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Chemistry and Catalytic Properties of Ruthenium and Osmium Complexes. 2.[1a] Synthesis and Characterization of New Mononuclear and Dinuclear Complexes with Hydride, Carboxylate, and Phosphine Ligands. X-ray Crystal and Molecular Structures of $OsBr(OCOMe)(CO)(PPh_3)_2$, $RuCl(OCOMe)(CO)(PPh_3)_2$, and $[PPh_3Me]^+[Ru_2Cl_2(\mu\text{-}Cl)_3(CO)_2(PPh_3)_2]^-$

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The synthesis and characterization of a number of new compounds are reported. $RuHBr(CO)(PPh_3)_3$ is prepared by reaction of $RuH(OCOMe)(CO)(PPh_3)_2$ with excess HBr, followed by treatment with H_2, NEt_3, and PPh_3. Halo–carboxylate complexes $MX(OCOR)(CO)(PPh_3)_2$ (M = Ru, X = Cl, R = CH_2Cl; M = Ru, X = Br, R = CH_3; M = Os, X = Cl, Br, R = CH_3) are obtained from the hydrides $MHX(CO)(PPh_3)_3$ by reaction with the appropriate acid, while hydrido–carboxylate complexes $RuH(OCOR)(CO)(PPh_3)_2$ (R = CMe_3, C_6H_{11}, CH_2Cl, CF_2Cl) result from the reaction of $RuH_2(CO)(PPh_3)_3$ with carboxylic acids. Also, a novel reaction of $RuHCl(CO)(PPh_3)_3$ with CF_3CO_2H, CH_2ClCO_2H, and HBF_4, leading to three new dinuclear compounds, is described. All complexes have been characterized by analytical and spectroscopic (IR and ^1H and ^{31}P NMR) methods. In addition, structural details for two mononuclear complexes and one dinuclear complex are presented. $OsBr(OCOMe)(CO)(PPh_3)_2$ crystallizes in the monoclinic space group $P2_1/n$ with a = 9.760 (2) Å, b = 20.379 (4) Å, c = 17.462 (3) Å, β = 96.45 (2)°, and Z = 4. The structure converged to a conventional R factor of 0.048 for 3923 observations and 195 variables. The five ligands about the osmium adopt a highly distorted octahedral arrangement with the phosphines occupying mutually cis positions and the carboxylate bound in an asymmetric bidentate manner. $RuCl(OCOMe)(CO)(PPh_3)_2$ crystallizes in the monoclinic space group $P2_1/c$ with a = 17.776 (5) Å, b = 9.696 (2) Å, c = 20.862 (6) Å, β = 106.35 (3)°, and Z = 4. The structure has been refined to a conventional R factor of 0.111 for 6769 observations and 213 parameters. The CO and Cl ligands exhibit positional disorder. The Ru atom shows a distorted octahedral environment with the phosphines occupying mutually trans positions cis to the carboxylate, which is bound in a bidentate symmetric manner. $[PPh_3Me]^+[Ru_2Cl_2(\mu\text{-}Cl)_3(CO)_2(PPh_3)_2]^-\cdot CH_2Cl_2$ crystallizes in the monoclinic space group $P2_1/n$ with a = 19.966 (10) Å, b = 14.383 (6) Å, c = 20.064 (6) Å, and β = 93.36 (4)°. The structure has been refined to R = 0.079 for 6581 independent diffractometer data and 349 parameters. The Ru···Ru distance is 3.257 (1) Å. The anion has noncrystallographic m symmetry (if one neglects the differences of PPh_3 conformations). The μ-Cl–Ru bond distances for the μ-Cl atoms trans to the PPh_3 groups are significantly longer than those for the μ-Cl atoms trans to the Cl ligands (2.488 (2) and 2.510 (2) Å compared with 2.405 (2) and 2.402 (2) Å).

The chemistry of the carbonyl–halide–phosphine complexes of Ru(II) and Os(II), as well as that of their hydride derivatives, is very rich and complex. The stoichiometries $MX_2(CO)(PR_3)_3$, $MX_2(CO)_2(PR_3)_2$, $MHX(CO)(PR_3)_3$, and $MHX(CO)_2(PR_3)_2$ in various isomeric forms have been synthesized and characterized.[2] Interaction of hydrido(phosphine)ruthenium complexes with carboxylic acids produces a wide range of mononuclear mono- or bis(carboxylato) derivatives;[3] reactions of this type of hydride with inorganic acids of noncoordinating anions has led to the isolation of mononuclear cationic species.[4]

Carboxylate derivatives of these and other platinum-metal complexes have attracted much attention in view of the variety of structures and extensive chemistry displayed by them.[3,5] Interest in hydrido and carboxylate complexes of Ru(II) and Os(II) is further enhanced by their catalytic activity in a number of important reactions.[5c,6]

In the following paper of this series we describe a systematic study of the catalytic properties of such complexes for the homogeneus hydrogenation of aldehydes and ketones.[6k] This paper describes the synthesis and spectroscopic characterization of a number of new mononuclear ruthenium(II) and osmium(II) complexes, as well as a novel reaction between $RuHCl(CO)(PPh_3)_3$ with strong organic and inorganic acids to yield anionic and cationic triply bridged *dinuclear* complexes. Additionally, structural details of two mononuclear and one dinuclear compounds are reported.

Results and Discussion

1. The Complex $RuHBr(CO)(PPh_3)_3$.

Reaction of $RuCl_3\cdot x H_2O$ with PPh_3 and aqueous HCHO in boiling 2-methoxyethanol affords $RuHCl(CO)(PPh_3)_3$ (**1a**) in high yields.[7] This is a

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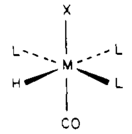
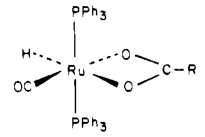
Table I. Selected IR[a] and ^{1}H and ^{31}P{^{1}H} NMR[b] Data for New Compounds

	^{1}H NMR						
	δ_{Me_4Si}			^{31}P{^{1}H} NMR,[c]	IR, cm^{-1}		
complex	R–CO_2	M–H	J_{P-H}, Hz	$\delta_{H_3PO_4}$	ν_{M-H}	ν_{CO}	$\nu_{(OCO)_a}$[d]
$RuH(OCOCMe_3)(CO)(PPh_3)_2$	0.2	−16.1	21.9		2000	1925	1510
$RuH(OCOCH_2Cl)(CO)(PPh_3)_2$	2.5	−16.9	20.2		2060	1940	1575
$RuH(OCOCF_2Cl)(CO)(PPh_3)_2$	...	−17.2 (br)	...		*e*	*e*	*e*
$RuH(OCOC_6H_{11})(CO)(PPh_3)_2$	0.7	−16.2	21.2		2025	1950	1525
$RuCl(OCOCH_2Cl)(CO)(PPh_3)_2$	2.4	...	...	33.9	...	1950	1545
$RuBr(OCOMe)(CO)(PPh_3)_2$	1.55	...	...	36.1	...	1960	1505
$OsBr(OCOMe)(CO)(PPh_3)_2$	2.35	...	...	8.5, −1.2[f]	...	1940	1530
$OsCl(OCOMe)(CO)(PPh_3)_2$	2.35	...	...	7.4, 0.07[f]	...	1940	1525

[a] In KBr disks. [b] In CD_2Cl_2 solution. [c] Positive values downfield from external 85% H_3PO_4. [d] Asymmetric mode; symmetric mode vibration usually obscured by PPh_3 bands. [e] Compound decomposes in Nujol mull or KBr disks. [f] Both signals observed as doublets, J_{P-P} = 10.0 Hz.

cream-colored stable solid, which has been used as a precursor to other compounds[3c,8] and as a catalyst in homogeneous reactions.[6f-k,9] The stereochemistry shown in **1a** has been suggested by analogy with the well-characterized complexes RuHCl(CO)($PMe_2Ph)_3$ (**1b**)[10] and $OsHBr(CO)(PPh_3)_3$ (**1c**),[11] since **1a** itself is an amorphous, rather insoluble material not amenable to X-ray or NMR studies.





2

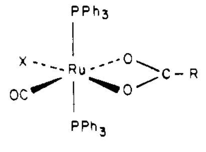
1a, M = Ru, X = Cl, L = PPh_3

1b, M = Ru, X = Cl, L = PMe_2Ph

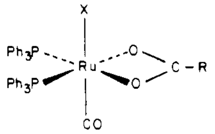
1c, M = Os, X = Br, L = PPh_3

1d, M = Ru, X = Br, L = PPh_3

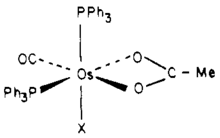
1e, M = Ru, X = I, L = PPh_3



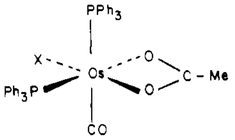
3a



3b



4a



4b

In our search for more soluble and more highly active catalysts we have attempted to prepare the unknown analogues RuHX(CO)($PPh_3)_3$ (X = Br (**1d**), I (**1e**)). Reaction of RuX_3, preformed or prepared in situ from $RuCl_3 \cdot xH_2O$ + LiX, with PPh_3 and HCHO in boiling 2-methoxyethanol affords low yields of impure materials. Simple halide exchange reactions of RuHCl(CO)($PPh_3)_3$ with LiX or NaX, a method known to be efficient for preparing the PMe_2Ph bromo and iodo analogues from the chlorinated complex,[10] also proved to be unsuccessful in this case.

The synthetic route we have devised for $RuHBr(CO)(PPh_3)_3$ (**1d**) involves reaction of $RuH(OCOMe)(CO)(PPh_3)_2$[3d] with an excess of HBr in refluxing methanol for 1 h; this yields an isoluble intermediate that we believe to be $[RuBr_2(CO)(PPh_3)_2]_2$ but have not isolated in a pure form (eq 1). This intermediate, suspended in toluene, is then reacted with H_2 at atmospheric pressure for 2 h in the presence of NEt_3 and PPh_3, to yield the desired product in ca. 70% yield (based on Ru) (eq 2). Analytically pure material is obtained by recrystallization from CH_2Cl_2/heptane mixtures. This method is not adequate for the iodo analogue **1e**, which we have not so far succeeded in preparing.

$$RuH(OCOMe)(CO)(PPh_3)_2 + 2HBr \rightarrow \tfrac{1}{2}\text{“}[RuBr_2(CO)(PPh_3)_2]_2\text{”} + H_2 + CH_3CO_2H \quad (1)$$

$$\tfrac{1}{2}\text{“}[RuBr_2(CO)(PPh_3)_2]_2\text{”} + H_2 + PPh_3 + NEt_3 \rightarrow RuHBr(CO)(PPh_3)_3 + Et_3N \cdot HBr \quad (2)$$

The spectroscopic properties of $RuHBr(CO)(PPh_3)_3$[12] agree with the stereochemistry shown in **1d**.

