

# Synthesis and spectral studies on $Ru_3(CO)_{12-n}$ ( $\mu$ -Ph<sub>2</sub>AsCH<sub>2</sub>AsPh<sub>2</sub>)(L) (n = 3, L: PPh<sub>3</sub>, PCy<sub>2</sub>Ph,P(OCH<sub>3</sub>)<sub>3</sub>); n = 4, L = Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>): crystal and molecular structures of $Ru_3(CO)_9$ ( $\mu$ -Ph<sub>2</sub>AsCH<sub>2</sub>AsPh<sub>2</sub>)(PCy<sub>2</sub>Ph) and $Ru_3(CO)_8$ ( $\mu$ -Ph<sub>2</sub>AsCH<sub>2</sub>AsPh<sub>2</sub>)( $\mu$ -Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>)

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Abstract—Mixed ligand triangulotriruthenium cluster carbonyls,  $Ru_3(CO)_9(\mu-Ph_2AsCH_2AsPh_2)(L)$  (L = PPh<sub>3</sub>, PCy<sub>2</sub>Ph, P(OCH<sub>3</sub>)<sub>3</sub>) and  $Ru_3(CO)_8(\mu-Ph_2AsCH_2AsPh_2)(\mu-Ph_2PCH_2PPh_2)$  were synthesised and characterised by microanalysis, IR, <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR spectrometry. Single crystal X-ray structure determination of  $Ru_3(CO)_9(\mu-Ph_2AsCH_2AsPh_2)(PCy_2Ph)$  and  $Ru_3(CO)_8(\mu-Ph_2AsCH_2AsPh_2)(\mu-Ph_2PCH_2PPh_2)$  are reported. In both the clusters, the triruthenium framework is planar. In  $Ru_3(CO)_9(\mu-Ph_2AsCH_2AsPh_2)(PCy_2Ph)$ , the monodentate phosphine occupies an equatorial position for steric reasons. The effect of trisubstitution is explicit in the highly significant differences observed in Ru—Ru distances (2.8301(6), 2.8653(7) and 2.8873(7) Å) in the present compound compared to  $Ru_3(CO)_{10}(\mu-Ph_2AsCH_2AsPh_2)$ . The observed Ru—As distances are 2.4508(7) and 2.4331(7) Å respectively and the Ru—P distance is 2.362(1) Å. In the case of  $Ru_3(CO)_8(\mu-Ph_2AsCH_2AsPh_2)(\mu-Ph_2PCH_2PPh_2)$ , the chelating ligands occupy four equatorial positions. Two of the Ru—Ru distances are similar in length (2.848(2), 2.850(2) and 2.828(2) Å). However, positional disorder is associated with As and P atoms. Other bond parameters are normal. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: crystal structure; steric effect; triruthenium; carbonyl cluster; phosphine substitution.

Synthetic and structural reports on substituted triangulotriruthenium clusters have always been on the rise for their interesting structural variations and related catalytic activity [1]. The metal-metal bond rupture in clusters under catalytic reaction conditions is of concern [2]. The stability of the clusters have been ensured by the presence of a bridging or a capping ligand. Identification of a new radical initiation synthetic route by the Adelaide group has enabled a host of new substituted triangulotriruthenium clusters to be identified and characterised [3,4]. A large number of substituted derivatives,  $Ru_3(CO)_{12-n}L_n$ (L = group 15 ligand) have been reported [5–7]. The effect of substitution on the triruthenium clusters manifests itself in many ways [8] with a decrease in the molecular symmetry. Also, introduction of a non-CO ligand, in general results in the lengthening of M—M bonds and only smaller molecules, such as isocyanides, occupy axial positions. However, the

