Journal of Organometallic Chemistry, 213 (1981) 139—150
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

SYNTHESIS AND STRUCTURE OF $FeRu_3(CO)_{13}(\mu\text{-}PPh_2)_2$; A "64-ELECTRON" CLUSTER COMPLEX WITH A PLANAR TRIANGULATED RHOMBOIDAL ARRAY OF METAL ATOMS *

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(Received October 20th, 1980)

Summary

The species $FeRu_3(CO)_{13}(\mu\text{-}PPh_2)_2$, synthesized from $Ru_3(CO)_{12}$ and $Fe(CO)_4(Ph_2P—PPh_2)$, has been characterized both spectroscopically and via a single-crystal X-ray structural analysis. This complex crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ [No. 2, C_i^1] with a = 10.066(3), b = 12.899(3), c = 17.003(4) Å, α = 111.89(2), β = 91.02(2), γ = 102.00(2)°, V = 1992.7(9) Å^3, Z = 2, ρ(obsd) = 1.79(2) g cm^{-3} and ρ(calcd) = 1.82 cm^{-3}. Diffraction data were collected with a Syntex P2_1 automated four-circle diffractometer and the structure was refined to R_F = 6.0% and R_{wF} = 3.6% for all 5213 reflections (R_F = 3.8%, R_{wF} = 3.6% for those 4140 reflections with $|F_0| > 3\sigma(|F_0|)$.

The metal atoms define a planar triangulated rhombus, with atoms Ru(1) and Ru(2) at the bridgehead, and Fe(1) and Ru(3) at the acute apices. Fe(1) is linked to four terminal carbonyl ligands and is associated with the heteronuclear bonds Fe(1)—Ru(1) = 2.861(1) Å and Fe(1)—Ru(2) = 2.868(1) Å. The ruthenium atoms are each bonded to three terminal carbonyl groups. The ruthenium—ruthenium distances are Ru(1)—Ru(2) = 3.098(1), Ru(1)—Ru(3) = 3.147(1), and Ru(2)—Ru(3) = 3.171(1) Å. The structure is completed by Ph_2P bridges across the Ru(1)—Ru(3) and Ru(2)—Ru(3) vectors (<Ru(1)—P(1)—Ru(3) = 84.89(5)° and <Ru(2)—P(2)—Ru(3) = 85.56(6)°).

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* Dedicated to the memory of the late Professor Paulo Chini.

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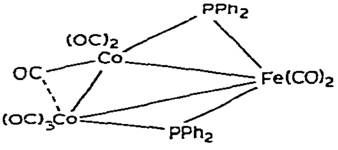
Introduction

The reaction of $Fe(CO)_4(Ph_2P{-}PPh_2)$ [1] with $Co_2(CO)_8$ has previously been shown to yield the heteronuclear metal cluster complex $FeCo_2(\mu_2\text{-}CO)(CO)_7(\mu\text{-}PPh_2)_2$ [2], which has structure I. In the course of extending our investigations of $Fe(CO)_4(Ph_2P{-}PPh_2)$, we found that it reacted with $Ru_3(CO)_{12}$ to form, inter alia, the species $FeRu_3(CO)_{13}(\mu\text{-}PPh_2)_2$. The synthesis and crystallographic characterization of this unusual 64-electron cluster are reported below.



(I)

Experimental

A. Synthesis of $FeRu_3(CO)_{13}(\mu\text{-}PPh_2)_2$

To 180 ml of cyclohexane under argon was added 0.64 g (1.0 mmol) of $Ru_3(CO)_{12}$ and 1.70 g (3.3 mmol) of $Fe(CO)_4(PPh_2{-}PPh_2)$. The mixture was refluxed for 16 h, producing a dark red solution. The cyclohexane was removed under vacuum, leaving a red, semi-crystalline product. This material was chromatographed over silica gel under argon with n-hexane and toluene. The following compounds were eluted in order and identified by mass spectra and infrared spectra of the carbonyl region: small yellow band, a mixture of $Ru(CO)_4(PPh_2{-}PPh_2)$, $FeRu(CO)_6(\mu\text{-}PPh_2)_2$, and $Ru_2(CO)_6(\mu_2\text{-}PPh_2)_2$; a small yellow-brown band, $Fe(CO)_4(PPh_2{-}PPh_2)$; a large magenta band, $FeRu_3(CO)_{13}(\mu_2\text{-}PPh_2)_2$. The last band was vacuum stripped free of solvent to give 0.9 g magenta powder. Dark red crystals of the compound were grown from n-hexane/diethyl ether mixed solvent at 0°C. The infrared spectrum of this complex is shown in Fig. 1. (Cyclohexane: ν(CO) 2074s, 2045vs, 2018s, 2009s, 1995s, 1988s, 1961w, 1949m cm^{-1})

B. Collection of the X-ray diffraction data

The selected crystal (a dark-red plate 0.23 × 0.20 × 0.09 mm^3) was sealed into a 0.2 mm diameter thin-walled glass capillary, which was then set into an aluminium pin on a eucentric goniometer and mounted on a Syntex $P2_1$ automated four-circle diffractometer. Crystal alignment, determination of the orientation matrix and accurate cell parameters, and data collection were all carried out as described previously [3]. Details are given in Table 1.

Data were corrected for the effects of absorption and for Lorentz and polarization effects. Redundant data were averaged ($R(I)$ = 1.62% for 357 averaged pairs) and were converted to unscaled $|F_0|$ values. Any reflection with $I < 0$ was assigned a value of $|F_0| = 0$.

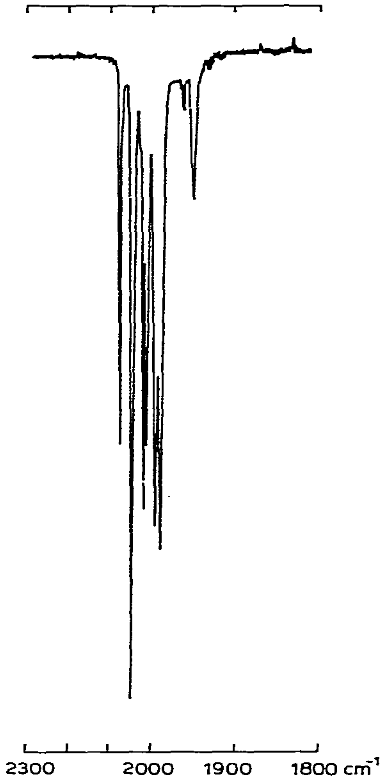


Fig. 1. Infrared spectrum (carbonyl stretching region) for $FeRu_3(CO)_{13}(\mu\text{-}PPh_2)_2$.

