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Reactivity of triosmium and triruthenium carbon radicals toward fluoro- and hexafluorobenzene

N. Hadj-Bagheri, D.S. Strickland, S.R. Wilson and J.R. Shapley *
School of Chemical Sciences, University of Illinois, Urbana, IL 61801 (USA)

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Abstract

The radicals $H_3M_3(CO)_9(\mu_3\text{-}C\cdot)$, generated by photolyzing a mixture of $Re_2(CO)_{10}$ and $H_3M_3(CO)_9(\mu_3\text{-}CBr)$ (M = Ru, Os), are found to add to C_6F_6 and C_6H_5F. With C_6F_6 the major products are the pentafluorophenyl derivatives $H_3M_3(CO)_9(\mu_3\text{-}CC_6F_5)$, whereas with C_6H_5F the major products are the phenyl derivatives $H_3M_3(CO)_9(\mu_3\text{-}CC_6H_5)$.

Introduction

We have reported [1] that the radical $H_3O_3(CO)_9(\mu_3\text{-}C\cdot)$ (1) can be generated by the photo-induced reaction of $Re_2(CO)_{10}$ (generating $\cdot Re(CO)_5$) with $H_3Os_3(CO)_9(\mu_3\text{-}CBr)$. The radical species **1** abstracts hydrogen from saturated hydrocarbons and also adds to benzene to give $H_3Os_3(CO)_9(\mu_3\text{-}CPh)$. The ruthenium analog **2** has been suggested as an intermediate in the reactions of $H_3Ru_3(CO)_9(\mu_3\text{-}CBr)$ with $HSnBu_3$ [2a] and with HSEt [2b]. In this paper we report on the reactivity of **1** and **2** toward fluorobenzene and hexafluorobenzene.

Results

Photolysis of $H_3Os_3(CO)_9(\mu_3\text{-}CBr)$ and $Re_2(CO)_{10}$ in hexafluorobenzene

When a solution of $H_3Os_3(CO)_9(\mu_3\text{-}CBr)$ and $Re_2(CO)_{10}$ in hexafluorobenzene under a CO atmosphere was photolyzed for a period of 5 hours, the color changed from pale yellow to dark orange. Examination revealed a mixture of products that could be separated by TLC. The major product from this reaction was $H_3Os_3(CO)_9(\mu_3\text{-}CC_6F_5)$, a pale yellow microcrystalline solid, which was obtained in 55% yield. The mass spectrum and analytical data suggested the proposed formulation. The IR spectrum of $H_3Os_3(CO)_9(\mu_3\text{-}CC_6F_5)$ in the ν(CO) region is very similar to that of other $H_3M_3(CO)_3(\mu_3\text{-}CR)$ clusters [2], and it displays a weak band at 1514 cm^{-1} in the region characteristic of fluoroaromatic ring absorptions [3]. The ^1H NMR spectrum consists of a singlet peak at δ −18.82, which is assigned to the hydride ligands bridging the osmium centers. The ^{19}F NMR spectrum of

