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Contribution from the Department of Chemistry,
 King's College, Strand, London WC2R 2LS

Complexes of the Platinum Metals. 9.¹ Chemistry of the Species $[M(OCOCF_3)_2CO(PPh_3)_2]$ and $[MH(OCOCF_3)CO(PPh_3)_2]$ ($M = Ru$ or Os)

ALAN DOBSON and STEPHEN D. ROBINSON*

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The complexes $[M(OCOCF_3)_2(CO)(PPh_3)_2]$ ($M = Ru$ or Os) and their alcoholysis products $[MH(OCOCF_3)(CO)(PPh_3)_2]$ react with carbon monoxide to yield the dicarbonyls $[M(OCOCF_3)_2(CO)_2(PPh_3)_2]$ and $[MH(OCOCF_3)(CO)_2(PPh_3)_2]$, respectively. The hydrides $[MH(OCOCF_3)(CO)(PPh_3)_2]$ add triphenylphosphine to form the species $[MH(OCOCF_3)(CO)(PPh_3)_3]$. Acetylacetonone (acac H) and hexafluoroacetylacetonone (facfac H) react with $[M(OCOCF_3)_2(CO)(PPh_3)_2]$ in boiling alcohol to form β -diketone complexes $[M(acac)(OCOCF_3)(CO)(PPh_3)_2]$ and $[M(facfac)(OCOCF_3)(CO)(PPh_3)_2]$, respectively; in the presence of potassium hydroxide, acetylacetonone affords the hydrides $[MH(acac)(CO)(PPh_3)_2]$. The complexes $[M(OCOCF_3)_2(CO)(PPh_3)_2]$ also react with sodium acetate in methanol and ethanol to yield the products $[M(OCOCH_3)_2(CO)(PPh_3)_2]$ and $[MH(OCOCH_3)(CO)(PPh_3)_2]$, respectively. Sodium nitrate in methanol affords the mixed nitrate/trifluoroacetato complexes $[M(NO_3)(OCOCF_3)(CO)(PPh_3)_2]$ and sulfur dioxide in methanol yields the mixed methylsulfonato/trifluoroacetato species $[M(SO_3CH_3)(OCOCF_3)(CO)(PPh_3)_2]$. The course of these reactions and the structure and stereochemistry of the products are discussed.

Introduction

We have recently reported² the synthesis and characterization of a wide range of perfluorocarboxylato complexes of the platinum group metals, and have shown³ that the bis-(trifluoroacetato) derivatives $[M(OCOCF_3)_2(CO)(PPh_3)_2]$ ($M = Ru, Os$) are homogeneous catalysts for the dehydrogenation of simple primary, secondary, and cyclic alcohols. The catalytic reaction involves alcoholysis to yield alkoxides $[M(OCHRR')(OCOCF_3)(CO)(PPh_3)_2]$ which subsequently undergo β -elimination to form an aldehyde ($R = H$) or ketone ($R \neq H$) and the isolable hydride intermediates $[MH(OCOCF_3)(CO)(PPh_3)_2]$.³

In this paper we report further studies on the chemical reactivity of the catalysts $[M(OCOCF_3)_2(CO)(PPh_3)_2]$ and the hydride intermediates $[MH(OCOCF_3)(CO)(PPh_3)_2]$. The reactions described were designed to yield information concerning other possible catalytic reactions, and to highlight the unusual reactivity of the monodentate carboxylate ligands in these complexes. Products isolated have been characterized by analytical and spectroscopic methods and, where possible, their stereochemistry has been assigned.

Several of the new complexes reported display stereochemical nonrigidity, in particular the intramolecular exchange of mono- and bidentate carboxylate and/or nitrate ligands.

Experimental Section

The complexes $[M(OCOCF_3)_2(CO)(PPh_3)_2]$ were prepared as previously described.² Reactions were performed under nitrogen, but, unless otherwise indicated, the products were manipulated in air. Systems involving the hydrides $[MH(OCOCF_3)(CO)(PPh_3)_2]$ were handled under strictly anaerobic conditions. Unless otherwise indicated, washings were performed using 2×2.5 cm³ of each solvent specified.

Analyses, by the microanalytical laboratory of the University College London, and melting points, taken in sealed tubes under nitrogen, are given in Table I. Infrared spectra of solid samples were obtained as Nujol mulls using a Perkin-Elmer 457 grating spectrometer. Proton and ³¹P NMR spectra were recorded at 90 and 36.43 MHz, respectively, using a Bruker HFX90 spectrometer. The ³¹P

NMR spectra were calibrated against external H₃PO₄ and values are quoted as the difference in ppm from this reference; shifts to high frequency are positive. Spectroscopic data are recorded in Tables II (infrared and ¹H NMR) and III (³¹P NMR).

Carbonylhydrido(trifluoroacetato)bis(triphenylphosphine)ruthenium(II), $[RuH(OCOCF_3)CO(PPh_3)_2]$. Carbonylbis(trifluoroacetato)bis(triphenylphosphine)ruthenium (0.2 g) was heated under reflux in ethanol (5.0 cm³) to give initially a bright yellow solution. This rapidly turned lime-green, and a pale yellow, crystalline solid began to precipitate. After 15 min the mixture was cooled, the *yellow crystals* were filtered off under nitrogen, washed successively with degassed methanol, water, and methanol, then dried in vacuo (yield 78%).

Carbonylhydrido(trifluoroacetato)bis(triphenylphosphine)osmium(II), $[OsH(OCOCF_3)CO(PPh_3)_2]$. Carbonylbis(trifluoroacetato)bis(triphenylphosphine)osmium (0.2 g) was heated under reflux in ethanol (5.0 cm³) for 20 min. During this time the initial complex dissolved to give a pale pink solution, from which *yellow crystals* rapidly precipitated. The mixture was allowed to cool, then the crystals were filtered off under nitrogen, washed successively with degassed methanol, water, and methanol, and dried in vacuo (yield 76%).

Carbonylhydrido(trifluoroacetato)tris(triphenylphosphine)ruthenium(II), $[RuH(OCOCF_3)CO(PPh_3)_3]$. Carbonylbis(trifluoroacetato)bis(triphenylphosphine)ruthenium (0.2 g) was added to a boiling solution of triphenylphosphine (0.2 g) in ethanol (10.0 cm³), and the mixture was heated under reflux for 20 min. The yellow coloration rapidly faded, and after 15 min *creamy-white crystals* began to precipitate. After 20 min the mixture was allowed to cool; then the crystals were filtered off, washed successively in methanol, water, and methanol, and dried in vacuo (yield 93%).

A similar procedure, employing carbonylbis(trifluoroacetato)bis(triphenylphosphine)osmium (0.2 g), gave creamy white crystals of **carbonylhydrido(trifluoroacetato)tris(triphenylphosphine)osmium(II)**, $[OsH(OCOCF_3)CO(PPh_3)_3]$ (yield 88%).

Dicarbonylbis(trifluoroacetato)bis(triphenylphosphine)ruthenium(II), $[Ru(OCOCF_3)_2(CO)_2(PPh_3)_2]$. Carbon monoxide was bubbled through a boiling solution of carbonylbis(trifluoroacetato)bis(triphenylphosphine)ruthenium (0.2 g) in benzene (10.0 cm³) to give an initial yellow coloration. Boiling was continued for 30 min, during which time the solution became colorless; the benzene was then removed by evaporation under reduced pressure. The resultant oil was crystallized from dichloromethane/methanol as *white crystals* which