TABLE 1

CRYSTALLOGRAPHIC DATA FOR THE X-RAY DIFFRACTION STUDY OF $FeRu_3(CO)_{13}(\mu\text{-}PPh_2)_2$

(A) Crystal parameters	
Temperature (°C)	24
Crystal system	triclinic
Space group	$P\bar{1}$ [C_i^1; No. 2]
a (Å)	10.066(3)
b (Å)	12.899(3)
c (Å)	17.003(4)
α (°)	111.89(2)
β (°)	91.02(2)
γ (°)	102.00(2)
V (Å^3)	1992.7(9)
Z	2
Mol.wt.	1093.36
ρ(obsd) (g/cm^3)	1.79(2)
ρ(calcd) (g/cm^3)	1.82
(B) Measurement of intensity data	
Diffractometer	Syntex $P2_1$
Radiation	Mo-$\overline{K_\alpha}$ ($\bar{\lambda}$ = 0.71073 Å)
Monochromator	Graphite, in equatorial mode
Reflections measured	$+h, \pm k, \pm l$
2θ range (°)	3°—45
Scan type	coupled θ(crystal)—2θ(counter)
Scan width (°)	symmetrical, [2.0 + $\Delta(\alpha_2 - \alpha_1)$]
Scan speed (deg/min)	3.0
No. reflections measured	5747
No. independent data	5213
Absorption coefficient (cm^{-1})	16.0

C. Solution and refinement of the structure

All subsequent calculations were performed using the CDC-6600-Cyber 173 computer at the Computer Center at SUNY-Buffalo. Programs used during the structural analysis were the following: LSHF (full-matrix least-squares refinement and structure factor calculations, by B.G. DeBoer), JIMDAP (Fourier synthesis, derived from A. Zalkin's FORDAP, by J.A. Ibers), STAN1 (distances and angles, with e.s.d.'s, by B.G. DeBoer), PLOD (least-squares planes, by B.G. DeBoer) and ORTEP-II (thermal ellipsoid plotting program, by C.K. Johnson).

The analytical scattering factors for neutral Ru, Fe, P, O, C and H [4a] were corrected for both the real, $\Delta f'$, and imaginary, $\Delta f''$, components of anomalous dispersion [4b].

The function minimized during least-squares refinement was $\Sigma w(|F_0| - |F_c|)^2$, where the weighting scheme is that derived from counting statistics along with a term including an "ignorance factor" (p) set at a value of 0.03.

Diffraction data were converted to an approximately absolute scale by means of a Wilson Plot, which also provided the overall isotropic thermal parameter ($\bar{B}$ = 2.74 Å^2). Interpretation of a three-dimensional Patterson map led to location of the four metal atoms in a planar rhomboidal array. A series of difference-Fourier syntheses, each phased by an increasing number of atoms, led to the location of all non-hydrogen atoms and establishment of the molecular stoichiometry as $FeRu_3(CO)_{13}(\mu\text{-}PPh_2)_2$. Refinement of the positional and anisotropic thermal parameters for all 56 non-hydrogen atoms and with all 20 hydrogen atoms included in calculated positions with d(C—H) = 0.95 Å [5] led to convergence with R_F = 6.0%, R_{wF} = 3.6% and GOF = 1.146 for 5213 reflections and 505 variables. (Discrepancy indices for those 4140 reflections having $|F_0| > 3\sigma(|F_0|)$ were R_F = 3.8%, R_{wF} = 3.6% and GOF = 1.182).

TABLE 2

POSITIONAL PARAMETERS FOR $FeRu_3(CO)_{13}(\mu\text{-}PPh_2)_2$

Atom	*x/a*	*y/b*	*z/c*	B (Å^2) [a]
Ru(1)	−0.09938(5)	0.05460(4)	−0.20005(3)	
Ru(2)	−0.02875(5)	0.29235(4)	−0.21373(3)	
Ru(3)	−0.30460(4)	0.11377(4)	−0.30974(3)	
Fe(1)	0.14138(8)	0.22649(8)	−0.11219(6)	
P(1)	−0.30926(14)	−0.04790(12)	−0.27620(9)	
P(2)	−0.20477(14)	0.30131(12)	−0.29870(10)	
C(1)	−0.1877(6)	0.1254(5)	−0.0996(4)	
O(1)	−0.2454(5)	0.1592(4)	−0.0431(3)	
C(2)	−0.0113(6)	−0.0140(5)	−0.3009(4)	
O(2)	0.0343(5)	−0.0623(4)	−0.3604(3)	
C(3)	−0.0562(6)	−0.0472(6)	−0.1566(5)	
O(3)	−0.0312(5)	−0.1111(5)	−0.1298(4)	
C(4)	−0.1202(6)	0.3592(5)	−0.1141(4)	
O(4)	−0.1746(5)	0.4041(4)	−0.0584(3)	
C(5)	0.0896(6)	0.4338(6)	−0.1893(4)	
O(5)	0.1617(5)	0.5204(4)	−0.1760(4)	
C(6)	0.0689(6)	0.2243(5)	−0.3102(4)	
O(6)	0.1270(5)	0.1913(4)	−0.3674(3)	
C(7)	−0.3950(6)	0.1752(5)	−0.2076(4)	
O(7)	−0.4485(4)	0.2116(4)	−0.1490(3)	

TABLE 2 (continued)

