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Novel Hydroxo- and Hydrido-Bridged Trinuclear Ruthenium-Iron Derivatives. X-ray Structure of FeRu$_2$(μ-OH)$_2$(CO)$_8$(PPh$_3$)$_2$

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Reaction of the trinuclear complexes FeRu$_2$(μ-Cl)$_2$(CO)$_8$L$_2$ (**1**) [L = PPh$_3$ (**a**), PMe$_3$ (**b**), AsPh$_3$ (**c**)] with aqueous sodium carbonate in acetone leads to the substitution of chloro bridges to afford the heteronuclear derivatives FeRu$_2$(μ-OH)$_2$nCO)$_8$L$_2$ (**2**) containing hydroxo bridging groups, whereas potassium iodide with **1a** leads to the cleavage of the Fe–Ru bonds and formation of the binuclear compound Ru$_2$I$_2$(CO)$_4$(PPh$_3$)$_2$ (**4**). A similar reaction of **1a** with aqueous Na$_2$CO$_3$, but in 2-propanol, gives the bis(μ-hydroxo) complex **2a** and a mixed hydrido–hydroxo bridged complex: FeRu$_2$(μ-H)(μ-OH)(CO)$_8$(PPh$_3$)$_2$ (**3**), for which the ^{1}H NMR shows coupling of the μ-H proton (δ −10.55) with two equivalent phosphorus nuclei. The complex FeRu$_2$(μ-OH)$_2$(CO)$_8$(PPh$_3$)$_2$ (**2a**) crystallized in space group $P2_1/n$ with cell dimensions a = 13.851 (8) Å, b = 17.852 (6) Å, c = 17.510 (9) Å, β = 95.21 (5)°, and Z = 4. Refinement based on 5678 independent reflections converged at R_w = 0.035. The trimetallic chain Ru–Fe–Ru shows equivalent Fe–Ru bonds at the position trans to each phosphorus–ruthenium bond [Fe–Ru(1) = 2.806 (1) Å and Fe–Ru(2) = 2.805 (1) Å with a Ru(1)–Fe–Ru(2) angle of 65.41 (1)°]. The hydroxo groups, which establish equivalent Ru–O bond lengths (average 2.12 Å), maintain the ruthenium atoms at a distance of 3.032 (1) Å, which is short for nonbonding ruthenium atoms.

Introduction

Metal carbonyl clusters have been shown to be efficient precursors, in basic media, for promoting the catalytic water gas shift reaction.[2-4] In the absence of other reactive sites this reaction likely proceeds via the nucleophilic attack of the hydroxide anion on a carbonyl ligand. Cleavage of the metal–metal bonds of the cluster precursor may also occur.[2-4]

We have shown recently that RuCl$_2$(PR$_3$)(arene) complexes could be partially dehalogenated to afford the heterotrinuclear derivatives FeRu$_2$(Cl)$_2$(CO)$_8$(PR$_3$)$_2$ (**1**), which contain bridging chloro groups.[5] We now report that complexes **1**, in basic media under conditions similar to those of the water gas shift reaction, may lead, without cleavage of the Fe–Ru bonds, to the formation of new heterotrinuclear complexes containing hydroxo bridging groups, FeRu$_2$(μ-OH)$_2$(CO)$_8$(PR$_3$)$_2$ (**2**), or containing mixed hydrido and hydroxo bridging groups, FeRu$_2$(μ-H)(μ-OH)(CO)$_8$(PPh$_3$)$_2$ (**3**), according to the nature of the solvent. These complexes of type **2** or **3** are actually the first examples of hydroxo-bridged heteropolymetallic complexes.[6] The X-ray structure of FeRu$_2$(μ-OH)$_2$(CO)$_8$(PPh$_3$)$_2$ (**2a**) shows that the hydroxo groups establish two bridges between the ruthenium atoms of the Ru–Fe–Ru bent chain.

Experimental Section

Syntheses. Derivatives FeRu$_2$(μ-OH)$_2$(CO)$_8$L$_2$ (2a-c). The derivatives **1a–c** were synthesized from RuCl$_2$(L)(arene) according to the general procedure.[5] To a solution of 500 mg of derivatives **1** in 40 mL of acetone was added 3 mL of an aqueous solution of Na$_2$CO$_3$ (0.5 M). The mixture was refluxed under a nitrogen atmosphere and the transformation was followed by using thin-layer chromatography. The acetone was then removed under vacuum, and the products were extracted with dichloromethane. The silica gel thick-layer chromatography (eluent 1:5 ether–hexane) allowed the isolation of an orange, air-stable compound **2**, which was crystallized in a hexane–dichloromethane mixture.

2a (L = PPh$_3$): reflux for 8 h; 65% yield; mp 180–185 °C dec; IR (Nujol) ν_{OH} 3625, 3575 cm^{-1}, ν_{CO} 2055 (s), 2020 (s), 1980 (s), 1963 (vs), 1950 (s), 1940 (s), 1925 (s), 1908 (s) cm^{-1}. Anal. Calcd for C$_{44}$H$_{32}$O$_{10}$P$_2$FeRu$_2$: C, 50.67; H, 3.07; P. 5.95; Fe, 5.38; Ru, 19.42. Found: C, 50.24; H, 3.10; P, 5.70; Fe, 5.37; Ru, 19.11.