Table I. Melting Point and Analysis Data^a

Complex	M	Mp, °C	C	H	P
[MH(OCOCF ₃)CO(PPh ₃) ₂]	Ru	219–218	61.0 (61.0)	4.0 (4.1)	8.1 (8.1)
	Os	237–238	54.7 (55.2)	3.7 (3.7)	7.1 (7.2)
[MH(OCOCF ₃)CO(PPh ₃) ₃]	Ru	200–202	66.5 (66.5)	4.5 (4.5)	8.7 (9.0)
	Os	252–253	61.4 (61.2)	4.1 (4.1)	8.2 (8.3)
[M(OCOCF ₃) ₂ (CO) ₂ (PPh ₃) ₂]	Ru	260–261	55.5 (55.5)	3.3 (3.3)	6.7 (6.8)
	Os	263–265	50.4 (50.6)	3.2 (3.0)	5.9 (6.2)
[MH(OCOCF ₃)(CO) ₂ (PPh ₃) ₂]	Ru	206–207	60.1 (60.4)	4.1 (3.9)	8.1 (7.8)
	Os	225–226	54.2 (54.3)	3.5 (3.5)	7.0 (7.0)
[M(OCOCH ₃) ₂ CO(PPh ₃) ₂]	Ru	210–212	63.5 (63.8)	4.7 (4.7)	8.3 (8.0)
	Os	235–237	57.0 (57.2)	4.2 (4.2)	6.6 (7.2)
[MH(OCOCH ₃)CO(PPh ₃) ₂]	Ru	235–237	65.7 (65.6)	4.8 (4.8)	8.5 (8.7)
	Os	257–258	58.2 (58.3)	4.3 (4.3)	9.1 (7.7)
[M(NO ₃)(OCOCF ₃)CO(PPh ₃) ₂]	Ru	201–202	56.4 (56.5)	3.6 (3.6)	1.7 (1.7) ^b
	Os	210–211	51.2 (51.0)	3.3 (3.3)	1.5 (1.5)
[M(OCOCF ₃)(SO ₃ CH ₃)CO(PPh ₃) ₂]	Ru	135–140	55.2 (55.1)	4.1 (4.0)	7.0 (7.1)
[M(acac)(OCOCF ₃)CO(PPh ₃) ₂]	Ru	130–131	60.2 (59.9)	4.3 (4.3)	7.2 (7.0)
	Os	120–121	52.6 (52.8)	3.9 (3.8)	6.1 (6.1)
[MH(acac)CO(PPh ₃) ₂]	Ru	200–201	66.8 (66.9)	5.0 (5.1)	8.5 (8.2)
	Os	223–224	59.6 (59.8)	4.6 (4.5)	7.2 (7.3)
[M(facfac)(OCOCF ₃)CO(PPh ₃) ₂]	Ru	220–223	54.3 (54.3)	3.3 (3.2)	6.7 (6.4)
	Os	230–233	49.8 (49.7)	3.0 (2.9)	5.8 (5.8)

^a Calculated figures in parentheses. ^b Nitrogen analysis.Table II. Infrared and ¹H NMR^a Spectroscopic Data

Complex	M	ν(MH)	ν(CO)	ν(OCO) _{asym}	τ(MH)	² J(PH)
[MH(OCOCF ₃)CO(PPh ₃) ₂]	Ru	2040	1943	1620	27.2 (t)	19.0
	Os	2137	1920	1610	31.1 (t)	17.0
[MH(OCOCF ₃)CO(PPh ₃) ₃]	Ru	2070	1927	1692	15.6	{110.0
	Os	2115	1915	{1700	(d of t)	{24.5
				{1684		{93.0
				{1684	(d of t)	{25.0
				{1678		
[M(OCOCF ₃) ₂ (CO) ₂ (PPh ₃) ₂]	Ru		{2065	{1684		
	Os		{1981	{1678		
			{2055	1686		
			{1961			
[MH(OCOCF ₃)(CO) ₂ (PPh ₃) ₂]	Ru		{1982	1700	14.1 (t)	19.2
	Os	1928	{2048		12.9 (t)	21.0
			{1985			
			{2045			
[M(OCOCH ₃) ₂ CO(PPh ₃) ₂]	Ru		1960	{1630		
	Os		1940	{1517		
				{1640		
				{1517		
[MH(OCOCH ₃)CO(PPh ₃) ₂]	Ru	2016	1928	1528	26.5 (t)	20.7
	Os	2110	1915	1528	29.7 (t)	16.5
[M(NO ₃)(OCOCF ₃)CO(PPh ₃) ₂]	Ru		1985	1708	ν(NO ₃) {1572 1255	
	Os		1962	1706	{1542	
					{1580 1225	
					{1541	
[M(OCOCF ₃)(SO ₃ CH ₃)CO(PPh ₃) ₂]	Ru		1982	1655	ν(SO ₂) ν(SO) {1235 987	
					{1190	
[M(acac)(OCOCF ₃)CO(PPh ₃) ₂]	Ru		1978	1697	ν(acac/facfac) 1585 1520	
	Os		1955	1700	1580 1520	
[MH(acac)(CO)(PPh ₃) ₂]	Ru	1938	1913		1595 1508	23.3 (t)
	Os	2042	1900		1588 1513	25.8 (t)
[M(facfac)(OCOCF ₃)CO(PPh ₃) ₂]	Ru		1990	1696	1631 1555	
	Os		1970	1705	1625 1558	

^a d = doublet, t = triplet; spectra recorded in CDCl₃.

were filtered off, washed successively in methanol, water, and methanol, and then dried in vacuo (yield 86%).

A similar procedure, employing carbonylbis(trifluoroacetato)-bis(triphenylphosphine)osmium(II) (0.2 g), gave white crystals of **dicarbonylbis(trifluoroacetato)bis(triphenylphosphine)osmium(II)**, [Os(OCOCF₃)₂(CO)₂(PPh₃)₂] (yield 73%).

Dicarbonylhydrido(trifluoroacetato)bis(triphenylphosphine)ruthenium(II), [RuH(OCOCF₃)(CO)₂(PPh₃)₂]. Carbon monoxide was bubbled through a boiling solution of carbonylhydrido(trifluoroacetato)bis(triphenylphosphine)ruthenium (0.2 g) (prepared as above) in benzene (10.0 cm³). The initial yellow coloration slowly faded,

after 30 min heating was stopped, and the benzene was removed by evaporation under reduced pressure. The resultant oil was crystallized from dichloromethane/methanol as *white crystals* which were filtered off, washed successively in methanol, water and methanol, and then dried in vacuo (yield 91%).

A similar procedure, employing carbonylhydrido(trifluoroacetato)bis(triphenylphosphine)osmium (0.2 g), gave white crystals of **dicarbonylhydrido(trifluoroacetato)bis(triphenylphosphine)osmium(II)** [OsH(OCOCF₃)(CO)₂(PPh₃)₂] (yield 82%).

Bis(acetato)carbonylbis(triphenylphosphine)ruthenium(II), [Ru(OCOCH₃)₂CO(PPh₃)₂]. Sodium acetate (0.4 g) and carbonyl-

bis(trifluoroacetato)bis(triphenylphosphine)ruthenium (0.4 g) were heated together in boiling methanol (10.0 cm³) for 90 min. During this period, a small quantity of a white solid was precipitated from the pale yellow solution. The mixture was then cooled, and the white solid (A) was filtered off, and the filtrate was reduced in volume by evaporation under reduced pressure, and then allowed to crystallize slowly from ca. 5 cm³ of methanol as pale yellow crystals (B). These were filtered off, washed successively with small volumes of methanol, water, and methanol, and then dried in vacuo (yield 60%). The pale yellow crystals (B) are the desired product; the white solid (A) was identified by IR and ¹H NMR spectroscopy as **carbonylhydrido-(acetato)bis(triphenylphosphine)ruthenium(II)** (yield 15%) and is identical with an authentic specimen.

Bis(acetato)carbonylbis(triphenylphosphine)osmium(II), [Os(OCOCH₃)₂CO(PPh₃)₂]. Sodium acetate (0.4 g) and carbonylbis(trifluoroacetato)bis(triphenylphosphine)osmium (0.32 g) were heated together in boiling acetone/methanol (10.0 cm³ of each) for 60 min. The acetone and methanol were then removed by evaporation under reduced pressure, and the resultant oil was crystallized from a minimum volume of methanol as *pale cream crystals*. These were filtered off, washed successively with small volumes of methanol, water, and methanol, and dried in vacuo (yield 84%).

Acetato carbonylhydridobis(triphenylphosphine)ruthenium(II), [RuH(OCOCH₃)CO(PPh₃)₂]. Sodium acetate (0.3 g) and carbonylbis(trifluoroacetato)bis(triphenylphosphine)ruthenium (0.3 g) were heated together under reflux in ethanol (10.0 cm³). A white solid rapidly precipitated from the yellow solution; after 10 min heating was stopped and the mixture was allowed to cool. The *white microcrystals* were filtered off, washed successively with methanol, water, and methanol, and dried in vacuo (93%).

A similar procedure, employing carbonylbis(trifluoroacetato)bis(triphenylphosphine)osmium (0.3 g), gave as white microcrystals **acetato carbonylhydridobis(triphenylphosphine)osmium(II)**, [OsH(OCOCH₃)CO(PPh₃)₂] (yield 92%).

Carbonyl(nitrato)(trifluoroacetato)bis(triphenylphosphine)ruthenium(II), [Ru(NO₃)(OCOCF₃)CO(PPh₃)₂]. Sodium nitrate (0.1 g) and carbonylbis(trifluoroacetato)bis(triphenylphosphine)ruthenium (0.2 g) were heated together in boiling methanol (10.0 cm³) to form a pale yellow solution. From this solution, a pale yellow solid slowly precipitated; after 15 min heating was stopped and the mixture was allowed to cool. The precipitate was filtered off, washed successively in methanol, water, and methanol, then recrystallized from dichloromethane/methanol as *large yellow crystals*, which were filtered off and dried in vacuo (yield 74%).

