

The Thermal and Photochemical Reactions of $[\text{Ru}_3(\text{CO})_{12}]$ with Tetraethyldiphosphite. X-ray Structure of $[\text{Ru}_3(\text{CO})_{10}\{\mu\text{-(EtO)}_2\text{POP(OEt)}_2\}]$

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Abstract

The thermal reaction (70 °C) of $[\text{Ru}_3(\text{CO})_{12}]$ with tetraethyldiphosphite $[(\text{EtO})_2\text{POP(OEt)}_2, \text{tedip}]$ (1/1 equivalent ratio) gives a mixture of at least five compounds which includes $[\text{Ru}_3(\text{CO})_{10}(\mu\text{-tedip})]$ (1), $[\text{Ru}_3(\text{CO})_8(\mu\text{-tedip})_2]$ (2) and $[\text{Ru}_3(\text{CO})_6(\mu\text{-tedip})_3]$ (3). However, under photochemical conditions (10 °C, mercury lamp) only $[\text{Ru}_3(\text{CO})_{10}(\mu\text{-tedip})]$ was produced. With higher proportions of tedip both the thermal and photochemical routes give mixtures of 1, 2 and 3 along with other unidentified products. Complex 2 could not be separated pure in any case. The structure of complex 1 has been determined by X-ray diffraction methods; it is similar to that of $[\text{Ru}_3(\text{CO})_{12}]$ in which two equatorial carbonyl groups have been replaced by the two P atoms of the tedip ligand.

Introduction

Fragmentation of the framework of triruthenium clusters can be easily achieved photochemically; in fact, irradiation of $[\text{Ru}_3(\text{CO})_{12}]$ in the presence of CO has been found to give $[\text{Ru}(\text{CO})_5]$ [1]. In addition, the photochemical reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with bis(diphenylphosphino)methane (dppm) gives $[\text{Ru}_3(\text{CO})_{10}(\mu\text{-dppm})]$ and $[\text{Ru}_2(\mu\text{-CO})(\text{CO})_4(\mu\text{-dppm})_2]$, depending on the reaction conditions [2]. However, after irradiation of $[\text{Ru}_3(\text{CO})_{12}]$ with different amounts of bis(dimethylphosphino)methane (dmpm) no fragmentation of the cluster framework was observed and only trinuclear products with different degrees of substitution were isolated [2]. The photochemical reactions of $[\text{Ru}_3(\text{CO})_{12}]$ with some diphosphazanes $[(\text{RO})_2\text{PN}(\text{Et})\text{P}(\text{OR})_2]$ have also been studied, affording $[\text{Ru}_3(\text{CO})_{10}\{\mu\text{-(RO)}_2\text{PN}(\text{Et})\text{P}(\text{OR})_2\}]$ and $[\text{Ru}_2(\mu\text{-CO})(\text{CO})_4\{\mu\text{-(RO)}_2\text{PN}(\text{Et})\text{P}(\text{OR})_2\}_2]$ depending on the cluster to ligand ratio

used [3]. The mononuclear species $[\text{Ru}(\text{CO})_3\{\text{Ph}_2\text{PN}(\text{Et})\text{PPh}_2\}]$ has also been prepared by irradiation of $[\text{Ru}_3(\text{CO})_{12}]$ with an excess of bis(diphenylphosphino)ethylamine [2].

On the other hand, the thermal reactions of $[\text{Ru}_3(\text{CO})_{12}]$ with dppm [4–9] and dmpm [10] have been extensively studied, and a range of trinuclear products, in which one, two or three bridging diphosphine ligands are in the positions originally occupied by two, four or six equatorial CO groups, have been isolated. With these two ligands no cluster fragmentation nor ligand degradation have been reported working at temperatures below 70 °C [5, 10]. However, at higher temperatures, $[\text{Ru}_3(\text{CO})_{10}(\mu\text{-dppm})]$ degrades to $[\text{Ru}_3\{\mu_3\text{-}\eta^3\text{-PhPCH}_2\text{-P}(\text{Ph})\text{C}_6\text{H}_4\}(\text{CO})_9]$ and $[\text{Ru}_3(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-PhPCH}_2\text{-PPh}_2)(\text{CO})_9]$ [11], whereas $[\text{Ru}_3(\text{CO})_{10}(\mu\text{-dmpm})]$ gives $[\text{Ru}_3(\mu\text{-H})(\mu_3\text{-}\eta^3\text{-Me}_2\text{PCHPM}_2)(\text{CO})_9]$ [10].