2b (L = PMe$_3$): reflux for 8 h; 55% yield; mp 167–169 °C; IR (Nujol) ν_{OH} 3640, 3625 cm^{-1}, ν_{CO} 2043 (s), 2020 (s), 1975 (sh), 1955 (vs), 1903 (s), 1895 (s), 1878 (s), 1867 (s) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.45 (d, $^2J_{\mathrm{P-H}}$ = 10.7 Hz, PMe$_3$), −2.16 (s, μ-OH); mass spectrum m/e (C$_{14}$H$_{20}$O$_{10}$P$_2$FeRu$_2$) 669.798 (calcd 669.796), (M − CO) 641, (M − 2CO) 613, (M − 3CO) 585, (M − 4CO) 557, (M − 5CO) 529, (M − 6CO) 501. Anal. Calcd for C$_{14}$H$_{20}$O$_{10}$P$_2$FeRu$_2$: C, 25.07; H, 2.98. Found: C, 24.85; H, 2.90.

2c (L = AsPh$_3$): reflux for 1 h; 95% yield; mp 165–170 °C dec; IR (Nujol) ν_{OH} 3620, 3570 cm^{-1}, ν_{CO} 2050 (s), 2010 (vs), 1980 (sh), 1968 (vs), 1948 (sh), 1940 (vs), 1915 (sh) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.23 (m, C$_6$H$_5$), −1.78 (s, μ-OH). Anal. Calcd for C$_{44}$H$_{32}$O$_{10}$As$_2$FeRu$_2$: C, 46.80; H, 2.83; Fe, 4.96. Found: C, 46.92; H, 3.07; Fe, 4.38.

Derivatives FeRu$_2$(μ-H)(μ-OH)(CO)$_8$(PPh$_3$)$_2$ (3). In a Schlenk tube, under a nitrogen atmosphere, 10 mL of an aqueous solution of Na$_2$CO$_3$ (0.5 M) was added to a solution of 0.5 g **1a** in 100 mL of 2-propanol. The mixture was refluxed for 24 h. After the evaporation of the 2-propanol followed by the extraction with dichloromethane, the products were chromatographed on silica gel thick layers. The red compound **3** (20 %) and the orange derivative **2a** (15%) were successively eluted (hexane–ether, 5:1), isolated, and crystallized in dichloromethane–hexane.

3: mp 170–175 °C dec; IR (Nujol) ν_{OH} 3558 cm^{-1}, ν_{CO} 2058 (s), 2022 (s), 1990 (s), 1970 (vs), 1960 (sh), 1935 (sh), 1930 (s) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.25 (m, C$_6$H$_5$), −1.75 (s, μ-OH), −10.55 (t, $^2J_{\mathrm{P-H}}$ = 4.2 Hz, μ-H). Anal. Calcd for C$_{44}$H$_{32}$O$_9$P$_2$FeRu$_2$:C, 51.56; H, 3.12. Found: C, 50.45; H, 3.54.

Derivative Ru$_2$I$_2$(CO)$_4$(PPh$_3$)$_2$ (4). A solution of 100 mg of compound **1a** and of an excess (240 mg) of potassium iodide in 20 mL of dimethoxyethane was refluxed for 1.5 h under a nitrogen atmosphere. The solution was then concentrated and chromatographed on a silica gel column (eluent hexane–ether). The yellow derivative **4** was then isolated and crystallized in a dichloromethane–ether mixture: 95% yield; mp 196–199 °C; IR (Nujol) 2026 (vs), 1986 (s), 1956 (vs), 1945 (w) cm^{-1}. Anal. Calcd for C$_{40}$H$_{30}$I$_2$O$_4$P$_2$Ru$_2$: C, 43.95; H, 2.74; I, 23.25; Ru, 18.49. Found: C, 43.37; H, 2.79; I, 21.12; Ru, 18.44.

Collection and Reduction of X-ray Data. Crystals of the title compound, FeRu$_2$(μ-OH)$_2$(CO)$_8$(PPh$_3$)$_2$ (**2a**), suitable for X-ray analysis were obtained by recrystallization from a mixture of hexane–dichloromethane. Preliminary photographic data showed that the crystal belonged to the monoclinic space group $P2_1/n$. Accurate cell parameters were obtained by a least-squares analysis of 25 carefully centered diffractometer reflections from diverse regions of reciprocal space. Table I gives the pertinent crystal data and all the details of