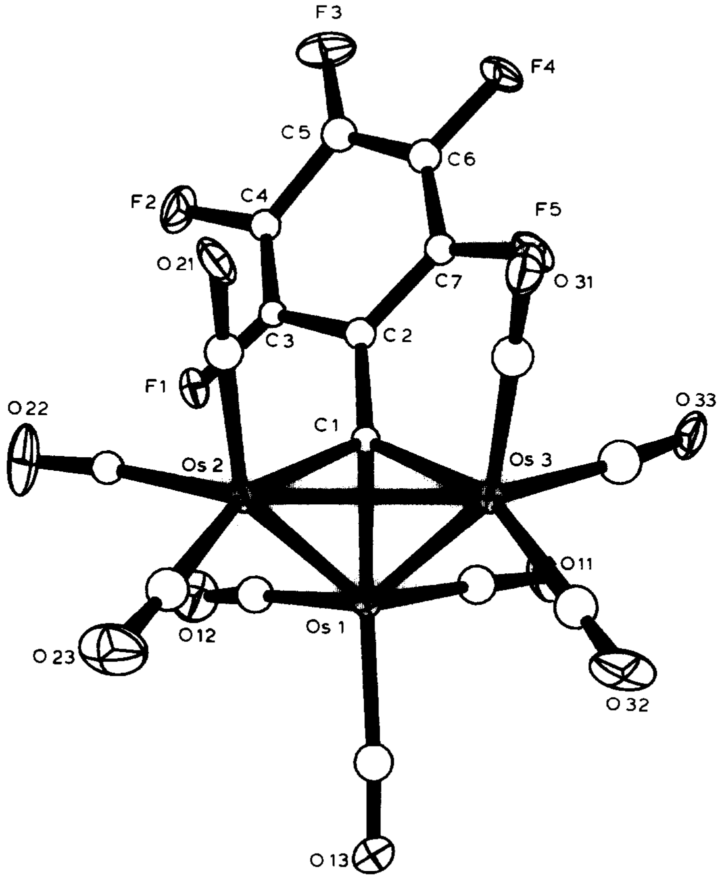


Fig. 1. ORTEP diagram showing geometry and atomic labeling scheme for $(\mu\text{-H})_3Os_3\text{-}(CO)_9(\mu_3\text{-}CC_6F_5)$. Important distances (Å) are: Os(1)–Os(2) = 2.873(2), Os(1)–Os(3) = 2.871(2), Os(2)–C(1) = 2.1(2), Os(2)–(1) = 2.2(1), Os(3)–C(1) = 2.2(2), and C(1)–C(2) = 1.5(3). Significant angles (deg) are Os(2)–Os(1)–Os(3) = 59.99(4), Os(1)–Os(2)–Os(3) = 59.96(4), Os(1)–Os(3)–Os(2) = 60.05(4), Os(1)–C(1)–Os(2) = 85(6), Os(1)–C(1)–Os(3) = 85(8), Os(2)–C(1)–Os(3) = 83(7), Os(1)–C(1)–C(2) = 133(16), Os(2)–C(1)–C(2) = 125(13), and Os(3)–C(1)–C(2) = 129(18).

$H_3Os_3(CO)_9(\mu_3\text{-}CC_6F_5)$ consists of a multiplet signal centered at −163.6 ppm (relative to $CFCl_3$), which compares with the position of free C_6F_6 at −162 ppm.

A second product from the reaction of $H_3Os_3(CO)_9(\mu_3\text{-}CBr)$ with $Re_2(CO)_{10}$ in C_6F_6 was $H_3Os_3(CO)_9(\mu_3\text{-}CF)$, identified by IR, and ^1H NMR spectroscopy [4]. A third product, isolated after TLC as a pale yellow solid, showed a molecular ion of *m/z* 1336 in its mass spectrum, which indicated the formulation $H_2Os_3Re(CO)_{14}(CC_6F_5)$. A small amount of a dark orange complex, previously shown to be $[H_3Os_3(CO)_9(\mu_3\text{-}CCO)]_2$ [1], was also isolated.

An X-ray crystallographic study of $H_3Os_3(CO)_9(\mu_3\text{-}CC_6F_5)$ was undertaken, and the resulting molecular structure is shown in Fig. 1. The framework of the cluster is an equilateral triangle of three osmium atoms, each with three terminal CO ligands. The geometry around each osmium center is pseudo-octahedral as expected. The Os–Os distances (avg. 2.87 Å) are typical for such structures with bridged Os–H–Os bonds [1,5,6]. The carbon center bridges the three metal centers in a symmetrical fashion; the average Os–C bond is 2.16 Å. The pentafluorophenyl ring is coordinated to the μ_3-C center such that the plane of the ring is essentially perpendicular to the plane of the osmium centers.

Reaction of $H_3Ru_3(CO)_9(\mu_3\text{-}CBr)$ and $Re_2(CO)_{10}$ in hexafluorobenzene

The interaction of $H_3Ru_3(CO)_9(\mu_3\text{-CBr})$ and $Re_2(CO)_{10}$ in hexafluorobenzene under irradiation resulted in the formation of a dark red solution and some reddish brown precipitate. TLC of the supernatant showed many products to be present, from which the major component, $H_3Ru_3(CO)_9(\mu_3\text{-CC}_6F_5)$, was isolated in 33% yield. The formulation of the compound was established by the microanalytical and mass spectra data; its IR (νCO) spectrum and ^{1}H NMR signal for the bridging hydride ligands are consistent with other compounds of this type [2]. The ^{19}F NMR spectrum showed the presence of a C_6F_5 ring. A ^{19}F NMR spectrum of the reaction mixture showed a signal at -75.3 ppm that is attributed to $H_3Ru_3(CO)_9(\mu_3\text{-CF})$, but this compound could not be isolated in pure form.

