Journal of Organometallic Chemistry, 235 (1982) 83—91
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

CLUSTER CHEMISTRY

X *. PREPARATION OF 1,2-BIS(DIPHENYLPHOSPHINO)ETHANE DERIVATIVES OF $Ru_3(CO)_{12}$: CRYSTAL AND MOLECULAR STRUCTURES OF $Ru_3(CO)_{10}(\mu\text{-}Ph_2PCH_2CH_2PPh_2)$

MICHAEL I. BRUCE *, TREVOR W. HAMBLEY, BRIAN K. NICHOLSON ** and
MICHAEL R. SNOW

Jordan Laboratories, Department of Physical and Inorganic Chemistry, University of Adelaide, Adelaide, South Australia 5001 (Australia)

(Received March 1st, 1982)

Summary

The reactions of dppe with $Ru_3(CO)_{12}$ catalysed by $Ph_2CO^{\cdot-}$ have been investigated. Under the appropriate conditions $Ru_3(CO)_{11}(PPh_2CH_2CH_2PPh_2)$ (with only one P atom coordinated), $[Ru_3(CO)_{11}]_2(\mu\text{-dppe})$ (with one dppe ligand bridging two $Ru_3(CO)_{11}$ clusters), $Ru_3(CO)_{10}(\mu\text{-dppe})$ and $Ru_3(CO)_8(\mu\text{-dppe})_2$ (both with dppe bridging Ru—Ru bonds) can all be isolated in good yields. A full X-ray crystallographic analysis of $Ru_3(CO)_{10}(\mu\text{-dppe})$ shows that it crystallizes in the triclinic system, space group $P\bar{1}$, a 10.615(2), b 11.769(6), c 16.584(4) Å, α 75.68(2), β 84.59(2), γ 69.64(2)°. The structure was refined to $R = 0.030$, $R_w = 0.034$ using 3558 data with $I \geqslant 2.5\,\sigma(I)$. The dppe ligand bridges a Ru—Ru bond (2.856(1) Å), occupying equatorial sites on adjacent Ru atoms. Other distances: non-bridged Ru—Ru bonds are 2.855(1), 2.847(1); Ru—P, 2.330(2) Å.

Introduction

The reactions of $Ru_3(CO)_{12}$ with bidentate ligands have not been extensively studied [2]. Reasonably detailed reports are available for $Ru_3(CO)_{10}(dppm)$ [3] *** and for derivatives $Ru_3(CO)_{10}(L_2)$ where L_2 = ffos, ffars or $f_6$fos [4]. More

---

[*] For part IX, see ref. 1.

[**] On leave from the University of Waikato, Hamilton, New Zealand.

[***] Abbreviations: dppe = 1,2-bis(diphenylphosphino)ethane, $Ph_2P(CH_2)_2PPh_2$; dppm = bis(diphenylphosphino)methane, $CH_2(PPh_2)_2$; ffars = 1,2-bis(dimethylarsino)tetrafluorocyclobut-1-ene $(Me_2As)\overline{C{=}C(AsMe_2)CF_2C}F_2$; ffos = 1,2-bis(diphenylphosphino)tetrafluorocyclobut-1-ene $(Ph_2P)\overline{C{=}C(PPh_2)CF_2C}F_2$; $f_6$fos = 1,2-bis(diphenylphosphino)hexafluorocyclopent-1-ene, $(Ph_2P)\overline{C{=}C(PPh_2)CF_2CF_2C}F_2$.

0022-328X/82/0000—0000/$02.75

highly substituted species $Ru_3(CO)_8(L_2)_2$ (L_2 = ffos, ffars) are also known [5] and very recently $Ru_3(CO)_8(dppm)_2$ has been briefly mentioned [6]. With dppe the only characterised derivative is $Ru_3(CO)_{10}(dppe)$ prepared in low yield (3%) by a thermal reaction between $Ru_3(CO)_{12}$ and dppe [7].

