethylamine (40% aq., 3.54 g) was heated overnight in a closed glass-lined reactor under nitrogen (800 psi) at 145°C. The yellow solid which separated upon cooling was filtered off, washed and recrystallized from acetone, **5** (70 mg, 66%) Anal. Found: C, 42.60; H, 4.28. $C_{12}H_{14}NO_4Ru$ calcd.: C, 42.73; H, 4.15%.

An identical product was obtained by treating **3** and **8** with triethylamine as described above. Complex **5** was transformed into **1** when exposed to CO in toluene at 145°C.

[Ru(PhCOO)(CO)₂MeOCMe₃]₂ (7). The polymer (**9**) (100 mg) was dissolved in a solution of methyl-t-butyl ether to give crystals of **7** (50 mg, 38%).

[Ru₂(PhCOO)₂(CO)₄Me₂CO]₂ (8). A mixture of dodecacarbonyltriruthenium (100 mg, 0.16 mmol) and benzoic acid (300 mg, 2.5 mmol) was heated for 16 h at 145°C in a closed glass-lined reactor. The orange-yellow solid was chromatographed (silica) and elution with 1/10 ether/petroleum ether gave an orange red substance (80 mg) which upon crystallization from acetone petroleum ether gave **8** (30 mg, 12%). Anal. Found: C, 40.25; H, 2.83. $C_{21}H_{16}O_9Ru_2$ calcd.: C, 41.04; H, 2.61%. (More **8** was recovered from the mother liquor from the recrystallization.) Elution of the column with ether gave **3** (28 mg, 15%).

[Ru(PhCOO)(CO)₂]ₙ (9). A mixture of dodecacarbonyltriruthenium (54 mg, 0.084 mmol), benzoic acid (31 mg, 0.25 mmol) , and toluene (2.5 ml) was refluxed for 47 h. The orange precipitate was filtered off, washed with dichloromethane, and dried in vacuo to give **9**, (27 mg, 38%). Anal. Found: C, 39.07; H, 1.69. $C_9H_5O_4Ru$ calcd.: C, 38.85; H, 1.80%. This substance was insoluble in non-ligating organic solvents.

Reaction in an open vessel. A mixture of dodecacarbonyltriruthenium (200 mg, 0.31 mmol) benzoic acid (183 mg, 1.5 mmol) and benzene (10 ml) was heated under reflux and the IR spectrum was recorded at intervals. After 2 h there were bands at 2100m, 2080s, 2060vs, 2035vs, 2005vs, 1695vs, 1550m, and 1415s cm^{-1} which show the presence of $H_4Ru_4(CO)_{12}$ (**1**) and benzoic acid. After 6 h there were bands at 2105m, 2082s, 2065s, 2040vs, 2005vs, 1970w, 1940m, 1695s, 1670m, 1555s, 1415vs cm^{-1}. Subsequently the band at 1670 cm^{-1} (**3**) increased with concomitant decrease of the free PhCOOH band (1695 cm^{-1}). After 48 h the homogeneous solution was evaporated and the residue was chromatographed as described above to give **2** and **3**.

4-Fluorobenzoate complexes

[Ru(4-FC₆H₄COO)(CO)₃]₂ (10). Dodecacarbonyltriruthenium (250 mg, 0.39 mmol) and 4-fluorobenzoic acid (250 mg, 1.8 mmol) were heated together at 145°C for 16 h in a closed glass-lined reactor. The solid was dissolved in hot benzene, to give a solution which had the IR spectrum of **10**. Attempted crystallization of **10** from benzene gave yellow crystals of **11** (133 mg, 34%). The triphenylphosphine derivative **13** (Table 1) was obtained by mixing equimolar quantities of **10** and triphenylphosphine in benzene at room temperature.

[Ru₂(4-FC₆H₄COO)₂(CO)₅(H₂O)] · 0.5C₆H₆ (11). A mixture of dodeca-carbonyltriruthenium (210 mg, 0.33 mmol), 4-fluorobenzoic acid (154 mg, 1.1 mmol)

and toluene (5 ml) was heated at 145°C for 16 h in a closed glass-lined reactor. The yellow crystals which separated upon cooling were filtered off and recrystallized from benzene to give **11** (160 mg, 48%). Anal. Found: C, 38.60; H, 1.59; F, 5.93. $C_{22}H_{13}F_2O_{10}Ru_2$ calcd.: C, 39.00; H, 1.92; F, 5.61%. ^{13}C NMR (90.56 MHz, $CDCl_3$) [19]: 115.11d (J(C–F) 21.7 Hz; C(3)), 128.42d (J 13 Hz; C(2)), 132.4d (J 9.0 Hz; C(1)), 165.5d (J 252.6 Hz; C(4)), 197.8m (CO). ^{19}F NMR (338.68 MHz, $CDCl_3$): −107.0s ($sw_{1/2}$ 30 Hz).