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trend in increase of M—M bond distances is only marginal. The group 15 ligands allow a degree of tuning of the reactivity of mixed ligand clusters [7]. In the case of a chelating ligand substituted cluster viz,  $Ru_3(CO)_{10}(\mu$ -Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>), only the equatorial position gets activated for subsequent substitution [8]. A number of substituted carbonyls such as  $Ru_3(CO)_9(\mu$ -Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>)L (L: P(OCH<sub>3</sub>)<sub>3</sub>) have been reported from our laboratory [9]. In continuation of our interest in the substituted clusters, we report the synthesis and characterisation of  $Ru_3(CO)_9(\mu$ -Ph<sub>2</sub>AsCH<sub>2</sub> AsPh<sub>2</sub>)(L) [L = PPh<sub>3</sub>, PCy<sub>2</sub>Ph (Cy: cyclohexyl), P(OCH<sub>3</sub>)<sub>3</sub>] and X-ray structures of  $Ru_3(CO)_9(\mu$ -Ph<sub>2</sub>AsCH<sub>2</sub>AsPh<sub>2</sub>)(PCy<sub>2</sub>Ph) and  $Ru_3(CO)_8(\mu$ -Ph<sub>2</sub>As CH<sub>2</sub>AsPh<sub>2</sub>)( $\mu$ -Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>).

## EXPERIMENTAL

## Materials

 $Ru_3(CO)_{12}$  (Aldrich),  $Ph_2AsCH_2AsPh_2(dpam)$ ,  $Ph_2PCH_2PPh_2(dppm)$ ,  $PCy_2Ph$  (Press Chemical Co) and  $P(OCH_3)_3$  (BDH) were used as received. Kieselgel  $60GF_{254}$  was used for TLC separations. The THF solvent was dried over sodium wire and freshly distilled for every reaction. Oxygen free nitrogen was used to maintain an inert atmosphere. Microanalysis was performed using a model  $240 \times A$  from Control Equipment Corporation. IR spectra were recorded with a Mattson 1000 FTIR spectrometer in a NaCl solution cell (0.1 mm). NMR spectra were recorded in CDCl<sub>3</sub> with a Bruker B2H 300/52.

(*Bis*(*diphenylarsino*)*methane*)*decacarbonylruthenium*(0),  $Ru_3(CO)_{10}(\mu$ -Ph<sub>2</sub>AsCH<sub>2</sub>AsPh<sub>2</sub>). The compound was prepared by using the phenylketyl initiator route as previously reported [4].

(Bis(diphenylarsino)methane)nonacarbonvl(triphenylphosphino)ruthenium(0),  $Ru_3(CO)_9(\mu-Ph_2As)$  $Ru_3(CO)_{10}(\mu-Ph_2AsCH_2AsPh_2)$  $CH_2AsPh_2)(PPh_3)$ . (100 mg, 0.0947 mmol) and PPh<sub>3</sub> (26 mg, 0.0995 mmol) were stirred THF (25 ml) under nitrogen. About 0.2 ml of diphenylketyl radical anion initiator was introduced into the reaction mixture under a current of nitrogen. The reaction mixture turned intense red. After 2 h of stirring, the solvent was removed under vacuum. The reaction mixture was separated using TLC (cyclohexane: acetone, 80:20). Three bands appeared including a minor quantity of the starting material. The major band (red)  $R_{\rm f} = 0.85$ , was separated and characterised. Yield = 47.5 mg, 38.9 %, m.p. 223–225° C. (Found : C, 48.40 ; H, 2.90 ; Calc.: C, 48.42; H, 2.89). IR (cyclohexane), v(CO) 2054 w, 1994 vs, 1976 vs, 1943 sh cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.3–7.7 (m, 25 H, Ph), δ 4.0 (s, 2H, CH<sub>2</sub>), <sup>13</sup>C NMR(CDCl<sub>3</sub>)  $\delta$  129.0–137.0 (m, Ph),  $\delta$  198.6 (m, CO), <sup>31</sup>P NMR(CDCl<sub>3</sub>)  $\delta$  35.5 (s, PPh<sub>3</sub>).