We have recently described [8] substitution of $Ru_3(CO)_{12}$ (and of other clusters) with Group V donor ligands catalysed by sodium benzophenone ketyl, $Na^+Ph_2CO^-$ under mild conditions. Specific products $Ru_3(CO)_{12-n}(L)_n$ (L = PR_3, R = alkyl, aryl; $P(OR)_3$, R = alkyl, aryl; $AsPh_3$, $SbPh_3$, n = 1—3) were obtained in stoichiometric reactions and in much higher yields than were previously possible in thermal or photochemical reactions.

We now report on the Ph_2CO^- catalysed reaction between $Ru_3(CO)_{12}$ and dppe, and describe the crystal structure of one of the products, $Ru_3(CO)_{10}$(μ-dppe).

Experimental

Substitution reactions were conducted under nitrogen, but subsequent workup was carried out without any precautions to exclude oxygen. Solvents were dried over Na wire, except for tetrahydrofuran (THF) which was freshly distilled from sodium benzophenone ketyl before use. Light petroleum refers to 40—60°C fraction. $Ru_3(CO)_{12}$ was prepared by a standard method [9] and dppe (Strem) was used as received.

Preparation of catalyst. A solution of benzophenone (90 mg, 0.5 mmol) in THF (20 cm^3) was stirred over sodium metal for one hour to give a purple solution assumed to be ca. 0.025 mol l^{-1} in Ph_2CO^-.

Preparation of $Ru_3(CO)_{11}(\eta^1$-dppe) (1)

A mixture of $Ru_3(CO)_{12}$ (100 mg, 0.156 mmol) and dppe (70 mg, 0.176 mmol) in THF (6 cm^3) was warmed to ca. 40°C to dissolve all of the carbonyl. A solution of Ph_2CO^- in THF was added dropwise from a syringe until the solution darkened and the 2061 cm^{-1} band of $Ru_3(CO)_{12}$ was absent (2—5 drops). Solvent was removed and the residue extracted with light petroleum (50 cm^3). After filtration the extract was cooled to —30°C to give a brick-red precipitate, characterised as $Ru_3(CO)_{11}(\eta^1\text{-}PPh_2CH_2CH_2PPh_2)$ (1), ν(CO) (hexane) 2097m, 2047s, 2026sh, 2018s, 2000w, 1990w cm^{-1}. Contamination with varying amounts of $Ru_3(CO)_{10}(\mu$-dppe), evidenced by the ν(CO) band at 2078 cm^{-1}, could not be avoided and acceptable C, H analyses were not obtained. (e.g. Found: C, 47.4; H, 3.1; $C_{37}H_{24}O_{11}P_2Ru_3$ calcd.: C, 44.02; H, 2.39%).

Preparation of $[Ru_3(CO)_{11}]_2(\mu$-dppe) (2)

A solution of $Ru_3(CO)_{12}$ (200 mg, 0.312 mmol) and dppe (61 mg, 0.150 mmol) in THF (10 cm^3) at 40°C was treated dropwise with Ph_2CO^- until all the $Ru_3(CO)_{12}$ was consumed (IR). Solvent was removed and the residue dissolved in benzene. Addition of EtOH and cooling gave orange crystals of $Ru_3(CO)_{11}(PPh_2CH_2CH_2PPh_2)Ru_3(CO)_{11}$ (2), (104 mg, 43%); ν(CO) (hexane) 2098m, 2048s, 2030s, 2028sh, 2017vs cm^{-1}; m.p. >145°C (dec.); Found: C, 36.45; H, 1.23; $C_{48}H_{24}O_{22}P_2Ru_6$ calcd.: C, 35.57; H, 1.49%.

