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XXXXVI *. SOME RUTHENIUM CARBONYL CLUSTER COMPLEXES CONTAINING ARYLDIAZO LIGANDS: X-RAY STRUCTURE OF $Ru_3(\mu_3\text{-}PPhCH_2PPh_2)(\mu\text{-}\eta^1\text{-}N{=}NC_6H_3Cl_2\text{-}2,4)(CO)_9$

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Summary

Reactions of $[Ru_3(\mu_3\text{-}EPhCH_2EPh_2)(CO)_9]^-$ (E = P or As) with $[ArN_2]^+$ (Ar = Ph or $C_6H_3Cl_2$-2,4) have given the aryldiazo-triruthenium complexes $Ru_3(\mu_3\text{-}EPhCH_2EPh_2)(\mu\text{-}\eta^1\text{-}N{=}NAr)(CO)_9$ (E = P, Ar = Ph or $C_6H_3Cl_2$-2,4; E = As, Ar = Ph). The X-ray structure of the dichlorophenyl complex shows a bent Ru_3 arrangement, the non-bonded Ru ··· Ru vector being spanned by the α-nitrogen of the N=NAr group and the phosphorus of the μ_3-phosphido-phosphine ligand. The complex is monoclinic, space group $P2_1/c$, with a 11.94(1), b 28.69(1), c 12.306(8) Å, β 117.98(5)°, $Z = 4$; 4739 observed data with $I > 3\sigma(I)$ were refined by block diagonal least-squares methods to $R = 0.035$, $R_w = 0.029$. On heating, the μ-η^1-N=NPh complexes undergo an internal cyclometallation reaction to give $Ru_3(\mu\text{-}H)(\mu_3\text{-}EPhCH_2EPh_2)(\mu\text{-}\eta^1,\eta^1\text{-}N{=}NC_6H_4)(CO)_8$, in which the α-nitrogen spans the non-bonded Ru ··· Ru vector, and the P (As) atom of the phosphido (arsenido) group bridges the adjacent Ru–Ru bond, which is also bridged by the H atom.

Introduction

Although extensive studies of mononuclear complexes containing nitrosyl (NO) or aryldiazo (ArN_2) ligands have shown the complementary nature of these two

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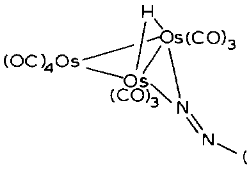
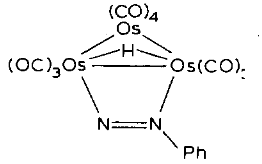
* For Part XXXXV, see ref. 5.

ligands [1,2] there are only two structurally characterised cluster complexes, $Os_3(\mu\text{-}H)(\mu\text{-}\eta^1\text{-}N{=}NC_6H_4Me\text{-}4)(CO)_{10}$ (**1**) [3] and $Os_3(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}N{=}NPh)(CO)_{10}$ (**2**) [4], containing the ArN_2 ligands. Compounds of the former type were obtained from reactions between aryldiazonium tetrafluoroborates and $Os_3(\mu\text{-}H)_2(CO)_{10}$, followed by addition of NH_3 to deprotonate the supposed $[Os_3H(N{=}NHAr)(CO)_{10}]^+$ intermediate. Irradiation of **1** affords the isomeric $\mu\text{-}\eta^2\text{-}N{=}NAr$ derivatives (**2**); the phenyl complex was also obtained from $Os_3(CO)_{10}(NCMe)_2$ and phenylhydrazine [4]. Pyrolysis of **2** regenerates **1**: both isomerisation reactions are intramolecular.



(1)



(2)