Reaction of $H_3Os_3(CO)_9(\mu_3\text{-}Br)$ and $Re_2(CO)_{10}$ in fluorobenzene

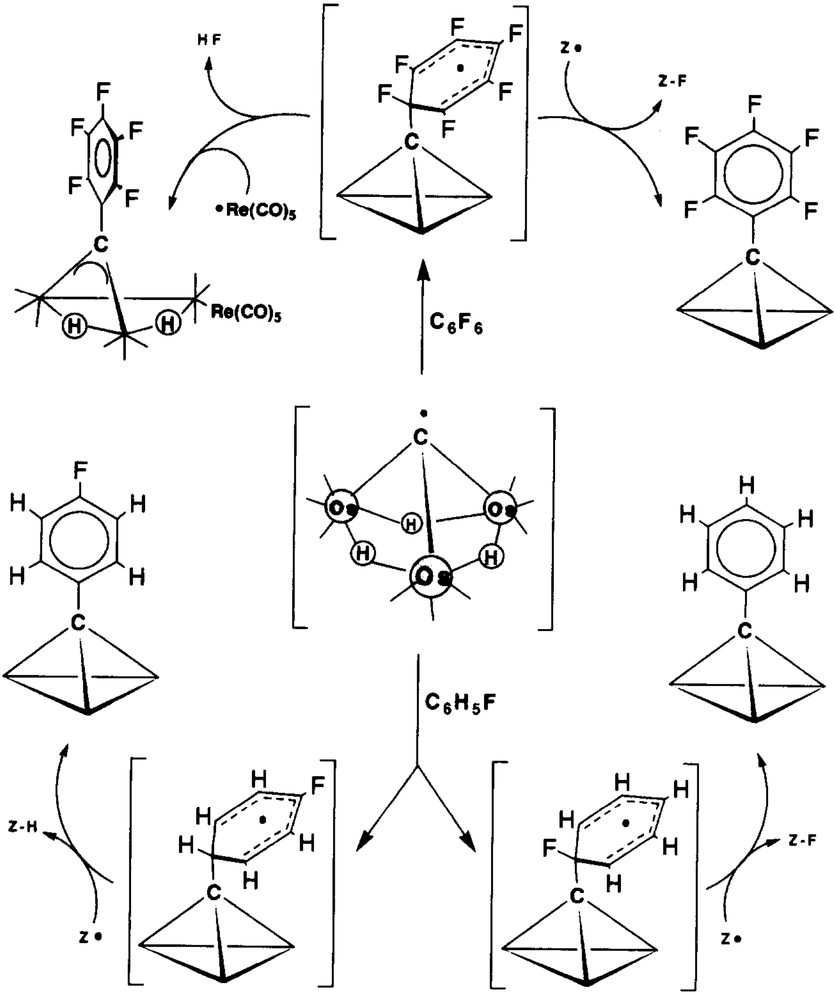
When a solution of $H_3Os_3(CO)_9(\mu_3\text{-CBr})$ and $Re_2(CO)_{10}$ in C_6H_5F under a CO atmosphere was photolyzed for a period totalling 10 hours, the ^{1}H NMR spectrum showed the formation of several products. Both $H_3Os_3(CO)_9(\mu_3\text{-CH})$ and $H_3Os_3(CO)_9(\mu_3\text{-CF})$ were formed in low yields, but the major component of the reaction mixture was $H_3Os_3(CO)_9(\mu_3\text{-CPh})$, subsequently isolated in 40% yield. A small amount of a fourth product, characterized as $H_3Os_3(CO)_9(\mu_3\text{-}C_6H_4F)$ was also formed. The ^{1}H NMR spectrum of $H_3Os_3(CO)_9(\mu_3\text{-CC}_6H_4F)$ consists of a signal at δ -18.61 (3H), due to the hydride ligands and two multiplet resonances centered at δ 7.52 (2H) and 7.70 (2H), due to the phenyl protons. The NMR data therefore lead us to conclude that the fluorophenyl moiety is coordinated to the triply bridging carbon in a *para* fashion. The ^{19}F NMR spectrum of $H_3Os_3(CO)_9(\mu\text{-CC}_6H_4F)$ displays a signal at -99.6 ppm, which compares with the position of free C_6H_5F at -113 ppm.