A single crystal obtained in this way was used for an X-ray diffraction study [10].

[Ru(4-FC$_6$H$_4$COO)(CO)$_2$4-FC$_6$H$_4$COOH]$_2$ (12). A mixture of dodeca-carbonyltriruthenium, (185 mg, 0.289 mmol) 4-fluorobenzoic acid (400 mg, 2.86 mmol), and toluene (5 ml) was refluxed for 3 h, after which the IR spectrum (toluene) showed bands 2100vs, 2070m, 2045vs, 2000vs, 1970vs, 1945s, 1695s, 1668vsbr, 1555m, 1400vs-br cm^{-1} which revealed the presence of $H_4Ru_4(CO)_{12}$, **11**, **12** and free acid. The free acid was precipitated by the addition of petroleum ether, and the solution was filtered then evaporated in vacuo. The residue was rapidly chromatographed on a short silica column. A yellow band eluted with dichloro-methane/petroleum ether gave **11** (35 mg, 13%). Elution with dichloromethane then gave a yellow oil, **12** (70 mg; 39%) which could not be crystallized. IR (Table 1). ^{19}F NMR (338. 68 MHz, $CDCl_3$): −104.3s ($sw_{1/2}$ 35 Hz), −106.75s ($sw_{1/2}$ 30 Hz). ^{13}C NMR (90.56 MHz, $CDCl_3$): 115.5d (J 21.7 Hz; C(3)), 115.9d (J 21.7 Hz; C(3)), 127.9d (J 12.7 Hz; C(2)), 128.7d (J 12.7 Hz; C(2)), 132.2d (J 9.1 Hz; C(1)), 133.1d (J 8.2 Hz; C(1)), 165.7d (J 253.5 Hz; C(4)), 166.6d (J 256.2 Hz; C(4)), 173.3s (COOH), 178.0s (COO), 200.1s (CO).

[Ru(4-FC$_6$H$_4$COO)(CO)$_2$]$_n$ (14). A mixture of dodecacarbonyltriruthenium (55 mg, 0.086 mmol), and 4-fluorobenzoic acid (36 mg, 0.257 mmol), and toluene (5 ml) was refluxed for 47 h. The orange precipitate (**14**) was filtered off, washed with dichloromethane and dried in vacuo (9 mg, 12%). Anal. Found: C, 36.74; H, 1.29. $C_9H_4O_4Ru$ calcd.: C, 36.49; H, 1.35%. The filtrate from the above crystallization was found to contain **11** and **12**.

4-Methoxybenzoato complexes

[Ru(4-MeOC$_6$H$_4$COO)(CO)$_3$]$_2$ (15). A mixture of dodecacarbonyltriruthenium (215 mg, 0.34 mmol) and anisic acid (155 mg, 1.02 mmol), and toluene (5 ml) was heated at 145°C for 16 h in a glass-lined closed reactor. The yellow solid **15** obtained upon cooling was filtered off and washed with toluene (250 mg, 74%). IR (Table 1). The triphenylphosphine derivative *[Ru(4-MeOC$_6$H$_4$COO)(CO)$_2$(Ph$_3$P)]$_2$ (19)* was obtained by treating **15** (8 mg, 0.012 mmol) in toluene (1 ml) at room temperature with a toluene solution of triphenylphosphine (0.3 ml, 0.08 M). Evaporation of the solvent and crystallization of the residue from benzene gave yellow crystals of **19** (Table 1).

[Ru$_2$(4-MeOC$_6$H$_4$COO)$_2$(CO)$_5$(H$_2$O)] (16). Attempted crystallization of **15** from toluene gave yellow crystals **16** containing 0.75 molecules of toluene (see NMR data, Table 1). Anal. Found: C, 43.24; H, 3.09. $C_{21}H_{16}O_{12}Ru_2 \cdot 0.75(C_7H_8)$ calcd.: C, 43.09; H, 3.01%. ^{13}C NMR (90.56 MHz, $CDCl_3$) [19]: 55.39 (MeO), 113.23 (C(3)), 125.9 (C(1)), 131.91 (C(2)), 162.99 (C(4)), 198.41 (CO).