Preparation of $Ru_3(CO)_{10}(\mu$-dppe) (3)

A mixture of $Ru_3(CO)_{12}$ (100 mg, 0.156 mmol) and dppe (70 mg, 0.17 mmol) in THF (6 cm^3) at 40° C was treated with a solution of $Ph_2CO^{\bar{\cdot}}$ in THF

TABLE 1

FINAL POSITIONAL PARAMETERS (X 10^4) FOR $Ru_3(CO)_{10}(\mu$-dppe)

Atom	x	y	z
Ru(1)	4736(1)	5881(1)	1994(1)
Ru(2)	3484(1)	8066(1)	2624(1)
Ru(3)	6047(1)	7674(1)	1828(1)
P(1)	3433(1)	4670(1)	2641(1)
P(2)	1322(1)	7992(1)	2929(1)
C(1)	1993(5)	5392(5)	3273(3)
C(2)	1012(5)	6626(5)	2768(4)
C(4)	4250(4)	3082(3)	4226(2)
C(5)	5007(4)	1991(3)	4747(2)
C(6)	5886(4)	1040(3)	4416(2)
C(7)	6007(4)	1180(3)	3564(2)
C(8)	5250(4)	2271(3)	3043(2)
C(3)	4371(4)	3222(3)	3374(2)
C(10)	2028(5)	3209(4)	2358(2)
C(11)	1365(5)	2783(4)	1886(2)
C(12)	1310(5)	3218(4)	1032(2)
C(13)	1918(5)	4079(4)	652(2)
C(14)	2581(5)	4505(4)	1124(2)
C(9)	2636(5)	4070(4)	1977(2)
C(16)	1454(3)	8115(4)	4594(2)
C(17)	962(3)	8145(4)	5391(2)
C(18)	—309(3)	8091(4)	5600(2)
C(19)	—1088(3)	8007(4)	5011(2)
C(20)	—595(3)	7977(4)	4213(2)
C(15)	675(3)	8031(4)	4004(2)
C(22)	—488(4)	10399(3)	2552(2)
C(23)	—1339(4)	11444(3)	2039(2)
C(24)	—1674(4)	11384(3)	1270(2)
C(25)	—1157(4)	10281(3)	1013(2)
C(26)	—306(4)	9236(3)	1525(2)
C(21)	29(4)	9295(3)	2295(2)
C(27)	6160(6)	4956(6)	2795(4)
C(28)	3365(6)	6945(5)	1213(3)
C(29)	5661(6)	4929(5)	1227(4)
C(30)	4207(5)	6741(5)	3575(3)
C(31)	2909(6)	9257(5)	1580(4)
C(32)	3353(6)	9375(5)	3133(3)
C(33)	6626(7)	7135(7)	2960(5)
C(34)	5899(7)	9362(7)	1783(4)
C(35)	7804(7)	6933(7)	1439(5)
C(36)	5356(7)	8081(7)	715(4)
O(1)	7012(5)	4320(5)	3241(4)
O(2)	2566(5)	7467(4)	705(3)
O(3)	6210(6)	4381(5)	743(3)
O(4)	4552(4)	6024(4)	4194(3)
O(5)	2510(5)	10015(4)	994(3)
O(6)	3293(5)	10148(4)	3449(3)
O(7)	7071(5)	6866(6)	3614(4)
O(8)	5809(7)	10353(5)	1756(4)
O(9)	8896(5)	6515(7)	1225(4)
O(10)	5030(6)	8356(6)	37(3)

until the carbonyl bands at 2061 and 2096 cm^{-1} were absent (0.1—0.2 cm^3). Solvent was removed and the residue recrystallized from toluene/light petroleum (1/2) to give red-brown crystals of $Ru_3(CO)_{10}(\mu$-dppe) (3) (79 mg, 52%), ν(CO) (hexane) 2080m, 2014vs, 1999s, 1981w, 1965w, 1935w cm^{-1}; m.p. 208—210°C (dec.). Found: C, 43.95; H, 2.34; $C_{36}H_{24}O_{10}P_2Ru_3$ calcd.: C, 44.04; H, 2.46%.

Preparation of $Ru_3(CO)_8(\mu$-dppe$)_2$ (4)

$Ru_3(CO)_{12}$ (100 mg, 0.156 mmol) and dppe (160 mg, 0.4 mmol) in THF (10 cm^3) was treated dropwise with $Ph_2CO^{\overline{\cdot}}$ solution (0.4 cm^3) over 15 min. Solvent was removed under vacuum and the residue recrystallized from toluene/light petroleum to give orange $Ru_3(CO)_8(dppe)_2$ (4) (116 mg, 53%), decomposed without melting. ν(CO) (CH_2Cl_2) 2055m, 1981s, 1952s, 1920sh cm^{-1}. Found: C, 53.79; H, 3.69; $C_{60}H_{48}O_8P_4Ru_3$ calcd.: C, 54.43; H, 3.65%.