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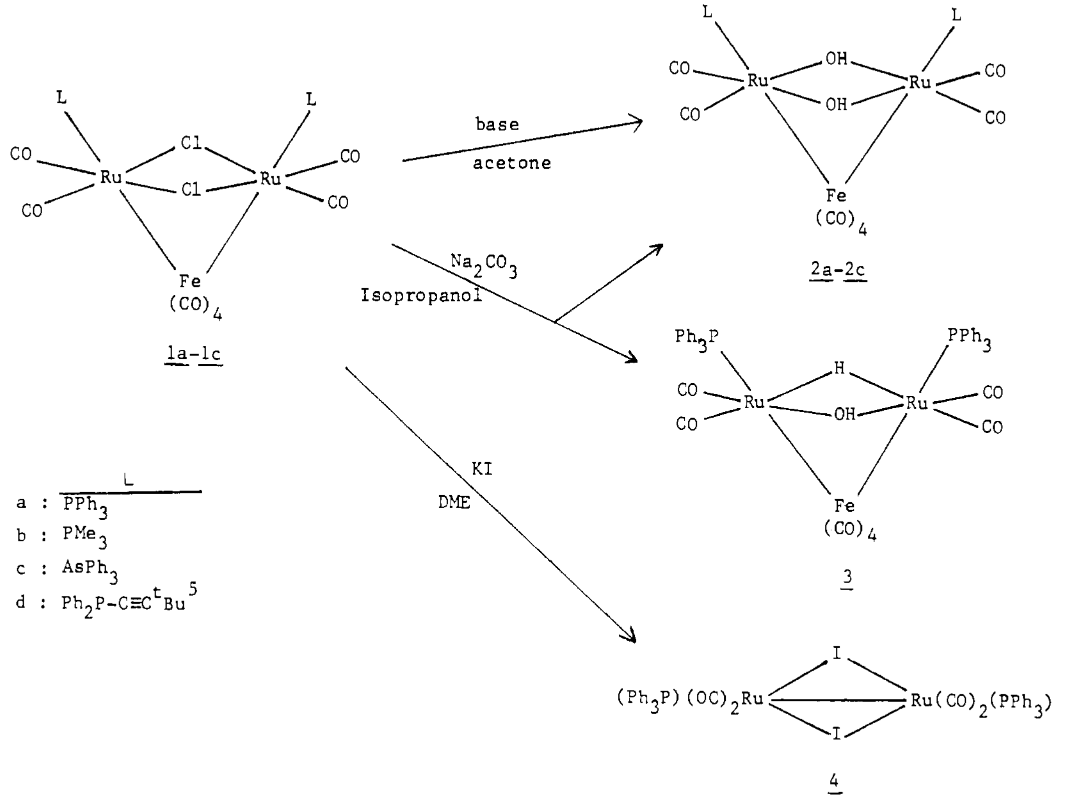
0020-1669/83/1322-0029$01.50/0

Scheme I



data collection. Intensity data were collected by using the $\omega/2\theta$ method on a Nonius CAD-4 automated diffractometer. All 5678 independent reflections measured having $I > 3\sigma_I$ were used in the structure solution and refinement. The data were corrected for Lorentz polarization and absorption effects. The three standard reflections monitored every hour of exposure did not show any significant changes in intensity throughout the course of data collection.

Solution and Refinement of the Structure. All calculations were performed on a PDP 11/60 computer with the SDP program package.[7] Analytical scattering factors for neutral atoms were used along with both real, $\Delta f'$, and imaginary, $\Delta f''$, correction factors for anomalous dispersion. The function minimized during least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where the weighting scheme was derived from counting statistics as $1/w = {}^1/_4(\sigma_I^2/I + p^2I)$ and the value of p was taken as 0.05.

Most atoms were found by using the Multan program in the most probable set. Refinement of the scale factor and positional and isotropic thermal parameters of these atoms led us to calculate a three-dimensional electron density difference map revealing the position of all remaining non-hydrogen atoms. Anisotropic refinement of all the atoms was performed before locating hydrogen atoms with the assumption of idealized geometry and d(C–H) = 0.95 Å. With isotropic thermal parameters fixed at 5.0 Å^2, these hydrogen atoms were refined such that their positional shifts were coupled to those of the carbon atom to which they were attached. Full-matrix least-squares refinement proceeded to convergence with $R = 0.030$, $R_w = 0.035$, and GOF = 0.994. A final difference Fourier synthesis revealed no significant peak, and the largest parameter shift was 0.4 times its esd in the last cycle of refinement. Table II lists the atomic parameters with their esd's. Bond distances and angles are given in Tables III and IV, respectively.

Results and Discussion

Synthetic Aspects. The readily available trinuclear derivatives $FeRu_2(\mu\text{-}Cl)_2(CO)_8(PR_3)_2$ (**1**), containing chloro groups bridging the ruthenium atoms of the bent Ru–Fe–Ru chain, can be easily transformed in a basic medium. The derivatives **1a**,[5] **1b**,[5] and **1c**[8] were refluxed in an acetone solution containing an aqueous solution of Na_2CO_3. They were progressively transformed, as indicated by thin-layer chromatography, into a new orange, air-stable compound, which was isolated by using silica gel chromatography. The derivatives **2a** (65%),[9] **2b** (55%), and **2c** (95%) were respectively obtained (Scheme I) and identified as shown in the scheme on the basis of analysis and of their infrared spectra, which showed terminal carbonyl absorption bands and two absorption bands corresponding to the hydroxo groups (Nujol): (**2a**) 3625, 3575 cm^{-1}; (**2b**) 3640, 3625 cm^{-1}; (**3c**) 3620, 3570 cm^{-1}.