(Bis(diphenylarsino)methane)nonacarbonyl(trimethylphosphite)ruthenium(0), Ru<sub>3</sub>(CO)<sub>9</sub>(µ-Ph<sub>2</sub>As CH<sub>2</sub>AsPh<sub>2</sub>)P(OCH<sub>3</sub>)<sub>3</sub>. Ru<sub>3</sub>(CO)<sub>10</sub>(µ-Ph<sub>2</sub>AsCH<sub>2</sub>AsPh<sub>2</sub>) (100 mg, 0.0947 mmol) and P(OCH<sub>3</sub>) <sub>3</sub> (12mg, 0.094 mmol) in THF (25 ml) was added with 0.2 ml of initiator solution. The resultant mixture was stirred for 30 min and then the solvent was removed under vacuum. The products were separated using TLC. Three bands appeared including a very small quantity of the starting material and the major band was separated ( $R_f = 0.50$ , benzene : ethanol; 90:10). Yield: 31.1 mg, 28.5%, m.p. 219°C (Found: C, 38.50; H, 2.72; Calc.: C, 38.49; H, 2.71). IR (cyclohexane)  $\nu$ (CO) 2083 w, 2067 w, 2040 w, 1988 s, 1967 vs, 1925 sh, 1912 sh cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.2–7.4 (m, 20H, Ph):  $\delta$  4.0 (s, 2H, CH<sub>2</sub>);  $\delta$  3.6–3.8 (m, 9H, CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  35.5–57.5 (d, P).

(Dicyclohexyl)phenylphosphino)(bis(diphenylarsino)methane) nonacarbonvlruthenium(0), Ru<sub>1</sub>  $(CO)_9(\mu-Ph_2AsCH_2AsPh_2)(PCy_2Ph)$ .  $Ru_3(CO)_{10}(\mu-$ Ph<sub>2</sub>AsCH<sub>2</sub>AsPh<sub>2</sub>) (100 mg, 0.0947 mmol) and PCy<sub>2</sub>Ph(27.3 mg, 0.0995 mmol) in dry THF (25 ml) were added with 0.1 ml initiator and stirred for 4 h. The product as a major band was separated by TLC which contained four bands in all with a very minor quantity of the starting material; dichloromethane : ethanol; 90 : 10;  $R_{\rm f} = 0.26$ ; yield, 53.0 mg., 43.2%; m.p. 214-216°C. Found, C, 47.95; H, 3.77; Calc., 47.97; H,3.79. IR (cyclohexane) v(CO) 2052 w, 1989 vs, 1973 vs, 1938 m cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ 7.25–7.45 (m, 25H, Ph);  $\delta$  4.0 (s, 2H, CH<sub>2</sub>);  $\delta$  1.52 (s, 22H, Cy). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  128.5–130.0 (d, Ph),  $\delta$  199.0 (m, CO); <sup>31</sup>P NMR (CDCl<sub>3</sub>)  $\delta$  41.5 (s, P).

(Bis(diphenylarsino)methane)(bis(diphenylphosphino)methane)octacarbonylruthenium(0),  $Ru_3(CO)_8$  $(\mu$ -Ph<sub>2</sub>AsCH<sub>2</sub>AsPh<sub>2</sub>) $(\mu$ -Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>). Ru<sub>3</sub>(CO)<sub>10</sub> $(\mu$ -Ph<sub>2</sub>AsCH<sub>2</sub>AsPh<sub>2</sub>) (100 mg, 0.0947 mmol) and Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub> (38.22 mg, 0.0994 mmol) in THF (25 ml) under dry nitrogen was added with 0.1 ml initiator and stirred for 6 h. The product as a major band was separated by TLC which contained five bands including trace amounts of the starting material; hexane: acetone; 80:20;  $R_f = 0.50$ ; yield, 44.2 mg, 35.5%, m.p. 240°C. IR (cyclohexane) v(CO) 2081 w, 2040 w, 2013 w, 1981 sh, 1963 vs, 1896 w cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.1–7.4(m, 40H, Ph);  $\delta$  5.85 (s, 2H, CH<sub>2</sub>);  $\delta$  3.6–3.8 (q, 2H, CH<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ 124.0–128 (m, Ph),  $\delta$  198.8 (m, CO); <sup>31</sup>P NMR (CDCl<sub>3</sub>)  $\delta$  18.0–24.0 (dd, P).