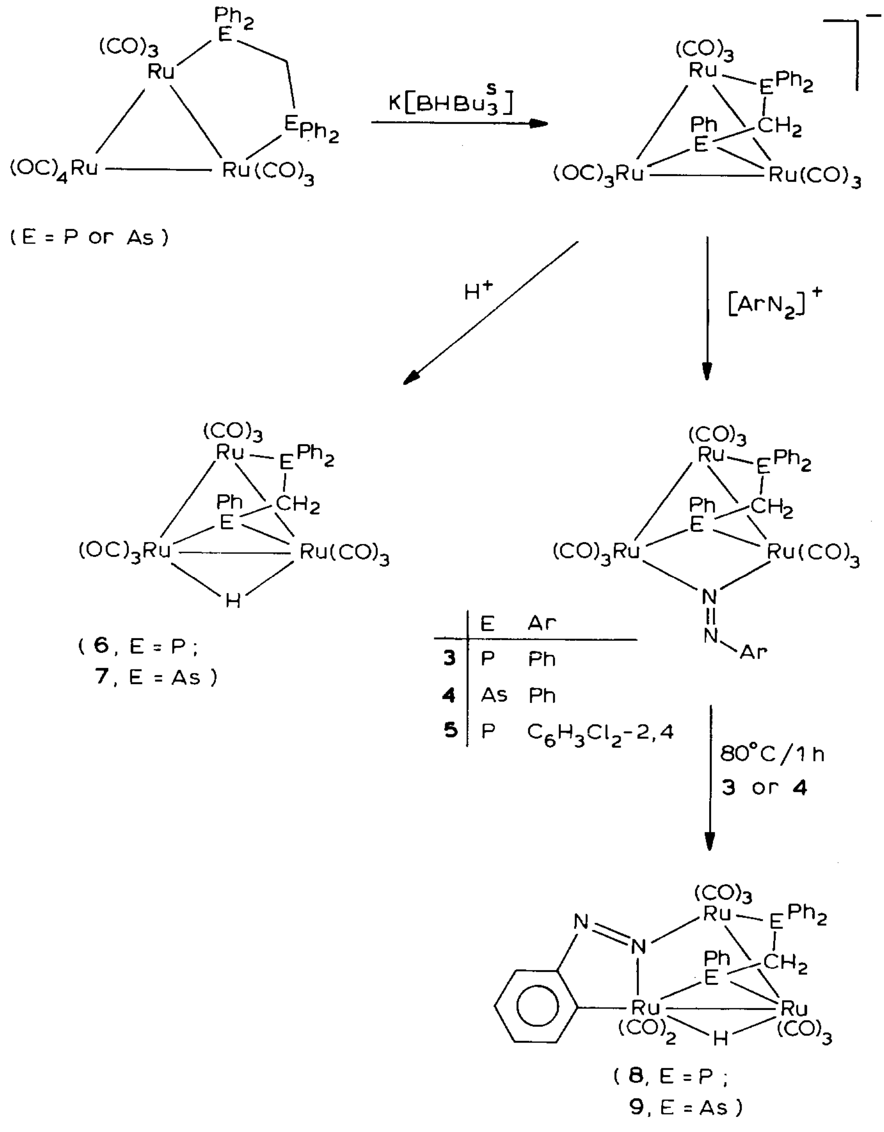
We have earlier described the synthesis of the cluster anion $[Ru_3(\mu_3\text{-}EPhCH_2EPh_2)(CO)_9]^-$ (E = P or As) and its reactions with various electrophiles [5]; this paper describes in detail the products obtained by treatment of the anions with aryldiazonium salts. In contrast with the osmium series, we find that further reaction of these complexes results not in isomerisation, but in a cyclometallation reaction. Some of these results have been reported in preliminary form [6].

Results and discussion

The reactions between $[Ru_3(\mu_3\text{-}EPhCH_2EPh_2)(CO)_9]^-$ and $[PhN_2][PF_6]$ or $[2,4\text{-}Cl_2C_6H_3N_2][BF_4]$ proceeded readily in tetrahydrofuran at room temperature to give yellow-orange complexes $Ru_3(\mu\text{-}\eta^1\text{-}N_2R)(\mu_3\text{-}EPhCH_2EPh_2)(CO)_9$ (R = Ph, E = P (**3**), As (**4**); R = $C_6H_3Cl_2$-2,4, E = P (**5**) (Scheme 1)), together with small amounts of the corresponding hydrido complexes **6** and **7**. The formation of the latter complexes is likely to have resulted from protonation of the cluster anions by HF which is present as a minor impurity in the aryldiazonium salts. Complexes **3**–**5** were identified by elemental microanalysis and from their spectral properties. Thus, four medium to strong $\nu(CO)$ bands are found between 2100–1950 cm^{-1}, and a strong band assigned to $\nu(N{=}N)$ coupled with the aryl ring modes occurs at 1575 cm^{-1} [7]. In their ^1H NMR spectra, the characteristic AB resonance for the CH_2 protons of the capping phosphido-phosphine ligand was found at δ ca. 4.5. The molecular structure of **5** was confirmed by a single-crystal X-ray study (see below).

We have no evidence for the formation of any complexes containing $\mu\text{-}\eta^2\text{-}N{=}NAr$ ligands analogous to the osmium complexes **2**.