2. Mononuclear Carboxylate Complexes. Robinson has reported[3d] the reactions of alkane- and arenecarboxylic acids with $RuHCl(CO)(PPh_3)_3$ and $RuH_2(CO)(PPh_3)_3$ to yield a variety of $RuCl(OCOR)(CO)(PPh_3)_2$ and $RuH(OCOR)(CO)(PPh_3)_2$ complexes, respectively. According to this report, osmium carbonyl hydride precursors *do not react* with nonfluorinated carboxylic acids to yield the corresponding osmium analogues;[3d] moreover, examples of osmium–carboxylate derivatives are rather scarce.[13]

As part of our systematic study of the catalytic properties of this type of compound,[6k] we have synthesized some new members of the ruthenium families by slight modifications of the original methods[3d,14] and characterized them by their spectroscopic properties shown in Table I. The new compound RuHBr(CO)($PPh_3)_3$ also reacts with acetic acid to yield the corresponding acetate derivative.

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(12) Vibrational spectroscopy: ν_{CO}, 1950 cm^{-1} (s); ν_{M-H}, 2020 cm^{-1} (w); ν_{Ru-Br}, 205 cm^{-1} (Raman); ν_{Ru-Cl} for RuHCl(CO)($PPh_3)_3$, 225 cm^{-1} (Raman). ^{1}H NMR (−20 °C, CD_2Cl_2): δ_{Me_4Si} −7.52 (dt, $J_{HP(trans)}$ = 101 Hz, $J_{HP(cis)}$ = 24 Hz). ^{31}P{^{1}H} NMR (−20 °C, CD_2Cl_2): $\delta_{H_3PO_4}$ 10.05 (t), 38.09 (d, J_{PP} = 16 Hz). NMR spectra at 25 °C are broad.

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Table II. Selected Interatomic Distances (Å) and Angles (deg) for $OsBr(OCOMe)(CO)(PPh_3)_2$

Os–P1	2.331 (2)	P1–Os–P2	101.8 (1)	Os–P1–C101	119.6 (3)
–P2	2.345 (2)	–Br	88.3 (1)	–C111	113.9 (3)
–O1	2.209 (6)	–C3	89.5 (3)	–C121	116.3 (3)
–O2	2.139 (6)	–O1	108.2 (2)	Os–P2–C201	118.4 (3)
–Br	2.562 (1)	–O2	164.6 (2)	–C211	108.9 (3)
–C3	1.795 (9)	P2–Os–Br	167.0 (1)	–C221	120.0 (3)
P1–C101	1.837 (9)	–C3	91.5 (3)	Os–C3–O3	173.7 (8)
–C111	1.840 (9)	–O1	85.4 (2)	Os–O1–C1	88.2 (5)
–C121	1.843 (10)	–O2	87.8 (2)	Os–O2–C1	92.5 (5)
P2–C201	1.834 (9)	Br–Os–C3	96.6 (3)	O1–C1–O2	119.0 (8)
–C211	1.846 (9)	–O1	83.8 (2)	–C2	120.7 (8)
–C221	1.840 (9)	–O2	80.7 (2)	O2–C1–C2	120.3 (8)
C3–O3	1.177 (11)	C3–Os–O1	162.3 (3)		
C1–O1	1.286 (11)	–O2	102.3 (3)		
–O2	1.244 (11)	O1–Os–O2	60.2 (2)		
–C2	1.559 (15)				

Table III. Selected Interatomic Distances (Å) and Angles (deg) for $RuCl(OCOMe)(CO)(PPh_3)_2$

Ru–P1	2.376 (2)	P1–Ru–P2	178.9 (1)	C3–Ru–O1	161.4 (9)
–P2	2.370 (2)	–Cl1	92.7 (1)	–O2	101.1 (9)
–O1	2.152 (6)	–Cl1′	87.3 (1)	C3′–Ru–O1	104.3 (7)
–O2	2.144 (6)	–C3	86.4 (8)	–O2	163.8 (7)
–Cl1	2.364 (6)	–C3′	90.6 (5)	O1–Ru–O2	60.3 (2)
–Cl1	2.332 (6)	–O1	93.5 (1)	Ru–P1–C101	113.5 (2)
–C3	1.744 (32)	–O2	85.7 (1)	–C111	115.3 (2)
–C3′	1.730 (20)	P2–Ru–Cl1	86.8 (1)	–C121	115.3 (2)
P1–C101	1.824 (8)	–Cl1′	93.8 (1)	Ru–P2–C201	113.6 (2)
–C111	1.814 (8)	–C3	94.7 (8)	–C211	113.7 (2)
–C121	1.822 (8)	–C3′	88.9 (5)	–C221	115.5 (3)
P2–C201	1.810 (8)	–O1	85.6 (1)	Ru–C3–O3	169.3 (24)
–C211	1.813 (8)	–O2	94.5 (1)	Ru–C3′–O3′	173.8 (17)
–C221	1.799 (9)	Cl1–Ru–C3	94.0 (9)	Ru–O1–C1	90.7 (5)
C3–O3	1.022 (38)	–O1	104.6 (2)	Ru–O2–C1	91.2 (5)
C3′–O3′	1.200 (26)	–O2	164.7 (2)	O1–C1–O2	117.8 (6)
C1–O1	1.264 (10)	Cl1′–Ru–C3′	94.9 (7)	–C2	122.5 (9)
–O2	1.258 (11)	–O1	160.8 (2)	O2–C1–C2	119.6 (8)
–C2	1.514 (15)	–O2	100.6 (2)		

The data for the hydrides $RuH(OCOR)(CO)(PPh_3)_2$ are in agreement with the stereochemistry **2**, as previously assigned by Robinson for analogous compounds.[3d,14] The spectroscopic data for $RuCl(OCOCH_2Cl)(CO)(PPh_3)_2$ and $RuBr(OCOMe)(CO)(PPh_3)_2$ are similar to those of previously known members of this series[3d] but do not allow one to distinguish between structures **3a** and **3b**; the former, containing the two phosphine ligands in mutually *trans* positions, has been confirmed by McGuiggan and Pignolet for the benzoate complex[15] and now by us for the compound $RuCl(OCOMe)(CO)(PPh_3)_2$ (vide infra).

More interestingly, we find that the osmium complexes $OsHX(CO)(PPh_3)_3$ (X = Cl, Br) *do react* with acetic acid in toluene to yield $OsX(OCOMe)(CO)(PPh_3)_2$. The spectroscopic properties of these complexes, also collected in Table I, suggest a different stereochemistry from that of the ruthenium series in that the two phosphine ligands occupy mutually cis positions (two doublets with $J_{P-P} \sim 10$ Hz in the ^{31}P spectrum); this evidence was, however, insufficient to distinguish between isomers **4a** and **4b**. Consequently, an X-ray diffraction study of the bromo compound was undertaken, and structure **4a** has been confirmed (vide infra).

This difference in stereochemistries for the ruthenium and osmium acetate complexes is reflected in their different catalytic behavior and presumably in their general reactivity, which appears to be largely dominated by the bidentate–monodentate carboxylate transformation.[6k] This opening of the carboxylate is in turn influenced by the labilizing influence of the ligands trans to the metal–oxygen bonds and the steric strain imposed by the ligand arrangement around the central metal atom.

3. Solid-State Structures of $OsBr(OCOMe)(CO)(PPh_3)_2$ and $RuCl(OCOMe)(CO)(PPh_3)_2$. $OsBr(OCOMe)(CO)(PPh_3)_2$ (4a).

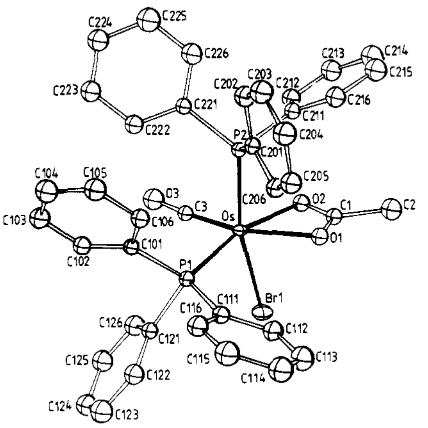

Figure 1. View of a $OsBr(OCOMe)(CO)(PPh_3)_2$ molecule with atom numbering.

The molecular structure of this mononuclear complex is shown in Figure 1, and selected distances and angles are listed in Table II. The five ligands about the osmium adopt a highly distorted octahedral arrangement, with the phosphines occupying mutually cis positions, in contrast with $RuCl(OCOMe)(CO)(PPh_3)_2$ and other similar ruthenium complexes in which the phosphines are located in a *trans* arrangement (vide infra). The acetate group is bonded in an asymmetric bidentate manner, with Os–O distances of 2.139 (6) and 2.209 (6) Å, comparable to those found for other osmium acetate complexes[13,16] and also in RuCl(OCOMe)-

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(15) McGuiggan, M. F.; Pignolet, L. H. *Cryst. Struct. Commun.* **1978**, *7*, 583–588.

(16) (a) Cotton, F. A.; Goodgame, D. M. L.; Soberberg, R. H. *Inorg. Chem.* **1963**, *2*, 1162. (b) Taylor, J. C.; Mueller, M. H.; Hitterman, R. L. *Acta Crystallogr.* **1966**, *20*, 842. (c) Behling, T.; Capparelli, M. V.; Skapski, A. C.; Wilkinson, G. *Polyhedron* **1982**, *1*, 840–841.

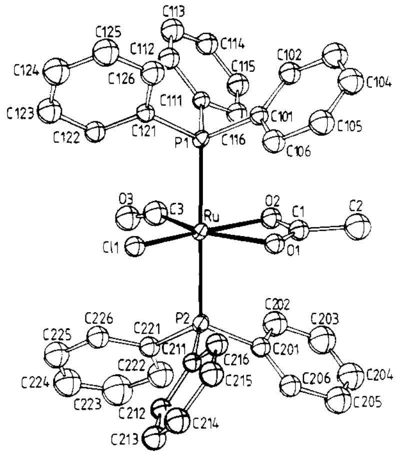


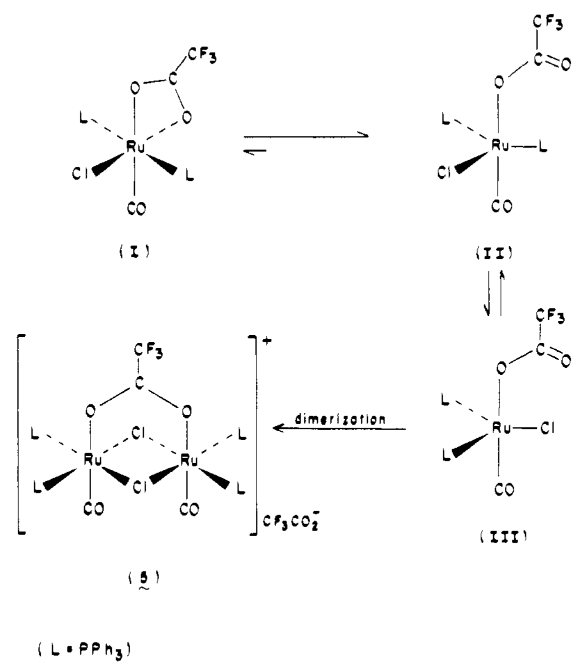
Figure 2. View of a $RuCl(OCOMe)(CO)(PPh_3)_2$ molecule with atom numbering. Deliberately only one of the two possible OC–Ru–Cl arrangements was drawn. In the other one CO and Cl ligands have exchanged their places.