Atom	*x/a*	*y/b*	*z/c*	*B* (Å^2) [a]
C(8)	−0.4674(6)	0.0740(5)	−0.3791(3)	
O(8)	−0.5687(4)	0.0497(4)	−0.4217(3)	
C(9)	−0.2050(6)	0.0600(5)	−0.4087(4)	
O(9)	−0.1490(4)	0.0320(4)	−0.4671(3)	
C(10)	0.0501(6)	0.2880(6)	−0.0239(4)	
O(10)	0.0066(5)	0.3305(4)	0.0390(3)	
C(11)	0.2168(6)	0.1589(6)	−0.2055(4)	
O(11)	0.2812(5)	0.1198(5)	−0.2601(3)	
C(12)	0.2033(7)	0.1485(6)	−0.0601(4)	
O(12)	0.2462(7)	0.1020(5)	−0.0231(4)	
C(13)	0.2737(7)	0.3532(6)	−0.0795(5)	
O(13)	0.3620(5)	0.4342(5)	−0.0563(4)	
C(14)	−0.4523(5)	−0.0856(5)	−0.2186(4)	
C(15)	−0.4342(6)	−0.1045(5)	−0.1448(4)	
C(16)	−0.5833(6)	−0.0981(5)	−0.2521(4)	
C(17)	−0.5444(6)	−0.1372(5)	−0.1058(4)	
C(18)	−0.6942(6)	−0.1320(6)	−0.2138(4)	
C(19)	−0.6754(7)	−0.1526(6)	−0.1410(4)	
C(20)	−0.3173(5)	−0.1884(5)	−0.3612(4)	
C(21)	−0.3459(6)	−0.2111(5)	−0.4454(4)	
C(22)	−0.3006(7)	−0.2785(5)	−0.3398(5)	
C(23)	−0.3544(7)	−0.3195(6)	−0.5073(4)	
C(24)	−0.3115(8)	−0.3868(6)	−0.4010(5)	
C(25)	−0.3386(7)	−0.4067(6)	−0.4838(5)	
C(26)	−0.1742(6)	0.3179(5)	−0.3998(4)	
C(27)	−0.2839(7)	0.2898(5)	−0.4592(4)	
C(28)	−0.0470(7)	0.3553(6)	−0.4202(5)	
C(29)	−0.2690(8)	0.2989(6)	−0.5367(4)	
C(30)	−0.0312(8)	0.3617(7)	−0.4996(6)	
C(31)	−0.1421(9)	0.3341(7)	−0.5553(5)	
C(32)	−0.3025(6)	0.4100(5)	−0.2523(4)	
C(33)	−0.2376(7)	0.5229(5)	−0.2050(4)	
C(34)	−0.4448(6)	0.3808(6)	−0.2662(4)	
C(35)	−0.3140(8)	0.6043(6)	−0.1709(4)	
C(36)	−0.5175(7)	0.4651(6)	−0.2333(5)	
C(37)	−0.4518(9)	0.5755(7)	−0.1850(5)	
HC(15)	−0.3440	−0.0938	−0.1208	4.49
HC(16)	−0.5964	−0.0827	−0.3017	4.75
HC(17)	−0.5307	−0.1500	−0.0551	5.34
HC(18)	−0.7840	−0.1416	−0.2379	5.59
HC(19)	−0.7521	−0.1767	−0.1150	5.71
HC(21)	−0.3602	−0.1509	−0.4615	5.14
HC(22)	−0.2817	−0.2647	−0.2814	5.90
HC(23)	−0.3712	−0.3337	−0.5660	6.02
HC(24)	−0.2988	−0.4473	−0.3849	6.55
HC(25)	−0.3470	−0.4819	−0.5256	6.12
HC(27)	−0.3724	0.2636	−0.4456	5.19
HC(28)	0.0304	0.3760	−0.3800	6.36
HC(29)	−0.3465	0.2815	−0.5761	6.08
HC(30)	0.0571	0.3869	−0.5140	7.63
HC(31)	−0.1304	0.3378	−0.6096	7.16
HC(33)	−0.1407	0.5443	−0.1962	5.39
HC(34)	−0.4908	0.3031	−0.2975	5.32
HC(35)	−0.2690	0.6816	−0.1377	6.60
HC(36)	−0.6141	0.4464	−0.2445	6.87
HC(37)	−0.5028	0.6318	−0.1606	7.50

[a] The phenyl hydrogen atoms are in their calculated positions (see text). They were assigned isotropic thermal parameters of 1.0 Å^2 greater than their respective carbon atom.