Complexes **3** and **4** undergo facile cyclometallation of the aryldiazo ligand on heating in refluxing cyclohexane (1 h) to give orange $Ru_3(\mu\text{-}H)(\mu\text{-}\eta^1,\eta^1\text{-}N_2C_6H_4)(\mu_3\text{-}EPhCH_2EPh_2)(CO)_8$ (E = P (**8**), As (**9**)) in high yields (Scheme 1). The $\nu(CO)$ spectra are more complex than those of complexes **3**–**5**, containing eight medium to strong bands, suggesting a considerable reduction in symmetry of the cluster. The ^1H NMR spectra confirm the presence of the metal-bonded hydrogen at δ −11.45 [dd, J(PH) 2.5 and 15.5 Hz] for **8** and δ −11.65(s) for **9**, together with the extended aromatic proton resonances between δ 7.10–8.25. An AB(XY) pattern at δ 2.45 for **8**, which is similar to that observed for complex **3**, and an AB quartet



	E	Ar
3	P	Ph
4	As	Ph
5	P	$C_6H_3Cl_2$-2,4

SCHEME 1. Formation and cyclometallation of aryldiazo-ruthenium complexes.

at δ 2.66 (J(AB) 12.9 Hz) for **9** can be assigned to the magnetically inequivalent methylene protons of the μ_3-$EPhCH_2EPh_2$ ligands. Again, the above formulation was confirmed by an X-ray structural study of $Ru_3(\mu$-$H)(\mu_3$-$AsPhCH_2AsPh_2)(\mu$-η^1, η^1-$N{=}NC_6H_4)(CO)_8$ (**9**) [6], which shows that cyclometallation of the aryldiazo ligand has occurred by oxidative addition of the *ortho*-C–H bond to Ru(3), the hydrogen (which was located and refined in the X-ray study) taking up a bridging position between Ru(3) and Ru(2). As can be seen by reference to Scheme 1, the cyclometallation reaction is accompanied by either a shift in the aryldiazo ligand with concomitant Ru–Ru bond cleavage and closure or a migration of the dephenylated μ_3-phosphido-phosphine and μ_3-arsenido-arsine ligands.

This reaction contrasts with the η^1- and η^2-ArN_2 interconversions observed in complexes such as **1** and **2** [4] and is characteristic of phenylazo ligands (such as azobenzene) on mononuclear complexes [11]. Indeed azobenzenes react with some ruthenium cluster complexes to give mononuclear cyclometallated derivatives [12]; in the present instance the μ_3-$EPhCH_2EPh_2$ ligand prevents cluster degradation.

Molecular structure of $Ru_3(\mu_3\text{-}PPhCH_2PPh_2)(\mu\text{-}\eta^1\text{-}N{=}NC_6H_3Cl_2\text{-}2,4)(CO)_9$ *(5)*

The crystal consists of discrete molecules of the complex, separated by normal Van der Waals distances; there are no abnormally short contacts. The molecular structure of **5** is shown in Fig. 1. The three metal atoms are arranged in a triangle, two edges of which are short enough (Ru(1)–Ru(2) 2.875(2), Ru(1)–Ru(3) 2.893(2) Å) to permit significant metal–metal bonding interaction. The third edge is bridged by the N=NAr ligand and by the phosphido group of the capping ligand. Each acts as a 3e-donor, and there is essentially no direct bonding interaction between the two metal atoms, which are separated by 3.321(2) Å. In $Ru_3(\mu\text{-}NO)_2(CO)_{10}$, the long Ru–Ru separation, which is bridged by the NO groups, is 3.15 Å [8], while in **9** (see below), the non-bonded ruthenium atoms are even further apart, at 3.547(1) Å. The coordination about each ruthenium atom in **5** is completed by three CO ligands, which give each metal atom approximate octahedral stereochemistry.

