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Reaction of triruthenium dodecacarbonyl with bis(dimethylphosphino)methane, bis(diphenylphosphino)methane and bis(diphenylphosphino)-ethylamine under photochemical conditions

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Abstract

The photochemical reactions of $[Ru_3(CO)_{12}]$ with the diphosphorus ligands $Me_2PCH_2PMe_2$, $Ph_2PCH_2PPh_2$ and $Ph_2PN(Et)PPh_2$ have been found to give tri-, di- or mono-nuclear products, depending on the reaction conditions and the ligand involved. Products isolated include $[Ru_3(CO)_{10}\{\mu\text{-}R_2PYPR_2\}]$ ($Y = CH_2$, $R = Me$ or Ph; $Y = N(Et)$, $R = Ph$), $[Ru_3(CO)_8\{\mu\text{-}R_2PYPR_2\}_2]$ ($Y = CH_2$, $R = Me$ or Ph), $[Ru_3(CO)_6\{\mu\text{-}R_2PYPR_2\}_3]$ ($Y = CH_2$, $R = Me$ or Ph), $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}Ph_2PCH_2PPh_2\}_2]$ and $[Ru(CO)_3\{Ph_2PN(Et)PPh_2\}]$. An X-ray crystallographic study has revealed that the diphosphazane ligand in $[Ru_3(CO)_{10}\{\mu\text{-}Ph_2PN(Et)PPh_2\}]$ is coordinated equatorially and that the Ru–Ru edge which it bridges is ca. 0.06 Å shorter than the average of the other two edges.

Introduction

The reaction of $[Ru_3(CO)_{12}]$ with the ditertiary phosphine $Ph_2PCH_2PPh_2$ under thermal conditions has received much attention and trinuclear products $[Ru_3(CO)_{10}\{\mu\text{-}Ph_2PCH_2PPh_2\}]$ (I; $Y = CH_2$, $R = Ph$), $[Ru_3(CO)_9\{\mu\text{-}Ph_2PCH_2PPh_2\}\{\eta^1\text{-}Ph_2PCH_2PPh_2\}]$, $[Ru_3(CO)_8\{\mu\text{-}Ph_2PCH_2PPh_2\}_2]$ (II; $Y = CH_2$, $R = Ph$), and $[Ru_3(CO)_6\{\mu\text{-}Ph_2PCH_2PPh_2\}_3]$ (III; $Y = CH_2$, $R = Ph$) in which two, three, four or six carbonyl groups have been replaced and in which the diphosphine functions as a monodentate and/or a bridging bidentate ligand, have been isolated and characterised [1–7].

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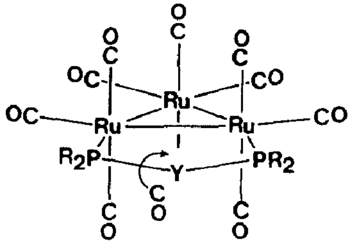
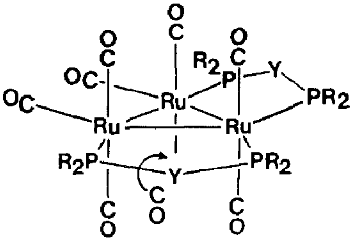


(I)



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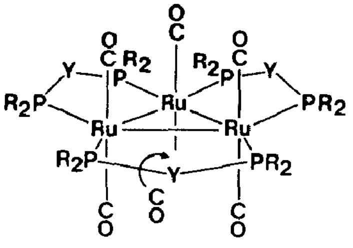


(III)

The reaction has been investigated kinetically [5] and the formation of $[Ru_3(CO)_8\{\mu\text{-}Ph_2PCH_2PPh_2\}_2]$ has been shown to occur by stepwise loss of carbon monoxide. The replacement of the first carbonyl is ligand dependent, but subsequent carbonyl replacement steps have been suggested to involve CO dissociation pathways. There was no evidence for cluster fragmentation under the conditions used, involving temperatures of between 30 and 70 °C. Degradation of the coordinated $Ph_2PCH_2PPh_2$ has been shown to occur under more forcing conditions, however. Thus thermolysis of $[Ru_3(CO)_{10}\{\mu\text{-}Ph_2PCH_2PPh_2\}]$ produces $[Ru_3\{\mu_3\text{-}\eta^3\text{-}PhPCH_2P(Ph)C_6H_4\}(CO)_9]$ in cyclohexane at 80 °C and $[Ru_3(\mu\text{-}H)\{\mu_3\text{-}\eta^2\text{-}PhPCH_2PPh_2\}(CO)_9]$ in toluene at 90 °C [8]. Also, heating of a solution of $[Ru_3(CO)_8\{\mu\text{-}Ph_2PCH_2PPh_2\}_2]$ in xylene at 100 °C for 1 h has been found to give $[Ru_3\{\mu\text{-}PPh\}\{\mu_3\text{-}\eta^2\text{-}CHPPh_2\}(CO)_7\{\mu\text{-}Ph_2PCH_2PPh_2\}]$ via $[Ru_3(\mu\text{-}H\{\mu_3\text{-}\eta^4\text{-}PhPCHP(Ph)C_6H_4\}(CO)_7\{\mu\text{-}Ph_2PCH_2PPh_2\}]$ as an intermediate [4,9].