TABLE 3

ANISOTROPIC THERMAL PARAMETERS [a] FOR THE NON-HYDROGEN ATOMS IN $FeRu_3(CO)_{13}$-(μ-$PPh_2)_2$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ru(1)	2.56(2)	3.48(2)	2.96(3)	0.67(2)	0.05(2)	1.37(2)
Ru(2)	2.57(2)	3.05(2)	3.15(3)	0.74(2)	−0.13(2)	0.90(2)
Ru(3)	2.32(2)	2.57(2)	2.14(2)	0.65(2)	0.12(2)	0.79(2)
Fe(1)	2.80(4)	4.30(5)	3.17(5)	0.93(3)	−0.60(3)	0.86(4)
P(1)	2.79(7)	2.84(7)	2.63(7)	0.70(6)	0.25(6)	1.16(6)
P(2)	2.51(7)	2.68(7)	2.81(7)	0.72(5)	0.12(6)	0.91(6)
C(1)	3.7(3)	4.1(3)	2.6(3)	−0.1(3)	−0.6(2)	1.1(3)
O(1)	5.6(3)	6.0(3)	3.3(2)	0.7(2)	1.2(2)	0.8(2)
C(2)	3.3(3)	3.7(3)	4.4(4)	0.9(2)	0.8(3)	1.6(3)
O(2)	5.4(3)	5.5(3)	5.9(3)	2.2(2)	2.4(2)	1.6(2)
C(3)	3.4(3)	6.3(4)	5.2(4)	1.6(3)	0.3(3)	2.9(3)
O(3)	6.6(3)	9.5(4)	10.4(4)	3.6(3)	1.6(3)	7.6(4)
C(4)	4.0(3)	4.0(3)	3.0(3)	1.5(3)	0.1(3)	1.0(3)
O(4)	6.8(3)	5.5(3)	4.0(3)	2.6(2)	0.9(2)	1.1(2)
C(5)	2.5(3)	4.5(4)	5.1(4)	0.4(3)	0.3(3)	0.6(3)
O(5)	4.1(2)	4.1(2)	10.3(4)	−0.1(2)	1.1(3)	1.1(3)
C(6)	3.4(3)	4.0(3)	4.0(4)	0.8(3)	0.1(3)	1.5(3)
O(6)	5.4(3)	6.1(3)	5.2(3)	2.3(2)	1.9(2)	2.6(2)
C(7)	3.1(3)	3.8(3)	2.4(3)	0.5(2)	0.1(2)	1.0(3)
O(7)	3.9(2)	6.2(3)	3.5(2)	1.8(2)	1.2(2)	1.0(2)
C(8)	3.5(3)	3.8(3)	1.8(3)	1.3(2)	0.3(2)	0.5(2)
O(8)	3.4(2)	8.1(3)	3.1(2)	1.3(2)	−0.7(2)	1.4(2)
C(9)	2.9(3)	3.2(3)	3.3(3)	1.0(2)	0.1(2)	0.6(3)
O(9)	5.0(2)	6.0(3)	3.3(2)	2.0(2)	1.6(2)	0.8(2)
C(10)	3.6(3)	5.4(4)	3.2(3)	1.3(3)	−1.1(3)	0.9(3)
O(10)	5.1(3)	8.0(3)	3.6(3)	1.9(2)	−0.6(2)	−0.1(2)
C(11)	3.2(3)	6.2(4)	4.3(4)	1.5(3)	−0.5(3)	1.9(3)
O(11)	3.9(2)	10.0(4)	4.6(3)	3.0(2)	0.3(2)	2.0(3)
C(12)	4.9(4)	7.0(4)	3.2(4)	2.8(3)	−0.4(3)	0.8(3)
O(12)	12.2(5)	10.5(4)	5.3(3)	6.9(4)	−0.9(3)	2.8(3)
C(13)	4.3(3)	6.3(4)	5.3(4)	1.0(3)	−0.9(3)	1.2(4)
O(13)	5.7(3)	8.1(4)	8.5(4)	−2.2(3)	−0.2(3)	1.3(3)
C(14)	3.1(3)	3.0(3)	2.7(3)	1.0(2)	0.2(2)	0.9(2)
C(15)	3.7(3)	4.0(3)	3.2(3)	1.0(2)	0.5(2)	1.8(3)
C(16)	3.4(3)	4.6(3)	3.0(3)	0.7(3)	0.1(2)	1.7(3)
C(17)	4.7(4)	5.6(4)	3.6(3)	1.5(3)	1.6(3)	2.6(3)
C(18)	2.5(3)	7.4(4)	4.6(4)	1.0(3)	0.8(3)	2.9(3)
C(19)	4.2(3)	5.9(4)	4.7(4)	1.0(3)	2.0(3)	2.5(3)
C(20)	2.8(3)	2.8(3)	3.1(3)	0.5(2)	0.6(2)	1.1(2)
C(21)	5.2(4)	3.1(3)	3.4(3)	0.7(3)	0.1(3)	0.8(3)
C(22)	7.7(5)	3.7(4)	4.0(4)	1.7(3)	1.3(3)	1.6(3)
C(23)	5.9(4)	4.7(4)	3.1(3)	1.1(3)	−0.7(3)	−0.2(3)
C(24)	8.7(5)	3.4(3)	6.5(5)	2.6(3)	2.1(4)	2.5(4)
C(25)	5.1(4)	3.2(3)	5.7(4)	0.9(3)	0.5(3)	0.1(3)
C(26)	3.2(3)	2.5(3)	3.8(3)	0.8(2)	0.5(2)	1.2(2)
C(27)	4.7(3)	4.4(3)	3.7(3)	0.4(3)	0.8(3)	2.0(3)
C(28)	3.8(3)	6.5(4)	7.0(5)	1.0(3)	0.8(3)	4.5(4)
C(29)	6.5(4)	4.9(4)	3.8(4)	0.5(3)	0.2(3)	2.0(3)
C(30)	4.7(4)	9.7(6)	9.2(6)	1.8(4)	3.2(4)	6.7(5)
C(31)	8.3(6)	7.9(5)	5.0(4)	3.0(4)	2.5(4)	4.0(4)
C(32)	3.6(3)	2.6(3)	2.5(3)	1.0(2)	0.2(2)	0.8(2)
C(33)	5.3(4)	4.0(3)	3.7(3)	1.5(3)	−0.3(3)	1.3(3)
C(34)	4.0(3)	4.0(3)	5.3(4)	2.0(3)	1.4(3)	1.8(3)
C(35)	9.6(5)	2.7(3)	4.3(4)	2.4(4)	−0.4(4)	0.8(3)
C(36)	4.8(4)	6.3(4)	8.3(5)	3.6(4)	2.8(4)	3.2(4)
C(37)	9.1(6)	6.3(5)	5.5(5)	4.9(5)	2.4(4)	2.0(4)

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[a] The anisotropic thermal parameters enter the expression for the calculated structure factor in the form $\exp[-0.25(h^2a^{*2}B_{11} + k^2b^{*2}B_{22} + l^2c^{*2}B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23})]$.

The largest peak on a final difference-Fourier synthesis had a peak height of 0.8 $e\text{Å}^{-3}$. The structure is thus complete. The usual tests of $\Sigma w(|F_0| - |F_c|)^2$ vs. $|F_0|$, $(\sin\theta)/\lambda$, sequence number and identity or parity class of the Miller indices showed no unusual trends; the weighting scheme is thus satisfactory.

Final positional parameters are collected in Table 2; anisotropic thermal parameters are listed in Table 3. Lists of observed and calculated structure facton are available on request (from M.R.C.).

Results and discussion

The crystal consists of discrete ordered units of $FeRu_3(CO)_{13}(\mu\text{-}PPh_2)_2$, which are mutually separated by normal Van der Waal's distances. Figure 2 shows the system used for numbering atoms within the $FeRu_3(CO)_{13}(\mu\text{-}P(C)_2)_2$ portion of the molecule, while Fig. 3 presents a stereoscopic view of the entire molecule. Interatomic distances and their estimated standard deviations (e.s.d.'s) are given in Table 4; interatomic angles are listed in Table 5.