The μ-N=NAr ligand is attached to Ru(1) and Ru(3) via atom N(1) (Ru(2)–N(1) 2.137(4), Ru(3)–N(1) 2.098(4) Å). The latter may be compared with values of

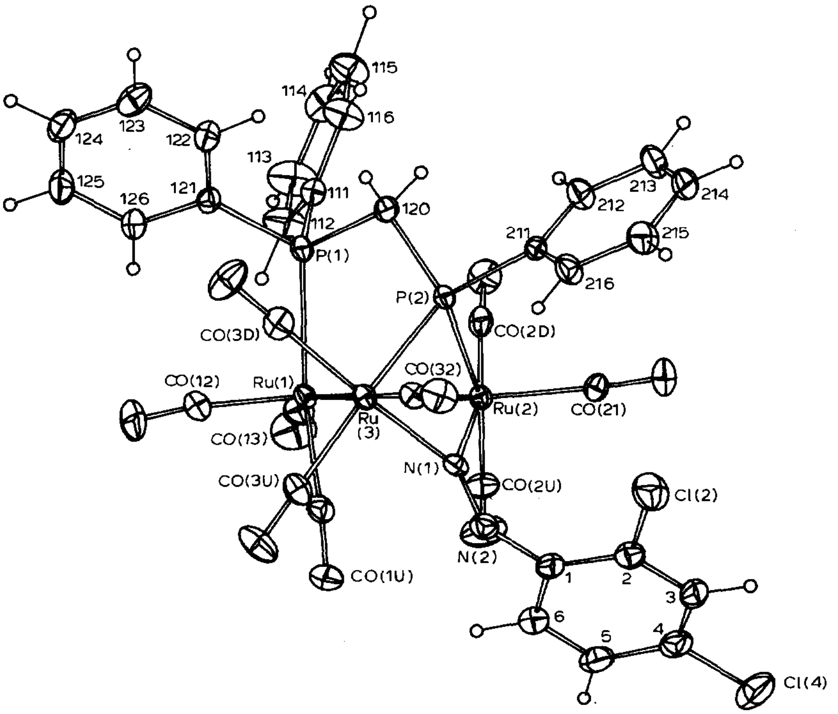
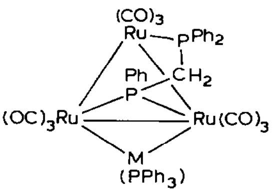
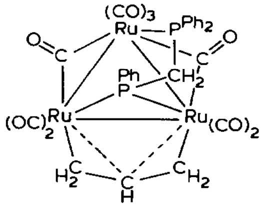


Fig. 1. A molecule of $Ru_3(\mu_3\text{-}PPhCH_2PPh_2)(\mu\text{-}\eta^1\text{-}N{=}NC_6H_3Cl_2\text{-}2,4)(CO)_9$ (**5**), showing the numbering scheme for the non-hydrogen atoms, together with 20% thermal ellipsoids.

2.092(5) and 2.065(7) Å found for similar bonds in **9**, or with the Os–N distances of 2.036(11) and 2.056(11) Å in **1** [3]. However, the lengthening of the bond to Ru(2) is noteworthy; no obvious explanation is apparent, but the asymmetry reflects in inverted fashion the difference in Ru(2)–P(2) and Ru(3)–P(2) distances. We have noted previously that the bridging groups in these types of complex are not symmetrically arranged, and that, for example, in complexes **10** the longer M–Ru distance (M = Cu, Ag or Au) involves the ruthenium with the shorter P–Ru separation [5].



(10)



(11)

There is an interesting difference in the conformation of the aryldiazo groups in the three complexes. In **5**, the 2,4-$Cl_2C_6H_3N_2$ group bridges Ru(2) ··· Ru(3) on the opposite side of the Ru_3 plane to the phosphido-phosphine ligand [dihedral Ru(1)Ru(2)Ru(3)/Ru(2)Ru(3)N(2) 122.6°], while in **9**, the $C_6H_4N_2$ group, which does not bridge the same Ru–Ru vector as the arsenido group, is bent up on the same side of the Ru_3 plane as the arsenido-arsine ligand [dihedral Ru(1)-Ru(2)Ru(3)/Ru(1)Ru(3)N(1) 156.3°]. In the osmium complex **1**, the dihedral angle between the corresponding planes is 105.74°. Within the aryldiazo ligand, the N(1)–N(2)-separation (1.230(5) Å) is similar to that found earlier in **9** (1.267(8) Å) and in **1** (1.238(18) Å); all distances are consistent with the presence of N=N double bonds. The ArN=N group is bent at the β-nitrogen (angle N(1)N(2)C(1) 116.8(4)°), and the angle subtended at N(1) is 103.3(1)° (cf. 118.6(3) in **9**, 87.2(5)° in **1**, but note that in the latter an Os–Os bond is present).