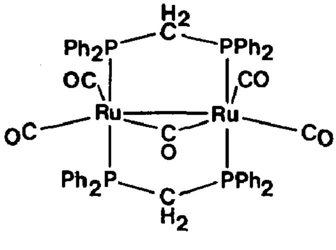
Recently Smith et al. have reported the synthesis of $[Ru_3(CO)_{10}\{\mu\text{-}Me_2PCH_2PMe_2\}]$ and $[Ru_3(CO)_8\{\mu\text{-}Me_2PCH_2PMe_2\}_2]$ by reaction of $[Ru_3(CO)_{12}]$ with $Me_2PCH_2PMe_2$ in THF under reflux and by reaction of $[Ru_3(CO)_{10}\{\mu\text{-}Me_2PCH_2PMe_2\}]$ with $Me_2PCH_2PMe_2$ in benzene at 60 °C respectively. As observed for their $Ph_2PCH_2PPh_2$ analogues, these compounds were shown to undergo degradation at higher temperature and in toluene under reflux to $[Ru_3(\mu\text{-}H)\{\mu_3\text{-}\eta^3\text{-}Me_2PCHPMe_2](CO)_9]$ and $[Ru_3(\mu\text{-}H)\{\mu_3\text{-}\eta^3\text{-}Me_2PCHPMe_2\}(CO)_7\{\mu\text{-}Me_2PCH_2PMe_2\}]$, respectively [10].

In contrast to the above thermal reactions, the photochemical reaction of $[Ru_3(CO)_{12}]$ with CO leads to fragmentation of the triruthenium framework and the formation of $[Ru(CO)_5]$ without detectable side reactions [11]. A mechanism involving non-radical intermediates has been proposed [12]. Fragmentation can also be effected thermally but at high temperatures. Thus treatment of $[Ru_3(CO)_{12-x}(PPh_3)_x]$ ($x = 0, 1, 2$ or 3) with CO and various monodentate phosphorus ligands in decalin at temperatures above 130 °C was found to give mononuclear products at rates that were independent of the concentration of the reactant nucleophile [13,14].

We have previously established that diphosphazane derivatives of diruthenium nonacarbonyl of the type $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (R = Me, Et, Pr^i, etc) can be readily synthesised by treating $[Ru_3(CO)_{12}]$ with the appropriate diphosphazane under photochemical conditions [15]. With the object of synthesising corresponding ditertiary phosphine-bridged derivatives we treated $[Ru_3(CO)_{12}]$ photochemically with $Ph_2PCH_2PPh_2$, as well as with $Me_2PCH_2PMe_2$ and $Ph_2PN(Et)PPh_2$. The results are reported here.

Results and discussion

Irradiation of a solution of $[Ru_3(CO)_{12}]$ and an equimolar amount of $Ph_2PCH_2PPh_2$ with UV light was found to give the known decacarbonyl derivative $[Ru_3(CO)_{10}\{\mu\text{-}Ph_2PCH_2PPh_2\}]$ (I; Y = CH_2, R = Ph) [1,2] without fragmentation of the triruthenium framework. However, treatment of $[Ru_3(CO)_{12}]$ with twice- or three-fold molar amounts of the ligand, in cyclohexane under photolytic conditions resulted in the separation from solution of a yellow-orange microcrystalline material that was characterised as the dinuclear pentacarbonyl derivative $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}Ph_2PCH_2PPh_2\}_2]$ (IV).



(IV)

The band pattern in the C–O stretching region of both the solid state and solution infrared spectra of this species is very similar to that for $[Fe_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}Ph_2PCH_2PPh_2\}_2]$ and for $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ [14] and on this basis is assumed to have a structure analogous to that established X-ray crystallographically for the latter [14] in which the two ruthenium atoms are bridged by a carbonyl as well by the two ditertiary phosphine ligands. Significantly, there was no evidence for the presence of $[Ru(CO)_4\{\eta^1\text{-}Ph_2PCH_2PPh_2\}]$ and/or $[Ru(CO)_3\{Ph_2PCH_2PPh_2\}]$ in solution, indicating that the mononuclear species, formed as a result of the fragmentation of $[Ru_3(CO)_{10}\{\mu\text{-}Ph_2PCH_2PPh_2\}]$, must rapidly associate.