[Ru(4-MeOC$_6$H$_4$COO)(CO)$_2$(4-MeOC$_6$H$_4$COOH)]$_2$ (17). A mixture of dodecacarbonyltriruthenium (100 mg, 0.156 mmol), anisic acid (370 mg, 2.43 mmol), and toluene (5 ml) was refluxed for 2 h. Unchanged anisic acid was filtered off after

cooling of the reaction mixture to room temperature, then hexane was added to the filtrate to give orange-brown crystals **17** containing 0.75 molecules of toluene (see NMR data, Table 1); these were washed with hexane (148 mg, 69%). Anal. Found: C, 49.75; H, 3.59. $C_{36}H_{30}O_{16}Ru_2 \cdot 0.75$ (C_7H_8) calcd.: C, 50.03; H, 3.64%.

[Ru(4-MeOC₆H₄COO)(CO)₂]ₙ (20). A mixture of dodecacarbonyltriruthenium (253 mg, 0.4 mmol), anisic acid (177 mg, 1.16 mmol), and toluene (5 ml) were refluxed for 3 h. The solvent was removed in vacuo to leave a brown oil (430 mg) which was dissolved in a mixture of dichloromethane/methyl-t-butyl ether (MTBE) and chromatographed on silica. The column was eluted with mixtures of MTBE and cyclohexane. $H_4Ru_4(CO)_{12}$ was obtained with a 10% and **16** with a 30% solvent mixture. With a 50% mixture, a yellow solution was obtained which upon evaporation gave a brown powder, **20** (100 mg), insoluble in non-ligating solvents (IR, Table 1). Dissolution of this powder in MTBE gave a crystalline product **18** (Table 1).

Pivalato complexes

[Ru₂(Me₃CCOO)(CO)₅H₂O] (21). A mixture of dodecacarbonyltriruthenium (335 mg, 0.52 mmol), pivalic acid (196 mg, 1.92 mmol), and benzene (5 ml) was refluxed for 4 h. The solution was set aside at room temperature for 24 h, then the yellow crystals of $H_4Ru_4(CO)_{12}$ (130 mg, 60%) were filtered off. The filtrate was evaporated and the residue was dissolved in dichloromethane and chromatographed on silica. Elution with dichloromethane/petroleum ether (1/1) gave a dark purple solid (140 mg); the IR (benzene): 2095s, 2085vs, 2040vs, 2005vs, 1945s, 1700m, 1675m, 1548s, 1428s cm^{-1}, identified a mixture of **21** and [Ru(Me₃CCOO)(CO)₃]₂ which could not be crystallized. Further elution of the column (dichloromethane) gave crystals of **22**, (75 mg, 13%).

[Ru(Me₃CCOO)(CO)₂Me₃CCOOH]₂ (22). A mixture of dodecacarbonyl-triruthenium (350 mg, 0.55 mmol) pivalic acid (1.32 g, 13 mmol), and toluene (5 ml) was heated in a closed glass-lined reactor under nitrogen at 145°C for 18 h. Ether was added to the cooled mixture and the orange crystals, **22** (218 mg, 31%) were filtered off, washed with hexane, and dried in vacuo. Anal. Found: C, 40.50; H, 5.11. $C_{12}H_{19}O_6Ru$ calcd.: C, 40.00; H, 5.28%. ^{13}C NMR (90.56 MHz, CDCl₃): 27.02 (CH₃), 27.73 (CH₃), 39.33 (Me₃C), 40.11 (Me₃C), 187.79 (COOH), 192.02 (COO), 200.58 (CO).

All the pivalic acid complexes resisted polymerization.

s-Butyrato complexes

[Ru(s-C₄H₉COO)(CO)₃]₂ (23). A suspension of **26** (10 mg) in cyclohexane was exposed to CO (250 psi) at 80°C for 3 h. The resulting yellow solution had an IR spectrum corresponding to **23** (Table 1).

[Ru₂(s-C₄H₉COO)₂(CO)₄(s-C₄H₉COOH)]₂ (25). A mixture of dodeca-carbonyltriruthenium (130 mg, 0.2 mmol) and 2-methylbutyric acid (290 mg, 2.84 mmol) was heated for 18 h at 145°C in a closed glass-lined reactor, then cooled. Crystallization from dichloromethane gave red crystals of **25** (126 mg, 67%), m.p. 240°C (dec.). Anal. Found: C, 36.87; H, 4.28, Ru, 32 (by AA). $C_{19}H_{28}O_{10}Ru_2$ calcd.: C, 36.89; H, 4.53; Ru, 32.69%. The complex was purified by chromatography on silica, no decomposition occurring. Its structure was determined by X-ray diffraction (Fig. 4) [11]. ^{13}C NMR (acetone-d_6, 22.63 MHz) [19]: 11.72, 12.13, 16.92, 17.96 (CH₃), 27.35, 28.25 (CH₂), 43.21, 44.19 (CH), 203 (CO).