### X-ray data collection

Determination of cell constants and data collection were carried out at room temperature (293 K) with Mo- $K_x$  radiation on a Siemens P4 diffractometer equipped with a graphite monochromator. Data were recorded by  $\theta/2\theta$  scan technique and were corrected for Lorentz and polarisation effects. The structure was solved by direct methods with SHELXTL-PC [11] and refined by full-matrix least squares technique on  $F^2$ with SHELXL93 [12]. All the hydrogens were fixed

	1	2	
Empirical formula	$C_{52}H_{49}As_2O_9PRu_3$	$C_{58}H_{44}As_2O_8P_2Ru_3$	
M	1301.9	1383.7	
Crystal system	triclinic; P-1	orthorhombic; Pca21	
a (Å)	12.570(1)	21.586(2)	
$b(\mathbf{A})$	12.902(1)	15.839(2)	
$c(\mathbf{A})$	16.949(2)	18.383(1)	
$\alpha$ (°)	92.07(1)	90	
$\beta$ (°)	110.50(1)	90	
γ (°)	98.14(1)	90	
$U(\mathbf{\hat{A}})$	2537.8(4)	6285.2(1)	
$D_{\rm c}/({\rm Mg}~{\rm m}^{-3})$	1.704	1.453	
Z	2	4	
$\mu$ (Mo- $K_{x}$ ) (cm <sup>-1</sup> )	22.61	23.21	
Scan mode	$\theta/2\theta$	heta/2 heta	
<i>T</i> (°K)	293(2)	293(2)	
$\theta$ range (°)	1.60-27.50	1.59-27.58	
Recorded reflections	11,868	8573	
Independent reflections	10,382 [R(int) = 0.0288]	7574 [ $R(int) = 0.0336$ ]	
$[I > 2\sigma(I)]$			
Residual R, Rw	0.0360, 0.0941	0.0549, 0.1700	

geometrically with the HADD utility [11]. The relevant data collection and refinement parameters are given in Table 1.

# **RESULTS AND DISCUSSION**

Microanalysis of the compounds agreed well with the proposed molecular formulae for all the reported compounds within the experimental errors.

# IR spectra

Isolation of a number of specifically substituted derivatives of  $Ru_3(CO)_{12}$  has enabled a definitive v(CO) spectral information possible on different entities [4,6]. As the number of substituents increases, the frequencies of the bands decrease in magnitude in general. Similarly, as the basicity of the ligand increases, the frequencies of the bands show a decrease. In the present study, trisubstituted,  $Ru_3(CO)_9(\mu-Ph_2AsCH_2AsPh_2)(L)$  clusters show two strong bands of almost equal intensities characteristically, one band at ~ 1960 and the other at ~ 2000 cm<sup>-1</sup>. In the case of the tetra-substituted cluster, six bands were observed, of which the one at 1963 cm<sup>-1</sup> was the strongest and appears to be the characteristic band similar to earlier observations [4].

### NMR spectra

<sup>1</sup>H NMR spectra of all the compounds showed a multiplet around  $\delta$  7.0 characteristic of the phenyl

groups. Other than that, the signal at  $\delta$  4.0 is due to the CH<sub>2</sub> protons. For the methoxy protons, the signal appeared at  $\delta$  3.6–3.8. In the case of the dicyclohexylphenylphosphine-cluster the signal at 1.52 ppm corresponds to the cyclohexyl protons. <sup>13</sup>C NMR spectra of all the substituted clusters showed a prominent signal around  $\delta$  128.5–130.0 ppm characteristic of the phenyl carbons. The carbonyl carbons in all the clusters showed as a multiplet at  $\delta \sim 198.6$  ppm. In addition, the methoxy carbons appeared at  $\delta$  30.0 ppm for the corresponding cluster. <sup>31</sup>P NMR spectra showed signals at  $\delta$  values 35.5, 41.5 and 55.5–57.5 ppm for PPh<sub>3</sub>, PCy<sub>2</sub>Ph and P(OCH<sub>3</sub>)<sub>3</sub> substituted clusters respectively. The observed trend is in keeping with their relative basicities. In the case of  $Ru_3(CO)_8$  $(\mu$ -Ph<sub>2</sub>AsCH<sub>2</sub>AsPh<sub>2</sub>) $(\mu$ -Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>), <sup>1</sup>H NMR showed signals corresponding to phenyl and methylene protons at  $\delta$  values 7.1–7.4, 5.85 (Ph<sub>2</sub>AsCH<sub>2</sub> AsPh<sub>2</sub>) and 3.6-3.8(Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>) respectively. In the range of  $\delta$ : 124.0–128.0, <sup>13</sup>C NMR spectrum showed signal due to phenyl carbons and <sup>31</sup>P NMR spectrum showed signals due to the P atoms at 18.0-24.0 ppm split by by the methylene protons.