In contrast to what was observed for the corresponding reactions involving $Ph_2PCH_2PPh_2$, the photochemical reactions of $[Ru_3(CO)_{12}]$ with the more basic ditertiary phosphine $Me_2PCH_2PMe_2$ were found to afford only trinuclear products. In particular, UV irradiation of cyclohexane solutions of the parent dodecacarbonyl with an equimolar proportion, a two molar proportion, or an excess of the ligand gave, respectively, $[Ru_3(CO)_{10}\{\mu\text{-}Me_2PCH_2PMe_2\}]$ (I; $Y = CH_2$, $R = Me$), $[Ru_3(CO)_8\{\mu\text{-}Me_2PCH_2PMe_2\}_2]$ (II; $Y = CH_2$, $R = Me$) or $[Ru_3(CO)_6\{\mu\text{-}Me_2PCH_2PMe_2\}_3]$ (III; $Y = CH_2$, $R = Me$). The IR and NMR spectroscopic data for these three compounds are consistent with their coordinated diphosphine ligands occupying equatorial positions (I, II and III, respectively; $Y = CH_2$, $R = Me$), as observed for the corresponding $Ph_2PCH_2PPh_2$ derivatives [3,6,7]. In other words the stepwise replacement of carbonyl groups in $[Ru_3(CO)_{12}]$ by $Me_2PCH_2PMe_2$ takes place at equatorial sites.

Reaction of $[Ru_3(CO)_{12}]$ with an equimolar amount of the diphosphazane ligand $Ph_2PN(Et)PPh_2$ under photochemical conditions resulted in simple replacement of two carbonyl groups and formation of $[Ru_3(CO)_{10}\{\mu\text{-}Ph_2PN(Et)PPh_2\}]$. However, with a two molar or larger proportion of this ligand, cluster fragmentation occurs and the mononuclear species $[Ru(CO)_3\{Ph_2PN(Et)PPh_2\}]$ is produced.

Crystal structure of $[Ru_3(CO)_{10}\{\mu\text{-}Ph_2PN(Et)PPh_2\}]$

The molecular stereochemistry of $[Ru_3(CO)_{10}\{\mu\text{-}Ph_2PN(Et)PPh_2\}]$, as established X-ray crystallographically [16], is illustrated in Fig. 1. The structure is based on that of the parent $[Ru_3(CO)_{12}]$ molecule with the diphosphazane ligand in place of two equatorial carbonyl groups on adjacent ruthenium atoms. The edge of the triruthenium framework bridged by the diphosphazane ligand is 0.055(7) Å shorter than the average length of the other two edges (see Table 3 for selected parameters of the molecular geometry referred to in this section). This bond distance difference is much larger than that observed for $[Ru_3(CO)_{10}\{\mu\text{-}Ph_2PCH_2PPh_2\}]$ (0.017 Å) [3]

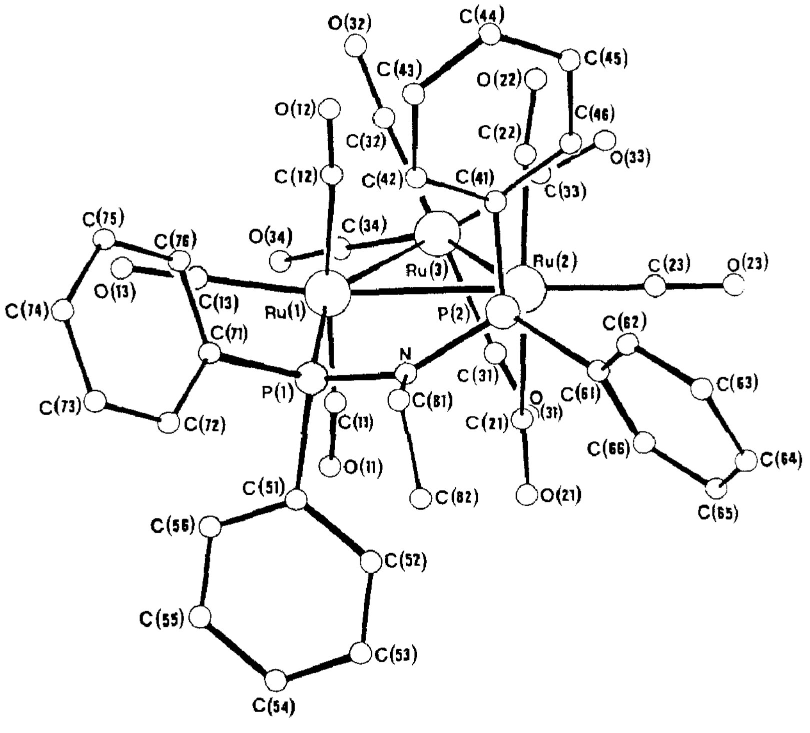


Fig. 1. The molecular stereochemistry of $[Ru_3(CO)_{10}\{\mu\text{-}Ph_2PN(Et)PPh_2\}]$.

and for $[Ru_3(CO)_8\{\mu\text{-}Ph_2PCH_2PPh_2\}_2]$ (0.028 Å) [6] and presumably reflects the smaller bite of the diphosphazane ligand (vide infra).