The same complex was obtained when a two- or a six-fold molar excess of the acid with respect to Ru was used. The triphenylphosphine complex **24** was obtained by treating **25** (12 mg, 0.0097 mmol) with PPh_3 (12 mg, 0.046 mmol) in benzene at room temperature for 2 h. The crystals were filtered off and washed with ether (16 mg, 79%). ^{13}C NMR ($CDCl_3$, 90.56 MHz) [19]: 11.72, 17.20 (CH_3), 27.28 (CH_2), 43.77 (CH), 128.09, 129.52, 133.89 (aromatic C), 194.39 (CO).

[Ru(s-C$_4$H$_9$COO)(CO)$_2$]$_n$ (26). A mixture of dodecacarbonyltriruthenium (318 mg, 0.497 mmol), 2-methylbutyric acid (200 mg, 1.96 mmol) and benzene (5 ml) was refluxed for 14 h, and the IR spectrum recorded at intervals. After 8 h IR (benzene) bands at 2095vs, 2080vs, 2060sh, 2030vs, 2005vs, 1970sh, 1940vs, 1710m, 1685s, 1555s, 1425s cm^{-1} showed the presence of $H_4Ru_4(CO)_{12}$, $[Ru(s-C_4H_9COO)(CO)_3]_2$ and **25**. The orange precipitate present after 14 h was filtered off and washed with benzene, **26** (275 mg, 72%). Anal. Found: C, 33.03; H, 3.48. $C_7H_9O_4Ru$ calcd.: C, 32.56; H, 3.49%.

The IR spectrum of the benzene filtrate showed the presence of **25**.

Exchange experiments

(a) With benzoic acid. To aliquots (2.0 ml) of a toluene solution of **1** (0.012 M) were added 0.25 ml portions of 0.18 and 0.36 M solutions of benzoic acid in toluene. The two solutions were kept under nitrogen at 85°C and the IR band of **1** at 2085 cm^{-1} was periodically monitored. After 24 h the absorption intensity of the first solution was ca. twice that of the second. A new band at 1945 cm^{-1} which formed and disappeared with time was assigned to a type II complex, $[Ru_2(PhCOO)_2(CO)_5(PhCOOH)]$.

(b) With pyridine. To aliquots (3.0 ml) of a toluene solution of **1** (0.005 M) at −20°C were added 0.3 ml portions of 0.1 and 0.2 M solutions of pyridine in toluene. After 5 min at −20°C temperature the first solution consisted of a mixture of $Ru_2(PhCOO)_2(CO)_5Py$ and $[Ru(PhCOO)(CO)_2Py]_2$, IR (toluene): 2085m, 2025vs, 1995m-s, 1980m-s, 1948sbr, 1940sh cm^{-1}, while the second solution contained only the latter bi-pyridine complex, IR (toluene): 2030vs, 1980m-s, 1950vs cm^{-1}. NMR (360 MHz, $CDCl_3$): 7.27 (t, J 7.5 Hz, $2H_m$), 7.39 (t, J 7.5 Hz, $1H_p$), 7.54 (t, J 6.2 Hz, 2H), 7.85 (d, J 7.5 Hz, $2H_o$), 7.94 (dt, J 6.2, 1.2 Hz, 1H), 8.94 (dd, J 6.2, 1.2 Hz, 2H). Only after 20 min, did the two solutions exhibit the same infrared spectrum.

$[Ru_2(PhCOO)_2(CO)_5Py]$ was prepared by mixing a toluene solution of **1** (3 ml, 0.0034 M) with a toluene solution of pyridine (0.1 ml, 0.2 M) at −20°C). IR (toluene) 2085s, 2025vs, 1995vs, 1940m cm^{-1}. NMR (360 MHz, $CDCl_3$): 7.31 (t, J 7.4 Hz, $4H_m$), 7.43 (t, J 7.4 Hz, $2H_p$), 7.56 (t, J 7.2 Hz, 2H), 7.90 (d, J 7.4 Hz, $4H_o$), 7.95 (t, J 7.2 Hz, 1H), 8.89 (brs, 2H).