We now report the reactions of tetraethyldiphosphite $[(\text{EtO})_2\text{POP(OEt)}_2, \text{tedip}]$ with $[\text{Ru}_3(\text{CO})_{12}]$ under thermal and photochemical conditions, along with the X-ray structure of $[\text{Ru}_3(\text{CO})_{10}(\mu\text{-tedip})]$. To our knowledge, no reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with a diphosphite has previously been reported.

Experimental

C and H analyses were obtained with a Perkin-Elmer 240-B microanalyzer. IR spectra were recorded with 0.1 mm CaF_2 solution cells on a Perkin-Elmer FT 1720-X spectrophotometer. ^1H and ^{31}P NMR spectra were recorded at 25 °C on a Bruker AC-300 spectrometer, being referenced ($\delta = 0$ ppm) to internal SiMe_4 and external 85% H_3PO_4 , respectively. Solvents were dried and distilled prior to use. $[\text{Ru}_3(\text{CO})_{12}]$ was prepared as published elsewhere [12]. Tetraethyldiphosphite was obtained from Aldrich and was stored under nitrogen in a Young tube. The reactions were carried out under nitrogen.

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The Thermal Reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with *tedip*

$[\text{Ru}_3(\text{CO})_{12}]$ (300 mg, 0.47 mmol) and *tedip* (124 mg, 0.48 mmol) were stirred in 50 ml of hexane at 70 °C for 2.5 h. The red–orange solution was cooled down to room temperature and neutral alumina (*c.* 1 g, activity I) was added. The mixture was vacuum evaporated to dryness and the residue was transferred to a chromatography column packed with neutral alumina (10 × 3 cm, activity I) in hexane. Hexane eluted a trace amount of $[\text{Ru}_3(\text{CO})_{12}]$ followed by a yellow band which on evaporation yielded $[\text{Ru}_3(\text{CO})_6(\mu\text{-tedip})_3]$ (**3**) (40 mg, 7%). *Anal.* Found: C, 29.4; H, 5.0. Calc. for $\text{C}_{30}\text{H}_{60}\text{O}_{21}\text{P}_6\text{Ru}_3$: C, 28.93; H, 4.85%. $\nu(\text{CO})$ (hexane, cm^{-1}): 2100w, 2047s, 2031s, 2016vs, 1997m, 1991m. ^1H NMR (CDCl_3 , δ , ppm): 4.03 (quintet, $^3J(\text{P-H}) = ^3J(\text{H-H}) = 7.1$ Hz, 2H), 1.55 (t, $^3J(\text{H-H}) = 7.1$ Hz, 3H); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , δ , ppm): 133.4(s). Further elution of the column with toluene/hexane (1/3) gave a yellow–orange band which on evaporation to dryness afforded $[\text{Ru}_3(\text{CO})_{10}(\mu\text{-tedip})]$ (**3**) (180 mg, 45%) as a red–orange solid. *Anal.* Found: C, 26.3; H, 2.4. Calc. for $\text{C}_{18}\text{H}_{20}\text{O}_{15}\text{P}_2\text{Ru}_3$: C, 25.69; H, 2.40%. $\nu(\text{CO})$ (hexane, cm^{-1}): 2091m, 2061w, 2009s, 1988m, 1975m. ^1H NMR (CDCl_3 , δ , ppm): 4.04 (m, 2H), 1.38 (t, $J = 7.1$ Hz, 3H). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , δ , ppm): 127.8(s). Further elution of the column with toluene gave a yellow band containing a small amount of an as yet unidentified compound which only has terminal carbonyls. Toluene/THF (5/1) eluted a brown band; the $^{31}\text{P}\{^1\text{H}\}$ NMR of this fraction indicated that it was a mixture of several compounds which contained $[\text{Ru}_3(\text{CO})_8(\mu\text{-tedip})_2]$ (**2**) (an AA'BB' pattern centered at δ 133 ppm).

When $[\text{Ru}_3(\text{CO})_{12}]$ (300 mg, 0.47 mmol) and *tedip* (124 mg, 144 mmol) were refluxed in 50 ml of hexane for 6 h, the complexes **1** (162 mg, 41%) and **3** (88 mg, 15%) could be isolated, but complex **2**, although detected by ^{31}P NMR spectroscopy, could not be separated.