#### X-ray crystal structures

The ORTEP plot of  $Ru_3(CO)_9(\mu-Ph_2AsCH_2AsPh_2)(PCy_2Ph)$  is shown in Fig. 1. The selected bond parameters are given in Table 2. The triangulotriruthenium framework is planar. The three Ru—Ru distances are 2.8301(6), 2.8653(7) and 2.8873(7) Å. All three distances are significantly different from each other. A comparison of the

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Fig. 1. ORTEP plot of Ru<sub>3</sub>(CO)<sub>9</sub>(µ-Ph<sub>2</sub>AsCH<sub>2</sub>AsPh<sub>2</sub>)(PCy<sub>2</sub>Ph).

Ru—Ru distances of  $Ru_3(CO)_{10}(\mu-Ph_2AsCH_2AsPh_2)$ [10] (2.817(1), 2.845(1), 2.840(1) Å) clearly shows that the dissimilarities have increased as a consequence of further substitution. Relatively, significant lengthening observed in Ru(1)-Ru(3) bond reflects itself in the shortening of the Ru(3)—Ru(2) bond. The equatorial Ru-C bond distances (mean : 1.853(6) Å) are shorter than the axial (mean: 1.922(6) Å) as observed in the parent  $Ru_3(CO)_{12}$  cluster [13]. The Ceq-Ru-Cax angles are close to 90° and Cax-Ru-—Cax angles are close to  $180^\circ$  excepting the ones associated with Ru(1) which show considerable deviations due to the bulky monodentate PCy<sub>2</sub>Ph. The Ru—P distance in the compound is 2.362(1) Å. The Ru-As distances in the present compound are 2.4508(7) and 2.4331(7) Å; which are asymmetric clearly compared to the distances observed in Ru<sub>3</sub>  $(CO)_{10}(\mu-Ph_2AsCH_2AsPh_2)$  (2.430(1), 2.422(1) Å) [10]. The substituent, (PCy<sub>2</sub>Ph) on Ru(1) is on an equatorial position for steric reasons and Ru-P- $(Cy_2Ph)$  bond is *trans* to the Ru<sub>3</sub>As<sub>2</sub> plane. The cyclohexyl rings are in the preferred chair conformation. The bond parameters associated with the phenyl rings are normal.

The ORTEP plot of  $Ru_3(CO)_8(\mu-Ph_2AsCH_2)$ 

 $AsPh_2$  ( $\mu$ -Ph\_2PCH\_2PPh\_2) is shown in Fig. 2 and selected bond parameters are given in Table 3. The triangulotriruthenium frame work is planar as observed in the other structure. Two of the Ru-Ru distances are similar, viz. 2.850(2) and 2.848(2) Å whereas the third bond is significantly shorter (2.828(2) Å) than the other two. The two chelating ligands occupy equatorial positions. However, unlike the case of the PCy<sub>2</sub>Ph analogue, the bond distances are not affected to a greater extent compared to the  $Ru_3(CO)_{12}$  [13],  $Ru_3(CO)_{10}(dppm)$  [14] and  $Ru_3$ (CO)<sub>10</sub>(dpam) [10]. The equatorial Ru-C bonds are shorter (mean: 1.83(2) Å) and the axial Ru-C bonds are longer (mean: 1.90(2) Å). Positional disorder associated with arsenic and phosporous atoms in the present structure excludes a rigorous comparison of the bond parameters. The distances corresponding to As(1) and As(2) on the basis of a higher site occupancies (site occupancies: As(1): 0.6333, As(2): 0.6333) from the metal centre are 2.394(2) and 2.404(2) Å. Similarly, Ru-P distances correponding to higher site occupancies are 2.359(3) and 2.345(3) Å. The bond parameters associated with the phenyl rings are normal.