The $FeRu_3$ core of the molecule is essentially planar (r.m.s. deviation = 0.024 Å: see Table 6); the phosphorus atoms of the $\mu\text{-}PPh_2$ groups are close to coplanar with the tetranuclear metal core as are the 5 equatorial carbonyl ligands. This is shown clearly in Fig. 4.

The four metal atoms define a planar triangulated rhombus, with atoms Ru(1) and Ru(2) at the bridgehead positions and atoms Fe(1) and Ru(3) at the acute apices of the rhombus. The iron atom is bonded to four terminal ligands

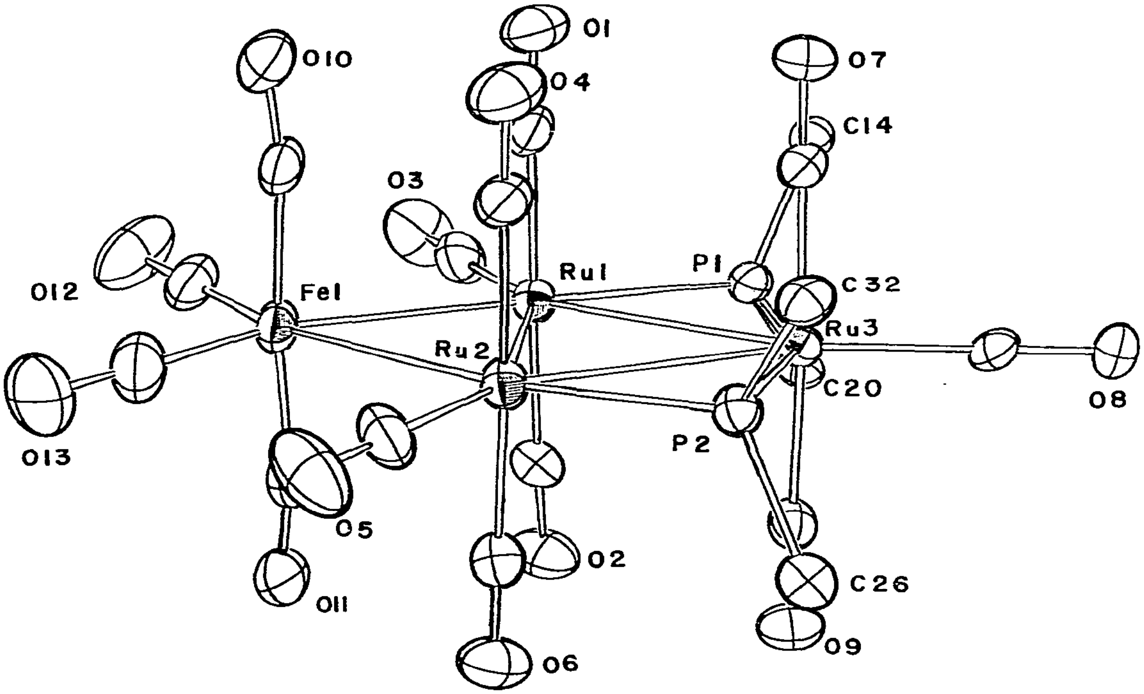

Fig. 2. Labelling of atoms in the $FeRu_3(CO)_{13}(\mu\text{-}P(C)_2)_2$ portion of the molecule (ORTEP-II diagram).

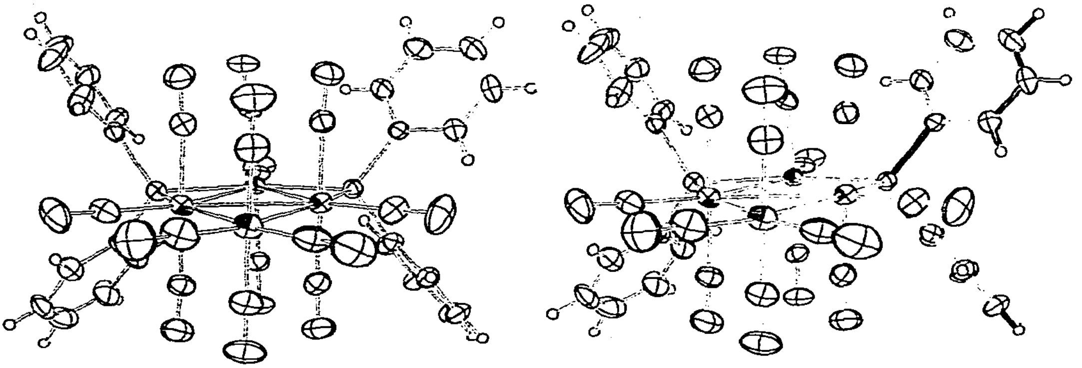

Fig. 3. Stereoscopic view of the $FeRu_3(CO)_{13}(\mu\text{-}PPh_2)_2$ molecule (ORTEP-II diagram).

and is linked to the triruthenium fragment solely through the bonds Fe(1)—Ru(1) = 2.861(1) Å and Fe(1)—Ru(2) = 2.868(1) Å. Each ruthenium atom is linked to three terminal carbonyl ligands. In addition, two diphenylphosphido ligands (derived initially from $Fe(CO)_4(Ph_2P{-}PPh_2)$) have been transferred completely to the triruthenium portion of the structure and bridge the Ru(1)—Ru(3) and Ru(2)—Ru(3) vectors. Angles at the bridging phosphorus atoms are <Ru(1)—P(1)—Ru(3) = 84.89(5)° and <Ru(2)—P(2)—Ru(3) = 85.56(6)°. The ruthenium—ruthenium distances, Ru(1)—Ru(2) = 3.098(1), Ru(1)—Ru(3) = 3.147(1), and Ru(2)—Ru(3) = 3.171(1) Å are all longer than the average Ru—Ru distance of 2.854 Å found in $Ru_3(CO)_{12}$ [6].