Reaction of $H_3Ru_3(CO)_9(\mu_3\text{-}CBr)$ and $Re_2(CO)_{10}$ in fluorobenzene

The photolysis of $H_3Ru_3(CO)_9(\mu_3\text{-CBr})$ and $Re_2(CO)_{10}$ in fluorobenzene resulted in a mixture of compounds which could not be cleanly separated by TLC. The ^{1}H NMR spectrum of the first broad band indicated the presence of $H_3Ru_3(CO)_9(\mu_3\text{-CH})$ and $H_3Ru_3(CO)_9(\mu_3\text{-CPh})$ as well as starting material. The ^{19}F NMR spectrum of the second band consisted of signals at -75.3 and -100 ppm which indicated a mixture of $H_3Ru_3(CO)_9(\mu_3\text{-CF})$ and $H_3Ru_3(CO)_9(\mu_3\text{-CC}_6H_4F)$. These products could not be further separated and characterized.

Discussion

Studies of the reactivity of various radicals with hexafluorobenzene have shown that addition to the aromatic ring takes place to give adduct-perfluorocyclohexadienyl radical intermediates [7]. These species typically undergo dimerization, but defluorination can occur when radicals capable of abstracting fluorine atoms are present. In this respect neither triphenylmethyl [8] nor the bridgehead adamantyl [9] radicals show evidence for fluorine abstraction, but the trimethylsilyl radical does [10]. In the present trimetallic carbon systems, the observation of $H_3M_3(CO)_9(\mu_3$-$CF)$ as one of the products suggests a role for the $M_3C\cdot$ radical in fluorine abstraction. However, the amount of $H_3M_3(CO)_9(\mu_3$-$CF)$ observed is always significantly less than that of $H_3M_3(CO)_9(\mu_3$-$CC_6F_5)$ formed, so other radicals must play the dominant role. The most likely candidate is the pentacarbonyl rhenium radical, which is present in relatively high concentrations under the chosen reaction conditions. However, identification of $Re(CO)_5F$, which is unstable and not expected to survive the workup conditions [11], has not proved possible by ^{19}F NMR spectroscopy or mass spectrometry of the product mixture. The formation of the diketone dimer $[H_3Os_3(CO)_9(\mu_3$-$CCO)]_2$ has been observed previously [1], and its presence in this reaction suggests that carbon monoxide can compete with hexafluorobenzene in trapping $H_3Os_3(CO)_9(\mu_3$-$C\cdot)$.



Scheme 1.

The products formed in addition to $H_3M_3(CO)_9(\mu_3\text{-}CC_6F_5)$ are more clearly defined for the triosmium system, and a summary set of reactions is shown in Scheme 1. The structure proposed for the mixed-metal product $H_2Os_3Re(CO)_{14}(CC_6F_5)$ is based on the structure established for $H_2Os_3(CO)_9(CC_6H_4CH_3)W(CO)_3(C_5H_5)$ [12] together with the spectroscopic data, which indicate (a) two inequivalent hydride ligands, (b) a fluoroaromatic ring, and (c) an intact $Re(CO)_5$ moiety. The mechanism suggested for the formation of this product involves elimination of the hydrogen fluoride from the intermediate hexafluorocyclohexadienyl radical, which moves the unpaired electron onto the osmium triangle, where coupling with a pentacarbonyl-rhenium radical generates the observed compound. This mechanism is certainly speculative, but similar intramolecular elimination of HF has been proposed in the reactions of hydroxyl [13] and cyclohexyl [14] radicals with fluoroaromatics. An alternative mechanism, suggested by a referee, is H-abstraction by $\cdot Re(CO)_5$ from $H_3Os_3(CO)_9(\mu_3\text{-}CC_6F_5)$ and coupling with a second $\cdot Re(CO)_5$. However, this seems unlikely, since no similar reaction is observed with $H_3Os_3(CO)_9(\mu_3\text{-}CX)$, X = Br, H, in the presence of $\cdot Re(CO)_5$ [1].