TABLE 2

SELECTED BOND LENGTHS AND ANGLES

Bond lengths: (Å)			
Ru(1)—Ru(2)	2.856(1)	Ru(1)—P(1)	2.330(2)
Ru(1)—Ru(3)	2.855(1)	Ru(2)—P(2)	2.330(2)
Ru(2)—Ru(3)	2.847(1)	P(1)—C(1)	1.842(5)
P(1)—C(3)	1.843(3)	P(1)—C(9)	1.843(6)
P(2)—C(2)	1.833(7)	P(2)—C(15)	1.856(4)
P(2)—C(21)	1.831(3)	C(1)—C(2)	1.551(6)
Ru—C distances vary from 1.882(6)—1.936(6), mean 1.903 Å			
C—O distances vary from 1.127(11)—1.152(6), mean 1.144 Å			
Bond angles: (°)			
Ru(1)—Ru(2)—Ru(3)	60.1(1)	Ru(1)—Ru(3)—Ru(2)	60.1(1)
Ru(2)—Ru(1)—Ru(3)	59.8(1)	Ru(1)—Ru(2)—P(2)	101.7(1)
Ru(2)—Ru(1)—P(1)	100.8(1)	Ru(3)—Ru(1)—P(1)	156.5(1)
Ru(3)—Ru(2)—P(2)	159.1(1)	Ru(1)—P(1)—C(1)	116.9(2)
Ru(2)—P(2)—C(2)	116.4(2)	P(1)—C(1)—C(2)	112.3(4)
P(2)—C(2)—C(1)	111.9(4)	Ru(1)—P(1)—C(3)	113.9(1)
Ru(1)—P(1)—C(9)	118.0(1)	Ru(2)—P(2)—C(15)	117.7(1)
Ru(2)—P(2)—C(21)	113.2(1)	C(1)—P(1)—C(3)	102.9(2)
C(2)—P(2)—C(15)	101.8(2)	C(1)—P(1)—C(9)	101.5(3)
C(2)—P(2)—C(21)	103.0(2)		
Dihedral angles (°)			
Ru(1)—Ru(2)—Ru(3)/C(29)—Ru(1)—P(1)	20.0		
Ru(1)—Ru(2)—Ru(3)/C(32)—Ru(2)—P(2)	15.9		
Ru(1)—Ru(2)—Ru(3)/C(34)—Ru(3)—C(35)	13.7		
Torsion angles (°)			
P(1)—Ru(1)/Ru(2)—P(2)	25.1	C(29)—Ru(1)/Ru(3)—C(35)	25.8
C(32)—Ru(2)/Ru(3)—C(34)	25.3	C(28)—Ru(1)/Ru(2)—C(31)	28.7
C(27)—Ru(1)/Ru(2)—C(30)	30.2	C(27)—Ru(1)/Ru(3)—C(33)	30.7
C(28)—Ru(1)/Ru(3)—C(36)	32.3	C(30)—Ru(2)/Ru(3)—C(33)	29.7
C(31)—Ru(2)/Ru(3)—C(36)	30.2		

Crystal structure of $Ru_3(CO)_{10}(\mu\text{-}dppe)$ *(3)*

Single crystals suitable for X-ray analysis were obtained as orange plates from CH_2Cl_2/light petroleum at —30° C. Preliminary precession photography indicated the triclinic system. Lattice parameters were determined from the setting angles of 25 reflections centred on a four-circle Enraf-Nonius CAD4 diffractometer using graphite monochromated Mo-K_α radiation.