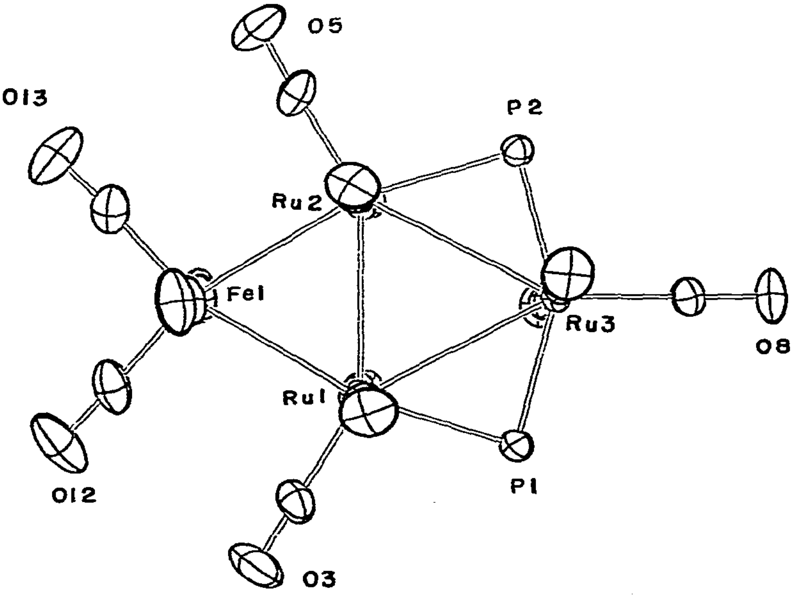

Fig. 4. The $FeRu_3(CO)_{13}(\mu\text{-}P)_2$ portion of the molecule, projected onto its $FeRu_3$ plane (ORTEP-II diagram).

TABLE 4

INTERATOMIC DISTANCES (Å) WITH E.S.D.'s FOR $FeRu_3(CO)_{13}(\mu\text{-}PPh_2)_2$

(A) Metal—metal distances			
Ru(1)—Ru(2)	3.098(1)	Fe(1)—Ru(1)	2.861(1)
Ru(1)—Ru(3)	3.147(1)	Fe(1)—Ru(2)	2.868(1)
Ru(2)—Ru(3)	3.171(1)		
(B) Metal—phosphorus distances			
Ru(1)—P(1)	2.313(2)	Ru(3)—P(1)	2.350(2)
Ru(2)—P(2)	2.315(2)	Ru(3)—P(2)	2.354(2)
(C) Metal—carbon and metal···oxygen distances			
Ru(1)—C(1)	1.942(7)	Ru(1)···O(1)	3.063(5)
Ru(1)—C(2)	1.939(6)	Ru(1)···O(2)	3.070(5)
Ru(1)—C(3)	1.846(7)	Ru(1)···O(3)	2.991(5)
Ru(2)—C(4)	1.939(6)	Ru(2)···O(4)	3.064(5)
Ru(2)—C(5)	1.853(6)	Ru(2)...O(5)	2.991(5)
Ru(2)—C(6)	1.941(7)	Ru(2)···O(6)	3.072(5)
Ru(3)—C(7)	1.950(6)	Ru(3)···O(7)	3.079(4)
Ru(3)—C(8)	1.863(5)	Ru(3)...O(8)	3.017(4)
Ru(3)—C(9)	1.949(6)	Ru(3)···O(9)	3.076(4)
Fe(1)—C(10)	1.786(7)	Fe(1)···O(10)	2.926(5)
Fe(1)—C(11)	1.772(7)	Fe(1)···O(11)	2.924(5)
Fe(1)—C(12)	1.758(7)	Fe(1)···O(12)	2.906(5)
Fe(1)—C(13)	1.774(7)	Fe(1)···O(13)	2.926(5)
(D) Carbon—oxygen distances			
C(1)—O(1)	1.124(7)	C(7)—O(7)	1.130(6)
C(2)—O(2)	1.133(7)	C(8)—O(8)	1.155(6)
C(3)—O(3)	1.145(7)	C(9)—O(9)	1.127(6)
C(4)—O(4)	1.128(7)	C(10)—O(10)	1.147(7)
C(5)—O(5)	1.139(7)	C(11)—O(11)	1.160(7)
C(6)—O(6)	1.133(7)	C(12)—O(12)	1.149(7)
		C(13)—O(13)	1.153(8)
(E) Phosphorus—carbon distances			
P(1)—C(14)	1.839(6)	P(2)—C(26)	1.833(6)
P(1)—C(20)	1.833(6)	P(2)—C(32)	1.826(5)
(F) Carbon—carbon distances in phenyl rings			
C(14)—C(15)	1.380(8)	C(26)—C(27)	1.375(8)
C(14)—C(16)	1.380(7)	C(26)—C(28)	1.370(8)
C(15)—C(17)	1.375(7)	C(27)—C(29)	1.375(8)
C(16)—C(18)	1.377(8)	C(28)—C(30)	1.393(9)
C(17)—C(19)	1.382(8)	C(29)—C(31)	1.348(9)
C(18)—C(19)	1.377(9)	C(30)—C(31)	1.347(10)
C(20)—C(21)	1.363(8)	C(32)—C(33)	1.381(8)
C(20)—C(22)	1.380(8)	C(32)—C(34)	1.395(8)
C(21)—C(23)	1.385(8)	C(33)—C(35)	1.388(9)
C(22)—C(24)	1.376(9)	C(34)—C(36)	1.387(8)
C(23)—C(25)	1.363(9)	C(35)—C(37)	1.351(10)
C(24)—C(25)	1.344(9)	C(36)—C(37)	1.362(10)
(G) C(axial)···C(axial) and O(axial)···O(axial) intramolecular contacts			
C(1)···C(4)	3.054(8)	O(1)···O(4)	3.200(6)
C(1)···C(7)	3.072(8)	O(1)···O(7)	3.038(6)
C(1)···C(10)	2.752(8)	O(1)···O(10)	2.917(7)
C(2)···C(6)	3.075(8)	O(2)···O(6)	3.258(6)
C(2)···C(9)	3.167(8)	O(2)···O(9)	3.298(6)
C(2)···C(11)	2.814(9)	O(2)···O(11)	3.006(7)
C(4)···C(7)	3.181(8)	O(4)···O(7)	3.209(6)
C(4)···C(10)	2.782(8)	O(4)···O(10)	2.959(7)
C(6)···C(9)	3.107(8)	O(6)···O(9)	2.111(7)
C(6)···C(11)	2.764(8)	O(6)···O(11)	2.887(6)