A similar procedure, employing carbonylbis(trifluoroacetato)bis(triphenylphosphine)osmium (0.2 g), gave pale cream crystals of **carbonyl(nitrato)(trifluoroacetato)bis(triphenylphosphine)osmium(II)**, [Os(NO₃)(OCOCF₃)CO(PPh₃)₂] (yield 82%).

Carbonyl(methylsulfonato)(trifluoroacetato)bis(triphenylphosphine)ruthenium(II), [Ru(CH₃SO₃)(OCOCF₃)CO(PPh₃)₂]. Methanol (10.0 cm³) was first saturated with sulfur dioxide, carbonylbis(trifluoroacetato)bis(triphenylphosphine)ruthenium (0.3 g) was then added, and the mixture was heated under reflux with continued passage of sulfur dioxide. After 15 min the pale yellow solution was cooled, and a fine white crystalline solid was precipitated. This solid was filtered off, washed successively with methanol, water, and methanol, and then recrystallized from dichloromethane/methanol as *white needles*, which were filtered off and dried in vacuo (yield 82%).

(Acetylacetonato)carbonyl(trifluoroacetato)bis(triphenylphosphine)ruthenium(II)-Dichloromethane (4/3), [Ru(CH₃COCHCOCH₃)(OCOCF₃)CO(PPh₃)₂·0.75CH₂Cl₂]. Acetylacetonone (0.5 cm³) and carbonylbis(trifluoroacetato)bis(triphenylphosphine)ruthenium (0.2 g) were heated together in refluxing ethanol (10.0 cm³) for 15 min. Evaporation of this mixture, under reduced pressure, gave an oil, which was crystallized from dichloromethane/hexane as *large yellow crystals*. These were filtered off, washed with a small volume of methanol, and dried in vacuo (yield 93%).

A similar procedure, employing carbonylbis(trifluoroacetato)bis(triphenylphosphine)osmium (0.2 g), gave pale cream crystals of **(acetylacetonato)carbonyl(trifluoroacetato)bis(triphenylphosphine)osmium(II)-dichloromethane (4/3)** [Os(CH₃COCHCOCH₃)(OCOCF₃)CO(PPh₃)₂·0.75CH₂Cl₂] (yield 81%).

(Acetylacetonato)carbonylhydridobis(triphenylphosphine)ruthenium(II), [RuH(CH₃COCHCOCH₃)CO(PPh₃)₂]. Acetylacetonone (0.1 g), potassium hydroxide (0.04 g), and carbonylbis(trifluoroacetato)bis(triphenylphosphine)ruthenium (0.2 g) were heated together

in boiling ethanol (5.0 cm³) for 20 min. During this time *white crystals* were precipitated from the solution. The mixture was then cooled and the crystals were filtered off, washed successively in methanol, water, and methanol, and then dried in vacuo (yield 93%).

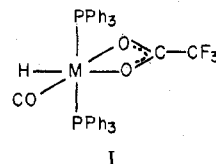
A similar procedure, employing carbonylbis(trifluoroacetato)bis(triphenylphosphine)osmium (0.2 g), gave pale yellow crystals of **(acetylacetonato)carbonylhydridobis(triphenylphosphine)osmium(II)**, [OsH(CH₃COCHCOCH₃)CO(PPh₃)₂] (yield 60%).

Carbonyl(hexafluoroacetylacetonato)(trifluoroacetato)bis(triphenylphosphine)ruthenium(II), [Ru(CF₃COCHCOCF₃)(OCOCF₃)CO(PPh₃)₂]. Hexafluoroacetylacetonone (0.5 cm³) and carbonylbis(trifluoroacetato)bis(triphenylphosphine)ruthenium (0.2 g) were heated together in boiling ethanol (5.0 cm³) for 20 min. The solution was then evaporated under reduced pressure to give an orange oil, which was crystallized from dichloromethane/hexane as *bright yellow-orange crystals*. These were filtered off, washed successively with small volumes of methanol, water, and methanol, and then dried in vacuo (yield 70%).

A similar procedure, employing carbonylbis(trifluoroacetato)bis(triphenylphosphine)osmium (0.2 g), gave bright yellow-orange crystals of **carbonyl(hexafluoroacetylacetonato)(trifluoroacetato)bis(triphenylphosphine)osmium(II)** [Os(CF₃COCHCOCF₃)(OCOCF₃)(CO)(PPh₃)₂] (yield 73%).

Results and Discussion

Carbonylhydrido(trifluoroacetato)bis(triphenylphosphine)ruthenium(II) and -osmium(II), [MH(OCOCF₃)(CO)(PPh₃)₂]. These pale yellow crystalline complexes, obtained by treating the precursors [M(OCOCF₃)₂(CO)(PPh₃)₂] with boiling ethanol, are air sensitive, blackening in a few hours in air and immediately on dissolution in the presence of oxygen. The loss of a trifluoroacetate ligand and the introduction of hydride can be attributed to alcoholysis followed by a β-elimination reaction.⁴ A more detailed account of this reaction and the catalytic alcohol dehydrogenation process derived from it has recently been given.³ Structure

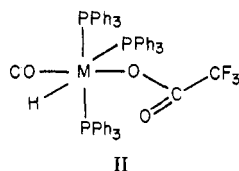


I is assigned on the basis of ¹H NMR spectra [$\tau(\text{RuH})$ 27.2 (t) (²J(PH)_{cis} = 19.0 Hz); $\tau(\text{OsH})$ 31.1 (t) (²J(PH)_{cis} = 17.0 Hz)], indicative of equivalent triphenylphosphine ligands and hydride trans to trifluoroacetate. Confirmation of this assignment is afforded by the ¹H decoupled ³¹P NMR spectrum of the ruthenium complex which displays only a single resonance [$\delta(\text{RuP})$ 43.40 ppm]. The complexes exhibit $\nu(\text{OCO})_{\text{asym}}$ at ca. 1615 cm⁻¹ indicative of a chelate mode of bonding for the trifluoroacetate ligand.^{2,5} These complexes are analogous to the acetato complex [RuH(OCOCH₃)(CO)(PPh₃)₂] obtained by the action of acetic acid on [RuH₂(CO)(PPh₃)₃];⁵ the cause of their air sensitivity is not immediately obvious.

The action of trifluoroacetic acid on the complexes [MH(OCOCF₃)(CO)(PPh₃)₂] in benzene leads to rapid regeneration of the bis(trifluoroacetato) complexes [M(OCOCF₃)₂(CO)(PPh₃)₂]. The hydrido complexes were also produced by the passage of a stream of dihydrogen through a solution of [M(OCOCF₃)₂(CO)(PPh₃)₂] in benzene and though not isolated were detected and identified in solution by their characteristic high-field ¹H NMR spectra.

Carbonylhydrido(trifluoroacetato)tris(triphenylphosphine)ruthenium(II) and -osmium(II), [MH(OCOCF₃)(CO)(PPh₃)₃]. These white air-stable crystalline complexes are produced in a manner similar to that described above for the bis(triphenylphosphine) complexes, but in the presence of excess triphenylphosphine. Their IR spectra indicate that the trifluoroacetate ligand is now monodentate, $\nu(\text{OCO})_{\text{asym}}$ ca.

1700 cm^{-1} . ^1H NMR spectra of the ruthenium complex $[\text{RuH}(\text{OCOCF}_3)(\text{CO})(\text{PPh}_3)_3]$ [$\tau(\text{RuH})$ 15.6 (doublet of triplets) ($^2J(\text{PH})_{\text{trans}} = \text{ca. } 110 \text{ Hz}$, $^2J(\text{PH})_{\text{cis}} = \text{ca. } 24.5 \text{ Hz}$)] indicate that the hydride ligand is trans to one phosphine and cis to two equivalent phosphines, thereby establishing stereochemistry II. However, the high-field RuH resonances

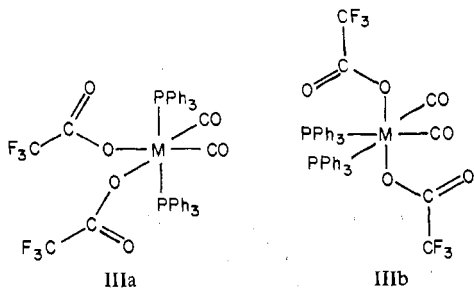


are broadened and in solution the complex slowly blackens in the absence of added triphenylphosphine. This is possibly due to phosphine dissociation and exchange, with the very air-sensitive bis(triphenylphosphine) complex $[\text{RuH}(\text{OCOCF}_3)(\text{CO})(\text{PPh}_3)_2]$ acting as an intermediate. The ^{31}P spectrum exhibits no obvious broadening [$\delta(\text{RuP})$ 41.0 (d), 18.7 ppm (t) ($^2J(\text{PP}') = 15.0 \text{ Hz}$)]]; however, this may simply reflect the larger frequency range involved in the ^{31}P spectra relative to the ^1H spectra.