$(CO)(PPh_3)_2$ (in the latter compound the metal–O distances are equal in length, however) (Table III). The longer Os–O bond is opposite to the carbonyl ligand; the two C–O distances are similar (1.286 (11) and 1.244 (11) Å), but the Os–O–C angles are different (88.2 (5) and 92.5 (5)°) due to the asymmetric binding to the metal. The Os–P bond lengths (2.331 (2) and 2.345 (2) Å) are slightly shorter than the Ru–P bond lengths in $RuCl(OCOMe)(CO)(PPh_3)_2$ (2.370 (2) and 2.376 (2) Å; Table III). The P–Os–P (101.8 (1)°), Br–Os–C3 (96.6 (3)°), and Br–Os–P2 (167.0 (1)°) angles are considerably distorted from ideal octahedral geometry in order to minimize the steric congestion arising from the meridional arrangement of three bulky ligands, i.e. two phosphines and a bromide. Further distortion from the octahedral structure is caused by the small bite angle of the acetate ligand (60.2 (2)°). Other bond distances and angles are normal.

$RuCl(OCOMe)(CO)(PPh_3)_2$ (3a). The molecular structure is shown in Figure 2, and selected distances and angles are listed in Table III. The central metal atom has a distorted octahedral coordination geometry, with the phosphines occupying mutually trans positions, cis to the carboxylate ligand, which is coordinated in a bidentate symmetric manner as in previously reported analogous ruthenium compounds.[15,17] The distortion from the octahedral structure arises essentially from the small angle subtended by the bidentate acetate (60.3 (2)°). Alternatively, this complex can be viewed as a pseudo-trigonal-bipyramidal species, with the bidentate acetate occupying one coordination site.[16] The structure is disordered in that ca. 50% of the molecules have the arrangement shown in Figure 2 and the other 50% have the CO and Cl groups in exchanged positions. McGuiggan and Pignolet report that in the structurally very similar compound $RuCl(OCOC_6H_5)(CO)(PPh_3)_2$ "the distances involving the ruthenium carbonyl groups are unreasonable".[15] It seems likely to us that in that structure the same type of positional disorder (perhaps to a different degree) is present as in $RuCl(OCOMe)(CO)(PPh_3)_2$. The two Ru–P distances (2.376 (2) and 2.370 (2) Å) as well as the distances and angles of the RuOCOMe unit (Ru–O1 = 2.152 (6) Å, Ru–O2 = 1.144 (6) Å, O1–Ru–O2 = 60.3 (2)°) compare well with the corresponding values of related compounds.[15,17]

4. Dinuclear Complexes. The known chemistry of dinuclear ruthenium complexes containing tertiary phosphines is rather limited,[18] possibly due to the lack of general synthetic routes to such compounds. We have found that interaction of the ruthenium hydride **1a** with strong acids leads to the formation of this type of dimeric species in what appears to be a new preparative method of general applicability.

Scheme I



Reaction of 1a with CF_3CO_2H. The interaction of $RuHCl(CO)(PPh_3)_3$ with CF_3CO_2H in 2-methoxyethanol has been reported to yield a "rather intractable material of apparent stoichiometry $RuCl(OCOCF_3)(CO)(PPh_3)_2{\cdot}0.5CF_3CO_2H$".[3c] We find that when a mixture of **1a** and trifluoroacetic acid in toluene is refluxed, or better heated to 150 °C for 2 h in a sealed tube or autoclave, the metal compound slowly goes into solution and a yellow color develops. After proper workup, high yields (ca. 80%) of the product can be isolated as yellow needles. Analytical data are consistent with the stoichiometry $RuCl(OCOCF_3)(CO)(PPh_3)_2{\cdot}CF_3CO_2H$; molecular weight values in solution (1200) as well as cyclic voltammetry studies[19a] suggest, but do not conclusively establish, a dinuclear formulation. The spectroscopic properties of the compound[19b] do not allow an unambiguous structural assignment.

An X-ray diffraction study of this compound confirmed a dinuclear cationic formulation as shown in **5** (Scheme I), with a trifluoroacetate anion and two molecules of trifluoroacetic acid of crystallization. The quality of the structure, however, is poor due to the low quality of the crystals (R = 0.142 and $R_w(F)$ = 0.154 for 6367 reflections, 112 atoms, and 489 parameters). Gentle reflux of this compound with an excess of $LiPF_6$ in toluene yields the PF_6 salt of the complex.

The structure **5**, containing two chloride bridges and *one single* carboxylate bridge, is interesting in that it represents, to our knowledge, the first example of a dinuclear ruthenium complex with a single carboxylate bridge. In fact, despite the very large number of dinuclear transition-metal carboxylate complexes that have been structurally characterized,[5c,5f,20] the occurrence of single carboxylate bridges is indeed very rare,[21] since they normally appear in pairs.

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(17) (a) Clark, G. R.; Waters, J. M.; Whittle, K. R. *J. Chem. Soc., Dalton Trans.* **1975**, 2556–2560. (b) Skapski, A. C.; Stephens, F. A. *J. Chem. Soc., Dalton Trans.* **1974**, 390–395.

(18) Bennet, M. A.; Bruce, M. I.; Matheson, T. W. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Abel, E. W., Stone, F. G. A., Eds.; Pergamon Press: London, New York, 1982; Vol. 4, p 835.

(19) (a) Cyclic voltammograms of this complex show two independent waves corresponding to two metal centers. The redox process is, however, not reversible, and therefore no $E_{1/2}$ values could be obtained. (b) IR: ν_{CO}, 1980 and 1975 cm^{-1}; $\nu_{OCO(asym)}$), 1645 cm^{-1}. $^{31}P\{^1H\}$ NMR: $\delta_{H_3PO_4}$ 36.9 (s).

(20) Cotton, F. A. *Chem. Soc. Rev.* **1975**, *4*, 27–54.

(21) The only other examples of which we are aware are $Re_2OCl_5(OCOEt)(PPh_3)_2$ (structure determined by X-rays: Cotton, F. A.; Fuxman, B. M. *Inorg. Chem.* **1968**, *7*, 1784–1792) and $[Rh_2(OCOR)(P\text{-}P)_2(CO)_2]^+$ (structures assigned by NMR: Mague, J. T.; De Vries, S. H. *Inorg. Chem.* **1983**, *21*, 1632–1638). A trinuclear complex with a single acetate bridge, $W_3O_3Cl_5(OCOMe)(PBu_3)_3$, has also been reported (X-ray structure: Cotton, F. A.; Felthouse, T. R.; Lay, D. G. *J. Am. Chem. Soc.* **1980**, *102*, 1431–1433).

Although no accurate bond distances could be obtained, the long Ru–Ru distance (3.624 (3) Å) indicates that there is no direct metal–metal interaction. Similar long distances have been found for the doubly bridged oxo-tricentered $Ru_3O(OCOMe)_6(PPh_3)_6$ (Ru–Ru = 3.3 Å)[22] while shorter Ru–Ru distances are observed for the metal–metal bonded "$Ru_2(OCOR)_4$" units (Ru–Ru = 2.24–2.29 Å),[23] the dinuclear species $[Ru(OCOPh)(CO)_2(PhCO_2H)]_2$ (Ru–Ru = 2.64 Å),[24a] three tetranuclear species $[Ru_2(\textit{sec}\text{-}C_4H_9CO_2)_2(CO)_4(\textit{sec}\text{-}C_4H_9CO_2H)]_2$ (Ru–Ru = 2.63 Å),[24a] $[Ru_2(CO)_4(OCOMe)_2(PBu_3)]_2$ (Ru–Ru = 2.68 Å),[24b] and $[Ru_2(CO)_4(OCOC_3H_6COO)(PBu_3)_2]_2$ (Ru–Ru = 2.73 Å),[24b] and the related osmium compound $Os_2(OCOMe)_2(CO)_6$ (Os–Os = 2.73 Å).[25]

The formation of this cationic dimer can be easily explained by the sequence of reactions depicted in Scheme I. The hydride complex **1a** reacts with CF_3CO_2H to yield (I), in an manner analogous to the reactions with nonfluorinated acids.[3d] Species I exists in a bidentate–monodentate equilibrium in solution, probably largely displaced toward the monodentate form (II); isomerization of this pentacoordinate intermediate produces III, which then dimerizes to **5** with loss of one trifluoroacetate ligand. All these steps have been previously well documented for closely related complexes (e.g. $RuH(OCOCF_3)(CO)(PPh_3)_2$ and $Ru(OCOCF_3)_2(CO)(PPh_3)_2$[5d,26]) except for the dimerization reaction, which occurs for other acids like CH_2ClCO_2H and HBF_4 (vide infra) and by thermal treatment of a number of phosphine complexes of Ru.[2,27,28]

Reaction of 1a with CH_2ClCO_2H. When **1a** is refluxed together with chloroacetic acid in toluene, solutions ranging in color from yellow to dark red are formed. The yellow solutions are usually obtained when the acid:Ru molar ratio is ~3, the reaction time is 10 min, and a moderate reflux is maintained. These solutions contain the mononuclear complex $RuCl(OCOCH_2Cl)(CO)(PPh_3)_2$ (Table I), together with small amounts of a second, red product. The latter is obtained as the major product when the reaction is carried out with a large (10-fold) excess of chloroacetic acid at 150 °C for 2 h. The red solutions resulting from this reaction are evaporated to produce a dark red oil, which is dissolved in CH_2Cl_2; addition of heptane and slow evaporation affords dark red crystals of the product.[29]

An X-ray analysis of this compound reveals another dinuclear structure in which the metal complex exists as the *anion* $[Ru_2Cl_2(\mu\text{-}Cl)_3(CO)_2(PPh_3)_2]^-$ (**6**) with PPh_3Me^+ as the counteraction. This structure, although carboxylate-free, is not without interest, especially since it contains the basic unit "$Ru_2(\mu\text{-}Cl)_2(CO)_2(PPh_3)_2$" also present in complexes **5** (vide supra) and (**7**) (vide infra).

Furthermore, although a number of triply chloride-bridged dinuclear ruthenium compounds have been reported in the literature,[30,31] they are normally neutral or cationic and only two of them, viz $RuCl(PPh_3)_2(\mu\text{-}Cl)_3Ru(PPh_3)_2$[30] and $RuCl(PPh_3)_2(\mu\text{-}Cl)_3Ru(CS)(PPh_3)_2$,[31] have been characterized crystallographically.