Table I. Relevant Crystallographic Data

compound	$Ru_2Fe(\mu\text{-}OH)_2(CO)_8(PPh_3)_2$
formula	$Ru_2FeP_2O_{10}C_{44}H_{32}$
fw	1040.67
a	13.851 (8) Å
b	17.852 (6) Å
c	17.510 (9) Å
β	95.21 (5)°
V	4156.4 Å^3
Z	4
F(000)	2080
density (calcd)	1.66 g cm^{-3}
abs coeff	11.92 cm^{-1}
space group	$P2_1/n$
cryst size	(0.15 × 0.18 × 0.20) mm
radiation	Mo Kα
monochromator	graphite
cryst-counter dist	173 mm
scan angle	(1.00 + 0.35 tan θ)°
max scan time	60 s
receiving aperture	(2.10 + 0.40 tan θ) mm
no. of data collected	6813
no. of obsd data	5678
no. of refined variables	533
$R = \Sigma\|\Delta F\|/\Sigma\|F_o\|$	0.030
$R_w = (\Sigma w\|\Delta F\|^2/\Sigma w\|F_o\|^2)^{1/2}$	0.035

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Table II. Positional Parameters and Their Estimated Standard Deviations

atom	x	y	z	atom	x	y	z
Ru(1)	0.10279 (2)	0.29504 (2)	0.62647 (1)	C(31)	−0.2319 (3)	0.4298 (3)	0.9157 (2)
Ru(2)	0.07185 (2)	0.45297 (2)	0.68347 (1)	C(32)	−0.2108 (3)	0.4521 (2)	0.8435 (2)
Fe	0.24910 (3)	0.40743 (3)	0.62232 (3)	C(33)	−0.1986 (2)	0.4840 (2)	0.6721 (2)
				C(34)	−0.2173 (3)	0.4153 (2)	0.6375 (2)
P(1)	−0.02380 (6)	0.20278 (5)	0.63684 (5)	C(35)	−0.3069 (3)	0.4009 (2)	0.5943 (3)
P(2)	−0.08045 (6)	0.49485 (5)	0.73280 (5)	C(36)	−0.3792 (3)	0.4564 (3)	0.5836 (3)
O(1H)	0.0771 (2)	0.3452 (1)	0.7334 (1)	C(37)	−0.3609 (3)	0.5253 (3)	0.6181 (3)
O(1)	0.3533 (3)	0.5530 (2)	0.6379 (2)	C(38)	−0.2715 (3)	0.5396 (2)	0.6624 (2)
O(2H)	−0.0037 (2)	0.3817 (1)	0.5998 (1)	C(39)	−0.0700 (2)	0.5948 (2)	0.7567 (2)
O(2)	0.3007 (2)	0.3488 (2)	0.7783 (1)	C(40)	−0.0617 (3)	0.6201 (2)	0.8317 (2)
O(3)	0.4060 (2)	0.3258 (2)	0.5507 (2)	C(41)	−0.0419 (4)	0.6947 (2)	0.8492 (2)
O(4)	0.1254 (2)	0.4424 (2)	0.4787 (1)	C(42)	−0.0300 (3)	0.7452 (2)	0.7911 (3)
O(5)	0.1441 (2)	0.2489 (2)	0.4677 (2)	C(43)	−0.0396 (3)	0.7211 (2)	0.7166 (2)
O(6)	0.2649 (2)	0.1896 (2)	0.6886 (3)	C(44)	−0.0612 (3)	0.6472 (2)	0.6989 (2)
O(7)	0.1949 (2)	0.5274 (2)	0.8147 (2)	H(1)	0.0674 (0)	0.3247 (0)	0.7841 (0)
O(8)	0.0953 (2)	0.5893 (2)	0.5863 (2)	H(2)	−0.0639 (0)	0.3858 (0)	0.5637 (0)
C(1)	0.3116 (3)	0.4961 (2)	0.6332 (2)	H(3)	0.0962 (0)	0.1175 (0)	0.5421 (0)
C(2)	0.2773 (3)	0.3722 (2)	0.7186 (2)	H(4)	0.1399 (0)	−0.0107 (0)	0.5304 (0)
C(3)	0.3439 (3)	0.3563 (2)	0.5790 (2)	H(5)	0.0746 (0)	−0.0977 (0)	0.6100 (0)
C(4)	0.1726 (3)	0.4283 (2)	0.5358 (2)	H(6)	−0.0178 (0)	−0.0648 (0)	0.7066 (0)
C(5)	0.1273 (3)	0.2663 (2)	0.5276 (2)	H(7)	−0.0577 (0)	0.0665 (0)	0.7259 (0)
C(6)	0.2035 (3)	0.2289 (2)	0.6651 (2)	H(8)	−0.1947 (0)	0.1047 (0)	0.6029 (0)
C(7)	0.1486 (3)	0.5000 (2)	0.7637 (2)	H(9)	−0.3267 (0)	0.0962 (0)	0.5003 (0)
C(8)	0.0838 (3)	0.5383 (2)	0.6241 (2)	H(10)	−0.3348 (0)	0.1872 (0)	0.4029 (0)
C(9)	0.0161 (3)	0.1041 (2)	0.6351 (2)	H(11)	−0.2208 (0)	0.2844 (0)	0.4073 (0)
C(10)	0.0737 (3)	0.0807 (2)	0.5779 (2)	H(12)	−0.0883 (0)	0.2949 (0)	0.5049 (0)
C(11)	0.0961 (3)	0.0063 (2)	0.5692 (3)	H(13)	−0.2193 (0)	0.2510 (0)	0.6925 (0)
C(12)	0.0619 (3)	−0.0458 (2)	0.6172 (3)	H(14)	−0.2698 (0)	0.2703 (0)	0.9208 (0)
C(13)	0.0068 (4)	−0.0242 (2)	0.6753 (3)	H(15)	−0.1547 (0)	0.2475 (0)	0.9240 (0)
C(14)	−0.0179 (3)	0.0510 (2)	0.6841 (2)	H(16)	0.0044 (0)	0.2012 (0)	0.9152 (0)
C(15)	−0.1311 (3)	0.2011 (2)	0.5635 (2)	H(17)	0.0598 (0)	0.1805 (0)	0.7920 (0)
C(16)	−0.2009 (3)	0.1432 (2)	0.5610 (2)	H(18)	0.0321 (0)	0.4294 (0)	0.8631 (0)
C(17)	−0.2760 (3)	0.1380 (2)	0.5021 (2)	H(19)	−0.0044 (0)	0.3913 (0)	0.9879 (0)
C(18)	−0.2830 (3)	0.1902 (3)	0.4441 (2)	H(20)	−0.1712 (0)	0.3946 (0)	1.0232 (0)
C(19)	−0.2152 (4)	0.2479 (3)	0.4460 (2)	H(21)	−0.3017 (0)	0.4280 (0)	0.9273 (0)
C(20)	−0.1384 (3)	0.2533 (2)	0.5052 (2)	H(22)	−0.2644 (0)	0.4601 (0)	0.0029 (0)
C(21)	−0.0751 (2)	0.2126 (2)	0.7291 (2)	H(23)	−0.1658 (0)	0.3745 (0)	0.6460 (0)
C(22)	−0.1715 (3)	0.2388 (2)	0.7370 (2)	H(24)	−0.3165 (0)	0.3540 (0)	0.5668 (0)
C(23)	−0.2013 (3)	0.2526 (2)	0.8100 (2)	H(25)	−0.4487 (0)	0.4448 (0)	0.5568 (0)
C(24)	−0.1363 (3)	0.2386 (2)	0.8740 (2)	H(26)	−0.4115 (0)	0.5650 (0)	0.6137 (0)
C(25)	−0.0405 (3)	0.2124 (2)	0.8670 (2)	H(27)	−0.2577 (0)	0.5883 (0)	0.6865 (0)
C(26)	−0.0088 (3)	0.1995 (2)	0.7953 (2)	H(28)	−0.0661 (0)	0.5843 (0)	0.8754 (0)
C(27)	−0.1113 (3)	0.4544 (2)	0.8244 (2)	H(29)	−0.0380 (0)	0.7131 (0)	0.9045 (0)
C(28)	−0.0352 (3)	0.4313 (2)	0.8783 (2)	H(30)	−0.0160 (0)	0.7957 (0)	0.8040 (0)
C(29)	−0.0572 (3)	0.4088 (3)	0.9512 (2)	H(31)	−0.0335 (0)	0.7604 (0)	0.6765 (0)
C(30)	−0.1563 (3)	0.4095 (3)	0.9701 (2)	H(32)	−0.0712 (0)	0.6312 (0)	0.6440 (0)