The high-field ^1H NMR spectrum of the osmium complex $[\text{OsH}(\text{OCOCF}_3)(\text{CO})(\text{PPh}_3)_3]$ [$\tau(\text{OsH})$ 16.3 (doublet of triplets) ($^2J(\text{PH})_{\text{trans}} = 93.0 \text{ Hz}$, $^2J(\text{PH})_{\text{cis}} = 25.0 \text{ Hz}$)] is again indicative of stereochemistry II but exhibits no broadening of the resonances. The osmium complex does not blacken in solution, even in the absence of added triphenylphosphine; this behavior probably reflects the generally lower lability of osmium complexes relative to their ruthenium analogues. The stereochemistry is again supported by ^{31}P NMR data [$\delta(\text{OsP})$ 13.8 (d), 0.34 ppm (t) ($^2J(\text{PP}') = 12.0 \text{ Hz}$)]. This complex is identical to that made by the action of trifluoroacetic acid on $[\text{OsH}_2(\text{CO})(\text{PPh}_3)_3]$ in cold benzene.²

Both the ruthenium and osmium complexes can be produced from the corresponding bis(triphenylphosphine) species $[\text{MH}(\text{OCOCF}_3)(\text{CO})(\text{PPh}_3)_2]$ by the action of excess triphenylphosphine in boiling benzene. Thus, in ethanol, the hydride species $[\text{MH}(\text{OCOCF}_3)(\text{CO})(\text{PPh}_3)_2]$ is probably first formed from $[\text{M}(\text{OCOCF}_3)_2(\text{CO})(\text{PPh}_3)_2]$ by alcoholysis and is then attacked by the excess triphenylphosphine present to produce the tris(triphenylphosphine) complexes $[\text{MH}(\text{OCOCF}_3)(\text{CO})(\text{PPh}_3)_3]$. This is confirmed by the failure of triphenylphosphine to add to the bis(trifluoroacetato) complexes $[\text{M}(\text{OCOCF}_3)_2(\text{CO})(\text{PPh}_3)_2]$ in nonalcoholic media.

Dicarbonylbis(trifluoroacetato)bis(triphenylphosphine)ruthenium(II) and -osmium(II), $[\text{M}(\text{OCOCF}_3)_2(\text{CO})_2(\text{PPh}_3)_2]$. These white air-stable crystalline complexes are produced by the action of carbon monoxide on solutions of $[\text{M}(\text{OCOCF}_3)_2(\text{CO})(\text{PPh}_3)_2]$ in boiling benzene. They are identical (in respect of their melting points and IR spectra) to the complexes produced by the action of trifluoroacetic acid on $[\text{Ru}(\text{CO})_3(\text{PPh}_3)_2]$ and $[\text{OsH}_2(\text{CO})_2(\text{PPh}_3)_2]$, respectively, and are similarly assigned either stereochemistry IIIa or IIIb.²

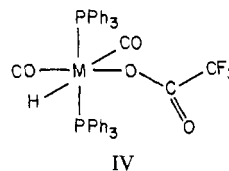


Both trifluoroacetato ligands are now monodentate, $\nu(\text{OCO})_{\text{asym}}$ ca. 1680 cm^{-1} ; the presence of two strong $\nu(\text{CO})$ vibrations at ca. 2060 and 1970 cm^{-1} indicates that the

carbonyl ligands are mutually cis and probably situated trans to the carboxylate ligands (stereochemistry IIIa). If these reactions are repeated in ethanol then the ruthenium dicarbonyl $[\text{Ru}(\text{OCOCF}_3)_2(\text{CO})_2(\text{PPh}_3)_2]$ is produced cleanly; the osmium product, however, exhibits extra vibrations in the $\nu(\text{CO})$ and $\nu(\text{OsH})$ regions of its IR spectrum, characteristic of $[\text{OsH}(\text{OCOCF}_3)(\text{CO})_2(\text{PPh}_3)_2]$ (vide infra).

The dicarbonyls $[\text{M}(\text{OCOCF}_3)_2(\text{CO})_2(\text{PPh}_3)_2]$ are themselves resistant to attack by alcohol; therefore, in the case of osmium, the alcohol is presumably able to compete with carbon monoxide in attacking the initial complex $[\text{Os}(\text{OCOCF}_3)_2(\text{CO})(\text{PPh}_3)_2]$. The hydrido complex $[\text{OsH}(\text{OCOCF}_3)(\text{CO})(\text{PPh}_3)_2]$ thus formed is then capable of reaction with carbon monoxide to produce the dicarbonyl-hydride noted above. Consequently the hydrido complexes $[\text{MH}(\text{OCOCF}_3)(\text{CO})(\text{PPh}_3)_2]$ were themselves treated with carbon monoxide.

Dicarbonylhydrido(trifluoroacetato)bis(triphenylphosphine)ruthenium(II) and -osmium(II), $[\text{MH}(\text{OCOCF}_3)(\text{CO})_2(\text{PPh}_3)_2]$. These white crystalline complexes are stable for a period of weeks in air, but in solution they are rapidly attacked by oxygen. They are produced by the action of carbon monoxide on the hydride complexes $[\text{MH}(\text{OCOCF}_3)(\text{CO})(\text{PPh}_3)_2]$ in boiling benzene. Their high-field ^1H NMR spectra are indicative of hydride cis to two equivalent triphenylphosphine ligands [$\tau(\text{RuH})$ 14.1 (t) ($^2J(\text{PH}) = 19.2 \text{ Hz}$); $\tau(\text{OsH})$ 12.9 (t) ($^2J(\text{PH}) = 21.0 \text{ Hz}$)]. The very low values obtained for $\tau(\text{MH})$ virtually exclude the possibility that hydride is trans to trifluoroacetate, and, assuming that the formulation $[\text{MH}(\text{OCOCF}_3)(\text{CO})_2(\text{PPh}_3)_2]$ is correct (good analytical correlation was obtained), the stereochemistry is probably IV with carbonyl trans to hydride and the triphenylphosphine ligands mutually trans.

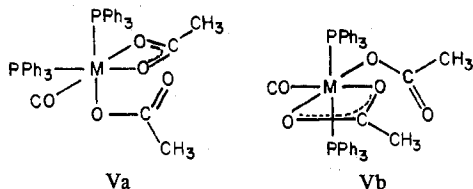


However, these complexes could conceivably be formulated as seven-coordinate fluxional trihydrides of stoichiometry $[\text{MH}_3(\text{OCOCF}_3)(\text{CO})(\text{PPh}_3)_2]$. This formulation is consistent with the analytical data and the low τ value of the hydride resonance recorded for the complexes,⁶ but is difficult to reconcile with the method of preparation described above, and in view of the failure of the complex to react with trifluoroacetic acid in boiling benzene is considered improbable. The trihydride formulation is also refuted by the NMR integration ratios; however, such ratios are frequently unreliable because of large differences in the relaxation times of the ^1H nuclei concerned.⁷

We are therefore unable to offer an adequate explanation for the high-field NMR data recorded for these complexes. The values of $\tau(\text{MH})$ are unexpectedly low even for hydride trans to carbonyl and are unusual in that $\tau(\text{OsH})$ is lower than $\tau(\text{RuH})$ for analogous complexes.^{8,9} The infrared spectra of these complexes also merit comment; in the region 2100–1900 cm^{-1} the osmium complex exhibits three strong vibrations attributable to $\nu(\text{CO})$ [2045 and 1985 cm^{-1}] and $\nu(\text{OsH})$ [1928 cm^{-1}] as expected for stereochemistry IV.¹⁰ However, the corresponding ruthenium complex displays only two bands in this region [2048 and 1982 cm^{-1}] both attributable to $\nu(\text{CO})$. The infrared absorption associated with the RuH stretching vibration must either be very weak or must occur at relatively high frequency and be masked by one of the $\nu(\text{CO})$ absorptions. The latter phenomenon has previously been reported for the closely related complexes $[\text{RuH}_2(\text{CO})_2(\text{PR}_3)_2]$ (R = Et or Ph).¹¹ For both complexes the ^{31}P NMR (^1H decoupled)

spectra exhibit the expected single resonance [$\delta(\text{RuP})$ 43.2, $\delta(\text{OsP})$ 15.4 ppm].