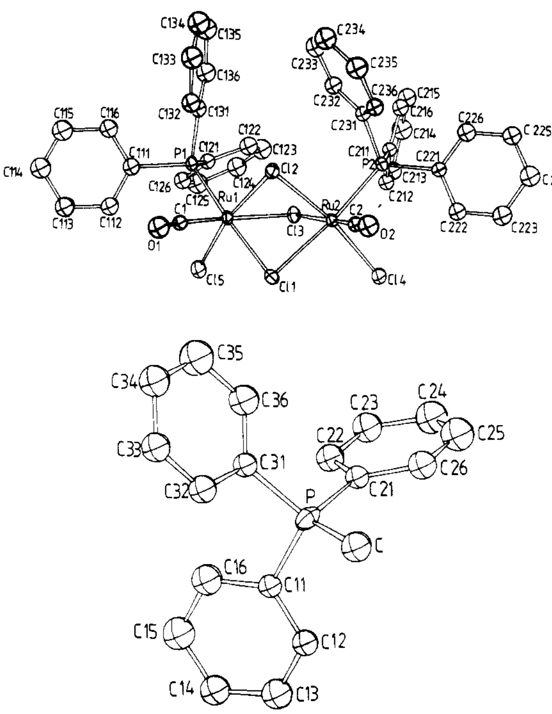
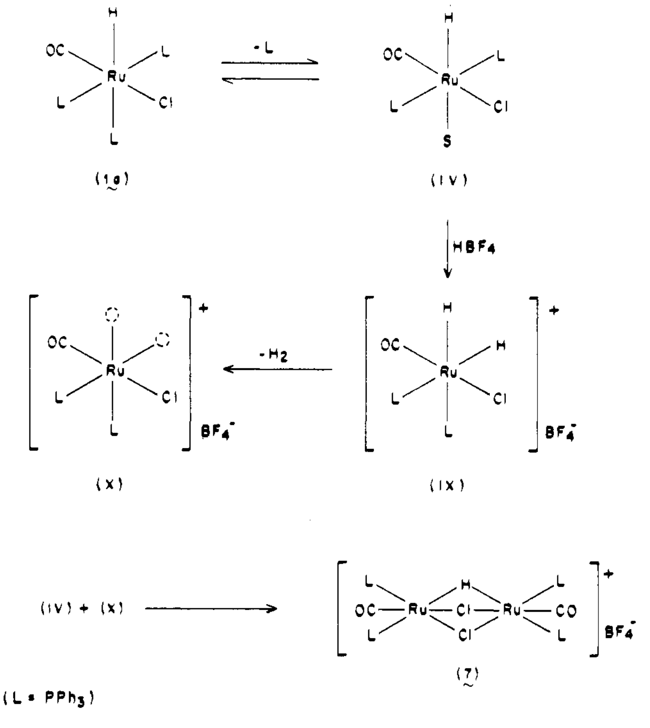


Figure 3. View of the cation and anion of the compound $[PPh_3Me]^+[Ru_2(\mu\text{-}Cl)_3Cl_2(CO)_2(PPh_3)_2]^-\cdot CH_2Cl_2$ with atom numbering.

Scheme II



Selected bond distances and angles are collected in Table IV. Atom numbering is shown in Figure 3.

The dinuclear anion consists of two approximately octahedral fragments sharing one face occupied by three chloride ligands. The Ru–Ru distance (3.257 (1) Å) is slightly shorter than those found in previously reported analogous compounds (3.35 and 3.36 Å),[30,31] but is too long for any direct metal–metal interaction.

The anion has (noncrystallographic) mirror symmetry. This is at least true if the differences in the conformation of both PPh_3 ligands are not taken into account. It is interesting to note that

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[22] (a) Norman, J. G.; Spencer, A.; Wilkinson, G. *J. Chem. Soc., Chem. Commun.* **1971**, 967–968. (b) Cotton, F. A.; and Norman, J. G., Jr. *Inorg. Chim. Acta* **1972**, *6*, 411–419.

[23] (a) Benett, M. J.; Caulton, K. G.; Cotton, F. A. *Inorg. Chem.* **1969**, *8*, 1–6. (b) Bino, A.; Cotton, F. A.; Felthouse, I. R. *Inorg. Chem.* **1979**, *18*, 2599–2604.

[24] (a) Rotem, M.; Shvo, Y.; Goldberg, I.; Shmueli, U. *Organometallics* **1984**, *3*, 1758–1759. (b) Bianchi, M.; Matteoli, U.; Frediani, P.; Piacenti, F.; Mardelli, M.; Pelizzi, G. *Chim. Ind. (Milan)* **1981**, *63*, 475–481.

[25] Bullit, J. G.; Cotton, F. A. *Inorg. Chim. Acta* **1971**, *5*, 406–412.

[26] Creswell, F. J.; Dobson, A.; Moore, D. S.; Robinson, S. D. *Inorg. Chem.* **1979**, *18*, 2055–2059.

[27] Wilkinson, G., Abel, E. W., Stone, F. G. A., Eds. "Comprehensive Organometallic Chemistry"; Pergamon Press: London, New York, 1982; Vol. 4.

[28] Armist, P. W.; Boyd, A. S. F.; Stephenson, T. A. *J. Chem. Soc., Dalton Trans.* **1975**, 1663–1672.

[29] The reaction is sensitive to some undetermined factor apparently not related to the presence of oxygen or moisture. This may cause reproducibility problems as a different, lighter red oil, which cannot be crystallized and appears to contain a mixture of compounds, is sometimes obtained.

[30] Alcock, N. W.; Raspin, K. A. *J. Chem. Soc. A* **1968**, 2108–2133.

[31] Fraser, J. F.; Gould, R. O. *J. Chem. Soc., Dalton Trans.* **1974**, 1139–1141.

Table IV. Selected Interatomic Distances (Å) and Angles (deg) for $[PPh_3Me]^+[Ru_2Cl_2(\mu\text{-}Cl)_3(CO)_3(PPh_3)_2]^-\cdot CH_2Cl_2$

		Anion			
Ru1···Ru2	3.257 (1)	Ru1-Cl1-Ru2	81.3 (1)	Cl1-Ru2-Cl2	80.2 (1)
Ru1-Cl1	2.488 (2)	Ru1-Cl2-Ru2	85.3 (1)	-Cl3	80.7 (1)
-Cl2	2.405 (2)	Ru1-Cl3-Ru2	82.9 (1)	-Cl4	91.0 (1)
-Cl3	2.454 (2)	Ru1-C1-O1	172.0 (10)	-C2	94.5 (3)
-Cl5	2.394 (3)	Ru2-C2-O2	178.6 (10)	-P2	174.1 (1)
-C1	1.906 (10)	Cl1-Ru1-Cl2	80.6 (1)	Cl2-Ru2-Cl3	80.6 (1)
-P1	2.282 (3)	-Cl3	81.4 (1)	-Cl4	167.9 (1)
Ru2-Cl1	2.510 (2)	-Cl5	92.2 (1)	-C2	93.4 (3)
-Cl2	2.402 (2)	-C1	91.5 (3)	-P2	94.1 (1)
-Cl3	2.469 (2)	-P1	176.9 (1)	Cl3-Ru2-Cl4	89.8 (1)
-Cl4	2.387 (3)	Cl2-Ru1-Cl3	80.9 (1)	-C2	172.9 (3)
-C2	1.871 (10)	-Cl5	168.0 (1)	-P2	96.8 (1)
-P2	2.284 (2)	-C1	93.5 (3)	Cl4-Ru2-C2	95.5 (3)
P1-C111	1.857 (11)	-P1	97.3 (1)	-P2	94.4 (1)
-C121	1.823 (10)	Cl3-Ru1-Cl5	88.5 (1)	C2-Ru2-P2	87.5 (3)
-C131	1.828 (11)	-C1	171.6 (3)		
P2-C211	1.836 (10)	-P1	96.0 (1)		
-C221	1.821 (9)	Cl5-Ru1-C1	96.4 (3)		
-C231	1.836 (9)	-P1	89.4 (1)		
C1-O1	0.943 (14)	C1-Ru1-P1	90.9 (3)		
C2-O2	1.021 (13)				
		Cation			
P-C	1.807 (13)	C-P-C11	109.6 (5)		
-C11	1.780 (10)	-C21	109.7 (5)		
-C21	1.787 (10)	-C31	107.6 (5)		
-C31	1.787 (10)	C11-P-C21	109.3 (5)		
		-C31	110.0 (5)		
		C21-P-C31	110.6 (5)		
		CH_2Cl_2 Molecule			
C′-Cl′1	1.802 (18)	Cl′1-C′-Cl′2	109.0 (10)		
-Cl′2	1.718 (18)				

there are altogether 11 possible isomers for an anion of type **6**, namely five racemates and one meso form. Evidently only the meso form has been formed, or at least isolated. The μ-Cl-Ru bond lengths depend strongly on the nature of the ligands trans to μ-Cl: they are shortest for X = Cl (2.405 (2) and 2.402 (2) Å) and longest for X = PPh_3 (2.488 (2) and 2.510 (2) Å). Values for X = CO are intermediate (2.454 (2) and 2.469 (2) Å). The (uncorrected) C-O bond lenghts for the carbonyl ligands are rather short. This shortenning, however, can be explained by the relatively high thermal vibrations of the O atoms. Other molecular features of the anion and the cation are normal.

Reaction of 1a with HBF_4. In view of the results obtained for carboxylic acids, we extended our study to the interaction of **1a** with an inorganic acid of a noncoordinating anion, namely HBF_4.

When a mixture of **1a** and aqueous HBF_4 in 2-methoxyethanol is refluxed for ca. 1 h, a yellow solution is formed. Addition of water causes precipitation of a yellow powder, which is recrystallized from CH_2Cl_2/heptane mixtures. Analytical, electrochemical,[19a] and spectroscopic[32] data are consistent with the cationic dinuclear structure **7** (Scheme II). Gentle reflux of this salt with $LiPF_6$ results in exchange of the anion; the PF_6 complex affords yellow prisms, which have been subjected to an X-ray analysis.

The crystals, however, rapidly lose the CH_2Cl_2 of crystallization. Consistent with this the atoms of the CH_2Cl_2 have large thermal vibrations. Also, the F atoms of the anion and some of the phenyl carbon atoms of the complex cation vibrate considerably, and the respective bond distances are therefore of low accuracy. Nevertheless, the overall geometry of the dinuclear cation corresponds to **7**, as proposed from the NMR data.[32] The Ru-Ru distance (2.842 (1) Å) is considerably shorter than those found for compounds **5** and **6**, and falls on the limit for a metal-metal bond; the poor quality of the structure, however, precludes a definitive statement in this respect. In the closely related complexes $[RuCl(CO)_2(P\text{-}t\text{-}Bu_2\text{-}o\text{-}Tol)]_2$[33] and $[RuBr(CO)_2(P\text{-}t\text{-}Bu_3)]_2$[34] the metal-metal bond distances are 2.63 and 2.67 Å.