(c) With 4-methylbenzoic acid. A mixture of $[Ru(PhCOO)(CO)_2(PhCOOH)]_2$ (**3**), (20 mg, 0.025 mmol) 4-methylbenzoic acid (12 mg, 0.088 mmol), and benzene (5 ml) was refluxed for 4 h. Chromatography of the solution on silica and elution with 1/4 dichloromethane/petroleum ether gave **27** (12 mg, 56%, Table 1).

(d) With pivalic acid. $[Ru(PhCOO)(CO)_2(PhCOOH)]_2$ (11 mg, 0.014 mmol) was stirred overnight at room temperature with pivalic acid in toluene (1 ml, 0.02 M). The solvent was removed in vacuo to give a mixture of $[Ru_2(PhCOO)_2(CO)_4(PhCOOH)(Me_3CCOOH)]$, benzoic acid, and pivalic acid. NMR (360 MHz, $CDCl_3$): 1.07 (s, pivalic acid), 1.28 (s, 9H), 7.38 (t, J 7.9 Hz, $4H_m$, bridging benzoate), 7.49 (t,

J 7.7 Hz, $2H_p$, bridging benzoate and $4H_m$ benzoic acid), 7.64 (t, J 7.7 Hz, $2H_p$, benzoic acid), 7.86 (d, J 7.9 Hz, $4H_o$ bridging benzoate), 8.14 (d, J 7.7 Hz, $4H_o$ benzoic acid).

(e) With pivalic acid. $Ru(4\text{-}MeOC_6H_4COO)(CO)_2(4\text{-}MeOC_6H_4COOH)]_2$ (**17**) (37 mg, 0.04 mmol) was stirred overnight at room temperature with pivalic acid (1 ml, 0.08 M solution in dichloromethane). Addition of cyclohexane gave a mixture of white (anisic acid) and yellow crystals. Crystallization from toluene gave **22** (15 mg, 52%).

(f) With acetic acid. A mixture of $[Ru_2(PhCOO)_2(CO)_5H_2O]$ (**2**) (23 mg, 0.038 mmol) and 2 ml acetic acid was refluxed. The polymer **9** separated quantitatively after 2 h.

References

1 M. Rotem and Y. Shvo, Organometallics, 2 (1983) 1689.

2 G.R. Crooks, B.F.G. Johnson, J. Lewis and I.G. Williams, J. Chem. Soc. (A), (1969) 2761.

3 H. Schumann, H. Opitz and J. Pickardt, J. Organomet. Chem., 128 (1977) 253.

4 H. Schumann and J. Opitz, Chem. Ber., 113 (1980) 989.

5 M. Bianchi, G. Menchi, F. Francalanci and F. Piacenti, J. Organomet. Chem., 188 (1980) 109.

6 M. Bianchi, U. Matteoli, P. Ferdiani, F. Piacenti, M. Nardelli and G. Pellizzi, La Chimica E L'industria, 63 (1981) 475.

7 M. Bianchi, P. Ferdiani, U. Matteoli, G. Menchi, F. Piacenti and G. Pettrucci, J. Organomet. Chem., 259 (1983) 207.

8 U. Matteoli, G. Menchi, P. Ferdiani, M. Bianchi and F. Piacenti, J. Organomet. Chem., 285 (1985) 281.

9 G. Süss-Fink, G. Hermann and P. Morys, J. Organomet. Chem., 284 (1985) 263.

10 M. Rotem, I. Goldberg and Y. Shvo, Inorg. Chim. Acta, 97 (1985) L27.

11 M. Rotem, Y. Shvo, I. Goldberg and U. Shmueli, Organometallics, 3 (1984) 1758.

12 K. Nakamoto, Infrared and Raman Spectra of Inorganic Coordination Compounds, Wiley-Interscience, 2nd Ed. 1970, New York, p. 219.

13 S.D. Robinson and M.F. Uttley, J. Chem. Soc., Dalton Trans., (1973) 1912.

14 A.R. Chakravarty, F.A. Cotton, D.A. Tocher and J.H. Tocher, Organometallics, 4 (1985) 8.

15 G. Valle, V. Peruzzo, G. Tagliavini and P. Ganis, J. Organomet. Chem., 276 (1984) 325.

16 D.J. Darensbourg, Adv. Organomet. Chem., 21 (1982) 113; J.D. Atwood, M.J. Wovkulich and D.C. Sonnenberger, Acc. Chem. Res., 16 (1983) 350.

17 F. Basolo, Inorg. Chim. Acta, 100 (1985) 33.

18 N. Walker and D. Stuart, Acta Crystallogr., Sect. A, 39 (1983) 158.

19 Because of insufficient number of scans and due to the long relaxation time, the ^{13}C NMR signal of the carboxylate carbon could not be observed.