Crystal data. $C_{36}H_{24}O_{10}P_2Ru_3$, M_r = 981.7, triclinic, space group $P\bar{1}$. a 10.615(2), b 11.769(6), c 16.584(4) Å; α 75.68(2)°, β 84.59(2)°, γ 69.64(2)°; U 1882.0 Å^3, D_m 1.69, D_c 1.73 g cm^{-3} for $Z = 2$; $F(000) = 964$; μ(Mo-K_α) = 12.7 cm^{-1}, T 23° C. Intensity data were collected in the range $1.5° < \theta < 22.5°$ using an $\omega - n/3\,\theta$ scan, where the optimum value of n was found to be 3 by peak analysis. Horizontal counter apertures and ω scan angles of (2.4 + 0.5 tan θ) mm and (1.0 + 0.3 tan θ)° respectively were used. Data reduction was performed using programme SUSCAD [10] which also applied Lorentz and polarisation corrections. The data were not corrected for absorption because of the small crystal size and low absorption coefficient. A total of 4542 unique reflections were collected, of which 3558 with $I > 2.5\ \sigma(I)$ were used in the analysis.

Solution and refinement

The positions of the three Ru atoms were found by direct methods using MULTAN [11]. All other non-hydrogen atoms were revealed by a subsequent

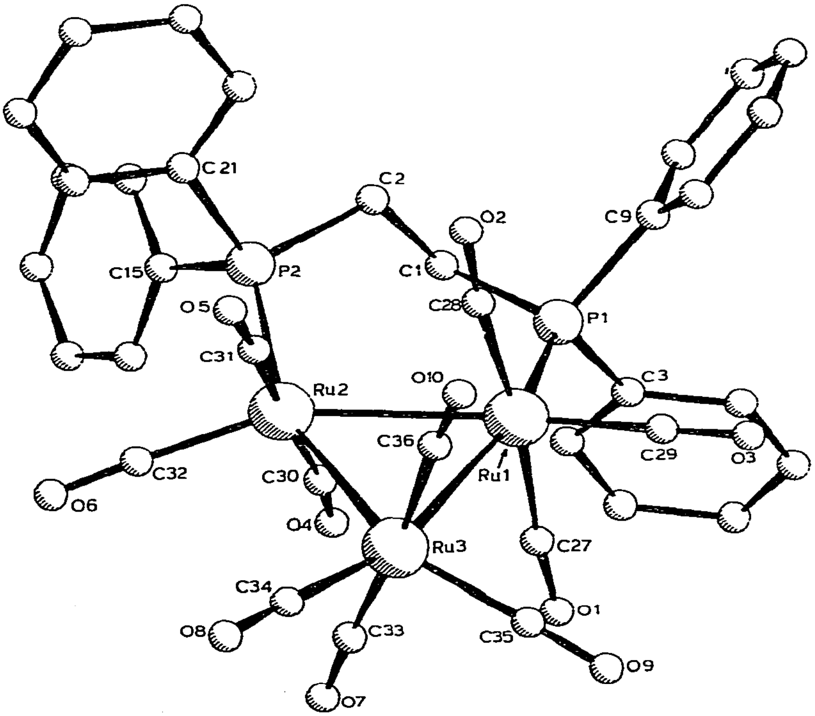


Fig. 1. PLUTO plot of the molecular structure of $Ru_3(CO)_{10}(dppe)$ (2).

difference Fourier phased on the heavy atom positions. In the final cycle of blocked full-matrix least-squares refinement phenyl rings were treated as rigid planar groups (C—C 1.38 Å), with isotropic temperature factors, hydrogen atoms were included in calculated positions (C—H 0.95 Å) and all other atoms were assigned anisotropic temperature factors. A weighting scheme was applied and refined to $w = 1.82(\sigma^2(F_o) + 0.0002(F_o)^2)^{-1}$. Final convergence gave R = 0.030, R_w = 0.034, with no parameter shifting by more than 0.5σ. A final difference map showed no peaks >0.6e Å^{-3}. Calculations were carried out using the SHELX [12] system of programmes and diagrams were prepared using PLUTO [13].

Positional parameters from the final cycle of refinement are given in Table 1 and selected bond lengths and angles in Table 2. A diagram of the molecule, showing the atom-labelling scheme, is given in Fig. 1. Lists of observed and calculated structure factors and thermal parameters can be obtained from the authors on request.