Bis(acetato)carbonylbis(triphenylphosphine)ruthenium(II) and -osmium(II), $[\text{M}(\text{OCOCH}_3)_2(\text{CO})(\text{PPh}_3)_2]$. These air-stable crystalline complexes are prepared by the action of sodium acetate on the corresponding bis(trifluoroacetate) complexes, $[\text{M}(\text{OCOCF}_3)_2(\text{CO})(\text{PPh}_3)_2]$, in boiling methanol.¹² IR spectra indicate the presence of both mono- and bidentate acetate ligands, i.e., $\nu(\text{OCO})_{\text{asym}}$ 1635 and 1517 cm^{-1} . ^1H NMR spectra of samples at 300 K exhibit a single resonance for the two methyl groups [τ 8.67 (Ru); τ 8.50 (Os)]. A decrease in sample temperature causes the single methyl resonance to broaden in each instance; further lowering of sample temperature effects decoalescence producing two sharp well-defined methyl resonances [coalescence temperature ca. 274 K (Ru), 291 K (Os); limiting separation of methyl resonances, 28 Hz (Ru) and 38 Hz (Os)]. ^{31}P NMR spectra also exhibit such temperature dependence; each complex exhibits a single resonance at 300 K [$\delta(\text{RuP})$ 47.92, $\delta(\text{OsP})$ 5.09 ppm]. At lower temperatures (ca. 213 K) both complexes give rise to an AB quartet [$\delta(\text{RuP})$ 45.73 and 49.36 ppm ($^2J(\text{PP}') = 24.4$ Hz); $\delta(\text{OsP})$ 4.19 and 6.66 ppm ($^2J(\text{PP}') = 7.3$ Hz)]. Thus ^1H and ^{31}P NMR spectral data are consistent with the fluxional stereochemistry (Va) analogous to that recently established for the bis(trifluoroacetato) precursors $[\text{M}(\text{OCOCF}_3)_2(\text{CO})(\text{PPh}_3)_2]$,² in which the mono- and bidentate acetate ligands undergo a rapid intramolecular exchange.¹³

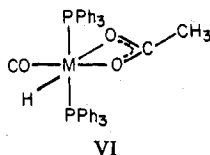


An apparently isomeric complex $[\text{Ru}(\text{OCOCH}_3)_2(\text{CO})(\text{PPh}_3)_2]$ has recently been reported by Wilkinson et al.,¹⁴ however, this species exhibits only one methyl resonance in its ^1H NMR spectrum at temperatures as low as 213 K. This species was assigned stereochemistry Vb by analogy with the similar formimidoyl complex $[\text{Ru}(\text{OCOCH}_3)(\text{HC}=\text{NR})(\text{CO})(\text{PPh}_3)_2]$ whose structure has been obtained by x-ray diffraction.¹⁵

The reaction of $[\text{Ru}(\text{OCOCF}_3)_2(\text{CO})(\text{PPh}_3)_2]$ with sodium acetate in boiling methanol also produced a small quantity of $[\text{RuH}(\text{OCOCH}_3)(\text{CO})(\text{PPh}_3)_2]$, identical to an authentic specimen. Since neither $[\text{Ru}(\text{OCOCH}_3)_2(\text{CO})(\text{PPh}_3)_2]$ nor $[\text{Ru}(\text{OCOCF}_3)_2(\text{CO})(\text{PPh}_3)_2]$ is attacked by boiling methanol alone, the formation of hydride is presumably due to sodium acetate functioning as the base in an alcoholysis reaction.

(Acetato)carbonylhydridobis(triphenylphosphine)ruthenium(II) and -osmium(II), $[\text{MH}(\text{OCOCH}_3)\text{CO}(\text{PPh}_3)_2]$. These white air-stable crystalline complexes are produced by the action of sodium acetate on the corresponding bis(trifluoroacetato) complexes, $[\text{M}(\text{OCOCF}_3)_2(\text{CO})(\text{PPh}_3)_2]$, in ethanol solution. Presumably, in the presence of sodium acetate (a weak base) ethanol removes a trifluoroacetate ligand by solvolysis to yield an ethoxide; this subsequently undergoes a β -elimination to form the observed hydrido complex.^{3,4}

The complexes are assigned stereochemistry VI on the basis of their high-field ^1H NMR spectra [$\tau(\text{RuH})$ 26.5 (t) ($^2J(\text{PH})_{\text{cis}} = 20.7$ Hz); $\tau(\text{OsH})$ 29.7 (t) ($^2J(\text{PH})_{\text{cis}} = 16.5$ Hz)].



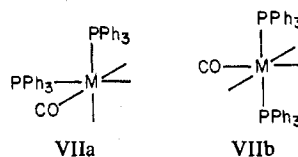
The ruthenium complex is identical to that previously obtained by the action of acetic acid on $[\text{RuH}_2(\text{CO})(\text{PPh}_3)_3]$.⁵ Unlike their trifluoroacetato analogues they are not further attacked by their respective acid to produce the corresponding bis(carboxylato) complexes; acetic acid is probably too weak to promote further protonation and subsequent elimination of the hydride ligands as dihydrogen.

Carbonylnitrato(trifluoroacetato)bis(triphenylphosphine)ruthenium(II) and -osmium(II), $[\text{M}(\text{NO}_3)(\text{OCOCF}_3)(\text{CO})(\text{PPh}_3)_2]$. These air-stable yellow (Ru) and cream (Os) crystalline complexes are produced by the action of sodium nitrate on $[\text{M}(\text{OCOCF}_3)_2(\text{CO})(\text{PPh}_3)_2]$ in boiling methanol. No hydrido complexes were detected, in contrast to the analogous reaction involving sodium acetate, where $[\text{RuH}(\text{OCOCH}_3)(\text{CO})(\text{PPh}_3)_2]$ was produced in small quantities. The absence of hydridic products presumably reflects the nonbasic character of sodium nitrate.

The high value of $\nu(\text{OCO})_{\text{asym}}$, ca. 1710 cm^{-1} , and its large separation from $\nu(\text{OCO})_{\text{sym}}$ at ca. 1415 cm^{-1} , i.e., 300 cm^{-1} , is indicative of a monodentate mode of coordination for the trifluoroacetate ligand. Thus to conserve the normal six-coordination characteristic of Ru(II) complexes the nitrate ligand is presumably bidentate. The highest frequency vibration assignable to coordinated nitrate ligand is ca. 1580 cm^{-1} and the lowest is ca. 1225 cm^{-1} . This large separation, ca. 350 cm^{-1} , and the proximity of the highest frequency vibration to 1600 cm^{-1} support the conclusion that the nitrate ligand is bidentate.¹⁶

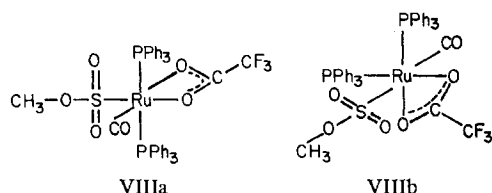
^{31}P NMR spectra at 300 K exhibit broadened singlet resonances for both the ruthenium and osmium complexes [$\delta(\text{RuP})$ 46.4, $\delta(\text{OsP})$ 1.41 ppm]. This strongly suggests a type of equilibrium mechanism similar to the one previously described for the bis(carboxylato) complexes, $[\text{M}(\text{OCOR})_2(\text{CO})(\text{PPh}_3)_2]$ (R = CF₃ or CH₃). Indeed, a decrease in sample temperature produces a complex sharp spectrum; further sharpening is noted as the temperature is lowered.¹³ However, the ruthenium complex $[\text{Ru}(\text{NO}_3)(\text{OCOCF}_3)(\text{CO})(\text{PPh}_3)_2]$ exhibits an additional sharp resonance masked at 300 K by the broad resonance that is not split at low sample temperature. This resonance is possibly due to an isomer containing mutually trans triphenylphosphine ligands and from integrations of the resonances accounts for approximately 20% of the ^{31}P concentration.

Thus the majority of the product from the above reactions can be assigned stereochemistry VIIa analogous to the bis(trifluoroacetato) complexes $[\text{M}(\text{OCOCF}_3)_2(\text{CO})(\text{PPh}_3)_2]$,² while the remainder is possibly of stereochemistry VIIb. The exact configuration of the trifluoroacetate and nitrate ligands (in the solid state) cannot be assigned for the major product except to say that they share the fac arrangement of available coordination sites.