Formation of this dinuclear complex can be explained by the reactions in Scheme II. Reaction of HBF_4 with one molecule of $RuHCl(CO)(PPh_3)_2$ (IV), formed by phosphine dissociation from **1a**, forms a cationic dihydride (IX), which readily loses hydrogen to yield the highly unsaturated species X. This reactive intermediate (X) then couples with a second molecule of the 16-electron hydride (IV) to produce the cationic dinuclear complex **7**. Protonation, hydrogen elimination, and dimerization steps similar to these are well documented.[28,30,31]

This reaction is in contrast with the previously reported cases of similar compounds, viz. $RuH(OAc)(PPh_3)_3$[4a] and $RuH_2(CO)(PPh_3)_3$,[4b] which yield *mononuclear* cationic species upon interaction with HBF_4 or HPF_6.

Conclusion

The chemistry of mononuclear hydrido and carboxylato phosphine complexes of Ru and Os has been extended by the synthesis and characterization of a number of new compounds, as summarized in Scheme III. In opposition to previous reports, osmium hydrides have been found to react with acetic acid to yield the corresponding carboxylate complexes $OsX(OCOMe)(CO)(PPh_3)_2$, in an fashion analogous to the reactions of ruthenium hydride derivatives. The stereochemistry adopted by these osmium acetate complexes differs from that of analogous ruthenium carboxylate compounds in that the phosphines occupy mutually cis positions in the former and trans in the latter. Also in contrast with the known reactivity of ruthenium hydrides toward acids, yielding neutral or cationic mononuclear compounds, we have demonstrated three examples of a novel reaction of $RuHCl(CO)(PPh_3)_3$ with strong acids leading to anionic and cationic dinuclear complexes. The unit "$Ru_2(\mu\text{-}Cl)_2(CO)_2(PPh_3)_2$", present in all cases, seems to confer a particular stability to the dinuclear structure, while the third bridging group as well as the remaining

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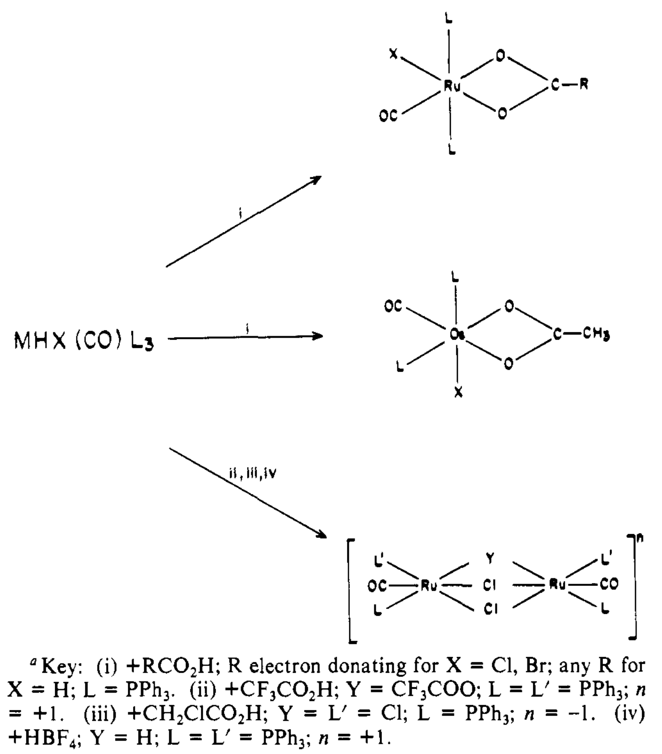
(32) IR: ν_{CO}, 1970 cm^{-1} (s); ν_{BF}, ~1100 cm^{-1}. ^1H NMR: δ_{Me_4Si} −13.2 (tt, J_{HP} = 10 and 43 Hz). $^{31}P\{^1H\}$ NMR: AA′BB′ pattern; $\delta_{H_3PO_4}$ 44.4, 28.5 (J_{AB} = 10 Hz, $J_{AB'}$ = 14 Hz).

(33) Gill, D. F.; Mason, R.; Shaw, B. L.; Thomas, K. H. *J. Organomet. Chem.* **1972**, *40*, C67-C69.

(34) Schumann, H.; Opitz, J.; Pickard, J. *Chem. Ber.* **1980**, *113*, 1385.

Scheme III[a]



[a] Key: (i) +RCO_2H; R electron donating for X = Cl, Br; any R for X = H; L = PPh_3. (ii) +CF_3CO_2H; Y = CF_3COO; L = L' = PPh_3; *n* = +1. (iii) +CH_2ClCO_2H; Y = L' = Cl; L = PPh_3; *n* = −1. (iv) +HBF_4; Y = H; L = L' = PPh_3; *n* = +1.

terminal ligands may be varied. We are presently extending the applications of this method to the synthesis of other dinuclear complexes, as well as studying the reactivity of the new compounds; these aspects will be the subject of future reports.

The following paper describes some of the catalytic properties of the new complexes.

Experimental Section

Manipulations were routinely carried out under nitrogen or argon by using conventional Schlenck techniques or a drybox. Solvents were dried by known procedures and distilled under nitrogen prior to use. Infrared spectra were taken as KBr disks on Perkin-Elmer 337 and 577 spectrometers. ^1H NMR spectra were recorded at 60 MHz (Bruker WP60) and ^{31}P spectra at 28.24 or 34.8 MHz (Bruker WP60 or Varian XL100, respectively). Elemental analyses were performed by Pascher Analitische Laboratory (Germany).

$RuHBr(CO)(PPh_3)_3$ (1d). Hydrobromic acid (2.4 mL, excess) was added to a suspension of $RuH(OAc)(CO)(PPh_3)_2$[3c] (0.92 g, 1.29 mmol) in methanol (35 mL), and the mixture was refluxed for ca. 1 h. During this time a color change from white to tan was observed in the insoluble solid. The solvent was removed, and toluene (40 mL), triphenylphosphine (1 g, 30 mmol), and triethylamine (0.5 mL) were added. The resulting solution was refluxed for ca. 2 h while hydrogen was bubbled through it. During this time the color changed from yellow to orange to red. On cooling, the solution was concentrated to half its volume and pentane added until the light brown product deposited; the solid was filtered, washed with cold toluene, methanol, water, methanol, and pentane, and dried in vacuo (yield 70%). Analytical pure material was obtained by recrystallization from CH_2Cl_2/heptane mixtures. Anal. Calcd for $C_{55}H_{46}BrOP_3Ru$: C, 66.3; H, 4.6; Br, 8.0; P 9.3; Ru, 10.1; mol wt., 996. Found: C, 66.2; H, 4.7; Br, 7.8; p, 9.3; Ru, 10.4; mol wt, 679.

This complex has also been prepared by others[35] by carbonylation of $RuHBr(PPh_3)_3$; in our hands, this reaction produced lower yields (~ 35–40%) than our method.

$RuCl(OCOCH_2Cl)(CO)(PPh_3)_2$. $RuHCl(CO)(PPh_3)_3$[7] (0.95 g, 1.1 mmol), chloroacetic acid (3 mmol), and toluene (35 mL) were heated under reflux for 10 min, during which a yellow-brown solution was formed and a small amount of a black solid deposited. The solution was filtered, and the solvent was evaporated under vacuum until precipitation began (ca. 50% volume). At this point heptane (25 mL) was added to complete precipitation. The beige solid was filtered off, washed with methanol, water, methanol, and pentane, and dried in vacuo. Analytically pure material was obtained by recrystallization from dichloromethane/heptane mixtures. Yield: 65% (based on Ru). Anal. Calcd for $C_{39}H_{32}Cl_2OP_2Ru$: C, 59.9; H, 4.1; Cl, 9.1; P, 7.9; Ru, 12.9; mol wt, 782. Found (mean of duplicate analyses): C, 60.0; H, 4.2; Cl, 9.8; P, 7.9; Ru, 12.9; mol wt, 580. *Note*: Larger amounts of chloroacetic acid, longer refluxing times, or excessively high temperatures led to solutions varying in color from reddish yellow to deep red. These solutions contain mixtures of varying amounts of $RuCl(OCOCH_2Cl)(CO)(PPh_3)_2$ and the deep red dimer $[Ru_2Cl_2(CO)_2(PPh_3)_2(\mu\text{-}Cl)_3][PPh_3Me]$ (vide infra).

$RuH(OCOR)(CO)(PPh_3)_2$. These compounds were prepared by slight modifications of the method reported by Robinson for the acetate analogue[3c] as follows: $RuH_2(CO)(PPh_3)_3$ (0.67 g, 0.7 mmol) was dissolved in toluene (7.5 mL) and a 10-fold molar excess of the appropriate acid (7 mmol) was added. The mixture was refluxed for 15 min; the resulting yellow solution was filtered at room temperature and concentrated to ca. 50% of the original volume and methanol (5–10 mL) added to precipitate the product in a microcrystalline form (all the compounds are pale yellow to yellow). The solid was filtered, washed with methanol, water, and methanol, and dried in vacuo. If further purification was desired the solid was dissolved in toluene (*ca.* 5 mL) and precipitated by slow addition of heptane or petroleum ether. For R = CMe_3 the yield was 56%, and for R = C_6H_{11} it was 66%.

For R = CH_2Cl and CF_2Cl toluene was replaced by ethanol as the solvent, and the reflux time was 60 min. (Yield: 76% and 54%, respectively.)

No satisfactory analytical data could be obtained for these compounds, which darken after a few hours even under inert atmosphere at room temperature. Characterization of these complexes was based on their spectroscopic properties (Table I) and by analogy with similar known compounds.[3c]

$OsBr(OCOMe)(CO)(PPh_3)_2$. Acetic acid (15 mmol), $OsHBr(CO)(PPh_3)_3$[11] (0.85 g, 0.75 mmol), and toluene (20 mL) were placed in a stainless-steel autoclave, together with a stirring bar. The autoclave was flushed three times with nitrogen at ca. 500 psig, the pressure was released, and then the autoclave was heated in an oil bath at 150 °C for 2 h with constant stirring. The resulting pale yellow solution was filtered and concentrated to ca. 50% its original volume, and heptane (ca. 10 mL) was added to precipitate the product. The compound can be purified by recrystallization from hot toluene or from CH_2Cl_2/heptane mixtures. Anal. Calcd for $C_{39}H_{33}BrO_3P_2Os$: C, 53.1; Br, 9.1; P, 7.0; Os, 21.6; mol wt, 881. Found: C, 54.1; Br, 9.0; P, 6.8; Os, 20.6; mol wt, 827. $OsCl(OCOMe)(CO)(PPh_3)_2$ and $RuX(OCOMe)(CO)(PPh_3)_2$ (X = Cl, Br) were prepared by analogous procedures, starting from $OsHCl(CO)(PPh_3)_3$ and $RuHX(CO)(PPh_3)_3$, respectively, and characterized by their spectroscopic properties. All of these complexes may also be prepared by refluxing the mixtures in conventional Schlenk equipment under inert atmosphere, but yields are better in the autoclave at 150 °C.