Results and discussion

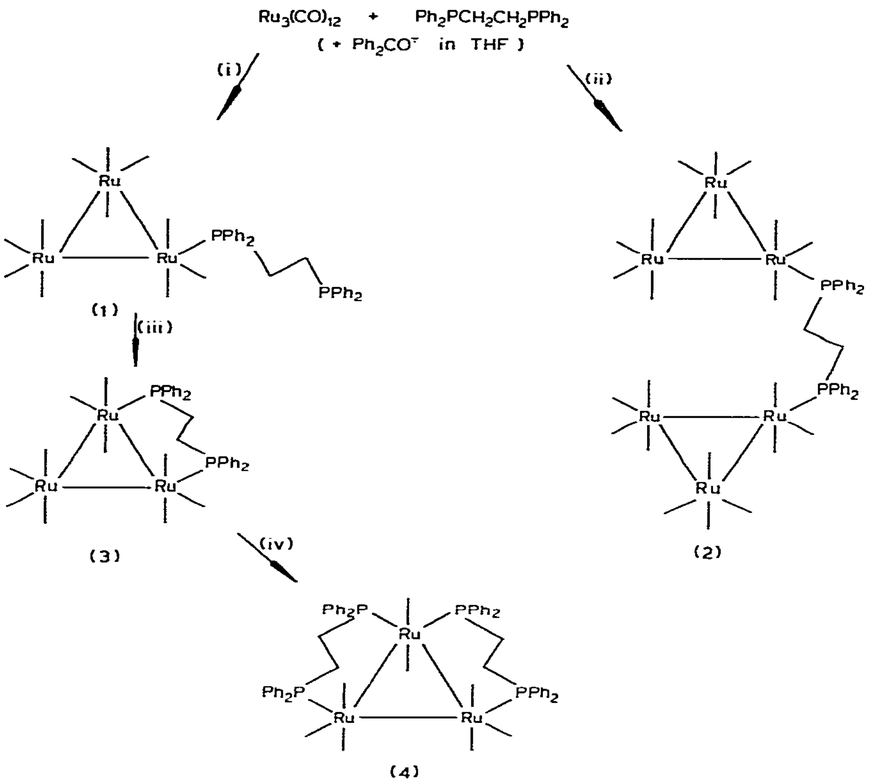
The replacement of CO ligands on $Ru_3(CO)_{12}$ by dppe proceeds cleanly under mild conditions in THF when catalysed by $Ph_2CO^{\cdot-}$. The products obtained depend on the stoichiometry of the reagents and the amount of catalyst added; results are summarised in Scheme 1.

Using a 1/1 ratio of $Ru_3(CO)_{12}$ to dppe and a minimum of catalyst the substitution reaction gives a species characterised as $Ru_3(CO)_{11}(PPh_2CH_2CH_2PPh_2)$ (**1**) in which only one phosphorus atom of dppe is coordinated to the Ru triangle, the other being non-coordinated. This assignment is based mainly on the infrared ν(CO) pattern which closely matches that of $Ru_3(CO)_{11}(PPh_3)$ [7,14]. Isolation of **1** depends on its moderate solubility in light petroleum, in contrast to species with bidentate dppe groups which are poorly soluble in non-polar solvents. In solution at room temperature **1** is slowly transformed to $Ru_3(CO)_{10}$-(μ-dppe) (**3**) so pure samples of **1** are not readily isolated but with care yields of up to 65% of >90% purity (by infrared) can be obtained.

Additional evidence that substitution with the diphosphine occurs stepwise is provided by the reaction of $Ru_3(CO)_{12}$ with dppe in the ratio of 1/0.5. The $Ph_2CO^{\cdot-}$ catalysed reaction proceeds to give good yields of $[Ru_3(CO)_{11}]_2$-(μ-dppe) (**2**), with the dppe ligand bridging between two mono-substituted clusters. This shows that under these reaction conditions substitution by the pendant PPh_2 group of **1** is more favourable at another molecule of $Ru_3(CO)_{12}$ than at another Ru atom of **1**. This observation is in marked contrast to the behaviour found for thermal reactions between $Ru_3(CO)_{12}$ and phosphines but is consistent with the mechanism proposed for $Ph_2CO^{\cdot-}$ catalysed reactions [8].