The two phosphorus atoms are slightly staggered with respect to each other, lying above and below the triruthenium plane and giving a P(1)–Ru(1)–Ru(2)–P(2) torsion angle of 24.4° (Table 3). The P–Ru–$C(O)_{axial}$ bond angles are maintained at approximately 90° so that the axial carbonyls bonded to the ruthenium atoms containing the coordinated diphosphazane ligand also become staggered with respect to each other and with one carbonyl ligand on each ruthenium tilted towards the adjacent ruthenium–ruthenium bond. As illustrated, the effect of this is to tilt the axial carbonyls on Ru(3) in order to maintain acceptable C...C and O...O non-bonded distances, and to move the equatorial carbonyls on this ruthenium out of the triruthenium plane. Staggered configurations have also been observed for $[Ru_3(CO)_{10}\{\mu\text{-}Ph_2PCH_2PPh_2\}]$ [3] and $[Ru_3(CO)_8\{\mu\text{-}Ph_2PCH_2PPh_2\}_2]$ [6] although the carbonyl groups in the parent compound $[Ru_3(CO)_{12}]$ adopt an eclipsed configuration [17]. The mean Ru–C(O) distance for the axial carbonyl groups is 1.938(6) Å while that for the equatorial carbonyls is 0.036 Å shorter, viz. 1.902(9) Å. Differences between the Ru–C(O) bond distances for axial and equatorial carbonyls have been noted previously for $[Ru_3(CO)_{12}]$ [17] and $[Ru_3(CO)_{10}\{\mu\text{-}Ph_2PCH_2PPh_2\}]$ [3], and are readily accounted for in terms of a smaller redistribution of electron density from the metal d_π orbitals to the π^* orbitals of the axial carbonyls as a result of the mutual *trans* disposition of the latter.

The mean C...C distance for the axial carbonyl groups is 2.83(2) Å whereas the mean O...O distance for these groups is 3.15(4) Å, indicating that these carbonyls are bent away from each other owing to repulsion between adjacent oxygen atoms. A similar bending is observed for the equatorial carbonyls, but is not as pronounced, as reflected by the mean deviation of the Ru–C–O bond angle from 180° being 6.4(8)° for the axial carbonyls and 1.7(3)° for the equatorial carbonyls (Table 3). A similar bonding effect has been noted previously for $[Ru_3(CO)_{12}]$ [17].

The P–N–P bond angle for the coordinated diphosphazane ligand is 118.0(5)°, and consistent with this the methylene carbon of the ethyl group lies essentially in the PNP plane. The nitrogen can thus be considered to be formally sp^2 hybridised, which would account for the fact that the average P–N distance of 1.720 Å in this compound is shorter than the corresponding average P–C(H) distance of 1.849 Å in $[Ru_3(CO)_{10}\{\mu\text{-}Ph_2PCH_2PPh_2\}]$. The shorter P–N distance in diphosphazane ligands is responsible for their having a smaller bite than corresponding ditertiary phosphines.

Four of the five atoms in the dimetallo-ligand ring, viz. Ru(1), P(1), N and P(2), are essentially coplanar, with Ru(2) lying 0.90 Å out of the least-squares plane defined by these four atoms. Relevant torsion angles are given in Table 3. Four of the five atoms in the dimetallo-ligand ring in the corresponding $Ph_2PCH_2PPh_2$ complex $[Ru_3(CO)_{10}\{\mu\text{-}Ph_2PCH_2PPh_2\}]$ [3] are also coplanar, but it is one of the phosphorus atoms, P(2), that lies out of the plane, by a distance of 0.75 Å. The relevant torsion angles for this complex * are given for comparison in square

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* These torsion angles were calculated from the published atomic coordinates and in doing so a misprint was noted in reference 3. Corrected fractional coordinates for P(1), namely $x = -0.0022(1)$, $y = 0.0993(1)$ and $z = 0.30151(6)$, were obtained from the authors.

brackets in Table 3 (read C(11) in place of N). The dimetallo-ligand ring in this compound is substantially more puckered than that in $[Ru_3(CO)_{10}\{\mu\text{-}Ph_2PN(Et)PPh_2\}]$ (see Table 3).