Synthesis of 5. $RuHCl(CO)(PPh_3)_3$ (0.84 mmol), trifluoroacetic acid (1.0 mmol), and toluene (50 mL) were placed in a glass-lined stainless-steel autoclave. After the autoclave was flushed three times with nitrogen, the mixture was heated to 150 °C with constant magnetic stirring in an oil bath for 2 h. The solution was allowed to cool slowly overnight to room temperature, yielding yellow crystals of **5**. If needed, the solid was redissolved in hot toluene, and the solution was filtered and left to cool slowly overnight. The crystals were filtered off, washed with cold diethyl ether, and dried under vacuum (yield 90%). Mp: 234–236 °C. Anal. Calcd for $C_{78}H_{61}Cl_2F_6O_6P_4Ru_2$: C, 53.7; H, 3.4; Cl, 3.9; F, 12.5; P, 6.8; mol wt, 1832. Found: C, 53.9; H, 3.5; Cl, 4.1; F, 12.2; P, 6.7; mol wt, 1200.

Synthesis of 6. In a procedure analogous to that described above for **5**, $RuHCl(CO)(PPh_3)_3$ (0.84 mmol) was reacted with chloroacetic acid (8.4 mmol) to yield a red solution. The solvent was removed under vacuum, and a dark oil was obtained. The oil was dissolved in dichloromethane, and heptane was carefully added to the solution so that two layers were formed. Slow liquid–liquid diffusion and evaporation through a syringe needle at room temperature resulted in the formation of large dark red crystals of **6**, suitable for X-ray diffraction. Yield: 20–25%.

Synthesis of 7. HBF_4 (40% aqueous, 2 mL) was added to a suspension of $RuHCl(CO)(PPh_3)_3$ (1.0 mmol) in 2-methoxyethanol (40 mL), and the mixture was refluxed for 2 h. The resulting yellow solution was allowed to cool to room temperature, and water was added until precipitation of the yellow powder was complete. The solid was filtered and dried under vacuum. Yield: 96%. The compound may be obtained as yellow prisms by recrystallization from dichloromethane/heptane mixtures (slow liquid–liquid diffusion) in an inert atmosphere. Mp: 234–235 °C. Anal. Calcd for $C_{74}H_{61}BCl_2F_4O_2P_4Ru_2$: C, 60.6; H, 4.2; B, 0.7; Cl, 4.8; F, 5.2; P, 8.5; Ru, 13.8. Found: C, 58.4; H, 4.4; B, 0.7; Cl, 4.8; F, 5.2; P, 8.3; Ru, 12.9.

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(35) James, B. R., personal communication.

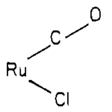
Table V. Crystallographic Details for $\mathrm{OsBr(OCOCH_3)(CO)(PPh_3)_2}$, $\mathrm{RuCl(OCOCH_3)(CO)(PPh_3)_2}$, and $\mathrm{[PPh_3Me]^+[Ru_2Cl_2(\mu\text{-}Cl)_3(CO)_2(PPh_3)_2]^- \cdot CH_2Cl_2}$

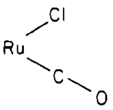
	$\mathrm{OsBr(OCOCH_3)(CO)(PPh_3)_2}$ (**4a**)	$\mathrm{RuCl(OCOCH_3)(CO)(PPh_3)_2}$ (**3a**)	$\mathrm{[PPh_3Me]^+[Ru_2Cl_2(\mu\text{-}Cl)_3(CO)_2(PPh_3)_2]^- \cdot CH_2Cl_2}$ (**6**)
formula	$\mathrm{BrC_{39}H_{33}O_3OsP_2}$	$\mathrm{C_{39}ClH_{33}O_3P_2Ru}$	$\mathrm{C_{58}Cl_7H_{50}O_2P_3Ru_2}$
fw	881.7	748.2	1322.26
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$	$P2_1/c$
a, Å	9.760 (2)	17.776 (5)	19.966 (10)
b, Å	20.379 (4)	9.696 (2)	14.383 (6)
c, Å	17.462 (3)	20.862 (6)	20.064 (6)
β, deg	96.45 (2)	106.35 (3)	93.36 (4)
V, Å^3	3451.2	3448.2	
Z	4	4	4
d_{calcd}, g/cm^3	1.697	1.441	1.527
μ(Mo Kα), cm^{-1}	47.8	5.8	8.8
cryst dimens, mm	0.2 × 0.2 × 0.3	0.08 × 0.2 × 0.2	0.16 × 0.22 × 0.25
scan mode	$\theta/2\theta$	$\theta/2\theta$	$\theta/2\theta$
data collcd	$\pm h,+k,+l$	$\pm h,+k,+l$	$\pm h,\pm k,\pm l$
2θ range, deg	$4 \le 2\theta \le 44$	$4 \le 2\theta \le 60$	$4 \le 2\theta \le 46$
no. of unique data	4216	10024	7958
no. of data with $I \ge \sigma(I)$	3923	6769	6581
no. of params	195	212	349
R	0.048	0.111	0.079
$R_w(F)$	0.054	0.123	0.084

X-ray Crystallography of 3a and 4a. Pale yellow crystals of $\mathrm{OsBr(OCOCH_3)(CO)(PPh_3)_2}$ (**4a**) were grown by slow evaporation of dichloromethane/heptane mixtures, and orange crystals of $\mathrm{RuCl(OCOCH_3)(CO)(PPh_3)_2}$ (**3a**) were grown by slow cooling of toluene solutions from 100 °C to room temperature.

The X-ray measurements were carried out on a Phillips PW 1100 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å) at 20 °C. Crystal data and parameters of the data collection are shown in Table V. Unit cell constants were obtained by least-squares refinement of the setting of 19 (Os complex) and 14 reflections (Ru complex). Three control reflections were monitored every hour for both compounds. No significant deviations in their intensities were observed. Empirical absorption corrections were applied for the Os complex by using the program DIFABS written by Walker and Stuart.[36] No absorption corrections were applied to the data of the Ru complex since μ was small.

The structures were solved via Patterson syntheses, which yielded the positions of the metal atoms. The remaining non-hydrogen atoms were located via difference syntheses. Hydrogen atoms were ignored in all stages. Scattering factors for neutral atoms were taken from Cromer et al.[37,38] No extinction corrections were introduced. For $\mathrm{OsBr(OCOCH_3)(CO)(PPh_3)_2}$, the Os and Br atoms were refined with anisotropic and the other non-hydrogen atoms with isotropic temperature factors. For $\mathrm{RuCl(OCOCH_3)(CO)(PPh_3)_2}$ after the majority of atoms was located, it became obvious that the CO and Cl ligands are disordered; in some molecules the first and in some other molecules the second of the following arrangements are realized:





The disordered part of the molecule was then treated as a superposition of the two above arrangements with each C, O, and Cl atom having an occupancy factor of 0.5. The Ru and P atoms were refined with anisotropic and the other non-hydrogen atoms, including the disordered ones, with isotropic temperature factors. The half-occupied atoms were far enough separated from one another so as to allow convergence of their positional parameters to stereochemically reasonable values (d(Ru–Cl) $\simeq$ 2.35 Å, d(Ru–CO) $\simeq$ 1.74 Å). The occupation factors were held constant at 0.5. Tables VI and VII list the final parameters for the two compounds. The computations were performed with the SHELX program system.[39]

Table VI. Atom Coordinates and Isotropic Temperature Factors[a] (Å^2 × 10^3) of $\mathrm{OsBr(OCOCH_3)(CO)(PPh_3)_2}$

atom	x	y	z	U
Os	0.4490 (1)	0.2160 (1)	0.1527 (1)	23 (1)
Br	0.5788 (1)	0.1073 (1)	0.1756 (1)	46 (1)
C1	0.6298 (9)	0.2501 (5)	0.2599 (5)	32 (2)
C2	0.7463 (12)	0.2696 (6)	0.3243 (7)	53 (3)
O1	0.5114 (6)	0.2312 (3)	0.2770 (4)	34 (2)
O2	0.6500 (6)	0.2532 (3)	0.1908 (4)	35 (2)
C3	0.4471 (9)	0.2170 (4)	0.0499 (5)	28 (2)
O3	0.4561 (8)	0.2218 (3)	−0.0166 (5)	54 (2)
P1	0.2436 (2)	0.1565 (1)	0.1391 (1)	28 (1)
C101	0.0896 (9)	0.1917 (5)	0.0840 (5)	29 (2)
C102	0.0592 (10)	0.1779 (5)	0.0062 (6)	38 (2)
C103	−0.0491 (12)	0.2085 (5)	−0.0396 (7)	49 (3)
C104	−0.1350 (12)	0.2525 (6)	−0.0034 (7)	58 (3)
C105	−0.1068 (12)	0.2688 (6)	0.0729 (7)	55 (3)
C106	0.0114 (10)	0.2385 (5)	0.1192 (6)	38 (2)
C111	0.1832 (9)	0.1325 (5)	0.2312 (5)	35 (2)
C112	0.2832 (10)	0.1213 (5)	0.2943 (6)	44 (3)
C113	0.2424 (12)	0.1031 (6)	0.3655 (7)	62 (3)
C114	0.1041 (14)	0.0980 (7)	0.3759 (7)	69 (4)
C115	0.0025 (13)	0.1094 (6)	0.3125 (8)	65 (3)
C116	0.0439 (11)	0.1259 (5)	0.2399 (6)	47 (3)
C121	0.2469 (9)	0.0774 (5)	0.0882 (5)	31 (2)
C122	0.1554 (10)	0.0276 (5)	0.1050 (6)	46 (3)
C123	0.1438 (13)	−0.0304 (6)	0.0611 (7)	61 (3)
C124	0.2302 (11)	−0.0404 (6)	0.0016 (6)	52 (3)
C125	0.3243 (12)	0.0098 (6)	−0.0153 (6)	53 (3)
C126	0.3324 (11)	0.0673 (5)	0.0297 (6)	48 (3)
P2	0.3684 (2)	0.3244 (1)	0.1531 (1)	26 (1)
C201	0.2390 (9)	0.3454 (4)	0.2176 (5)	29 (2)
C202	0.1754 (11)	0.4082 (5)	0.2101 (6)	48 (3)
C203	0.0881 (12)	0.4263 (6)	0.2666 (7)	60 (3)
C204	0.0650 (12)	0.3849 (6)	0.3252 (7)	59 (3)
C205	0.1277 (11)	0.3230 (5)	0.3312 (6)	50 (3)
C206	0.2174 (10)	0.3030 (5)	0.2774 (6)	42 (3)
C211	0.5122 (9)	0.3787 (5)	0.1901 (5)	31 (2)
C212	0.6234 (10)	0.3857 (5)	0.1483 (6)	40 (2)
C213	0.7368 (11)	0.4263 (6)	0.1766 (6)	52 (3)
C214	0.7345 (12)	0.4575 (6)	0.2465 (7)	61 (3)
C215	0.6250 (12)	0.4499 (6)	0.2897 (7)	57 (3)
C216	0.5110 (10)	0.4108 (5)	0.2624 (6)	45 (3)
C221	0.3045 (9)	0.3648 (4)	0.0619 (5)	30 (2)
C222	0.2142 (10)	0.3323 (5)	0.0087 (6)	39 (2)
C223	0.1531 (11)	0.3636 (5)	−0.0590 (6)	49 (3)
C224	0.1918 (12)	0.4274 (6)	−0.0739 (7)	54 (3)
C225	0.2847 (13)	0.4627 (7)	−0.0204 (7)	68 (4)
C226	0.3412 (11)	0.4303 (6)	0.0491 (6)	52 (3)

[a] For Os and Br the equivalent isotropic temperature factors are listed.