The Photochemical Reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with *tedip*

$[\text{Ru}_3(\text{CO})_{12}]$ (300 mg, 0.47 mmol) and *tedip* (124 mg, 0.48 mmol) were irradiated with a 400 W mercury lamp in 50 ml of THF, at 10 °C, for 1.5 h. The solution was worked up as above. The products from the chromatography were a trace amount of $[\text{Ru}_3(\text{CO})_{12}]$ and complex **1** (300 mg, 76%).

When $[\text{Ru}_3(\text{CO})_{12}]$ (300 mg, 0.47 mmol) and *tedip* (372 mg, 1.44 mmol) were irradiated in 50 ml of THF, at 10 °C, for 6 h, the complexes **1** (146 mg, 37%) and **3** (106 mg, 18%) were isolated, but complex **2**, although detected, could not be separated.

Crystal Structure Determination of $[\text{Ru}_3(\text{CO})_{10}(\mu\text{-tedip})]$ (**1**)

Crystal data

$\text{C}_{18}\text{H}_{20}\text{O}_{15}\text{P}_2\text{Ru}_3$, $M = 841.5$, monoclinic, $a = 8.650(2)$, $b = 17.652(2)$, $c = 19.542(4)$ Å, $\beta = 97.48(3)^\circ$, cell dimensions from least-squares refinements of 25 reflections in the range $14 \leq \theta \leq 15^\circ$, $U = 2958(1)$, $Z = 4$, $D_c = 1.89$ g cm^{-3} , $F(000) = 1640$, space group $P2_1/n$, $\lambda(\text{Mo K}\alpha) 0.71069$ Å, $\mu(\text{Mo K}\alpha) 16.5$ cm^{-1} .

A deep red crystal of compound **1** (0.3 × 0.3 × 0.3 mm) was grown from methanol at –20 °C. Data were collected at room temperature on a CAD4 Enraf Nonius diffractometer ($\omega/2\theta$ mode) using Mo K α radiation (graphite monochromator) and scan width $1.2 + 0.34\tan\theta$. 5189 reflections were collected in the range $1.5 \leq \theta \leq 25^\circ$, 2577 reflections (with $F \geq 2\sigma(F)$) were used for computations. An empirical (ψ -scan based) absorption correction [13] was applied (max. 1.03, min. 1.00). The structure was solved by direct methods with SHELX [14] and subsequent Fourier maps. Least-squares refinements (345 parameters) were made with an approximation in two blocks to the normal matrix. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions ($\text{C-H} = 0.96$ Å, overall temperature factor 0.8 Å²), and their coordinates (not refined) were recalculated after each cycle. The weighting scheme was $w = w'[1 - \{(AF)/6\sigma(F_o)\}^2]$ [15], where $w' = 1/E^2 \sum_{r=1}^n ArTr(\vec{x})$ with three coefficients Ar (5.000, –2.892, 3.817) for the Chebyshev polynomial $ArTr(x)$ [$x = F_c/F_c(\text{max})$]. Refinements converged at R 0.035 (R_w 0.037). All calculations were performed with CRYSTALS [16]. Scattering factors, with correction for anomalous dispersion were also from CRYSTALS.

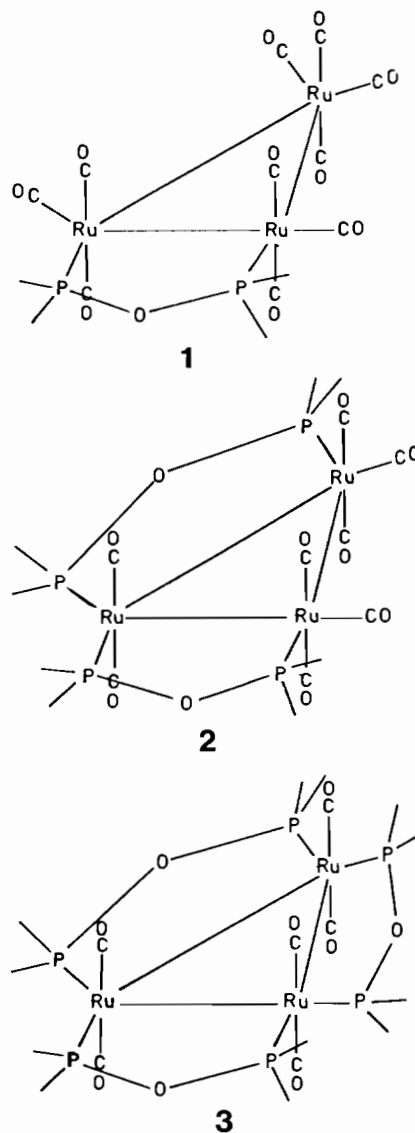
Fractional atomic coordinates and selected interatomic distances and angles are listed in Tables 1 and 2, respectively. See also 'Supplementary Material'.