Therefore, the steric effects due to the presence of

	1.0(1(6)		1.004(0)
Ru(1)— $C(2)$	1.861(6)	Ru(1) - C(3)	1.924(6)
Ru(1)C(1)	1.923(6)	Ru(1) - P(1)	2.3622(14)
Ru(1)— $Ru(2)$	2.8301(6)	Ru(1) - Ru(3)	2.8873(7)
Ru(2)-C(5)	1.875(6)	Ru(2)— $C(4)$	1.926(7)
Ru(2)-C(6)	1.933(7)	Ru(2)— $As(1)$	2.4331(7)
Ru(2)— $Ru(3)$	2.8653(7)	Ru(3)-C(8)	1.859(6)
Ru(3)—As(2)	2.4508(7)	As(1) - C(17)	1.941(5)
As(1) - C(11)	1.950(5)	As(1) - C(10)	1.974(6)
As(2)—C(23)	1.940(6)	As(2)—C(29)	1.952(5)
As(2)—C(10)	1.983(5)	P(1)-C(35)	1.838(6)
P(1) - C(41)	1.838(6)	P(1)—C(47)	1.852(6)
C(2) - Ru(1) - P(1)	96.3(2)	C(3) - Ru(1) - P(1)	91.7(2)
C(1) - Ru(1) - P(1)	93.7(2)	C(2) - Ru(1) - Ru(2)	98.0(2)
C(3) - Ru(1) - Ru(2)	82.3(2)	C(1) - Ru(1) - Ru(2)	92.4(2)
P(1) - Ru(1) - Ru(2)	164.24(4)	C(2) - Ru(1) - Ru(3)	158.1(2)
C(3) - Ru(1) - Ru(3)	87.8(2)	C(1) - Ru(1) - Ru(3)	90.4(2)
P(1) - Ru(1) - Ru(3)	105.24(4)	Ru(2) - Ru(1) - Ru(3)	60.14(2)
C(5) - Ru(2) - As(1)	108.1(2)	C(4)— $Ru(2)$ — $As(1)$	88.0(2)
C(6) - Ru(2) - As(1)	88.6(2)	C(5) - Ru(2) - Ru(1)	95.7(2)
C(4) - Ru(2) - Ru(1)	85.6(2)	C(6) - Ru(2) - Ru(1)	96.8(2)
As(1)— $Ru(2)$ — $Ru(1)$	155.55(2)	C(5) - Ru(2) - Ru(3)	154.1(2)
C(4) - Ru(2) - Ru(3)	96.8(2)	C(6) - Ru(2) - Ru(3)	81.8(2)
As(1)— $Ru(2)$ — $Ru(3)$	96.58(2)	Ru(1)— $Ru(2)$ — $Ru(3)$	60.92(2)
C(8) - Ru(3) - As(2)	102.1(2)	C(7) - Ru(3) - As(2)	92.0(2)
C(9) - Ru(3) - As(2)	93.7(2)	C(8) - Ru(3) - Ru(2)	164.8(2)
C(7) - Ru(3) - Ru(2)	84.7(2)	C(9) - Ru(3) - Ru(2)	94.3(2)
As(2) - Ru(3) - Ru(2)	92.84(2)	C(8) - Ru(3) - Ru(1)	106.2(2)
C(7) - Ru(3) - Ru(1)	87.6(2)	C(9) - Ru(3) - Ru(1)	87.0(2)
As(2) - Ru(3) - Ru(1)	151.70(2)	Ru(2)— $Ru(3)$ — $Ru(1)$	58.94(2)
As(1) - C(10) - As(2)	113.4(3)		()
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Table 2. Selected bond distances (Å) and angles (°) for Ru<sub>3</sub>(CO)<sub>9</sub>(µ-Ph<sub>2</sub>AsCH<sub>2</sub>AsPh<sub>2</sub>)(PCy<sub>2</sub>Ph)



Fig. 2. ORTEP plot of Ru<sub>3</sub>(CO)<sub>8</sub>(µ-Ph<sub>2</sub>AsCH<sub>2</sub>AsPh<sub>2</sub>)(µ-Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>).