Table III. Selected Bond Distances and Esd's (Å)

Ru(1)-Ru(2)	3.032 (1)	Ru(2)-Fe	2.805 (1)
Ru(1)-Fe	2.806 (1)	Ru(2)-P(2)	2.400 (1)
Ru(1)-P(1)	2.379 (1)	Ru(2)-O(1H)	2.112 (2)
Ru(1)-O(1H)	2.130 (2)	Ru(2)-O(2H)	2.124 (2)
Ru(1)-O(2H)	2.124 (2)	Ru(2)-C(7)	1.862 (4)
Ru(1)-C(5)	1.862 (4)	Ru(2)-C(8)	1.859 (4)
Ru(1)-C(6)	1.869 (4)	O(1H)-O(2H)	2.569 (3)
Fe-C(1)	1.791 (5)	Fe-C(3)	1.784 (4)
Fe-C(2)	1.806 (4)	Fe-C(4)	1.788 (4)
P(1)-C(9)	1.841 (4)	P(2)-C(27)	1.840 (4)
P(1)-C(15)	1.835 (4)	P(2)-C(33)	1.831 (3)
P(1)-C(21)	1.819 (3)	P(2)-C(39)	1.836 (4)
C(1)-O(1)	1.157 (4)	C(2)-O(2)	1.143 (4)
C(3)-O(3)	1.142 (5)	C(4)-O(4)	1.160 (5)
C(5)-O(5)	1.137 (5)	C(6)-O(6)	1.129 (5)
C(7)-O(7)	1.149 (4)	C(8)-O(8)	1.144 (4)

Table IV. Interbond Angles and Standard Deviations (Deg) within the Organometallic Moiety