Results and Discussion

The reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with *tedip* in refluxing hexane has been found to give a mixture of compounds, even carrying out the reaction with a 1/1 mol ratio of the reactants. Column chromatography of the mixture allowed the isolation of $[\text{Ru}_3(\text{CO})_{10}(\mu\text{-tedip})]$ (**1**) and $[\text{Ru}_3(\text{CO})_6(\mu\text{-tedip})_3]$ (**3**) (Scheme 1). The complex $[\text{Ru}_3(\text{CO})_8(\mu\text{-tedip})_2]$ (**2**) was also produced in the reaction, but it could not be obtained pure. The relative amounts of these products depended on the proportion of the reactants, complex **1** being always the major component of the mixtures. As expected, no fragmentation of

TABLE 1. Fractional atomic coordinates and thermal parameters for $[\text{Ru}_3(\text{CO})_{10}(\mu\text{-tedip})]$ (1)

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> (eq)
Ru(1)	0.20602(8)	0.21375(3)	0.09549(3)	0.0562
Ru(2)	-0.00388(8)	0.23065(3)	0.19294(3)	0.0568
Ru(3)	0.00489(8)	0.34179(3)	0.08839(3)	0.0614
O(1)	-0.0278(8)	0.1011(4)	0.0221(4)	0.0934
O(2)	0.4496(8)	0.3233(4)	0.1661(4)	0.1020
O(3)	0.377(1)	0.2199(5)	-0.0304(4)	0.1234
O(4)	0.2715(9)	0.2844(4)	0.2943(4)	0.1054
O(5)	-0.222(1)	0.2892(6)	0.2904(5)	0.1371
O(6)	-0.2897(8)	0.1773(4)	0.0964(4)	0.0921
O(7)	-0.166(1)	0.2551(5)	-0.0350(4)	0.1115
O(8)	-0.287(1)	0.4300(5)	0.1099(5)	0.1177
O(9)	0.178(1)	0.4274(4)	0.2101(4)	0.1116
O(10)	0.162(1)	0.4425(5)	-0.0063(4)	0.1315
C(1)	0.053(1)	0.1453(5)	0.0498(4)	0.0682
C(2)	0.352(1)	0.2849(5)	0.1418(5)	0.0745
C(3)	0.316(1)	0.2184(6)	0.0175(5)	0.0844
C(4)	0.175(1)	0.2664(5)	0.2538(5)	0.0729
C(5)	-0.142(1)	0.2676(6)	0.2531(5)	0.0900
C(6)	-0.178(1)	0.1983(5)	0.1291(4)	0.0702
C(7)	-0.099(1)	0.2825(5)	0.0125(5)	0.0775
C(8)	-0.182(1)	0.3954(5)	0.1019(5)	0.0855
C(9)	0.118(1)	0.3900(5)	0.1674(6)	0.0801
C(10)	0.101(1)	0.4028(6)	0.0285(5)	0.0906
P(1)	0.3200(3)	0.1177(1)	0.1592(1)	0.0649
P(2)	0.0498(3)	0.1108(1)	0.2279(1)	0.0620
O(11)	0.2089(6)	0.0761(3)	0.2072(3)	0.0714
O(12)	0.4640(7)	0.1427(3)	0.2110(3)	0.0813
C(12)	0.551(1)	0.0901(7)	0.2608(6)	0.1003
C(15)	0.551(2)	0.123(1)	0.3287(7)	0.1364
O(13)	0.387(1)	0.0456(4)	0.1255(5)	0.1130
C(13)	0.334(2)	0.0042(9)	0.0766(9)	0.1597
C(16)	0.400(2)	-0.0723(3)	0.0777(9)	0.1438
O(22)	-0.0745(6)	0.0521(3)	0.1960(3)	0.0717
C(22)	-0.055(1)	-0.0315(5)	0.2067(6)	0.0942
C(25)	-0.103(2)	-0.0676(7)	0.1385(7)	0.1380
O(23)	0.082(1)	0.0881(4)	0.3059(4)	0.1159
C(23)	0.038(2)	0.119(1)	0.3625(6)	0.1290
C(26)	0.063(2)	0.080(1)	0.4250(6)	0.1387



Scheme 1.