TABLE 5

SELECTED INTRAMOLECULAR ANGLES (in deg.), WITH E.S.D.'s FOR $FeRu_3(CO)_{13}(\mu\text{-}PPh_2)_2$

(A) Intermetallic angles			
Ru(2)—Ru(1)—Ru(3)	61.03(2)	Ru(1)—Ru(2)—Ru(3)	60.26(2)
Ru(2)—Ru(1)—Fe(1)	57.38(3)	Ru(1)—Ru(2)—Fe(1)	57.16(3)
Ru(3)—Ru(1)—Fe(1)	118.38(3)	Ru(3)—Ru(2)—Fe(1)	117.39(3)
Ru(1)—Ru(3)—Ru(2)	58.71(2)	Ru(1)—Fe(1)—Ru(2)	65.45(3)
(B) Ruthenium—phosphorus—ruthenium angles			
Ru(1)—P(1)—Ru(3)	84.89(5)	Ru(2)—P(2)—Ru(3)	85.56(6)
(C) Metal—metal—phosphorus angles			
Ru(3)—Ru(1)—P(1)	48.05(4)	Ru(3)—Ru(2)—P(2)	47.74(4)
Ru(2)—Ru(1)—P(1)	106.06(4)	Ru(1)—Ru(2)—P(2)	108.00(5)
Fe(1)—Ru(1)—P(1)	166.13(4)	Fe(1)—Ru(2)—P(2)	165.01(4)
Ru(1)—Ru(3)—P(1)	47.07(4)	Ru(2)—Ru(3)—P(2)	46.70(2)
Ru(2)—Ru(3)—P(1)	105.77(4)	Ru(1)—Ru(3)—P(2)	105.41(4)
(D) Metal—metal—carbon angles			
Ru(2)—Ru(1)—C(1)	87.09(18)	Ru(1)—Ru(2)—C(4)	91.61(18)
Ru(2)—Ru(1)—C(2)	92.01(17)	Ru(1)—Ru(2)—C(6)	87.27(18)
Ru(2)—Ru(1)—C(3)	149.72(21)	Ru(1)—Ru(2)—C(5)	150.55(21)
Ru(3)—Ru(1)—C(1)	89.40(17)	Ru(3)—Ru(2)—C(4)	90.97(18)
Ru(3)—Ru(1)—C(2)	89.92(18)	Ru(3)—Ru(2)—C(6)	90.56(18)
Ru(3)—Ru(1)—C(3)	149.22(21)	Ru(3)—Ru(2)—C(5)	149.12(21)
Fe(1)—Ru(1)—C(1)	85.86(17)	Fe(1)—Ru(2)—C(4)	88.92(17)
Fe(1)—Ru(1)—C(2)	93.90(18)	Fe(1)—Ru(2)—C(6)	88.46(18)
Fe(1)—Ru(1)—C(3)	92.34(21)	Fe(1)—Ru(2)—C(5)	93.48(21)
Ru(1)—Ru(3)—C(7)	88.34(17)	Ru(2)—Ru(3)—C(7)	89.28(16)
Ru(1)—Ru(3)—C(8)	150.70(18)	Ru(2)—Ru(3)—C(8)	150.59(18)
Ru(1)—Ru(3)—C(9)	90.48(17)	Ru(2)—Ru(3)—C(9)	87.40(17)
Ru(1)—Fe(1)—C(10)	90.84(20)	Ru(2)—Fe(1)—C(10)	88.25(20)
Ru(1)—Fe(1)—C(11)	84.02(21)	Ru(2)—Fe(1)—C(11)	88.07(20)
Ru(1)—Fe(1)—C(12)	96.81(24)	Ru(2)—Fe(1)—C(13)	96.43(24)
Ru(1)—Fe(1)—C(13)	161.58(24)	Ru(2)—Fe(1)—C(12)	162.20(24)
(E) Carbon—metal—carbon angles			
C(1)—Ru(1)—C(2)	179.06(29)	C(4)—Ru(2)—C(6)	177.36(26)
C(1)—Ru(1)—C(3)	91.04(28)	C(4)—Ru(2)—C(5)	89.97(27)
C(2)—Ru(1)—C(3)	89.88(28)	C(6)—Ru(2)—C(5)	89.83(27)
C(7)—Ru(3)—C(8)	91.23(23)	C(9)—Ru(3)—C(8)	91.35(24)
C(7)—Ru(3)—C(9)	176.61(24)		
C(10)—Fe(1)—C(11)	174.59(29)		
C(10)—Fe(1)—C(12)	90.71(30)	C(11)—Fe(1)—C(12)	91.58(30)
C(10)—Fe(1)—C(13)	91.91(32)	C(11)—Fe(1)—C(13)	92.45(30)
C(12)—Ce(1)—C(13)	101.37(33)		
(F) Phosphorus—ruthenium—carbon angles			
P(1)—Ru(1)—C(1)	90.73(17)	P(2)—Ru(2)—C(4)	89.45(18)
P(1)—Ru(1)—C(2)	89.29(19)	P(2)—Ru(2)—C(6)	93.18(18)
P(1)—Ru(1)—C(3)	101.17(21)	P(2)—Ru(2)—C(5)	101.42(21)
P(1)—Ru(3)—C(7)	87.68(17)	P(2)—Ru(3)—C(7)	90.36(17)
P(1)—Ru(3)—C(8)	103.64(18)	P(2)—Ru(3)—C(8)	103.89(19)
P(1)—Ru(3)—C(9)	93.84(17)	P(2)—Ru(3)—C(9)	86.89(17)
(G) Phosphorus—ruthenium—phosphorus angle			
P(1)—Ru(3)—P(2)	152.44(6)		
(H) Metal—carbon—oxygen angles			
Ru(1)—C(1)—O(1)	175.1(6)	Ru(3)—C(8)—O(8)	179.5(4)
Ru(1)—C(2)—O(2)	174.6(6)	Ru(3)—C(9)—O(9)	177.2(6)
Ru(1)—C(3)—O(3)	179.1(5)	Fe(1)—C(10)—O(10)	171.3(6)
Ru(2)—C(4)—O(4)	174.9(6)	Fe(1)—C(11)—O(11)	171.6(6)
Ru(2)—C(5)—O(5)	178.5(10)	Fe(1)—C(12)—O(12)	177.0(8)
Ru(2)—C(6)—O(6)	175.3(6)	Fe(1)—C(13)—O(13)	177.4(9)
Ru(3)—C(7)—O(7)	178.9(8)		
(I) Angles around phosphorus			
Ru(1)—P(1)—C(14)	118.94(18)	Ru(2)—P(2)—C(26)	120.86(19)
Ru(1)—P(1)—C(20)	117.77(18)	Ru(2)—P(2)—C(32)	118.64(19)
Ru(3)—P(1)—C(14)	115.93(18)	Ru(3)—P(2)—C(26)	115.67(19)
Ru(3)—P(1)—C(20)	120.21(19)	Ru(3)—P(2)—C(32)	116.74(19)
C(14)—P(1)—C(20)	100.34(25)	C(26)—P(2)—C(32)	100.41(25)