Experimental

The ligands $Me_2PCH_2PMe_2$ and $Ph_2PCH_2PPh_2$ were obtained commercially while $Ph_2PN(Et)PPh_2$ was synthesised by a published method [18]. All reactions were performed under nitrogen in freshly distilled solvents. Chromatographic separations were on silica gel columns with mixtures of dichloromethane and light petroleum as eluents. IR spectra (Table 1) were recorded with 0.5 mm NaCl cells on a Philips Pye Unicam SP3-200 instrument. $^{31}P\{H\}$ NMR spectra were recorded on a Varian FT80A instrument. Microanalyses were performed by the Microanalytical Section of the Department of Chemistry, University of Natal, Pietermaritzburg.

Synthesis of $[Ru_3(CO)_{10}\{\mu\text{-}R_2PYPR_2\}]$ ($Y = CH_2$, $R = Me$ and Ph; $Y = N(Et)$, $R = Ph$)

A stirred solution of $[Ru_3(CO)_{12}]$ (0.32 g, 0.05 mmol) and an equimolar amount of $Me_2PCH_2PMe_2$ (0.07 g, 0.05 mmol) or $Ph_2PCH_2PPh_2$ (0.19 g, 0.05 mmol) or $Ph_2PN(Et)PPh_2$ (0.21 g, 0.05 mmol) in cyclohexane (ca. 150 cm^3) was irradiated with ultraviolet light (Philips 125W lamp) under argon for 3–5 hours. The solution was filtered, the filtrate evaporated under reduced pressure, and the residue chromatographed on a silica gel column. The product from the major band was crystallised from dichloromethane/light petroleum. $[Ru_3(CO)_{10}\{\mu\text{-}Me_2PCH_2PMe_2\}]$: Yield: 60%. Analysis: C, 25.3; H, 2.1. $C_{15}H_{14}O_{10}P_2Ru_3$ calcd.: C, 25.0; H, 1.90%. $[Ru_3(CO)_{10}\{\mu\text{-}Ph_2PCH_2PPh_2\}]$: Yield: 80%. Analysis: C, 43.1; H, 2.2. $C_{35}H_{22}O_{10}P_2Ru_3$ calcd.: C, 43.4; H, 2.3%. $[Ru_3(CO)_{10}\{\mu\text{-}Ph_2PN(Et)PPh_2\}]$: Yield: 75%. Analysis: C, 43.1; H, 2.9; N, 1.5. $C_{36}H_{25}O_{10}NP_2Ru_3$ calcd.: C, 43.3; H, 2.6; N, 1.4%.

Table 1

Infrared and $^{31}P\{H\}$ NMR spectroscopic data

Compound		ν(C–O) (cm^{-1}) [a,b]	δ($^{31}P\{H\}$) (ppm) [c]
$[Ru_3(CO)_{10}\{\mu\text{-}R_2PYPR_2\}]$			
Y	R		
CH_2	Ph	2080m, 2004s, 1960m, sh	14.1s [d]
	Me	2074m, 1997s, 1958m,sh	−11.9s [d]
N(Et)	Ph	2080s, 2004s, 1966m,sh	84.1s [d]
$[Ru_3(CO)_8\{\mu\text{-}Me_2PCH_2PMe_2\}_2]$		2020m, 1955s, 1890w,sh	−8.7 (AA′BB′ pattern) [d]
$[Ru_3(CO)_6\{\mu\text{-}Me_2PCH_2PMe_2\}_3]$		1905s, 1850vw	−7.3s [e]
$[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}Ph_2PCH_2PPh_2\}_2]$		1970ms, 1926s, 1905ms, 1882m,sh, 1700m	27.6s [e]
$[Ru(CO)_3\{Ph_2PN(Et)PPh_2\}]$		1998s, 1928s, 1912s	44.4s [d]

[a] Measured in CH_2Cl_2. [b] Abbreviations: s, strong; m, medium; w, weak; sh, shoulder. [c] Abbreviation: s, singlet. [d] Measured in chloroform-d_1. [e] Measured in acetone-d_6.

Synthesis of [$Ru_3(CO)_8\{\mu$-$Me_2PCH_2PMe_2\}_2$]

A stirred solution of [$Ru_3(CO)_{12}$] (0.32 g, 0.05 mmol) and a two molar proportion of $Me_2PCH_2PMe_2$ (0.15 g, 0.11 mmol) in cyclohexane (ca. 150 cm^3) was irradiated with ultraviolet light (Philips 250W lamp) under argon for 7–8 h. The solution was filtered, evaporated under reduced pressure, and then chromatographed. The product isolated from the major band was crystallised from acetone/light petroleum. [$Ru_3(CO)_8\{\mu$-$Me_2PCH_2PMe_2\}_2$]: Yield: 65%. Analysis: C, 26.6; H, 3.5. $C_{18}H_{28}O_8P_4Ru_3$ calcd.: C, 27.0; H, 3.5%.