The photo-induced reactions in fluorobenzene offered several prospects for examining regioselectivity. Interestingly, the major aromatic derivatives formed are the phenyl complexes $H_3M_3(CO)_9(\mu_3\text{-}CC_6H_5)$, which presumably result from an intermediate cyclohexadienyl radical following fluorine abstraction [7]. Again, $H_3M_3(CO)_9(\mu_3\text{-}CF)$ is an observed product but in amounts too small to be the primary fluorine abstraction product. The fluorophenyl complex $H_3Os_3(CO)_9(\mu_3\text{-}CC_6H_4F)$ is accompanied by a comparable amount of $H_3Os_3(CO)_9(\mu_3\text{-}CH)$, which is likely the primary hydrogen abstraction product. If the 4:1 phenyl-to-fluorophenyl ratio observed for the products reflects the initial ratio for attack of $H_3Os_3(CO)_9(\mu_3\text{-}C\cdot)$ on the fluorobenzene ring, rather strong nucleophilic behavior is implied for this radical. Nucleophilicity has been suggested for purely organic bridgehead radicals [15], but it may be that the nucleophilic character is more pronounced with these trimetallocarbon radicals due to the electron withdrawing nature of the ancillary carbonyl ligands.

Experimental

General procedures

$H_3M_3(CO)_9(\mu_3\text{-}CBr)$, M = Ru, Os, were prepared according to the literature methods [2]. $Re_2(CO)_{10}$ (Strem Chemicals) was used as received. Hexafluorobenzene was purchased from Aldrich and used without further purification. Preparative-scale thin-layer-chromatography (TLC) was carried out in air with reagent-grade solvents on Merck Silica Gel 60-GF254 with fluorescent indicator. Multiple elution with petroleum ether was used to separate compounds with similar R_f values; increasing proportions of dichloromethane in petroleum ether were used to elute more slowly-moving components. Merck pre-coated TLC sheets, Silica Gel 60-F_{254} (0.2 mm) were used for analytical TLC. Colorless bands were visualized using a UVSL-25 mineral light.

Infrared spectra were recorded on a Perkin–Elmer 1750 FT-IR spectrometer. ^1H NMR spectra were obtained with a General Electric QE-300 (300 MHz) instrument. $^{19}F\{^1H\}$ NMR spectra were recorded at 338.2 MHz on a Nicolet 360 instrument with $CFCl_3$ as external reference. Mass spectra (electron impact) were obtained on a

Varian MAT CH-5 mass spectrometer by the staff of the Mass Spectroscopy Laboratory of the School of Chemical Sciences. Elemental analyses were performed in the Microanalytical Laboratory of the School of Chemical Sciences.

In each of the sealed tube photolysis experiments, starting materials and solvent were placed in a medium-walled NMR tube fitted with a vacuum line adapter. After three freeze-pump-thaw degassing cycles, carbon monoxide was added to 1 atm, the tube closed to the vacuum line, and the solvent frozen in a liquid nitrogen bath before the tube was sealed. Photolysis reactions were carried out using an Ace-Hanovia 450W medium-pressure mercuryvapor lamp.

Reaction of $H_3Os_3(CO)_9(\mu_3\text{-}CBr)$ and $Re_2(CO)_{10}$ in hexafluorobenzene

A solution of $H_3Os_3(CO)_9(\mu_3\text{-}CBr)$ (35 mg, 0.038 mmol) and $Re_2(CO)_{10}$ (24 mg, 0.038 mmol) in hexafluorobenzene (0.5 ml) was sealed under an atmosphere of carbon monoxide in an NMR tube. Photolysis for 5 h produced an orange solution and some off-white precipitate. The orange solution mixture was separated by TLC to give several bands. $H_3Os_3(CO)_9(\mu_3\text{-}CC_6F_50$ (21 mg, 0.021 mmol, 55%) was collected as a yellow microcrystalline solid. $H_3Os_3(CO)_9(\mu_3\text{-}CF)$ (5 mg, 0.006 mmol, 15%) was separated as a colorless band trailing the major product. The third major band, very pale yellow in color, gave upon re-TLC $H_2Os_3Re(CO)_{14}CC_6F_5$ (15%). Finally, $[H_3Os_3(CO)_9(\mu_3\text{-}CCO)]_2$ (4 mg, 0.002 mmol, 3%) was collected from a slow-moving band as an orange solid.