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(36) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found Crystallogr.* **1983**, *A39*, 158.

(37) Cromer, D. T.; Mabb, J. B. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 321.

(38) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

(39) Sheldrick, G. M. "SHELX-76 Program for Crystal Structure Determination"; Cambridge University: Cambridge, England, 1976.

Table VII. Atom Coordinates[a] and Isotropic Temperature Factors[b] ($Å^2 \times 10^3$) of $RuCl(OCOCH_3)(CO)(PPh_3)_2$

atom	*x*	*y*	*z*	*U*
Ru	0.2598 (1)	−0.0007 (1)	0.2488 (1)	31 (1)
P1	0.1528 (1)	−0.0135 (2)	0.1504 (1)	33 (1)
O2	0.2527 (3)	0.2183 (6)	0.2337 (3)	48 (1)
C1	0.2113 (5)	0.2308 (9)	0.2733 (4)	48 (2)
O1	0.1961 (3)	0.1231 (5)	0.3015 (3)	43 (1)
C2	0.1796 (7)	0.3714 (12)	0.2840 (6)	82 (3)
C101	0.0661 (4)	0.0799 (8)	0.1569 (4)	39 (2)
C102	0.0276 (5)	0.1743 (9)	0.1075 (5)	56 (2)
C103	−0.0393 (6)	0.2445 (11)	0.1145 (5)	71 (3)
C104	−0.0645 (7)	0.2197 (12)	0.1696 (6)	75 (3)
C105	−0.0292 (6)	0.1281 (11)	0.2169 (5)	71 (3)
C106	0.0392 (6)	0.0571 (10)	0.2120 (5)	57 (2)
C111	0.1707 (4)	0.0597 (7)	0.0761 (3)	36 (1)
C112	0.1499 (5)	−0.0079 (9)	0.0154 (5)	54 (2)
C113	0.1619 (6)	0.0548 (11)	−0.0405 (5)	68 (3)
C114	0.1967 (5)	0.1859 (10)	−0.0361 (5)	59 (2)
C115	0.2173 (6)	0.2528 (10)	0.0235 (5)	63 (2)
C116	0.2037 (5)	0.1928 (9)	0.0798 (4)	53 (2)
C121	0.1176 (4)	−0.1871 (8)	0.1248 (4)	41 (2)
C122	0.1720 (5)	−0.2878 (9)	0.1255 (4)	52 (2)
C123	0.1467 (6)	−0.4234 (11)	0.1032 (5)	71 (3)
C124	0.0696 (7)	−0.4495 (13)	0.0806 (6)	79 (3)
C125	0.0160 (7)	−0.3542 (13)	0.0801 (6)	81 (3)
C126	0.0380 (6)	−0.2152 (11)	0.1023 (5)	64 (2)
P2	0.3649 (1)	0.0114 (2)	0.3482 (1)	37 (2)
C201	0.3870 (5)	0.1852 (8)	0.3796 (4)	44 (2)
C202	0.4031 (7)	0.2840 (12)	0.3360 (6)	75 (3)
C203	0.4185 (8)	0.4209 (14)	0.3583 (7)	96 (4)
C204	0.4149 (8)	0.4552 (14)	0.4180 (7)	87 (4)
C205	0.3998 (7)	0.3621 (12)	0.4630 (6)	80 (3)
C206	0.3844 (5)	0.2221 (9)	0.4429 (4)	53 (2)
C211	0.3473 (5)	−0.0841 (8)	0.4173 (4)	41 (2)
C212	0.4055 (5)	−0.1588 (9)	0.4623 (4)	54 (2)
C213	0.3875 (6)	−0.2325 (10)	0.5133 (5)	64 (2)
C214	0.3130 (7)	−0.2317 (11)	0.5201 (6)	73 (3)
C215	0.2543 (6)	−0.1499 (11)	0.4769 (5)	67 (3)
C216	0.2716 (5)	−0.0793 (9)	0.4247 (5)	55 (2)
C221	0.4567 (5)	−0.0580 (9)	0.3427 (4)	45 (2)
C222	0.5235 (8)	0.0162 (13)	0.3554 (7)	86 (4)
C223	0.5937 (9)	−0.0518 (17)	0.3505 (8)	14 (5)
C224	0.5930 (8)	−0.1890 (14)	0.3367 (7)	93 (4)
C225	0.5251 (7)	−0.2662 (12)	0.3201 (6)	76 (3)
C226	0.4567 (6)	−0.1983 (10)	0.3239 (5)	59 (2)
Cl1	0.2414 (3)	−0.2303 (7)	0.2796 (2)	47 (1)
Cl1′	0.3407 (4)	−0.0617 (5)	0.1826 (2)	37 (1)
O3′	0.2383 (9)	−0.2879 (17)	0.2832 (7)	65 (4)
C3′	0.2429 (10)	−0.1687 (21)	0.2691 (9)	46 (4)
O3	0.3607 (11)	−0.0814 (19)	0.1769 (9)	77 (7)
C3	0.3189 (16)	−0.0480 (27)	0.1983 (14)	77 (8)

[a] For Ru, P1, and P2 the equivalent isotropic temperature factors are listed. [b] Atoms Cl1, C3, O3, Cl1′, C3′, and O3′ were given occupation factors of 0.5. Together they represent one carbonyl and one Cl ligand.

X-ray Crystallography of $[PPh_3Me]^+[Ru_2Cl_2(\mu\text{-}Cl)_3(CO)_2(PPh_3)_2]^-\cdot CH_2Cl_2$ (6). Dark red crystals of this compound containing the anion **6** and obtained from a dichloromethane/heptane solution were sealed in glass capillaries. Rotation and Weissenberg photographs indicated that the space group is $P2_1/c$ (systematic absences *h*0*l*, *l* odd, and 0*k*0, *k* odd). Unit cell dimensions were determined by least-squares refinement of the diffraction geometry for 20 reflections, centered on a Philips PW 1100 diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71069 Å).

An irregularly-shaped crystal fragment was chosen for collection of intensity data (PW 1100 instrument, Mo Kα radiation, graphite monochromator). The intensities of three check reflections measured every 60 reflections indicated that no crystal decomposition occurred during the data collection.

The *I* and $\sigma(I)$ values were corrected for Lorentz and polarization effects but not for absorption.

The structure was solved by Patterson and Fourier techniques and refined by least-squares techniques using anisotropic thermal parameters for the Ru, Cl and P atoms and isotropic temperature factors for the remaining non-hydrogen atoms. Hydrogen atoms were ignored. Scattering factors for neutral atoms were taken from Cromer et al.[37,38] Final parameters are listed in Table VIII.

Table VIII. Atom Coordinates[a] and Isotropic Temperature Factors ($Å^2$) of $[PMePh_3]^+[Ru_2Cl_2(\mu\text{-}Cl)_3(CO)_2(PPh_3)_2]^-\cdot CH_2Cl_2$