Synthesis of [$Ru_3(CO)_6\{\mu$-$Me_2PCH_2PMe_2\}_3$]

A stirred solution of [$Ru_3(CO)_{12}$] (0.32 g, 0.05 mmol) and $Me_2PCH_2PMe_2$ (0.30 g, 0.22 mmol) in cyclohexane (ca. 150 cm^3) was irradiated with ultraviolet light (Philips 250W lamp) under argon for 10–12 hours. The solution was filtered, evaporated under reduced pressure, and chromatographed on a silica gel column. The product isolated from the major band could not be obtained analytically pure but was identified spectroscopically as [$Ru_3(CO)_6\{\mu$-$Me_2PCH_2PMe_2\}_3$]. Yield: 35%.

Synthesis of [$Ru_2(\mu$-$CO)(CO)_4\{\mu$-$Ph_2PCH_2PPh_2\}_2$]

A stirred solution of [$Ru_3(CO)_{12}$] (0.32 g, 0.05 mmol) and $Ph_2PCH_2PPh_2$ (0.61 g, 0.16 mmol) in cyclohexane (ca. 150 cm^3) was irradiated with UV light (Philips 125W lamp) under argon for 8 h. The yellow-orange microcrystalline product that separated out was washed with small quantities of cyclohexane and dried in vacuo. Yield: 65%. Analysis: C, 60.1; H, 3.8. $C_{55}H_{44}O_5P_4Ru_2$ calcd.: C, 59.5; H, 4.0%.

Synthesis of [$Ru(CO)_3\{Ph_2PN(Et)PPh_2\}$]

A stirred solution of [$Ru_3(CO)_{12}$] (0.64 g, 0.10 mmol) and $Ph_2PN(Et)PPh_2$ (0.90 g, 0.22 mmol) in cyclohexane (ca. 150 cm^3) was irradiated with UV light (Philips 250 W lamp) under argon for 6 h. The red-brown solid that separated was recrystallised from dichloromethane/light petroleum. Yield: 75%. Analysis: C, 58.1; H, 4.1; N, 4.6. $C_{29}H_{25}NO_3P_2Ru$ calcd.: C, 58.2; H, 4.2; N, 4.7%.

Crystal structure determination of [$Ru_3(CO)_{10}\{\mu$-$Ph_2PN(Et)PPh_2\}$]

Crystal data. $C_{36}H_{25}NO_{10}P_2Ru_3$, $M = 996.76$, dark red needle-shaped crystal of dimensions 0.37 × 0.18 × 0.08 mm grown from dichloromethane/hexane, triclinic, space group $P\bar{1}$, a 14.732(3), b 12.386(3), c 10.982(3) Å, α 104.53(2), β 100.64(2), γ 94.89(2)°, V 1888.1 Å^3, $Z = 2$, D_m 1.73, D_c 1.74 g cm^{-3}, μ(Mo-K_α) 12.7 cm^{-1}, $F(000) = 980.0$.

Intensity data were collected on a Philips PW1100 four-circle diffractometer using graphite-monochromated Mo-K_α radiation (λ 0.71069 Å). Diffraction intensities were measured in the range $2 \leq \theta \leq 23°$ using the ω–2θ scan technique. Three standard reflections, measured every hour, showed no decrease in intensity during data collection. Lorentz and polarisation but no absorption corrections were applied. Of the 5295 unique reflections 3538 were classed as observed ($I > 5\sigma(I)$) and these were used for the solution and refinement of the structure. The structure was solved by Patterson methods and refined by least squares methods [19]. All non-hydrogen atoms were assigned anisotropic thermal parameters. The thermal parameters of the hydrogen atoms of the phenyl rings were constrained to be equal

(*Continued on p. 402*)

Table 2

Fractional atomic coordinates and equivalent isotropic temperature factors for $[Ru_3(CO)_{10}\{\mu\text{-}Ph_2PN(Et)PPh_2\}]$