For $H_3Os_3(CO)_9(\mu_3\text{-}CC_6F_5)$: IR ($CH_2Cl_2$): ν(CO) 2113w, 2085s, 2081w,sh, 2023s, 2013m, 1986vw, 1514w cm^{-1}. Anal. Found: C, 19.11; H, 0.27. $C_{16}H_3O_9F_5Os_3$ calcd.: C, 19.13; H, 0.30%. Mass spectrum: m/z 1006 (M^+, ^{192}Os). ^{1}H NMR ($CDCl_3$): δ −18.82 (s, 3H). $^{19}F\{^1H\}$ NMR ($CDCl_3$): δ −163.6 (m, 5F). For $H_2Os_3Re(CO)_{14}(CC_6F_5)$: ^{1}H NMR ($CDCl_3$): δ −17.98 (s, 1H); −20.70 (s, 1H). IR (C_6H_{12}): ν(CO) 2123w, 2097s, 2079s, 2043s, 2026vs, 2017s, 2012s,sh, 1991m, 1967vw, 1951w cm^{-1}. Mass spectrum: m/z 1336 (M^+, ^{192}Os, ^{187}Re). The other products, $H_3Os_3(CO)_9(\mu_3\text{-}CF)$ and $[H_3Os_3(CO)_9(\mu_3\text{-}CCO)]_2$, were characterized by comparison of their IR and ^{1}H NMR spectra with literature data [4,1].

Reaction of $H_3Ru_3(CO)_9(\mu_3\text{-}CBr)$ and $Re_2(CO)_{10}$ in hexafluorobenzene

A solution of $H_3Ru_3(CO)_9(\mu_3\text{-}CBr)$ (40 mg, 0.061 mmol) and $Re_2(CO)_{10}$ (40 mg, 0.061 mmol) in hexafluorobenzene (0.5 ml) was sealed under an atmosphere of carbon monoxide in an NMR tube. Photolysis for 3 h produced an orange solution and some dark red precipitate. TLC of the supernatant resulted in several overlapping bands. The first yellow band could be separated and $H_3Ru_3(CO)_9(\mu_3\text{-}CC_6F_5)$ (14 mg, 0.02 mmol, 33%) was isolated as a yellow solid. The other components were not adequately characterized, but the presence of $H_3Ru_3(CO)_9(\mu_3\text{-}CF)$ was indicated by ^{19}F NMR (δ −75.3, s).

For $H_3Ru_3(CO)_9(\mu_3\text{-}CC_6F_5)$: IR (in CH_2Cl_2): ν(CO) 2111w, 2087s, 2038s cm^{-1}. Anal. Found: C, 26.31; H, 0.68. $C_{16}H_3O_9F_5Ru_3$ calcd: C, 26.05; H, 0.41%. Mass spectrum: m/z 738 (M^+, ^{102}Ru). ^{1}H NMR ($CDCl_3$): δ −17.87 (s, 3H). $^{19}F\{^1H\}$ NMR ($CDCl_3$): δ −163.4 (m, 5F).

Reaction of $H_3Os_39CO)_9(\mu_3\text{-}CBr)$ and $Re_2(CO)_{10}$ in fluorobenzene

A solution of $H_3Os_3(CO)_9(\mu_3\text{-}CBr)$ (35 mg, 0.038 mmol) and $Re_2(CO)_{10}$ (40 mg, 0.043 mmol) in fluorobenzene (0.5 ml) was sealed under an atmosphere of carbon monoxide in an NMR tube. Photolysis for 10 h produced a dark red solution and some off-white precipate. The reaction mixture was separated by TLC to give five major bands. The first colorless band contained the starting material $H_3Os_3(CO)_9(\mu_3\text{-}CBr)$ (4 mg, 0.04 mmol, 9%). The second colorless band was $H_3Os_3(CO)_9(\mu_3\text{-}CH)$ (4 mg, 0.005 mmol, 10%). The third colorless band contained $H_3Os_3(CO)_9(\mu_3\text{-}CF)$ (2 mg, 0.002 mmol, 5%). The major colorless band was $H_3Os_3(CO)_9(\mu_3\text{-}CC_6H_5)$ (15 mg, 0.015 mmol, 40%). The fifth, pale yellow band was characterized as $H_3Os_3(CO)_9(\mu_3\text{-}CC_6H_4F)$ (4 mg, 0.004 mmol, 9%).

For $H_3Os_3(CO)_9(\mu_3\text{-}CC_6H_4F)$: IR($CH_2Cl_2$): ν(CO) 2110w, 2082s, 2022s, 2073w, 1992w cm^{-1}. Anal. Found: C, 21.22; H, 0.95. $C_{16}H_7O_9FOs_3$ calcd.: C, 20.60; H, 0.76%. ^1H NMR ($CDCl_3$): δ 7.2 (μ, 4H); −18.61 (s, 3H). $^{19}F\{^1H\}$ NMR ($CDCl_3$): δ −99.6(s). The other products were characterized by IR and ^1H NMR spectroscopy and comparison with literature data.