With a 1/1 ratio of $Ru_3(CO)_{12}$ to dppe and a generous aliquot of catalyst the reaction proceeds through the intermediacy of **1** to give $Ru_3(CO)_{10}(\mu$-dppe) (**3**), apparently identical to the product obtained in low yields by a thermal route. The orange complex is air-stable, only sparingly soluble in non-polar solvents but very soluble in aromatic or halocarbon solvents.

It has been shown [15] that there are two isomers of $H_4Ru_4(CO)_{10}$(dppe); one in which the dppe ligand chelates to one Ru atom and the other in which



SCHEME 1. Reactions of $Ru_3(CO)_{12}$ and dppe. Conditions (i) Ru_3/dppe = 1/1, 40°C, minimum catalyst, 5 min; (ii) Ru_3/dppe = 2/1, 40°C; (iii) Ru_3/dppe = 1/1, 40°C, excess catalyst, 10 min; (iv) Ru_3/dppe = 1/2, 25°C, excess catalyst, 15 min.

the dppe ligand bridges a Ru—Ru bond. Similar alternatives can be proposed for $Ru_3(CO)_{10}$(dppe) with added complications arising from the possibility of coordination of the phosphorus atoms at equatorial or axial sites. Since these isomers could not be distinguished by spectroscopic means a crystal structure analysis was performed. This showed that in the solid state the dppe ligand bridges a Ru—Ru bond with both phosphorus atoms coordinated equatorially (vide infra). Since both the solution and the solid phase (Nujol mull) infrared spectra of $Ru_3(CO)_{10}$(dppe) are similar, it appears this isomer is also the dominant one in solution, although the other isomers may also be present.

When a mixture of $Ru_3(CO)_{12}$ and dppe in the ratio 1/2.5 was treated with excess catalyst two molecules of dppe were incorporated in the cluster. Again a number of different isomers can be proposed since analysis cannot distinguish between $Ru_3(CO)_x(dppe)_2$ (x = 9 or 10). However the infrared spectrum of the product shows a carbonyl stretching pattern very similar to that reported for $Ru_3(CO)_8(ffars)_2$ which was shown by an X-ray structure determination [5] to have two bridging bidentate ligands occupying equatorial sites. Accordingly we assign structure **4** to $Ru_3(CO)_8(\mu\text{-dppe})_2$.

Structure of $Ru_3(CO)_{10}(\mu\text{-}dppe)$ *(3)*

The molecular structure (Fig. 1) is derived from that of $Ru_3(CO)_{12}$ by replacement of an equatorial CO group on each of two Ru atoms by the Ph_2P groups of the dppe ligand. There is an approximate C_2 axis through the Ru(3) atom and the mid-points of the Ru(1)—Ru(2) and C(1)—C(2) bonds. This is the same structure as that found [4] for $Ru_3(CO)_{10}$(ffars) and that proposed [3] for $Ru_3(CO)_{10}$(dppm) on the basis of NMR spectroscopy.

The Ru_3 triangle is little affected by substitution with dppe, the average Ru—Ru distance (2.853 Å) being not significantly different from that found for $Ru_3(CO)_{12}$ (2.851 Å) [16] and, surprisingly, considerably shorter than that found in $Ru_3(CO)_{11}(PPh_3)$ (2.88 Å) [17]. Individual Ru—Ru distances vary little from the mean, in contrast to those [4] in $Ru_3(CO)_{10}$(ffars) where the bridged Ru—Ru bond is nearly 0.06 Å longer than the other two. This is probably due to the variable 'bite' of the dppe ligand compared with the relatively rigid ffars, rather than to electronic differences.

The Ru—P, Ru—C and C—O bond lengths (Table 2) are unremarkable.