	x	y	z	B_{eq} (Å^2)
Ru(1)	−0.22510(5)	0.35819(7)	0.13189(8)	3.32
Ru(2)	−0.20439(6)	0.13047(7)	0.09538(8)	3.30
Ru(3)	−0.15590(7)	0.24517(8)	−0.08445(9)	4.80
P(1)	−0.31144(16)	0.35375(20)	0.28622(23)	2.97
P(2)	−0.22741(16)	0.14867(20)	0.30160(23)	3.01
N	−0.2986(5)	0.2453(6)	0.3562(7)	3.38
O(11)	−0.3996(6)	0.3094(7)	−0.0840(8)	5.36
O(12)	−0.0371(5)	0.4058(6)	0.3216(8)	5.03
O(13)	−0.2173(7)	0.6048(7)	0.1385(10)	7.52
O(21)	−0.4130(6)	0.0716(6)	−0.0278(8)	5.04
O(22)	0.0102(5)	0.1728(7)	0.1753(8)	5.66
O(23)	−0.1809(6)	−0.1158(7)	0.0152(11)	7.76
O(31)	−0.3302(8)	0.0904(9)	−0.2532(9)	7.73
O(32)	0.0285(8)	0.3921(10)	0.0698(11)	8.72
O(33)	−0.0456(9)	0.0809(10)	−0.2296(12)	11.17
O(34)	−0.1969(8)	0.4224(8)	−0.2277(10)	8.02
C(11)	−0.3331(9)	0.3211(8)	−0.0061(11)	4.53
C(12)	−0.1059(8)	0.3841(8)	0.2490(11)	3.88
C(13)	−0.2199(8)	0.5128(10)	0.1348(10)	4.58
C(21)	−0.3362(8)	0.0975(8)	0.0170(10)	3.79
C(22)	−0.0682(8)	0.1641(8)	0.1447(10)	4.16
C(23)	−0.1902(7)	−0.0235(10)	0.0429(12)	5.07
C(31)	−0.2692(10)	0.1459(12)	−0.1824(12)	5.74
C(32)	−0.0414(12)	0.3395(12)	0.0195(13)	6.82
C(33)	−0.0862(10)	0.1414(11)	−0.1776(13)	6.65
C(34)	−0.1794(10)	0.3555(12)	−0.1735(12)	5.80
C(41)	−0.1205(7)	0.1865(7)	0.4234(9)	3.41
C(42)	−0.0994(7)	0.2846(8)	0.5216(10)	3.69
C(43)	−0.0158(8)	0.3075(9)	0.6111(11)	4.51
C(44)	0.0495(7)	0.2363(11)	0.5984(12)	4.90
C(45)	0.0324(7)	0.1412(11)	0.5006(12)	5.25
C(46)	−0.0523(7)	0.1151(9)	0.4135(11)	4.48
C(51)	−0.4359(7)	0.3405(8)	0.2156(9)	3.51
C(52)	−0.4935(6)	0.2375(8)	0.1809(9)	3.43
C(53)	−0.5836(7)	0.2270(10)	0.1156(11)	4.51
C(54)	−0.6187(8)	0.3152(11)	0.0821(11)	4.97
C(55)	−0.5641(8)	0.4171(10)	0.1137(11)	5.28
C(56)	−0.4725(7)	0.4308(9)	0.1839(11)	4.55
C(61)	−0.2793(7)	0.0201(8)	0.3316(10)	3.46
C(62)	−0.2501(7)	−0.0069(9)	0.4457(11)	4.07
C(63)	−0.2904(8)	−0.1042(10)	0.4651(13)	5.79
C(64)	−0.3601(10)	−0.1755(10)	0.3690(14)	6.57
C(65)	−0.3890(10)	−0.1490(11)	0.2577(14)	6.63
C(66)	−0.3487(8)	−0.0528(10)	0.2396(11)	4.98
C(71)	−0.2948(6)	0.4775(8)	0.4231(9)	3.46
C(72)	−0.3677(7)	0.5108(9)	0.4827(10)	4.09
C(73)	−0.3517(8)	0.6000(10)	0.5899(12)	5.21
C(74)	−0.2645(8)	0.6613(9)	0.6406(11)	4.75
C(75)	−0.1920(7)	0.6309(8)	0.5808(10)	3.98
C(76)	−0.2081(7)	0.5419(8)	0.4736(10)	3.73
C(81)	−0.3264(8)	0.2456(9)	0.4799(10)	4.93
C(82)	−0.4254(8)	0.1949(13)	0.4686(14)	7.56

Table 3

Selected interatomic distances, interatomic angles and torsion angles for $[Ru_3(CO)_{10}\{\mu\text{-}Ph_2PN(Et)PPh_2\}]$ [a]