TABLE 2. Selected bond distances, angles and torsion angles for $[\text{Ru}_3(\text{CO})_{10}(\mu\text{-tedip})]$ (1)

Bond distances (Å)					
Ru(1)	Ru(2)	2.8131(9)	Ru(1)	Ru(3)	2.8446(9)
Ru(1)	C(1)	1.92(1)	Ru(1)	C(2)	1.92(1)
Ru(1)	C(3)	1.90(1)	Ru(1)	P(1)	2.254(2)
Ru(2)	Ru(3)	2.8408(9)	Ru(2)	C(4)	1.93(1)
Ru(2)	C(5)	1.90(1)	Ru(2)	C(6)	1.91(1)
Ru(1)	P(2)	2.253(2)	Ru(3)	C(7)	1.94(1)
Ru(3)	C(8)	1.92(1)	Ru(3)	C(9)	1.92(1)
Ru(3)	C(10)	1.96(1)	P(1)	O(11)	1.606(6)
P(1)	O(12)	1.564(6)	P(1)	O(13)	1.576(8)
P(2)	O(11)	1.604(6)	P(2)	O(22)	1.563(6)
P(2)	O(23)	1.566(7)			

(continued)

TABLE 2. (continued)

Bond angles (°)							
Ru(3)	Ru(1)	Ru(2)	60.28(2)	C(1)	Ru(1)	Ru(2)	85.1(2)
C(1)	Ru(1)	Ru(3)	95.6(2)	C(2)	Ru(1)	Ru(2)	93.2(3)
C(2)	Ru(1)	Ru(3)	82.2(3)	C(2)	Ru(1)	C(1)	177.7(4)
C(3)	Ru(1)	Ru(2)	166.6(3)	C(3)	Ru(1)	Ru(3)	107.1(3)
C(3)	Ru(1)	C(1)	92.3(4)	C(3)	Ru(1)	C(2)	89.0(4)
P(1)	Ru(1)	Ru(2)	88.88(6)	P(1)	Ru(1)	Ru(3)	147.75(1)
P(1)	Ru(1)	C(1)	90.5(2)	P(1)	Ru(1)	C(2)	91.0(3)
P(1)	Ru(1)	C(3)	104.3(3)	Ru(3)	Ru(2)	Ru(1)	60.4(2)
C(4)	Ru(2)	Ru(1)	85.1(3)	C(4)	Ru(2)	Ru(3)	97.0(3)
C(5)	Ru(2)	Ru(1)	165.9(3)	C(5)	Ru(2)	Ru(3)	106.6(3)
C(5)	Ru(2)	C(4)	91.4(4)	C(6)	Ru(2)	Ru(1)	92.9(3)
C(6)	Ru(2)	Ru(3)	80.2(3)	C(6)	Ru(2)	C(4)	177.2(4)
C(6)	Ru(2)	C(5)	90.0(4)	P(2)	Ru(2)	Ru(1)	88.84(6)
P(2)	Ru(2)	Ru(3)	147.43(6)	P(2)	Ru(2)	C(4)	90.2(3)
P(2)	Ru(2)	C(5)	104.9(3)	P(2)	Ru(2)	C(6)	91.8(3)
Ru(2)	Ru(3)	Ru(1)	59.31(2)	C(7)	Ru(3)	Ru(1)	80.0(3)
C(7)	Ru(3)	Ru(2)	97.2(2)	C(8)	Ru(3)	Ru(1)	154.8(3)
C(8)	Ru(3)	Ru(2)	98.0(3)	C(8)	Ru(3)	C(7)	93.3(4)
C(9)	Ru(3)	Ru(1)	93.9(3)	C(9)	Ru(3)	Ru(2)	77.7(3)
C(9)	Ru(3)	C(7)	173.5(4)	C(9)	Ru(3)	C(8)	91.3(4)
C(10)	Ru(3)	Ru(1)	99.8(3)	C(10)	Ru(3)	Ru(2)	155.0(3)
C(10)	Ru(3)	C(7)	91.8(4)	C(10)	Ru(3)	C(8)	104.7(4)
C(10)	Ru(3)	C(9)	91.5(4)	O(11)	P(1)	Ru(1)	114.5(2)
O(12)	P(1)	Ru(1)	113.5(2)	O(12)	P(1)	O(11)	103.7(3)
O(13)	P(1)	Ru(1)	122.3(3)	O(13)	P(1)	O(11)	99.0(4)
O(13)	P(1)	O(12)	101.2(4)	O(11)	P(2)	Ru(2)	115.6(2)
O(22)	P(2)	Ru(2)	113.4(2)	O(22)	P(2)	O(11)	102.4(3)
O(23)	P(2)	Ru(2)	122.6(3)	O(23)	P(2)	O(11)	95.7(4)
O(23)	P(2)	O(22)	104.1(4)	P(2)	O(11)	P(1)	124.8(3)
Torsion angles (°)							
C(1)	Ru(1)	Ru(2)	C(6)	22.2(4)			
C(1)	Ru(1)	Ru(3)	C(7)	23.4(4)			
C(2)	Ru(1)	Ru(2)	C(4)	21.8(4)			
C(2)	Ru(1)	Ru(3)	C(9)	25.0(4)			
C(3)	Ru(1)	Ru(3)	C(10)	19.3(4)			
C(4)	Ru(2)	Ru(3)	C(9)	21.9(4)			
C(5)	Ru(2)	Ru(3)	C(8)	17.8(4)			
C(6)	Ru(2)	Ru(3)	C(7)	25.0(4)			
P(1)	Ru(1)	Ru(2)	P(2)	21.09(8)			
C(2)	Ru(1)	P(1)	O(12)	1.3(4)			
C(6)	Ru(2)	P(2)	O(22)	5.9(4)			