Reaction of $H_3Ru_3(CO)_9(\mu_3\text{-}CBr)$ and $Re_2(CO)_{10}$ in fluorobenzene

A solution of $H_3Ru_3(CO)_9(\mu_3\text{-}CBr)$ (30 mg, 0.046 mmol) and $Re_2(CO)_{10}$ (30 mg, 0.043 mmol) in fluorobenzene (0.5 ml) was sealed under an atmosphere of carbon monoxide in an NMR tube. Photolysis for 2 h produced a dark red solution and a considerable amount of brown precipitate. TLC of the solution produced numerous bands which did not separate very well in spite of repetitive elution. The IR and ^1H NMR spectra of the first major band indicated a mixture of $H_3Ru_3(CO)_9(\mu_3\text{-}CH)$ and $H_3Ru_3(CO)_9(\mu_3\text{-}CBr)$ (total mass 5 mg). The second band appeared to contain $H_3Ru_3(CO)_9(\mu_3\text{-}CPh)$ as the major component; however both $H_3Ru_3(CO)_9(\mu_3\text{-}CC_6H_4F)$ and $H_3Ru_3(CO)_9(\mu_3\text{-}CF)$ were also present. Data for this band were as follows: IR (CH_2Cl_2): ν(CO) 2106vw, 2080s,br, 2035s,br, 2030m, 2019m, 1993w cm^{-1}. ^1H NMR ($CDCl_3$): δ −17.49 (s, $H_3Ru_3(CO)_9(\mu_3-CPh)$; −17.52 (s, $H_3Ru_3(CO)_9(\mu_3\text{-}CC_6H_4F)$); −17.84 (s, $H_3Ru_3(CO)_9(\mu_3\text{-}CF)$). $^{19}F\{^1H\}$ NMR ($CDCl_3$): δ −75.3 (br, s, $H_3Ru_3(CO)_9(\mu_3\text{-}CF)$); −100 ($H_3Ru_3(CO)_9(\mu\text{-}CC_6H_4F)$). Repeated TLC of the product mixture did not result in clean separation of $H_3Ru_3(CO)_9(\mu_3\text{-}CC_6H_4F)$.

X-Ray crystallographic study on $H_3Os_3(CO)_9(\mu_3\text{-}CC_6F_5)$

Crystal data. $C_{16}H_3O_9F_5Os_3$, MW 1004,79, monoclinic, $P2_1/c$, $a = 12.127(10)$, $b = 9.386(5)$, $c = 18.298(15)$ Å, $\beta = 98.92(6)°$, $V = 2058(4)$ Å^3, $Z = 4$, $\rho(\text{calc}) = 3.243$ g cm^{-3}, $T = 223$ K, $\mu(\text{Mo-}K_\alpha) = 185.87$ cm^{-1}. Enraf-Nonius CAD4F diffractometer, graphite monochromator, $\lambda = 0.71073$ Å, crystal transparent yellow prism (0.2 × 0.2 × 0.4 mm), 3312 data collected ($2.0 < 2\theta < 46.0°$), 2128 observed reflections ($I_o > 2.58\sigma(I_o)$), $R_i = 0.055$. The data were corrected for Lorentz and polarization effects, anomalous dispersion, extinction, and absorption (numerical; max, min transmission factors = 0.084, 0.018); no crystal decay was observed.

Structure solution and refinement. The structure was solved by direct methods (SHELXS-86); correct positions for the osmium atoms were deduced from an *E*-map. Subsequent least-squares-difference Fourier calculations gave positions for the remaining non-hydrogen atoms. The hydrogen atom positions never surfaced in electron density maps. In the final cycle of least squares carbon atoms were refined with isotropic thermal coefficients and anisotropic thermal coefficients were refined for the remaining atoms. The highest residual electron density in the final difference Fourier map was located in the vicinity of the osmium atoms. Successful conver-