Ru(2)-Ru(1)-Fe	57.28 (1)	Ru(1)-Ru(2)-Fe	57.31 (1)
Ru(2)-Ru(1)-P(1)	119.99 (2)	Ru(1)-Ru(2)-P(2)	123.61 (3)
Ru(2)-Ru(1)-O(1H)	44.14 (6)	Ru(1)-Ru(2)-O(1H)	44.63 (6)
Ru(2)-Ru(1)-O(2H)	44.47 (6)	Ru(1)-Ru(2)-O(2H)	44.48 (6)
Fe-Ru(1)-P(1)	176.66 (3)	Fe-Ru(2)-O(1H)	84.05 (6)
Fe-Ru(1)-O(1H)	83.70 (6)	Fe-Ru(2)-O(2H)	85.84 (6)
Fe-Ru(1)-O(2H)	85.82 (6)	Fe-Ru(2)-P(2)	178.24 (3)
P(1)-Ru(1)-O(1H)	92.96 (7)	P(2)-Ru(2)-O(1H)	97.60 (7)
P(1)-Ru(1)-O(2H)	93.16 (7)	P(2)-Ru(2)-O(2H)	94.01 (6)
O(1H)-Ru(1)-O(2H)	74.27 (9)	O(1H)-Ru(2)-O(2H)	74.65 (9)
Ru(1)-Fe-Ru(2)	65.41 (1)		
C(5)-Ru(1)-C(6)	88.9 (2)	C(7)-Ru(2)-C(8)	89.0 (2)
C(1)-Fe-C(2)	98.8 (2)	C(2)-Fe-C(3)	97.0 (2)
C(1)-Fe-C(4)	97.5 (2)	C(3)-Fe-C(4)	96.8 (2)
Ru(1)-O(1H)-Ru(2)	91.23 (8)	Ru(1)-O(2H)-Ru(2)	91.05 (8)

In addition, in the mass spectrum of the volatile derivative **2b** were observed the molecular ion, *m/e* 669.798 (calcd 669.796), and the ions corresponding to the successive loss of six carbonyls. The ^{1}H NMR spectrum of compound **2b** showed one doublet at δ 1.45 ($CDCl_3$; $^{2}J_{P-H}$ = 10.7 Hz), indicating the equivalence of the PMe_3 groups. A high-field, broad singlet, observed at δ −2.16 (**2b**) or at δ −1.78 (**2c**), disappeared when D_2O was added to the $CDCl_3$ solution and was attributed to the protons of the hydroxo bridges. The structure of **2a** was confirmed by an X-ray diffraction determination.

The derivative **2a** was also obtained by treatment of **1a** with aqueous Na_2CO_3 in dimethoxyethane on reflux or with an excess of *n*-Bu_4NOH in acetone at room temperature. Under these conditions the rate of formation of **2a** was increased without any significant modification of the yield.

The transformation **1** → **2** actually corresponds to a simple nucleophilic substitution at the ruthenium atoms of the halo

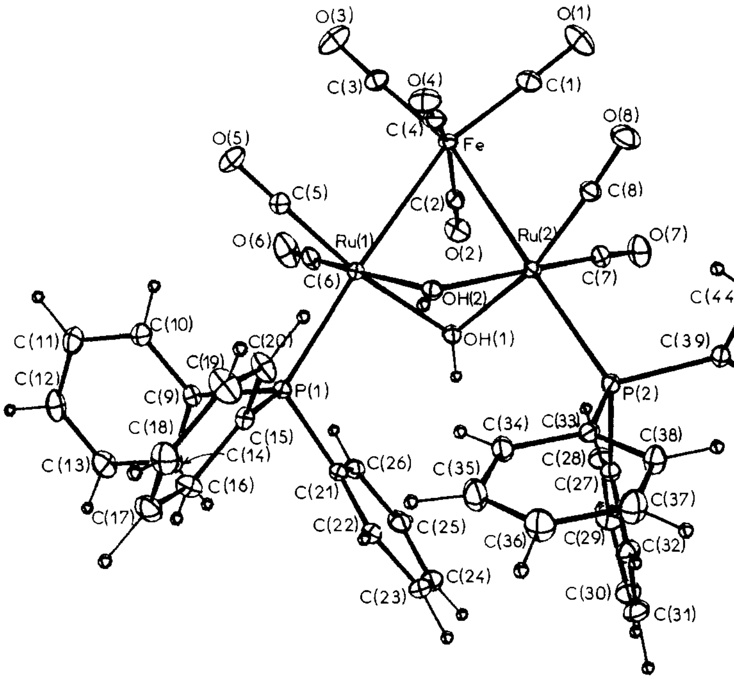

Figure 1. Molecular structure of $FeRu_2(\mu\text{-}OH)_2(CO)_8(PPh_3)_2$ (**2a**).

bridges by the hydroxo bridging groups. Under the same conditions, under acetone reflux, the reaction is faster and the yield is higher starting from **1c** (L = $AsPh_3$) than from **1a** (L = PPh_3) or **1b** (L = PMe_3). Since the cone angles for $AsPh_3$ and PPh_3 are similar,[10] more facile displacement of the chloride in **1c** may be related to a greater cis weakening of Ru–Cl bonds in the arsine complex. There is evidence for greater s-orbital participation in arsenic–metal bonds than in the phosphorus–metal bonds.[11]

The substitution of the chloro bridges by the hydroxide anion takes place without the cleavage of the Ru–Fe–Ru bent chain, whereas the attempted substitution of the chloride of compound **1a** by treatment with potassium iodide in dimethoxyethane led to the cleavage of the Fe–Ru bonds and to the formation of the binuclear derivative **4** (Scheme I) with 95% yield. The structure of **4** containing a Ru–Ru bond was established on the basis of elemental analysis and by the presence of four carbonyl absorption bands. The structure corresponds to that proposed for $Ru_2Cl_2(CO)_4(P\text{-}t\text{-}Bu_3)_2$ prepared recently by carbonylation of $RuCl_3$.[12]