the cluster framework was observed, since the refluxing temperature of hexane (69 °C) is not high enough to produce the break up of the Ru–Ru bonds [5]. Although the tedip ligand in compounds 1–3 remains intact, ligand degradation during the reaction cannot be ruled out, since some other products of the reaction could not be identified. Thermal degradation of coordinated tedip has not yet been reported, although it is well known for dmpm [10] and dppm [11].

When $[\text{Ru}_3(\text{CO})_{12}]$ was irradiated with tedip, in a 1/1 mol ratio, complex 1 was formed selectively. However, an increase of the proportion of tedip in the photochemical reactions led to mixtures where-

from complexes 1 and 3 could be separated, and complex 2 could be identified spectroscopically. In this case, although only trinuclear products were observed, cluster fragmentation cannot be excluded since some other products still remain unidentified. Moreover, it is known that the photochemical reactions of $[\text{Ru}_3(\text{CO})_{12}]$ with excess of dppm or diphosphazanes produce $[\text{Ru}_2(\mu\text{-CO})(\text{CO})_4(\mu\text{-L}_2)_2]$ ($\text{L}_2 = \text{dppm}$ [2] or $(\text{RO})_2\text{PN}(\text{Et})\text{P}(\text{OR})_2$ [3]).

Very recently, it has been shown that irradiation of $[\text{Ru}_3(\text{CO})_{10}(\mu\text{-dppm})]$ [17] under carbon monoxide gives $[\text{Ru}(\text{CO})_5]$ and $[\text{Ru}_2(\mu\text{-CO})(\text{CO})_6(\mu\text{-dppm})]$ [18]. However, under identical conditions, complex 1 remains unaltered.

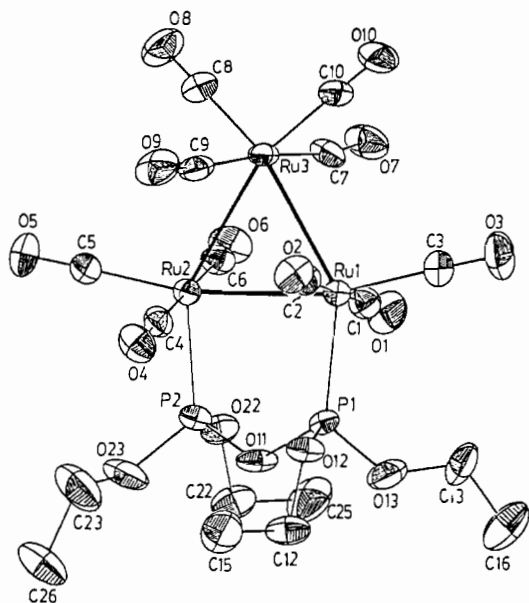


Fig. 1. ORTEP diagram of $[\text{Ru}_3(\text{CO})_{10}(\mu\text{-tedip})]$ (**1**) with the atomic numbering scheme.