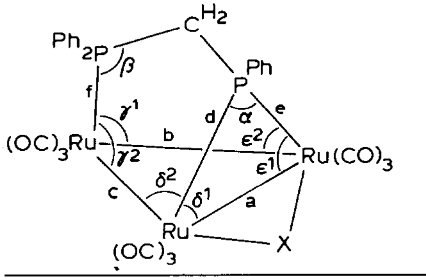
The geometry of the μ_3-$PPhCH_2PPh_2$ in **5** is compared with those of the same ligand in the complexes $Ru_3(\mu\text{-}H)(\mu_3\text{-}PPhCH_2PPh_2)(CO)_9$ (**6**) [9], $MRu_3(\mu_3\text{-}PPhCH_2PPh_2)(CO)_9(PPh_3)$ (M = Cu, Ag and Au) (**10**) [5] and $Ru_3(\mu\text{-}C_3H_5)(\mu_3\text{-}PPhCH_2PPh_2)(CO)_9$ (**11**) [10], in Table 1. The most obvious difference is the lengthening of Ru(2)–Ru(3) vector, which results in an opening of the Ru(2)P(2)Ru(3) angle (α) by some 10°. There have been many structural studies of complexes containing phosphido-bridged metal–metal bonds, and these have all followed the empirical correlation first established by Dahl and coworkers [12], who pointed out that metal–metal bonding interactions occurred when the M–M vector subtended a sharply acute angle at the μ-phosphido P atom. The results obtained for the five complexes mentioned above also fit in with this pattern, as does that for complex **9** (angle Ru(2)As(2)Ru(3) 77.2(1)°). However, in this case, although the aryldiazo group spans two formally non-bonded rutheniums (Ru(1) and Ru(3)), the phenylarsenido group bridges a bonded pair of metal atoms (Ru(2) and Ru(3)).

Molecular structure of $Ru_3(\mu\text{-}H)(\mu_3\text{-}AsPhCH_2AsPh_2)(\mu\text{-}\eta^1,\eta^1\text{-}N{=}NC_6H_4)(CO)_8$ *(9)*

The structure of a molecule of **9** is shown in Fig. 2. While some details have already been reported, it is useful to compare the structure of this complex with that

TABLE 1

GEOMETRY OF μ_3-$PPhCH_2PPh_2$ LIGANDS ON Ru_3 CLUSTERS



X =	$N{=}NC_6H_3Cl_2$ (5) [a]	H (6) [b]	$Cu(PPh_3)$ (10, M = Cu) [c]	$Ag(PPh_3)$ (10, M = Ag) [c]	$Au(PPh_3)$ (10, M = Au) [c]	C_3H_5 (11) [d]	(14) [e]
Bond distances (Å)							
a	3.321(2)	2.820(1)	2.885(1)	2.944(1)	2.942(1)	2.887(1)	3.0367(5)
b	2.893(2)	2.890(1)	2.873(1)	2.873(1)	2.867(1)	2.853(1) [g]	2.8361(2)
c	2.875(2)	3.012(1) [f]	2.896(1)	2.894(1)	2.891(1)	2.853(1) [g]	2.8361(2)
d	2.367(2)	2.306(1)	2.336(2)	2.349(2)	2.348(2)	2.359(1)	2.2958(6)
e	2.374(2)	2.332(1)	2.316(2)	2.328(2)	2.320(2)	2.344(1)	2.3262(6)
f	2.415(2)	2.384(1)	2.415(2)	2.432(2)	2.419(2)	2.411(1)	2.3863(6)
Bond angles (°)							
α	88.93(6)	74.89(2)	76.64(6)	78.03(7)	78.12(5)	75.7(1)	
β	109.2(2)	113.24(7)	112.0(2)	111.7(3)	111.7(2)		
γ^1	91.34(7)	93.08(1)	92.74(6)	92.76(6)	92.89(5)		
γ^2	91.63(6)	90.79(1)	89.86(6)	88.78(6)	88.60(5)		
δ^1	45.61(5)	52.98(1)	51.99(5)	51.31(6)	51.37(4)		52.63(1)
δ^2	75.14(5)	79.09(1)	78.33(5)	78.57(5)	78.49(4)		77.16(2)
ϵ^1	45.45(3)	52.13(1)	51.37(5)	50.66(6)	50.51(4)		51.67(1)
ϵ^2	74.70(5)	76.13(1)	78.51(5)	78.70(6)	78.57(5)		81.96(2)

[a] This work. [b] Reference 9. [c] Reference 5. [d] Reference 10. [e] Reference 13. [f] H bridges this bond. [g] Bridged by CO.