atom	*x*	*y*	*z*	*U*
		Anion		
Ru1	0.2904 (0)	0.0298 (1)	0.1059 (0)	0.030 (1)
Ru2	0.2270 (0)	0.2386 (1)	0.1016 (0)	0.026 (1)
Cl1	0.1901 (1)	0.0926 (2)	0.0414 (1)	0.036 (2)
Cl2	0.3343 (1)	0.1782 (2)	0.0746 (1)	0.036 (2)
Cl3	0.2453 (1)	0.1261 (2)	0.1938 (1)	0.037 (2)
Cl4	0.1158 (1)	0.2655 (2)	0.1347 (1)	0.046 (3)
Cl5	0.2282 (1)	−0.0988 (2)	0.1461 (2)	0.053 (3)
P1	0.3828 (1)	−0.0205 (2)	0.1680 (1)	0.036 (2)
P2	0.2715 (1)	0.3648 (2)	0.1574 (1)	0.030 (2)
C1	0.3203 (5)	−0.0313 (7)	0.0288 (5)	0.038 (2)
O1	0.3302 (5)	−0.0572 (6)	−0.0126 (5)	0.075 (3)
C2	0.2188 (5)	0.3133 (7)	0.0252 (5)	0.038 (2)
O2	0.2155 (4)	0.3536 (6)	−0.0167 (4)	0.069 (2)
C111	0.4162 (5)	−0.1368 (7)	0.1476 (5)	0.046 (3)
C112	0.3758 (5)	−0.2019 (8)	0.1124 (5)	0.050 (3)
C113	0.4039 (6)	−0.2859 (9)	0.0944 (6)	0.060 (3)
C114	0.4724 (7)	−0.3060 (10)	0.1109 (7)	0.072 (4)
C115	0.5108 (7)	−0.2419 (9)	0.1470 (7)	0.072 (4)
C116	0.4838 (6)	−0.1560 (8)	0.1675 (6)	0.056 (3)
C121	0.3680 (5)	−0.0281 (7)	0.2567 (5)	0.041 (2)
C122	0.3629 (6)	0.0554 (8)	0.2933 (6)	0.056 (3)
C123	0.3433 (6)	0.0495 (9)	0.3603 (6)	0.066 (3)
C124	0.3293 (6)	−0.0335 (9)	0.3868 (6)	0.068 (3)
C125	0.3318 (7)	−0.1168 (9)	0.3507 (7)	0.072 (4)
C126	0.3526 (5)	−0.1132 (8)	0.2843 (6)	0.050 (3)
C131	0.4587 (5)	0.0494 (7)	0.1626 (5)	0.045 (3)
C132	0.4763 (6)	0.0711 (8)	0.0964 (6)	0.059 (3)
C133	0.5377 (7)	0.1187 (10)	0.0891 (7)	0.078 (4)
C134	0.5793 (7)	0.1396 (10)	0.1432 (7)	0.080 (4)
C135	0.5632 (7)	0.1202 (10)	0.2056 (7)	0.076 (4)
C136	0.5003 (6)	0.0722 (9)	0.2188 (6)	0.064 (3)
C211	0.2771 (5)	0.3583 (6)	0.2489 (5)	0.034 (2)
C212	0.2275 (5)	0.3086 (7)	0.2811 (5)	0.042 (2)
C213	0.2316 (6)	0.3041 (8)	0.3509 (6)	0.054 (3)
C214	0.2840 (6)	0.3497 (9)	0.3877 (7)	0.069 (4)
C215	0.3314 (6)	0.4007 (8)	0.3569 (6)	0.055 (3)
C216	0.3280 (5)	0.4048 (7)	0.2871 (5)	0.044 (3)
C221	0.2327 (5)	0.4782 (6)	0.1433 (5)	0.035 (2)
C222	0.1666 (5)	0.4863 (7)	0.1152 (5)	0.046 (3)
C223	0.1368 (6)	0.5718 (9)	0.1080 (6)	0.062 (3)
C224	0.1741 (6)	0.6532 (9)	0.1274 (6)	0.063 (3)
C225	0.2377 (6)	0.6460 (8)	0.1547 (6)	0.057 (3)
C226	0.2681 (5)	0.5576 (8)	0.1627 (6)	0.050 (3)
C231	0.3573 (5)	0.3842 (7)	0.1323 (5)	0.035 (2)
C232	0.4110 (5)	0.3377 (7)	0.1667 (5)	0.045 (3)
C233	0.4767 (6)	0.3469 (9)	0.1435 (6)	0.059 (3)
C234	0.4859 (7)	0.3974 (10)	0.0859 (7)	0.073 (4)
C235	0.4309 (7)	0.4442 (9)	0.0520 (7)	0.068 (4)
C236	0.3655 (5)	0.4351 (8)	0.0755 (5)	0.048 (3)
		Cation		
P	0.0034 (1)	−0.0196 (2)	0.1778 (2)	0.045 (3)
C11	−0.0675 (5)	0.0548 (7)	0.1819 (5)	0.039 (2)
C12	−0.0576 (6)	0.1495 (8)	0.1832 (6)	0.054 (3)
C13	−0.1139 (7)	0.2081 (9)	0.1901 (7)	0.070 (4)
C14	−0.1775 (7)	0.1733 (9)	0.1922 (7)	0.069 (4)
C15	−0.1874 (8)	0.0749 (11)	0.1897 (7)	0.082 (4)
C16	−0.1307 (7)	0.0152 (9)	0.1853 (7)	0.069 (4)
C21	0.0428 (5)	−0.0329 (7)	0.2595 (5)	0.043 (2)
C22	0.0037 (6)	−0.0624 (8)	0.3109 (6)	0.060 (3)
C23	0.0320 (7)	−0.0711 (9)	0.3761 (7)	0.067 (3)
C24	0.1005 (7)	−0.0497 (10)	0.3892 (7)	0.079 (4)
C25	0.1372 (8)	−0.0234 (10)	0.3380 (8)	0.084 (4)
C26	0.1109 (6)	−0.0133 (8)	0.2715 (6)	0.060 (3)
C31	−0.0220 (5)	−0.1300 (7)	0.1442 (5)	0.042 (2)
C32	−0.0518 (6)	−0.1321 (8)	0.0805 (6)	0.057 (3)
C33	−0.0672 (6)	−0.2173 (9)	0.0491 (6)	0.061 (3)
C34	−0.0525 (7)	−0.2993 (10)	0.0840 (7)	0.071 (4)
C35	−0.0238 (8)	−0.2973 (12)	0.1471 (8)	0.093 (5)
C36	−0.0075 (7)	−0.2105 (9)	0.1797 (7)	0.068 (3)
C	0.0621 (6)	0.0304 (9)	0.1227 (6)	0.064 (3)
		Methylene Chloride of Crystallization		
Cl′1	0.2212 (3)	−0.2635 (4)	−0.0306 (2)	0.124 (7)
Cl′2	0.0923 (2)	−0.1882 (5)	−0.0051 (3)	0.132 (7)
C′	0.1745 (9)	−0.1591 (12)	−0.0157 (9)	0.103 (5)

[a] For the Ru, Cl, and P atoms the equivalent isotropic temperature factors are listed.

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Registry No. **1a**, 16971-33-8; **1c**, 16971-32-7; **1d**, 100678-61-3; **2** (R = CMe_3), 100514-77-0; **2** (R = CH_2Cl), 100514-78-1; **2** (R = CF_2Cl), 100514-80-5; **2** (R = C_6H_{11}), 100514-76-9; **3a**, 100678-64-6; **4a** (X = Br), 100678-68-0; **4a** (X = Cl), 100514-81-6; **5**, 100700-64-9; **6**, 100762-93-4; **7**, 100762-95-6; $RuH(OAc)(CO)(PPh_3)_2$, 50661-73-9; $RuCl(OCOCH_2Cl)(CO)(PPh_3)_2$, 84079-95-8; $RuBr(OCOMe)(CO)(PPh_3)_2$, 100837-28-3; $RuH_2(CO)(PPh_3)_3$, 25360-32-1; $OsHCl(CO)(PPh_3)_3$, 16971-31-6.

Supplementary Material Available: Tables IX–XI, F_o/F_c values for $OsBr(OCOMe)(CO)(PPh_3)_2$, $RuCl(OCOMe)(CO)(PPh_3)_2$, and $[PPh_3Me]^+[RuCl_2(\mu\text{-}Cl)_3(CO)_2(PPh_3)_2]^-\cdot CH_2Cl_2$, Tables XII–XIV, anisotropic thermal parameters, and Table XV, phenyl C–C ring distances for **4a**, **3a**, and **6** (80 pages). Ordering information is given on any current masthead page.

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Chemistry and Catalytic Properties of Ruthenium and Osmium Complexes. 3. Development of Highly Active Systems for the Homogeneous Hydrogenation of Aldehydes and Ketones

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The catalytic hydrogenation of aldehydes and ketones to yield the corresponding alcohols exclusively is efficiently achieved by use of a series of 19 ruthenium and 4 osmium complexes containing hydride, phosphine, and carboxylate ligands, under moderate reaction conditions. For complexes $MHX(CO)(PR_3)_3$ the catalytic activity is dependent on X (halide) and independent of R. Evidence is presented for a mechanism involving $MHX(CO)(PR_3)_2$ as the active species and alkoxy–metal intermediates in the cycle. Carboxylate species $MX(OCOR)(CO)(PPh_3)_2$ show a catalytic behavior dependent on the stereochemistry of the complex, on X, and on the electronic nature of the R group. Correlations between k_{obsd} for the catalytic reaction and pK_a of the acid from which carboxylate ligands are derived have been found. This is explained in terms of a mechanism involving a bidentate–monodentate equilibrium for the carboxylate as a key step in the catalysis.

The homogeneous catalytic hydrogenation of aldehydes and ketones is of considerable interest in connection with industrially important reactions such as those involved in the oxo and aldox processes.[1] Furthermore, this reaction may also be of use in synthetic organic chemistry and as a simple model for the widely publicized CO hydrogenation reaction and its implications in Fischer–Tropsch and related chemistry.[2]

Examples of efficient homogeneous catalysts for the hydrogenation of aldehydes and ketones to their corresponding alcohols are still relatively scarce.[3] Prior to our initial reports on the use of hydrido–phosphine complexes of ruthenium,[4] the only compounds of this metal known to reduce aldehydes were $RuH_2(CO)_2(PPh_3)_2$,[5] $RuCl_2(PPh_3)_3$,[6] and $RuCl_2(CO)_2(PPh_3)_2$;[7] for ketone reduction, $RuCl_2(PPh_3)_3$,[8] $RuH_2(PPh_3)_4$,[9] and $H_4Ru_4(CO)_{12}$[10] had been mentioned in the literature. Since then other neutral[11] and anionic[12] hydrido–phosphine ruthenium complexes were reported to catalytically hydrogenate aldehydes and ketones. We have recently published some preliminary results on the use of carboxylate derivatives of ruthenium for aldehyde hydrogen-

Table I. Hydrogenation of Propionaldehyde[a]

catalyst		
no.	compd	10^2k_{obsd}, min^{-1}
1	$RuHCl(CO)(PPh_3)_3$	3.50 ± 0.32
2	$RuHBr(CO)(PPh_3)_3$	2.02 ± 0.10
3	$RuHCl(CO)(PCy_3)_2$	3.85 ± 0.57
4	$RuCl(OCOEt)(CO)(PPh_3)_2$	2.15 ± 0.22
5	$RuCl(OCOMe)(CO)(PPh_3)_2$	2.50 ± 0.25
6	$RuBr(OCOMe)(CO)(PPh_3)_2$	2.39 ± 0.15
7	$RuCl(OCOPh)(CO)(PPh_3)_2$	3.04 ± 0.30
8	$RuCl(OCOCH_2Cl)(CO)(PPh_3)_2$	5.03 ± 0.39
9	$[Ru_2(\mu\text{-}OCOCF_3)(\mu\text{-}Cl)_2(CO)_2(PPh_3)_4]CF_3CO_2$	3.16 ± 0.20
10	$[Ru_2(\mu\text{-}H)(\mu\text{-}Cl)_2(CO)_2(PPh_3)_4]BF_4$	1.33 ± 0.07
11	$RuH(OCOPh)(CO)(PPh_3)_2$	2.04 ± 0.19
12	$RuH(OCOEt)(CO)(PPh_3)_2$	2.22 ± 0.15
13	$RuH(OCOCy)(CO)(PPh_3)_2$	2.48 ± 0.16
14	$RuH(OCOCMe_3)(CO)(PPh_3)_2$	2.54 ± 0.21
15	$RuH(OCOMe)(CO)(PPh_3)_2$	2.54 ± 0.25
16	$RuH(OCOCH_2Cl)(CO)(PPh_3)_2$	2.62 ± 0.16
17	$RuH(OCOCHCl_2)(CO)(PPh_3)_2$	5.23 ± 0.59
18	$RuH(OCOCF_2Cl)(CO)(PPh_3)_2$	6.13 ± 0.42
19	$RuH(OCOCF_3)(CO)(PPh_3)_2$	6.70 ± 0.46
20	$OsHCl(CO)(PPh_3)_3$	2.16 ± 0.12
21	$OsHBr(CO)(PPh_3)_3$	1.75 ± 0.12
22	$OsCl(OCOMe)(CO)(PPh_3)_2$	3.39 ± 0.26
23	$OsBr(OCOMe)(CO)(PPh_3)_2$	2.59 ± 0.24

[a] In toluene; 150 °C; 30 atm of H_2; [substrate] = 1.4 M; [catalyst] = 1.4×10^{-3} M; selectivity >98% for *n*-PrOH.

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