Carbonyl(methylsulfonato)(trifluoroacetato)bis(triphenylphosphine)ruthenium(II)-Methanol Solvate, $[\text{Ru}(\text{SO}_3\text{CH}_3)(\text{OCOCF}_3)(\text{CO})(\text{PPh}_3)_2]\cdot\text{CH}_3\text{OH}$ (1/1). This white air-stable crystalline complex was obtained as a 1/1 methanol solvate by the treatment of $[\text{Ru}(\text{OCOCF}_3)_2(\text{CO})(\text{PPh}_3)_2]$ with sulfur dioxide in boiling methanol. Presumably the methylsulfonate ligand is produced by the insertion of sulfur dioxide into the metal-methoxide linkage of $[\text{Ru}(\text{OCOCF}_3)(\text{OMe})(\text{CO})(\text{PPh}_3)_2]$. Methanol is known to coordinate to $[\text{Ru}(\text{OCOCF}_3)_2(\text{CO})(\text{PPh}_3)_2]$ giving $[\text{Ru}(\text{OCOCF}_3)_2(\text{MeOH})(\text{CO})(\text{PPh}_3)_2]$ ¹⁷ which could then form $[\text{Ru}(\text{OCOCF}_3)-$

(OMe)(CO)(PPh₃)₂] by proton transfer and CF₃COOH elimination. The IR spectrum exhibits vibrations similar to those reported by Barlex and Kemmitt¹⁸ for the complex [Pt(SO₃CH₃)₂(PPh₃)₂] which was obtained by a similar procedure. IR vibrations are similarly assigned: $\nu(\text{SO}_2)_{\text{asym}}$ ca. 1235 cm⁻¹, $\nu(\text{SO}_2)_{\text{sym}}$ ca. 1190 cm⁻¹, and $\nu(\text{S-O})$ ca. 987 cm⁻¹. Such a spectrum is indicative of a monodentate S-bonded methylsulfonate ligand.^{18,19} The trifluoroacetate ligand exhibits $\nu(\text{OCO})_{\text{asym}}$ at ca. 1650 cm⁻¹ and thus cannot be readily assigned either a mono- or bidentate mode of coordination, but is probably bidentate. The ³¹P NMR spectrum of this complex exhibits a single resonance [$\delta(\text{RuP})$ 35.60 ppm] indicative of equivalent triphenylphosphine ligands; if the trifluoroacetate ligand is assumed to be bidentate then the possible stereochemistries are VIIIa and VIIIb, VIIIa being sterically preferred. ¹H NMR spectra exhibit two methyl resonances, one at ca. τ 7.2 attributed to CH₃SO₃ and one at ca. τ 6.65 attributable to solvated methanol.



Analogous reactions involving [Os(OCOCF₃)₂(CO)(PPh₃)₂] gave a white crystalline product which exhibited similar spectral properties to the ruthenium methylsulfonate complex [Ru(CH₃SO₃)(OCOCF₃)(CO)(PPh₃)₂] described above. However, analytically pure products could not be obtained and ¹H NMR spectra revealed the presence of a variety of methyl resonances.

(Acetylacetonato)carbonyl(trifluoroacetato)bis(triphenylphosphine)ruthenium(II) and -osmium(II)-Dichloromethane Solvates, [M(CH₃COCHCOCH₃)(CO)(OCOCF₃)(PPh₃)₂]-CH₂Cl₂. These air-stable yellow crystalline complexes were obtained from [M(OCOCF₃)₂(CO)(PPh₃)₂] by treatment with acetylacetonone in boiling ethanol (Ru) or 2-methoxyethanol (Os) and recrystallization from dichloromethane-hexane.

The trifluoroacetate ligand exhibits $\nu(\text{OCO})_{\text{asym}}$ at ca. 1700 cm⁻¹ and is therefore expected to be monodentate. The high-frequency vibrations attributable to the acetylacetonate ligand, ca. 1580 and 1520 cm⁻¹, are indicative of bidentate O,O coordination.²⁰ ¹H NMR spectra demonstrate the presence of the two acetylacetonate methyl resonances at ca. τ 8.27 and 8.38 for the osmium complex, and ca. τ 8.23 and 8.40 for the ruthenium complex; thus for both complexes the acetylacetonate ligand is trans to two dissimilar ligands. There are also resonances attributable to the CH proton of the acetylacetonate ligand [τ 5.0 (Os) and 5.1 (Ru)] and the CH₂ group of the solvated dichloromethane (ca. τ 4.7).

³¹P NMR spectra exhibit two doublet resonances [$\delta(\text{RuP})$ 45.0 (d) and 40.9 ppm (d) ($^2J(\text{PP}') = 27.0$ Hz); $\delta(\text{OsP})$ 0.8 (d) and -2.3 ppm (d) ($^2J(\text{PP}') = 11.0$ Hz)] indicative of nonequivalent triphenylphosphine ligands. The stereochemistry is thus either IXa or IXb. However, the small size of the chemical shift difference between the two P nuclei (Table III) suggests that their chemical environments are not substantially different and therefore favors stereochemistry IXb rather than IXa.

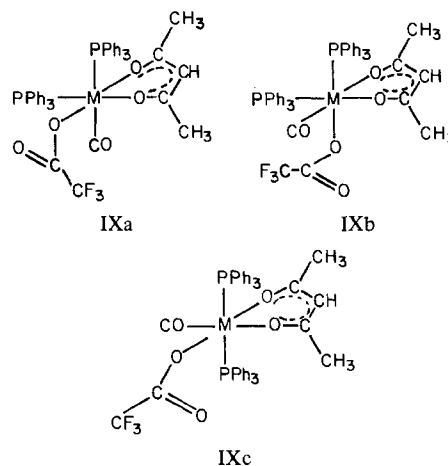
Stereochemistry IXb is also analogous to that found for the bis(trifluoroacetato) complexes [M(OCOCF₃)₂(CO)(PPh₃)₂]² and thus it may be considered as the probable configuration.

If reaction of the ruthenium complex is performed in a higher boiling alcohol, e.g., 2-methoxyethanol, then three additional resonances begin to appear in the ¹H NMR spectrum of the product. The new resonances at τ 8.27 and 8.73 are of equal intensity and ca. three times the intensity

Table III. ³¹P NMR Data^a

Complex	δ , ppm	$^2J(\text{PP}')$, Hz
[RuH(OCOCF ₃)CO(PPh ₃) ₂] ^b	43.40 (s)	
[RuH(OCOCF ₃)CO(PPh ₃) ₃]	{ 41.00 (d) 18.70 (t)	15.0
[OsH(OCOCF ₃)CO(PPh ₃) ₃]	{ 13.76 (d) 0.34 (t)	12.0
[RuH(OCOCF ₃)(CO) ₂ (PPh ₃) ₂]	43.16 (s)	
[OsH(OCOCF ₃)(CO) ₂ (PPh ₃) ₂]	15.41 (s)	
[RuH(OCOCH ₃)CO(PPh ₃) ₂]	44.50 (s)	
[Ru(NO ₃)(OCOCF ₃)CO(PPh ₃) ₂]	46.40 (br)	
[Os(NO ₃)(OCOCF ₃)CO(PPh ₃) ₂]	1.41 (br)	
[Ru(SO ₃ CH ₃)(OCOCF ₃)CO(PPh ₃) ₂]	35.60 (s)	
[Ru(acac)(OCOCF ₃)CO(PPh ₃) ₂]	{ 45.00 (d) 40.90 (d)	27.0
[Os(acac)(OCOCF ₃)CO(PPh ₃) ₂]	{ 0.80 (d) -2.30 (d)	11.0
[Ru(facfac)(OCOCF ₃)CO(PPh ₃) ₂]	41.40 (s)	
[Os(facfac)(OCOCF ₃)CO(PPh ₃) ₂]	{ -1.20 (d) -5.50 (d)	11.0

^a Recorded at 36.43 MHz in CDCl₃ solution at 25 °C and referenced to external H₃PO₄; all ¹H nuclei decoupled, CDCl₃ used to provide ²D field-frequency lock, couplings ± 0.5 Hz. ^b Except RuH(OCOCF₃)CO(PPh₃)₂, where C₆D₆ was used as solvent.