of **5** and also with that of $\overline{Ru(C_6H_4N{=}N}Ph)_2(CO)_2$ (**12**) [13]. The three ruthenium atoms again form an open triangle, with only two direct metal–metal interactions (Ru(1)–Ru(2) 2.903(1), Ru(2)–Ru(3), 3.055(1) Å); the non-bonded pair are separated by 3.547(1) Å. Compared with **5**, the major difference is that the arsenido group bridges a bonded pair of metal atoms (Ru(2)–As(2) 2.456(1), Ru(3)–As(2) 2.437(1) Å), while the aryldiazo group spans the Ru(1) ··· Ru(3) vector. The hydrogen atom bridges Ru(2)–Ru(3).

The geometry about Ru(3) resembles that found in **12**. Thus, the Ru(3)–N(1) distance (2.065(7) Å) is shorter than those in **12** (2.110(2), 2.158(3) Å), while the Ru(3)–C(46) separation (2.083(4) Å) is similar (2.048(3), 2.093(4) Å). The corresponding C–Ru–N angles are 77.4(2)° in **9**, 76.9(1) and 75.4(1)° in **12**, all being smaller than the ideal 90° because of the bite of the cyclometallated ligand. In both complexes, the N=N bonds are of similar lengths (1.267(8) in **9**, 1.279(4) and 1.291(3) in **12**) and the angles Ru–N=N (119.7(5)° in **9**, 117.5(2) and 118.4(2)° in **12**) show that no significant distortion of sp^2 geometry has occurred. These structural data are consistent with the conclusion drawn above, that the products

(Continued on p. 165)

TABLE 2

NON-HYDROGEN ATOM COORDINATES

Atom	*x*	*y*	*z*
Ru(1)	0.18096(4)	0.12538(2)	0.23504(4)
Ru(2)	0.04688(4)	0.07547(1)	0.34096(4)
Ru(3)	−0.02264(4)	0.18263(1)	0.22628(4)
C(12)	0.2167(6)	0.1710(2)	0.1454(5)
O(12)	0.2290(5)	0.1965(2)	0.0803(4)
C(13)	0.2812(5)	0.0725(2)	0.2422(5)
O(13)	0.3296(4)	0.0402(2)	0.2311(4)
C(1U)	0.0473(5)	0.1017(2)	0.0881(5)
O(1U)	−0.0293(4)	0.0872(2)	−0.0028(3)
C(21)	−0.0493(5)	0.0538(2)	0.4199(5)
O(21)	−0.0988(4)	0.0410(1)	0.4734(4)
C(2U)	0.0331(5)	0.0206(2)	0.2431(5)
O(2U)	0.0371(4)	−0.0126(2)	0.1954(4)
C(2D)	0.2031(5)	0.0528(2)	0.4660(5)
O(2D)	0.2942(4)	0.0380(1)	0.5435(4)
C(32)	−0.1595(5)	0.2166(2)	0.2296(5)
O(32)	−0.2403(4)	0.2379(2)	0.2279(4)
C(3U)	−0.0860(6)	0.1922(2)	0.0528(5)
O(3U)	−0.1246(5)	0.1980(2)	−0.0500(4)
C(3D)	0.0851(5)	0.2358(2)	0.2643(5)
O(3D)	0.1504(4)	0.2672(1)	0.2878(4)
P(1)	0.3281(1)	0.15731(5)	0.4327(1)
C(111)	0.4666(5)	0.1237(2)	0.5421(5)
C(112)	0.5257(6)	0.0927(2)	0.5026(6)
C(113)	0.6321(6)	0.0680(3)	0.5859(6)
C(114)	0.6799(6)	0.0758(2)	0.7069(6)
C(115)	0.6275(6)	0.1079(2)	0.7481(6)
C(116)	0.5206(6)	0.1312(2)	0.6655(5)
C(121)	0.4118(5)	0.2107(2)	0.4316(4)
C(122)	0.4214(5)	0.2499(2)	0.5015(5)
C(123)	0.4889(6)	0.2891(2)	0.4993(6)
C(124)	0.5499(6)	0.2889(2)	0.4293(6)
C(125)	0.5444(6)	0.2508(2)	0.3613(6)
C(126)	0.4757(5)	0.2119(2)	0.3617(5)
C(120)	0.2430(5)	0.1704(2)	0.5209(5)
P(2)	0.0790(1)	0.15099(5)	0.4281(1)
C(211)	0.0166(5)	0.1550(2)	0.5385(4)
C(212)	0.0808(5)	0.1331(2)	0.6515(5)
C(213)	0.0322(6)	0.1310(2)	0.7336(5)
C(214)	−0.0840(6)	0.1507(2)	0.7019(6)
C(215)	−0.1496(6)	0.1720(2)	0.5914(6)
C(216)	−0.0992(5)	0.1741(2)	0.5101(5)
N(1)	−0.1036(4)	0.1162(1)	0.2052(3)
N(2)	−0.2148(4)	0.1084(2)	0.1300(4)
C(1)	−0.2621(5)	0.0614(2)	0.1282(5)
C(2)	−0.3358(5)	0.0527(2)	0.1850(5)
Cl(2)	−0.3663(2)	0.09730(7)	0.2623(2)
C(3)	−0.3843(5)	0.0085(2)	0.1818(5)
C(4)	−0.3585(6)	−0.0262(2)	0.1196(5)
Cl(4)	−0.4150(2)	−0.08195(7)	0.1181(2)
C(5)	−0.2927(6)	−0.0172(2)	0.0560(5)
C(6)	−0.2445(5)	0.0270(2)	0.0604(5)