The Crystal Structure of $[\text{Ru}_3(\text{CO})_{10}(\mu\text{-tedip})]$ (**1**)

The X-ray structure of complex **1** is depicted in Fig. 1. The structure resembles that of $[\text{Ru}_3(\text{CO})_{12}]$ in which two equatorial carbonyl groups have been replaced by the tedip ligand. The structure is also related to those of $[\text{Ru}_3(\text{CO})_{10}(\mu\text{-dppm})]$ [7] and $[\text{Ru}_3(\text{CO})_{10}(\mu\text{-dppea})]$ [2] [dppea = bis(diphenylphosphino)ethylamine], but some points are worth noting.

In complex **1** the bridged Ru–Ru edge is 0.030 Å shorter (Table 2) than the average of the other two edges; this difference is in between those found in $[\text{Ru}_3(\text{CO})_{10}(\mu\text{-dppm})]$ (0.017 Å) and $[\text{Ru}_3(\text{CO})_{10}(\mu\text{-dppea})]$ (0.055 Å), suggesting that the bite of the tedip ligand is intermediate between those of dppm and dppea. In fact, although the distances P(1)–O(11) and P(2)–O(11) (av. 1.605 Å) are much shorter than those found between the bridging atom (X) and the phosphorous atoms in $[\text{Ru}_3(\text{CO})_{10}(\mu\text{-dppm})]$ (av. 1.849 Å) and in $[\text{Ru}_3(\text{CO})_{10}(\mu\text{-dppea})]$ (av. 1.720 Å), the angle P–X–P in the latter (X = N) (118°) is much more acute than that of the tedip ligand (X = O) (125°) in complex **1**.

Unlike in $[\text{Ru}_3(\text{CO})_{12}]$, where the carbonyl groups adopt an eclipsed configuration [19], in complex **1** the carbonyl groups are markedly staggered, with torsion angles (Table 2) which deviate *c.* 20° from the idealized eclipsed configuration. This distortion, which can be clearly seen in Fig. 2, has to be related to the strain imposed by the bridging ligand. The two P atoms are one above [+0.439(2) Å, P(2)] and the other below [–0.386(2) Å, P(1)] the tri-ruthenium plane, giving a P(1)–Ru(1)–Ru(2)–P(2)

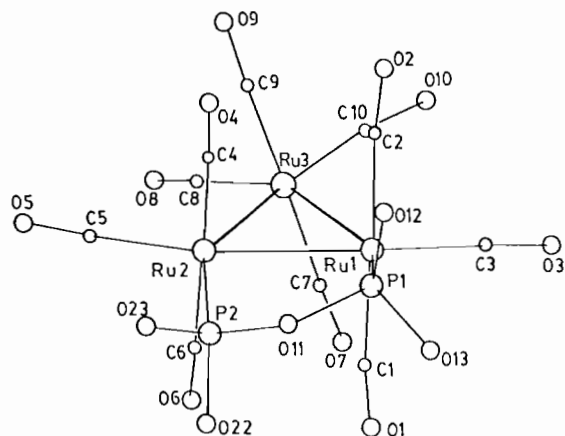


Fig. 2. Perspective view of $[\text{Ru}_3(\text{CO})_{10}(\mu\text{-tedip})]$ (**1**) showing the staggering of the CO ligands. The ethyl groups have been omitted for clarity.

torsion angle of 21.09(8)°. This angle is intermediate between those reported for $[\text{Ru}_3(\text{CO})_{10}(\mu\text{-dppm})]$ (19.1°) and $[\text{Ru}_3(\text{CO})_{10}(\mu\text{-dppea})]$ (24.4°), where the same type of distortion has been observed.

Supplementary Material

A complete table of fractional coordinates, including H atoms; a table of anisotropic thermal parameters, and a table of structure factors are available from the authors on request.

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