Bond distances (Å)			Mean
Ru–Ru	Ru(1)–Ru(2)	2.799(1)	2.799(1)
	Ru(1)–Ru(3)	2.848(1)	2.854(7)
	Ru(2)–Ru(3)	2.861(1)	
Ligand ring	Ru(1)–P(1)	2.307(3)	2.308(2)
	Ru(2)–P(2)	2.310(3)	
	P(1)–N	1.714(9)	1.720(6)
	P(2)–N	1.725(8)	
Ru–C (Axial)	Ru(1)–C(11)	1.917(11)	1.938(6)
	Ru(1)–C(12)	1.925(10)	
	Ru(2)–C(21)	1.937(11)	
	Ru(2)–C(22)	1.958(12)	
	Ru(3)–C(31)	1.944(12)	
	Ru(3)–C(32)	1.949(14)	
Ru–C (Eq.)	Ru(1)–C(13)	1.902(12)	1.902(9)
	Ru(2)–C(23)	1.890(12)	
	Ru(3)–C(33)	1.926(15)	
	Ru(3)–C(34)	1.889(15)	
C–O (Axial)	C(11)–O(11)	1.148(14)	1.132(4)
	C(12)–O(12)	1.132(13)	
	C(21)–O(21)	1.130(13)	
	C(22)–O(22)	1.130(14)	
	C(31)–O(31)	1.119(15)	
	C(32)–O(32)	1.133(18)	
C–O (Eq.)	C(13)–O(13)	1.126(15)	1.131(9)
	C(23)–O(23)	1.134(15)	
	C(33)–O(33)	1.110(20)	
	C(34)–O(34)	1.155(19)	
Non-bonded contacts (axial carbonyls) (Å)			
C...C	C(11)...C(31)	2.874	2.826(22)
	C(31)...C(21)	2.736	
	C(21)...C(11)	2.841	
	C(12)...C(32)	2.799	
	C(32)...C(22)	2.885	
	C(22)...C(12)	2.823	
O...O	O(11)...O(31)	3.241	3.150(41)
	O(31)...O(21)	3.005	
	O(21)...O(11)	3.238	
	O(12)...O(32)	3.065	
	O(32)...O(22)	3.219	
	O(22)...O(12)	3.134	
Bond angles (°)			
Ru_3 ring	Ru(1)–Ru(2)–Ru(3)	60.4(0)	60.6(3)
	Ru(2)–Ru(1)–Ru(3)	60.9(0)	
	Ru(1)–Ru(3)–Ru(2)	58.7(0)	58.7

continued

Table 3 (continued)

			Mean
Ligand ring	Ru(2)–Ru(1)–P(1)	91.9(1)	89.8(21)
	Ru(1)–Ru(2)–P(2)	87.7(1)	
	Ru(1)–P(1)–N	115.3(3)	116.0(8)
	Ru(2)–P(2)–N	116.8(3)	
	P(1)–N–P(2)	118.0(5)	
	P(1)–N–C(81)	122.8(7)	120.2(26)
	P(2)–N–C(81)	117.6(7)	
Bond angles (°)			
Ru–C–O (Axial)	Ru(1)–C(11)–O(11)	173.3(9)	173.6(8)
	Ru(1)–C(12)–O(12)	175.7(9)	
	Ru(2)–C(21)–O(21)	175.6(10)	
	Ru(2)–C(22)–O(22)	172.9(10)	
	Ru(3)–C(31)–O(31)	170.5(14)	
	Ru(3)–C(32)–O(32)	173.5(14)	
Ru–C–O (Eq.)	Ru(1)–C(13)–O(13)	178.7(11)	178.3(3)
	Ru(2)–C(23)–O(23)	178.0(12)	
	Ru(3)–C(33)–O(33)	178.9(14)	
	Ru(3)–C(34)–O(34)	177.7(13)	
Torsion angles (ligand ring) (°)			
	P(2)–Ru(2)–Ru(1)–P(1)	−24.4	[−19.1]
	Ru(2)–Ru(1)–P(1)–N	20.2	[0.0]
	Ru(1)–P(1)–N–P(2)	−2.4	[26.6]
	P(1)–N–P(2)–Ru(2)	−23.7	[−45.9]
	N–P(2)–Ru(2)–Ru(1)	30.8	[36.6]

[a] Standard deviations as estimated in the crystallographic least squares refinement, are given in parentheses. The mean values are means of chemically equivalent values. The standard error of the mean, given in parentheses, is calculated using $[\Sigma(x_i - \bar{x})^2/n(n-1)]$ for n values x_i. The torsion angles given in the square brackets are for $[Ru_3(CO)_{10}\{\mu\text{-}Ph_2PCH_2PPh_2\}]$.

for atoms in the same ring. Atomic scattering factors were taken from International Tables for X-ray Crystallography [20]. The refinement converged at a final conventional R factor of 0.048 ($R_w = 0.051$) for 478 refined parameters. The function minimised was $\Sigma w(|F_0| - |F_c|)^2$ with $w = [\sigma^2(F_0) + g|F_0|]^{-1}$ and $g = 0.0001$.

Fractional atomic coordinates and selected interatomic distances and angles are listed in Tables 2 and 3 respectively. Tables of thermal parameters and lists of observed and calculated structure factors are available from the authors.

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