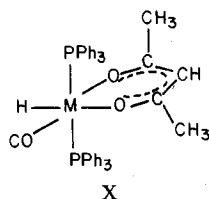
of the third new resonance at ca. τ 5.9. These three new resonances can be assigned to the two methyl groups and one C-H proton of an acetylacetonate ligand. If a reaction time of ca. 5 h is employed then this new species is the sole product. Analytical data establish this to be an isomer of the original complex, i.e., [Ru(CH₃COCHCOCH₃)(OCOCF₃)(CO)(PPh₃)₂]. ³¹P NMR spectra exhibit a single resonance, indicative of equivalent triphenylphosphine ligands [$\delta(\text{RuP})$ 30.22 ppm]. Thus this isomer appears to have stereochemistry IXc, containing mutually *trans*-phosphine ligands.

The osmium acetylacetonate complex [Os(CH₃COCHCOCH₃)(OCOCF₃)(CO)(PPh₃)₂] showed no such tendency to rearrange, probably reflecting the generally lower liability of osmium complexes. This tendency is also observed in the hexafluoroacetylacetonate complexes [M-(CF₃COCHCOCH₃)(OCOCF₃)(CO)(PPh₃)₂] discussed below, where the ruthenium complex more rapidly rearranges to the isomer containing mutually *trans*-triphenylphosphine ligands.

(Acetylacetonato)carbonylhydridobis(triphenylphosphine)ruthenium(II) and -osmium(II), [MH(CH₃COCHCOCH₃)CO(PPh₃)₂]. These white air-stable crystalline complexes were prepared from the corresponding bis(trifluoroacetato) complexes [M(OCOCF₃)₂(CO)(PPh₃)₂] by the action of acetylacetonone and potassium hydroxide in boiling ethanol. The presence of potassium hydroxide leads to the replacement of both trifluoroacetate ligands, one by acetylacetonate and the other by hydride. In the presence of base

and boiling ethanol the hydrido species is probably formed and is subsequently attacked by potassium acetylacetonate; this reaction is thus similar to that in the presence of sodium acetate described above. The formation of hydride in this instance can probably be attributed to the presence of base which can effectively remove the trifluoroacetic acid that would otherwise reattack the complex.

The high-field ^1H NMR spectrum [$\tau(\text{RuH})$ 23.3 (t) ($^2J(\text{PH}) = 20.5$ Hz); $\tau(\text{OsH})$ 25.8 (t) ($^2J(\text{PH}) = 17.0$ Hz)] is indicative of equivalent phosphine ligands and hydride trans to acetylacetonate. The chelate ring vibrations of acetylacetonate, ca. 1590 and 1510 cm^{-1} , are again indicative of O,O bidentate coordination.²⁰ Thus the stereochemistry is assigned as X.



The low-field ^1H NMR spectrum exhibits two resonances attributable to the acetylacetonate methyl groups [ca. τ 8.94 and 8.70] and a resonance attributable to the central CH group [τ 5.6]. These complexes thus have similar stereochemistry to the analogous trifluoroacetato complexes $[\text{MH}(\text{OCOCF}_3)(\text{CO})(\text{PPh}_3)_2]$.

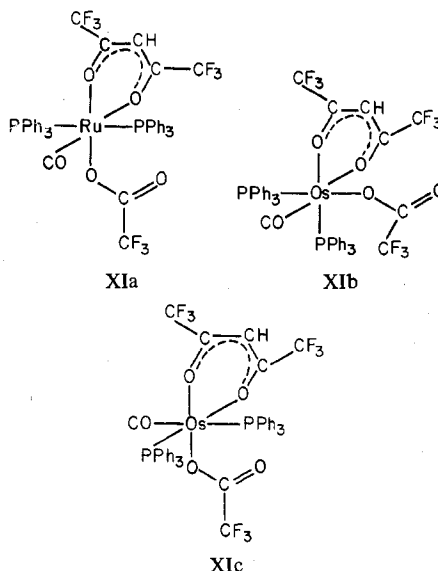
Carbonyl(hexafluoroacetylacetonato)(trifluoroacetato)-bis(triphenylphosphine)ruthenium(II) and -osmium(II), $[\text{M}(\text{CF}_3\text{COCHCOF}_3)(\text{OCOCF}_3)(\text{CO})(\text{PPh}_3)_2]$. These orange-yellow air-stable crystalline complexes are produced by the reaction of hexafluoroacetylacetonate on $[\text{M}(\text{OCOCF}_3)_2(\text{CO})(\text{PPh}_3)_2]$ in boiling ethanol. The hexafluoroacetylacetonate ligand again appears to be bidentate O,O coordinated; IR spectra exhibit vibrations at 1630 and 1550 cm^{-1} , which is consistent with this mode of bonding. These vibrations are at higher frequency than those exhibited by the corresponding acetylacetonate complexes, thus demonstrating the strong electron-withdrawing properties of the CF_3 groups, reflected by a weakening of the metal-oxygen bonds and strengthening of the C-O and C-C bonds.²¹ The corresponding decrease in electron density on the metal is exhibited by a slight increase in the carbonyl C=O stretching frequency of ca. 20 cm^{-1} relative to the analogous acetylacetonate complexes. The trifluoroacetate $\nu(\text{OCO})_{\text{asym}}$ vibrations are at high frequency (ca. 1700 cm^{-1}) consistent with a monodentate mode of coordination.⁵

^{31}P NMR spectra indicate the presence of nonequivalent triphenylphosphine ligands [$\delta(\text{OsP})$ -1.2 and -5.5 ppm (d) ($^2J(\text{PP}') = 11.0$ Hz)] for the osmium complex but equivalent triphenylphosphine ligands [$\delta(\text{RuP})$ 41.4 ppm (s)] for the ruthenium complex.

The ^{19}F NMR spectrum of the ruthenium complex exhibits three resonances of equal intensity; two are slightly broadened and are of similar appearance [7453 and 7420 Hz with respect to C_6F_6] and are thus assigned as the two CF_3 groups of the hexafluoroacetylacetonate ligand; the third resonance is very sharp [7457 Hz] and is assigned to the CF_3 group of the trifluoroacetate ligand. Thus the hexafluoroacetylacetonate ligand is trans to two dissimilar species and the stereochemistry can be assigned as XIa.

^{19}F NMR spectra of the osmium complex are similar with one very sharp resonance [7439 Hz, CF_3 of trifluoroacetate] and two slightly broadened resonances [7423 and 7419 Hz, CF_3 resonances of hexafluoroacetylacetonate ligand] all of equal intensity. The trifluoroacetate CF_3 resonance is again at a higher frequency than the CF_3 resonances of hexafluoroacetylacetonate, which is again trans to two dissimilar

ligands. For the osmium complex the stereochemistry cannot be definitely assigned and may be either XIb or XIc, with XIb preferred by analogy with $[\text{M}(\text{OCOCF}_3)_2(\text{CO})(\text{PPh}_3)_2]$ and $[\text{M}(\text{CH}_3\text{COCHCOCH}_3)(\text{OCOCF}_3)(\text{CO})(\text{PPh}_3)_2]$ (see above).



Both the ruthenium and the osmium complex probably initially form the *cis*-phosphine isomer XIb; the more labile ruthenium complex then rapidly rearranges to produce the *trans*-phosphine isomer [rearrangement was not detected for the osmium complex]. Similar behavior has been observed for a series of dithioformato²² and *N*-alkyl and *N*-aryl thioformamido complexes.²³ Both complexes exhibit a resonance at ca τ 4.4 in their ^1H NMR spectra, attributable to the central proton of the hexafluoroacetylacetonate ligand.