The displacement of the $Fe(CO)_4$ group during the formation of **4** is probably due to the large size of the iodide anion as compared to that of the hydroxide anion, although the derivative $FeRu_2(\mu\text{-}I)_2(CO)_8[P(OMe)_3]_2$ has been obtained but by partial dehalogenation of the complex of $RuI_2[P(OMe)_3](arene)$ according to the general route.[5]

The reaction of complex **1a** with aqueous Na_2CO_3, but in 2-propanol instead of acetone, leads to the formation of a new type of heterometallic complex, besides the expected formation of **2a**. The thick-layer chromatography of the reaction products allowed the separation of derivatives **3** and **2a**, which were obtained in 20% and 15% yields, respectively. The structure of the red compound **3**, which contains mixed hydroxo and hydrido bridges (Scheme I), has been elucidated on the basis of the analytical data and of the presence in the infrared spectrum of terminal carbonyl absorption bands and of only one O–H absorption band at 3558 cm^{-1} (Nujol). In addition, the ^1H NMR spectrum ($CDCl_3$) indicated the presence of two significant signals: (i) one singlet at δ −1.71, which disappeared when D_2O was added to the $CDCl_3$ solution and corresponded to the hydroxo proton, and (ii) one triplet at δ −10.55, being due to the hydrido bridge and resulting from its coupling ($^2J_{PH}$ = 4.2 Hz) with two identical phosphorus nuclei of the PPh_3 groups coordinated to each ruthenium atom. It is likely that the structure of **3** resembles that of **2a** and that found for the homotrinuclear complex $Os_2(\mu\text{-}H)(\mu\text{-}OMe)(CO)_{10}$.[13]

The formation of the $FeRu_2(\mu\text{-}H)(\mu\text{-}OH)$ moiety in derivative **3** may result from the substitution of one chloro bridge of **1a** by a hydroxide ion and of the second chloro group by the isopropoxy group, followed by the β elimination of the alkoxide moiety as it often occurs for the formation of hydridoruthenium derivatives.[14,15]

Description and Discussion of the Molecular Structure of $FeRu_2(\mu\text{-}OH)_2(CO)_8(PPh_3)_2$ (2a). A perspective view of the molecular geometry is illustrated in Figure 1. The structure shows a Ru–Fe–Ru bent chain with hydroxo groups bridging the ruthenium atoms. It can be compared directly to the structure established for a derivative of type **1**: $FeRu_2(\mu\text{-}Cl)_2(CO)_8(Ph_2PC{\equiv}C\text{-}t\text{-}Bu)_2$ (**1d**),[5] which has a similar Ru–Fe–Ru arrangement but has chloro groups bridging the ruthenium atoms. Both structures show phosphorus groups in a position trans with respect to the Fe–Ru bonds.

The main difference between the aggregates $FeRu_2(\mu\text{-}Cl)_2P_2$ of **1d** and $FeRu_2(\mu\text{-}OH)_2P_2$ of **2a** can be observed in Figure 2. The trimetallic Ru(1)–Fe–Ru(2) chain in **2a** has equivalent Fe–Ru bond lengths [Fe–Ru(1) = 2.806 (1) Å and Fe–Ru(2) = 2.805 (1) Å], which are similar of those of **1d**. However the Ru(1)–Fe–Ru(2) angle is 65.41 (1)° in **2a**, which is significantly smaller than the corresponding angle in **1d** [69.07(4)°]. Consequently the distance between the ruthenium atoms is much shorter in **2a** than in **1d** [Ru(1)···Ru(2) = 3.032 (1) Å in **2a** and 3.185 (2) Å in **1d**]. The Ru···Ru distance in **2a** can be compared to the Ru···Ru distances in $Ru_3(\mu\text{-}NO)_2(CO)_{10}$:[16] it is longer than the Ru···Ru bond lengths

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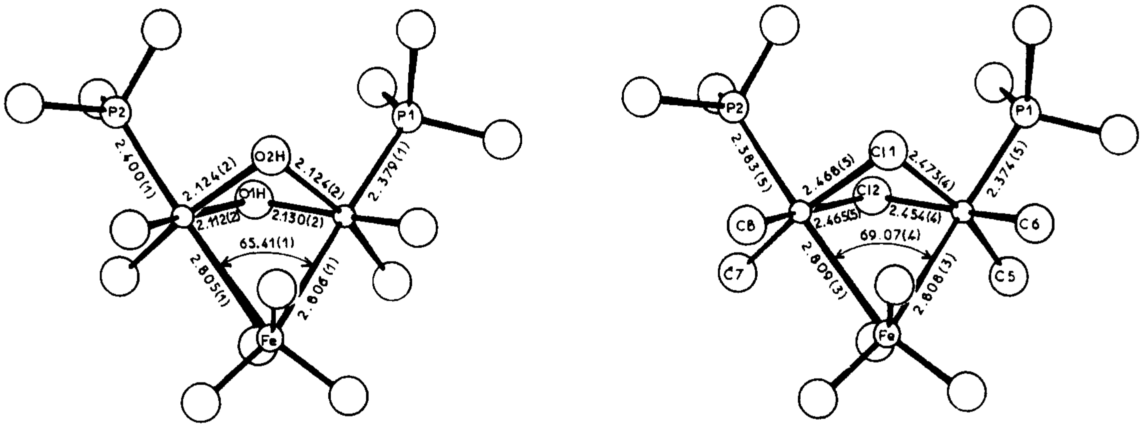

Figure 2. Heavy-atom skeleton of $FeRu_2(\mu\text{-}X)_2(CO)_8L_2$: comparison of **2a** (X = OH; L = PPh_3) and **1d**[5] (X = Cl; L = $Ph_2PC{\equiv}C\text{-}t\text{-}Bu$).