TABLE 6

THE METAL ATOM PLANE AND DEVIATIONS OF ATOMS THEREFROM

Plane: [a] $-0.5722X + 0.1937Y + 0.7969Z + 1.6846 = 0$

Atom	Dev. (Å)	Atom	Dev. (Å)
Ru(1)* [b]	−0.0241(5)	P(1)	0.0564(16)
Ru(2)*	−0.0237(5)	P(2)	0.0231(16)
Ru(3)*	+0.0223(5)		
Fe(1)*	+0.0255(9)		

[a] Cartesian (Å) coordinates. [b] Atoms marked with an asterisk were used in computing the least-squares plane.

The amassed literature on tetranuclear metal cluster compounds indicates that the skeletal bonding can usually be described in terms of localized two-center bonds [7]. Thus, a 60-electron count is normally associated with a tetrahedral cluster, a 62-electron count with a (planar or "butterfly") triangulated rhombus, and a 64-electron count with a metallo-ligated triangular (or, possibly, square) framework..

The present cluster has a formal electron count of 64 electrons (considering metals and ligands as neutral, we have four d^8 metal atoms, 2 electrons from each of the 13 carbonyl ligands and 3 electrons from each of the PPh_2 moieties), yet it takes up the geometry of the planar triangulated rhombus previously typified by the 62-electron species $[Re_4(CO)_{16}{}^{2-}]$ [8,9] and $HOs_3Re(CO)_{15}$ [10].

The present 64-electron complex has ruthenium—ruthenium distances which are rather longer than normal Ru—Ru single bonds (vide supra). It appears, therefore, that the two "extra" electrons occupy an antibonding orbital associated principally with the Ru_3 triangle and that the formal bond order of each of the three Ru—Ru linkages is reduced to only 2/3.

The cluster as a whole is symmetrical with approximate C_{2v} symmetry. The following additional point of interest should be noted.

(1) The axial metal—carbonyl linkages are generally longer than the corresponding equatorial metal—carbonyl distances. Thus Ru—CO (axial) distances at the bridgehead ruthenium atoms are Ru(1)—C(1) = 1.942(7), Ru(1)—C(2) = 1.939(6), Ru(2)—C(4) = 1.939(6), and Ru(2)—C(6) = 1.941(7) Å, (average = 1.940 ± 0.002 Å) as opposed to the Ru—CO (equ.) distances of Ru(1)—C(3) = 1.846(7) and Ru(2)—C(5) = 1.853(6) Å (average = 1.850 ± 0.005 Å). A similar pattern is discernible at the unique atom Ru(3), with the axial distances Ru(3)—C(7) = 1.950(6) and Ru(3)—C(9) = 1.949(6) Å (Ru—CO(axial) = 1.950 ± 0.001 Å) vs. the equatorial Ru(3)—C(8) bondlength of 1.863(5) Å. The pattern at Fe(1) is not so clearcut, but tends toward the same situation. A similar pattern occurs in $Ru_3(CO)_{12}$ and is caused there, as here, by the greater competition for $d_\pi—\pi^*$ bonding among the mutual *trans* pairs of axial M—CO linkages.

(2) The carbonyl ligands are all strictly of the terminal variety (There are no "semi-bridging" carbonyl ligands.) The M—C—O angles range from 171.3(6)° to 179.5(4)° and deviations from linearity are in all cases caused by intramolec-

ular oxygen...oxygen repulsions (see Table 4, section G). Thus the Fe(1)—C(10)—O(10) angle of 171.3(6)° results from the close contacts O(1)...O(10) = 2.917(7) and O(4)...O(10) = 2.959(7) Å while the Fe(1)—C(11)—O(11) angle of 171.6(6)° results from the repulsions O(2)...O(11) = 3.006(7) and O(6)...O(11) = 2.887(6) Å. Reciprocal repulsions cause distortions from linearity for the axial carbonyl ligands on Ru(1) and Ru(2), which have Ru—C—O angles in the range 174.6(6) to 175.3(6)°. The axial ligands on Ru(3) are not subjected to strong intramolecular repulsions and are close to linear [Ru(3)—C(7)—O(7) = 178.9(8)° and Ru(3)—C(9)—O(9) = 177.2(6)°] as are all of the equatorial Ru—C—O and Fe—C—O systems.

(3) The PPh_2 ligands occupy slightly asymmetrically bridging sites with the bonds to Ru(3) being slightly longer than the other two bonds [viz, Ru(3)—P(1) = 2.350(2) Å vs. Ru(1)—P(1) = 2.313(2) Å and Ru(3)—P(2) = 2.354(2) Å vs. Ru(2)—P(2) = 2.315(2) Å]. This presumably helps to remove electronic charge from Ru(3), which is the most "ligand-rich" of the four metal atoms.

(4) All other distances and angles are internally consistent and within the expected ranges, e.g., C—O = 1.124(7)—1.160(7) Å, P—C = 1.826(5)—1.839(6) Å, and C—C = 1.344(9) —1.395(8) Å.

Acknowledgements

This work was supported by the National Science Foundation (Grant CHE79-24560, to M.R.C.). Computing services were provided by the Computer Center of SUNY at Buffalo.

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