Registry No. $[\text{RuH}(\text{OCOCF}_3)\text{CO}(\text{PPh}_3)_2]$, 60451-51-6; $[\text{OsH}(\text{OCOCF}_3)\text{CO}(\text{PPh}_3)_2]$, 61966-65-2; $[\text{RuH}(\text{OCOCF}_3)\text{CO}(\text{PPh}_3)_3]$, 61966-66-3; $[\text{OsH}(\text{OCOCF}_3)\text{CO}(\text{PPh}_3)_3]$, 61990-11-2; $[\text{Ru}(\text{OCOCF}_3)_2(\text{CO})_2(\text{PPh}_3)_2]$, 56143-16-9; $[\text{Os}(\text{OCOCF}_3)_2(\text{CO})_2(\text{PPh}_3)_2]$, 56086-09-0; $[\text{RuH}(\text{OCOCF}_3)(\text{CO})_2(\text{PPh}_3)_2]$, 61951-05-1; $[\text{OsH}(\text{OCOCF}_3)(\text{CO})_2(\text{PPh}_3)_2]$, 62014-80-6; $[\text{Ru}(\text{OCOCH}_3)_2\text{CO}(\text{PPh}_3)_2]$, 61990-12-3; $[\text{Os}(\text{OCOCH}_3)_2\text{CO}(\text{PPh}_3)_2]$, 61990-13-4; $[\text{RuH}(\text{OCOCH}_3)\text{CO}(\text{PPh}_3)_2]$, 50661-73-9; $[\text{OsH}(\text{OCOCH}_3)\text{CO}(\text{PPh}_3)_2]$, 61951-06-2; $[\text{Ru}(\text{NO}_3)(\text{OCOCF}_3)\text{CO}(\text{PPh}_3)_2]$, 61951-07-3; $[\text{Os}(\text{NO}_3)(\text{OCOCF}_3)\text{CO}(\text{PPh}_3)_2]$, 61951-08-4; $[\text{Ru}(\text{OCOCF}_3)(\text{SO}_3\text{CH}_3)\text{CO}(\text{PPh}_3)_2]$, 61967-07-5; $[\text{Ru}(\text{acac})(\text{OCOCF}_3)\text{CO}(\text{PPh}_3)_2]$, 61951-09-5; $[\text{Os}(\text{acac})(\text{OCOCF}_3)\text{CO}(\text{PPh}_3)_2]$, 61951-10-8; $[\text{RuH}(\text{acac})(\text{OCOCF}_3)\text{CO}(\text{PPh}_3)_2]$, 61951-11-9; $[\text{OsH}(\text{acac})(\text{OCOCF}_3)\text{CO}(\text{PPh}_3)_2]$, 61950-99-0; $[\text{Ru}(\text{facfac})(\text{OCOCF}_3)\text{CO}(\text{PPh}_3)_2]$, 61951-03-9; $[\text{Os}(\text{facfac})(\text{OCOCF}_3)\text{CO}(\text{PPh}_3)_2]$, 61951-04-0; $[\text{Ru}(\text{OCOCF}_3)_2\text{CO}(\text{PPh}_3)_2]$, 38596-61-1; $[\text{Os}(\text{OCOCF}_3)_2\text{CO}(\text{PPh}_3)_2]$, 38596-63-3.

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Contribution from the Department of Chemistry,
 University of Washington, Seattle, Washington 98195

Comparison of Dioxygen and Ethylene as Ligands for Platinum(0)

JOE G. NORMAN, Jr.

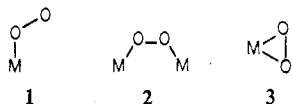
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The results of SCF-X α -SW calculations on the model chelated-O₂ complex Pt(PH₃)₂(O₂) and its ethylene analogue Pt(PH₃)₂(C₂H₄) are used to discuss the bonding, structure, and reactivity of dioxygen and ethylene complexes. Pt-O₂ and Pt-C₂H₄ covalent bonding is mainly due to mixing of metal 5d_{x²-y²} and 5d_{z²} orbitals with ligand bonding orbitals of both σ and π type. "Back-bonding" in Pt(PH₃)₂(O₂) amounts to essentially complete ionic transfer of two electrons from the Pt 5d_{xy} to the in-plane O₂ π^* orbital, with little covalent overlap between the two. However, such overlap is appreciable in Pt(PH₃)₂(C₂H₄), the electrons remaining chiefly in the d_{xy} orbital. Pt(PH₃)₂(O₂) is thus best formulated as a d⁸ system (Pt^{II}-O₂²⁻), and Pt(PH₃)₂(C₂H₄) as a d¹⁰ system (Pt⁰-C₂H₄). By extrapolation, the chelated-O₂ complexes of "d⁸" metals are best thought of as d⁶ systems (Co^{III}-O₂²⁻, etc.). The calculations agree well with electronic and x-ray photoelectron spectra. The influence of ligands trans to O₂ or C₂H₄ is used to explain why C₂H₄ is sometimes coordinated in, and sometimes perpendicular to, the molecular plane in complexes and why O₂ is sometimes monodentate and sometimes chelated. The energy-level diagram for Pt(PH₃)₂(O₂) is that of a nucleophile, the HOMO being strongly localized on O₂ as the out-of-plane π^* orbital and the two LUMO's being mainly Pt 5d_{xy} and O₂ σ^* , respectively. The mechanisms of SO₂ addition to chelated-O₂ complexes to form coordinated sulfate and the homogeneous catalysis of PPh₃ oxidation by Pt(PPh₃)₃ are discussed in these terms. Some Pt 5d \rightarrow P 3d π back-bonding is observed in the calculated electronic structures, as a replacement of 3s by 3d character in the phosphorus bonding functions. The implications of this result for the general question of metal-phosphorus bonding are discussed.

Introduction

The critical role played by transition metals in both biochemical and industrial processes involving molecular oxygen makes the chemistry of metal-dioxygen complexes especially important. Among the three coordination modes known for dioxygen—monodentate (1), bridging (2), and chelating



(3)—the first has particular significance because it almost certainly occurs (with M = Fe) in oxygenated heme proteins.^{1,2} However, the great majority of known dioxygen complexes contain chelated O₂; a recent review³ lists 43 x-ray structures of type 3 vs. 16 of types 1 and 2 combined.

Chelated-O₂ complexes fall naturally into two main groups: those of early transition metals in high oxidation states (e.g., [MoOF₄(O₂)]²⁻) and those of group 8 metals in lower oxidation states (e.g., Ir(PPh₃)₂(CO)(Cl)(O₂)). After several years of discussion, it now seems clear that both groups are best formulated as *peroxo* complexes, i.e., as containing O₂²⁻ covalently bound to metals in oxidation states $\geq 2+$.³⁻⁵ Consistently, the range of O-O distances in reliable structures is 1.40–1.52 Å (average 1.45 (2) Å),^{3,6} bracketing the value for peroxide ion, 1.49 Å. Though pleasing in its simplicity, this picture clearly does not describe the M-O₂ bonding in enough detail to resolve many important issues. For example, despite the similar structures of the early transition metal and group 8 complexes, the O₂ unit behaves formally as an electrophile in the former and as a nucleophile in the latter.^{7,8}

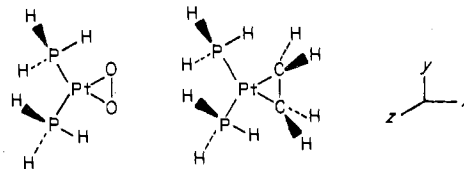
In order to provide a more sophisticated basis for discussing the chemistry of chelated-O₂ complexes in terms of electronic structure, I am carrying out SCF-X α -SW calculations⁹ on representative molecules. To exemplify group 8 complexes,

Pt(PPh₃)₂(O₂)¹⁰ is an obvious choice. Its structure is simple and accurately known by x-ray crystallography.¹¹ It participates in many well-defined reactions,^{7,12} sometimes as a homogeneous catalyst,¹³ which one might hope to explain. Moreover, it has an exact ethylene analogue, also structurally characterized,¹⁴ allowing a close comparison of the bonding of these two important π ligands. Pt(PPh₃)₂(C₂H₄) is interesting in its own right as the classic example of a d¹⁰ ethylene complex. This paper presents a comparison of calculations for the model compounds Pt(PH₃)₂L, L = O₂, C₂H₄. A very preliminary account of the results for Pt(PH₃)₂(O₂) has appeared.¹⁵

Experimental and Computational Section

Synthesis and Electronic Spectra. Pt[P(C₆H₅)₃]₂(O₂) was prepared by a published procedure.¹⁰ Electronic spectra for degassed methanol solutions under nitrogen were recorded from 700 to 210 nm using a Cary 14 instrument.

Initial Parameters. Calculations were made on the conformations of C_{2v} symmetry shown below (the molecular plane is *xy*). Bond



parameters used were Pt-O = 2.006 Å, Pt-P = 2.233 Å, O-O = 1.505 Å, and P-Pt-P = 101.23° for Pt(PH₃)₂(O₂), Pt-C = 2.11 Å, Pt-P = 2.27 Å, C-C = 1.43 Å, C-H = 1.08 Å, P-Pt-P = 111.6°, and H-C-H = 116° for Pt(PH₃)₂(C₂H₄), and P-H = 1.415 Å and H-P-H = 93.45° for both molecules. These were derived from the known structures of Pt(PPh₃)₂(O₂),¹¹ Pt(PPh₃)₂(C₂H₄),¹⁴ PH₃,¹⁶ and (for the C-H distance and H-C-H angle) (CH₂)₂O.¹⁷ A value $\alpha/2 = 28^\circ$ for the CC-CH₂ dihedral angle in Pt(PH₃)₂(C₂H₄) was obtained from a least-squares plot of $\alpha/2$ vs. C-C distance for eight alkene complexes for which this angle has been measured. Coordinates in