(average 2.87 Å) but significantly shorter than the nonbonded Ru···Ru distance (3.15 Å). In addition the Ru···Ru distance in **2a** is shorter or similar to Ru–Ru distances with which a bonding interaction has been associated such as 3.098 (1) Å in $FeRu_3(CO)_{13}(\mu\text{-}PPh_2)_2$,[17] 3.139 (1) and 3.05 (1) Å in $Ru_3(CO)_6(\mu\text{-}C_2\text{-}t\text{-}Bu)(\mu\text{-}\eta^2\text{-}C_2\text{-}t\text{-}Bu)(PPh_2)(Ph_2PC_2\text{-}t\text{-}Bu)$,[18] and 3.157 (1) or 3.025 (1) Å in $Ru_4(CO)_{13}(\mu\text{-}PPh_2)(\mu\text{-}\eta^2\text{-}C{\equiv}C\text{-}t\text{-}Bu)$;[19] therefore, although the Ru atoms are formally nonbonded in **2a**, the short Ru···Ru distance of 3.032 (1) Å is indicative of a bonding interaction.

In Ru–O bond lengths of the bridging hydroxo groups are essentially identical [Ru(1)–O(1H) = 2.130 (2) Å, Ru(1)–O(2H) = 2.124 (2) Å, Ru(2)–O(1H) = 2.112 (2) Å, Ru(2)–O(2H) = 2.124 (2) Å], and the Ru(1)–O–Ru(2) angles [91.23 (8)° for O(1H) and 91.05 (8)° for O(2H)] do not differ significantly. These angles are much larger than Ru(1)–Cl–Ru(2) in complex **1d** but are in the same range as the ru-(OH)–Ru angles of 89.0 (2) and 89.5 (2)° in $[Ru_2(\mu\text{-}OH)_3(PMe_3)_6]BF_4$,[20] in which the Ru···Ru distance of 3.004 (1) Å and the Ru–O bond lengths of 2.142 (2) and 2.134 (3) Å are also similar to those of **2a**. It thus appears that the nature of the bridge between the ruthenium atoms has an important influence on both the Ru–X bond length and the Ru–X–Ru angle. This influence may be essentially a reflection of the size of the bridging atom X. Consequently, the Ru···Ru distance should be in the same range for a given bridging group as is shown by the comparison of **2a** with $[Ru_2(\mu\text{-}OH)_2(PMe_3)_6]BF_4$.[20] Moreover, since the Fe–Ru distances appear to be insensitive to the nature of the bridging groups, the Ru···Ru distance determines the Ru–Fe–Ru angle (Figure 2).

In compound **2a** the Ru–P bond lengths P(1)–Ru(1) = 2.379 (1) Å and P(2)–Ru(2) = 2.400 (1) Å are similar to the corresponding Ru–P distances in **1d**, where the acetylenic phosphines are also trans to the Fe–Ru bonds. It thus appears that the nature of both the phosphorus groups and the bridging groups does not influence significantly these P–Ru bonds.

The coordination around the three metal atoms is such that derivative **2a** has approximate C_{2v} symmetry and each metal atom has a distorted octahedral stereochemistry; thus, the Fe–Ru(1)–P(1) and Fe–Ru(2)–P(2) angles 176.66 (3) and 178.24 (3)°, respectively, are slightly different from 180°. The P–Ru bonds are almost perpendicular to the Ru–O and Ru–CO bonds [P(1)–Ru(1)–O(1H) = 92.96 (7)°; P(1)–Ru(1)–O(2H) = 93.16 (7)°]. The two carbonyls bonded to each ruthenium atom are located at the position trans to the hydroxo bridging groups, but the phosphorus atoms are slightly out of the Ru(1)FeRu(2) plane.

The comparison between the structural data for the moieties $FeRu_2(\mu\text{-}Cl)_2P_2$ in **1d** and $FeRu_2(\mu\text{-}OH)_2P_2$ in **2a** shows that the formal substitution of the bridging chloro groups by the hydroxo groups does not modify significantly the arrangement of the molecule but leads to an important shortening of the Ru···Ru distance and, consequently, of the Ru(1)–Fe–Ru(2) angle. The replacement of the chloro bridges by the hydroxo groups affords a more compact $FeRu_2(\mu\text{-}X)_2$ aggregate, which may account for the higher thermal stability of compounds **2** as compared to precursors **1**.

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Registry No. 1a, 77187-25-8; **1b**, 77187-24-7; **1c**, 83268-99-9; **2a**, 78724-99-9; **2b**, 78725-00-5; **2c**, 83269-00-5; **3**, 83269-01-6; **4**, 78725-01-6; Ru, 7440-18-8; Fe, 7439-89-6.

Supplementary Material Available: Listings of observed and calculated structure factor amplitudes, thermal parameters, general temperature factors (Tables S_1 and S_2), and root-mean-square displacements of thermal vibrations (Table S_3) (35 pages). Ordering information is given on any current masthead page.

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