Ru(1)—C(2)	1.82(2)	Ru(1)—C(1)	1.90(2)
Ru(1) - C(3)	1.90(2)	Ru(1)— $As(1)$	2.394(2)
Ru(1) - P(1)	2.394(2)	Ru(1)— $Ru(3)$	2.848(2)
Ru(1) $Ru(2)$	2.850(2)	Ru(2) - P(3)	2.345(3)
Ru(2)—As(3)	2.345(3)	Ru(2)— $As(2)$	2.404(2)
Ru(2) - P(2)	2.404(2)	Ru(2)— $Ru(3)$	2.828(2)
Ru(3)—As(4)	2.359(3)	Ru(3)—P(4)	2.359(3)
$C(2) - R_{11}(1) - P(1)$	100.6(7)	$C(1) = R_{11}(1) = P(1)$	91 4(6)
C(3) - Ru(1) - P(1)	97.7(6)	C(2) = Ru(1) = Ru(3)	108.5(7)
C(1) = Ru(1) = Ru(3)	79.8(6)	C(3) - Ru(1) - Ru(3)	90.6(7)
$A_{s(1)} - R_{u(1)} - R_{u(3)}$	149.27(7)	P(1) - Ru(1) - Ru(3)	149.27(7)
C(2) - Ru(1) - Ru(2)	165.7(7)	C(1) - Ru(1) - Ru(2)	96.0(6)
C(3) - Ru(1) - Ru(2)	80.0(6)	$A_{s(1)} - R_{u(1)} - R_{u(2)}$	92.76(6)
P(1) - Ru(1) - Ru(2)	92.76(6)	Ru(3) - Ru(1) - Ru(2)	59.50(4)
P(3) - Ru(2) - As(2)	110.28(9)	As(3) - Ru(2) - As(2)	110.28(9)
P(3) - Ru(2) - P(2)	110.28(9)	As(3) - Ru(2) - P(2)	110.28(9)
P(3) - Ru(2) - Ru(3)	97.86(8)	$A_{s(3)}$ — $R_{u(2)}$ — $R_{u(3)}$	97.86(8)
As(2) - Ru(2) - Ru(3)	151.61(7)	P(2) - Ru(2) - Ru(3)	151.61(7)
P(3) - Ru(2) - Ru(1)	156.58(8)	As(3)— $Ru(2)$ — $Ru(1)$	156.58(8)
As(2) - Ru(2) - Ru(1)	92.33(7)	P(2) - Ru(2) - Ru(1)	92.33(7)
Ru(3)— $Ru(2)$ — $Ru(1)$	60.22(4)	As(4)— $Ru(3)$ — $Ru(2)$	90.80(7)
C(7)— $Ru(3)$ — $Ru(1)$	105.5(6)	C(6) - Ru(3) - Ru(1)	92.8(5)
As(4) - Ru(3) - Ru(1)	150.16(8)	P(4) - Ru(3) - Ru(1)	150.16(8)
Ru(2) - Ru(3) - Ru(1)	60.28(4)	P(4) - Ru(3) - Ru(2)	90.80(7)

Table 3. Selected bond distances (Å) and angles (°)<sup>*a*</sup> for  $Ru_3(CO)_8(\mu - Ph_2AsCH_2AsPh_2)$ ( $\mu - Ph_2PCH_2PPh_2$ )

 $PCy_2Ph$  in the strucure very clearly manifests itself in the dissimilarities associated with the Ru—Ru bonds but such a dissimilarity is reduced to a larger extent in the cluster with two chelating ligands, however disorder associated with the latter precludes a detailed comparison.

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<sup>&</sup>quot;Positional disorder is associated with As and P atoms and hence four Ru—As and four Ru—P bonds and related bond angles are listed.