In $Ru_3(CO)_{12}$ the carbonyl polyhedron approximates an anti-cuboctahedron with the equatorial ligands coplanar with, and the axial carbonyls normal to, the Ru_3 triangle [18]. Only small distortions of the ligand polyhedron are apparently found [15] for $Ru_3(CO)_{11}(PPh_3)$. In contrast the ligand polyhedron in $Ru_3(CO)_{10}(\mu$-dppe) is noticeably perturbed. This takes the form of a nearly equal twisting of each Ru atom by ca. 14—20° in the same sense to give torsion angles involving equatorial ligands on adjacent Ru atoms of 25—26° and torsion angles for axial carbonyls of 29—32° (Table 2).

This deformation clearly relieves non-bonded interactions between the dppe ligand and the CO groups. In particular major interactions involve the phenyl ring C(21—26) and the C(31)—O(5) carbonyl and the equivalent C(3—8) ring and the C(27)—O(1) carbonyl. A similar twisting has been previously described [4,5] for $Ru_3(CO)_{10}$(ffars) and $Ru_3(CO)_8(ffars)_2$.

Conclusion

This study is the first of several to be described which illustrate the wealth of chemistry which we are finding as a result of using mild conditions for cluster substitution. These enable a definition of the first products formed, which in turn can be examined further to cast more light on the complex changes which occur as, for example, temperatures are increased. In the present case, the thermal reaction between $Ru_3(CO)_{12}$ and dppe affords only a 3% yield of complex 3, together with much 'decomposition', which on further investigation would no doubt yield new complexes, as found recently with the analogous reaction of dppm [6].

Acknowledgement

Funding by the Australian Research Grants Committee is gratefully acknowledged. BKN is grateful for the granting of study leave by the University of Waikato.

References

1 Part IX: M.I. Bruce, J.G. Matisons and R.C. Wallis, Aust. J. Chem., 35 (1982) 935.
2 M.A. Bennett, M.I. Bruce and T.W. Matheson, in G. Wilkinson, F.G.A. Stone and E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Pergamon, Oxford, 1982, Chapter 32.
3 F.A. Cotton and B.E. Hanson, Inorg. Chem., 16 (1977) 3369.
4 W.R. Cullen and D.A. Harbourne, Inorg. Chem., 9 (1970) 1839; P.J. Roberts and J. Trotter, J. Chem. Soc. A, (1970) 3246.
5 P.J. Roberts and J. Trotter, J. Chem. Soc. A, (1971) 1479.
6 G. Lavigne and J.-J. Bonnet, Inorg. Chem., 20 (1981) 2713.
7 M.I. Bruce, G. Shaw and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1972) 2094.
8 M.I. Bruce, D. Kehoe, J. Matisons, B.K. Nicholson, M. Williams and P. Reiger, J. Chem. Soc., Chem. Commun., submitted.
9 M.I. Bruce, J.G. Matisons, B.W. Skelton, R.C. Wallis and A.H. White, Aust. J. Chem., submitted.
10 SUSCAD — 'Data reduction programme for the CAD 4 diffractometer', University of Sydney, 1976.
11 G. Germain, P. Main and M.M. Woolfson, Acta Crystallogr., A27 (1971) 368.
12 SHELX-76 — 'Programme for crystal structure determination', G.M. Sheldrick, University of Cambridge, 1976.
13 PLUTO — 'Programme for crystal and molecular plotting', W.D.S. Motherwell, University of Cambridge, 1977.
14 S.K. Malik and A. Poe, Inorg. Chem., 17 (1978) 1484.
15 M.R. Churchill and R.A. Lashewycz, Inorg. Chem., 17 (1978) 1950; M.R. Churchill, R.A. Lashewycz, J.R. Shapley and S.I. Richter, Inorg. Chem., 19 (1980) 1277.
16 M.R. Churchill, F.J. Hollander and J.P. Hutchinson, Inorg. Chem., 16 (1977) 2655.
17 E.J. Forbes, N. Goodhand, D.L. Jones and T.A. Hamor, J. Organometal. Chem., 182 (1979) 143.
18 R.E. Benfield and B.F.G. Johnson, Transition Met. Chem., 6 (1981) 131.