TABLE 3

RUTHENIUM AND PHOSPHORUS ATOM ENVIRONMENTS (The first column in each matrix is the ruthenium–ligand distance (Å); other entries are the angles (°) subtended at the ruthenium by the relevant atoms at the head of the row and column. The phosphorus environments are also given in this form)

Ru(1)	*r*	Ru(3)	P(1)	C(12)	C(13)	C(1U)
Ru(2)	2.875(2)	70.31(4)	91.63(7)	159.7(2)	93.1(2)	81.7(2)
Ru(3)	2.893(2)		91.34(6)	90.0(2)	161.9(2)	81.5(2)
P(1)	2.415(2)			94.0(2)	96.4(2)	171.5(2)
C(12)	1.885(7)				105.7(3)	90.6(3)
C(13)	1.909(6)					89.2(2)
C(1U)	1.890(5)					

Ru(2)	*r*	Ru(3)	P(2)	N(1)	C(21)	C(2U)	C(2D)
Ru(1)	2.875(2)	55.09(3)	75.14(5)	79.4(1)	169.0(2)	91.4(2)	89.6(2)
Ru(3)	3.321(2)		45.61(5)	37.9(1)	115.1(2)	123.7(2)	128.2(2)
P(2)	2.367(2)			75.6(1)	94.3(2)	166.3(2)	93.3(2)
N(1)	2.137(4)				95.1(2)	99.3(2)	166.1(2)
C(21)	1.922(7)					98.9(3)	94.2(3)
C(2U)	1.941(6)						89.4(2)
C(2D)	1.891(5)						

Ru(3)	*r*	Ru(2)	P(2)	N(1)	C(32)	C(3U)	C(3D)
Ru(1)	2.893(2)	54.60(2)	74.70(5)	79.6(1)	174.9(2)	90.5(2)	89.2(2)
Ru(2)	3.321(2)		45.45(3)	38.76(10)	120.4(2)	119.6(2)	129.1(2)
P(2)	2.374(2)			76.2(1)	101.2(2)	163.5(2)	95.4(2)
N(1)	2.098(4)				96.7(2)	94.2(2)	167.4(2)
C(32)	1.919(7)					93.2(3)	94.1(3)
C(3U)	1.922(6)						91.5(2)
C(3D)	1.906(6)						

P(1)	*r*	C(111)	C(121)	C(120)
Ru(1)	2.415(2)	121.2(2)	116.8(2)	109.2(2)
C(111)	1.840(4)		97.9(2)	103.3(3)
C(121)	1.833(6)			106.7(3)
C(120)	1.840(7)			

P(2)	*r*	Ru(3)	C(120)	C(211)
Ru(2)	2.367(2)	88.93(6)	117.4(2)	110.9(2)
Ru(3)	2.374(2)		114.1(2)	124.4(2)
C(120)	1.830(5)			101.9(3)
C(211)	1.833(7)			

Also:
N(1)–N(2), 1.230(5); N(2)–C(1), 1.460(7) Å;
Ru(2,3)–N(1)–N(2), 134.7(4), 121.9(3);
Ru(2)–N(1)–Ru(3), 103.3(1);
N(1)–N(2)–C(1), 116.8(4)°.
P(1)–C(20)–P(2), 107.1(3)°.