Table 1

Atomic coordinates and thermal parameters

Atom	x	y	z	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
Os1	0.74506(8)	0.9260(1)	0.12209(6)	0.0196(6)	0.0167(6)	0.0202(6)	−0.0001(5)	−0.0019(4)	0.0009(5)
Os2	0.72957(9)	0.7346(1)	−0.00157(5)	0.0237(6)	0.0204(7)	0.0159(6)	0.0008(5)	−0.0039(4)	0.0018(5)
Os3	0.92663(8)	0.7370(1)	0.10800(6)	0.0156(6)	0.0213(7)	0.0221(6)	0.0001(5)	−0.0006(4)	−0.0006(5)
F1	0.520(1)	0.680(2)	0.1087(8)	0.024(8)	0.03(1)	0.037(9)	0.008(8)	−0.009(7)	0.002(8)
F2	0.415(1)	0.478(2)	0.1738(9)	0.023(8)	0.05(1)	0.05(1)	0.000(9)	−0.003(8)	−0.015(8)
F3	0.535(2)	0.265(2)	0.2525(10)	0.07(1)	0.03(1)	0.05(1)	0.005(9)	0.03(1)	−0.015(10)
F4	0.759(1)	0.275(2)	0.2710(9)	0.04(1)	0.03(1)	0.05(1)	0.026(9)	−0.004(9)	−0.001(9)
F5	0.867(1)	0.473(2)	0.2111(8)	0.1028(8)	0.04(1)	0.045(10)	0.019(8)	0.007(7)	0.012(8)
O11	0.802(2)	0.952(2)	0.2891(9)	0.04(1)	0.06(2)	0.016(10)	0.01(1)	−0.000(8)	0.00(1)
O12	0.497(2)	0.979(3)	0.123(1)	0.05(1)	0.06(2)	0.06(1)	−0.01(1)	0.01(1)	0.01(1)
O13	0.790(2)	1.239(2)	0.091(10	0.04(1)	0.03(1)	0.05(1)	0.00(1)	−0.00(1)	−0.01(1)
O21	0.754(2)	0.423(2)	−0.044(1)	0.07(2)	0.03(1)	0.04(1)	−0.00(1)	−0.03(1)	0.02(1)
O22	0.478(2)	0.726(3)	−0.044(1)	0.04(1)	0.11(2)	0.02(1)	−0.02(1)	−0.009(10)	−0.01(1)
O23	0.757(2)	0.852(3)	−0.154(1)	0.12(2)	0.05(2)	0.04(1)	0.00(1)	0.01(1)	−0.01(2)
O31	0.997(1)	0.433(2)	0.082(1)	0.03(1)	0.04(1)	0.05(1)	−0.01(1)	−0.005(9)	0.00(1)
O32	1.136(2)	0.884(2)	0.065(1)	0.05(1)	0.05(2)	0.08(2)	0.03(1)	0.04(1)	−0.00(1)
O33	1.008(2)	0.707(2)	0.274(1)	0.04(1)	0.05(2)	0.03(1)	0.00(1)	−0.011(10)	−0.02(1)
C1	0.752(2)	0.704(3)	0.116(1)	0.016(6)					
C2	0.700(2)	0.589(3)	0.154(1)	0.021(6)					
C3	0.583(2)	0.583(3)	0.150(1)	0.016(5)					
C4	0.530(2)	0.484(3)	0.183(1)	0.022(6)					
C5	0.588(2)	0.365(3)	0.224(1)	0.028(7)					
C6	0.701(2)	0.380(3)	0.229(1)	0.025(6)					
C7	0.757(2)	0.483(3)	0.199(1)	0.021(6)					
C11	0.775(2)	0.943(3)	0.229(2)	0.034(7)					
C12	0.590(2)	0.952(3)	0.120(1)	0.030(7)					
C13	0.777(2)	1.124(3)	0.103(2)	0.031(7)					
C21	0.744(2)	0.541(3)	−0.030(2)	0.027(7)					
C22	0.575(2)	0.722(3)	−0.026(1)	0.022(6)					
C23	0.754(2)	0.805(3)	−0.098(2)	0.032(7)					
C31	0.971(2)	0.547(3)	0.092(2)	0.032(7)					
C32	1.064(3)	0.833(3)	0.080(2)	0.034(7)					
C33	0.982(3)	0.723(3)	0.211(2)	0.038(8)					

gence was indicated by the maximum shift/error for the last cycle. Final agreements factors were $R = 0.058$; $R_w = 0.066$. A final analysis of variance between observed and calculated structure factors showed a slight dependence on sin(θ). The accuracy of absorption correction was hampered by the rounded edges of the crystal. The high residual electron density ($+3.02 > e/\text{Å} > -3.73$) and relatively high agreement factors are most likely a direct consequence of this problem. Table 1 shows the final atomic coordinates and thermal parameters, and the molecular structure is displayed in Fig. 1.

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