TABLE 4

CARBONYL GEOMETRIES

Carbonyl	*r*(C–O) (Å)	Ru–C–O (°)
12	1.145(9)	172.9(5)
13	1.133(8)	171.2(4)
1U	1.140(6)	176.7(6)
21	1.132(9)	175.5(4)
2U	1.131(8)	172.9(4)
2D	1.140(6)	176.7(6)
32	1.133(8)	177.0(5)
3U	1.137(7)	179.3(6)
3D	1.136(7)	179.2(4)

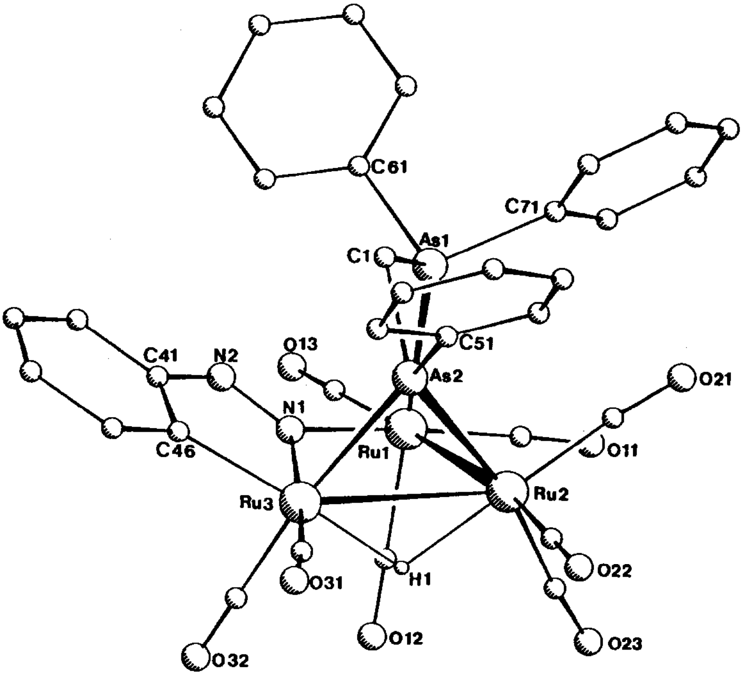
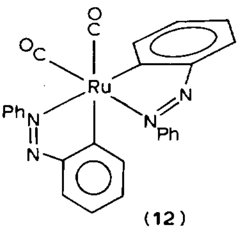


Fig. 2. A molecule of $Ru_3(\mu\text{-}H)(\mu_3\text{-}AsPhCH_2AsPh_2)(\mu\text{-}\eta^1,\eta^1\text{-}N{=}NC_6H_4)(CO)_8$ (**9**) showing atom numbering scheme (Ref. 6).

obtained from the cyclometallation reactions found for **3** and **4** have much in common with those found in mononuclear systems.



(12)

The arsenido-arsine ligand has been structurally characterised before in the complex $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}AsPhCH_2AsPh_2)_2(CO)_6$ (**13**) [14], the AsPh group bridging a bonded pair of metal atoms in this instance. The Ru(1)–As(1) distance of 2.498(1) Å in **9** is somewhat shorter than the separations of 2.523(2), 2.555(2) Å found in **13**, while the Ru(2)–As(2) and Ru(3)–As(2) bonds in **9** (2.456(1), 2.437(1) Å) are similar to the corresponding values found in **13** (2.454(2), 2.428(2) and 2.451(2), 2.470(2) Å). It is of interest that the Ru(μ-H)(μ-As)Ru separations (μ-As = bridging arsenido group) in the two complexes are 3.055(1) Å (in **9**) and 2.906(1) Å (in **13**); the former value is close to that found for the Ru–Ru bond in **13** which is bridged only by H (3.089(2) Å).

Experimental

The arenediazonium salts were either a commercial product, used as received ($[PhN_2][PF_6]$, Cationics Inc., Cleveland, Ohio 44143) or prepared by diazotising 2,4-dichloroaniline in aqueous HBF_4 solution with $NaNO_2$. The complexes $Ru_3(\mu$-dppm$)(CO)_{10}$ and $Ru_3(\mu$-dpam$)(CO)_{10}$ were prepared by published procedures [5]. Reagent grade solvents were dried and distilled before use. Reactions were carried out under an atmosphere of dry nitrogen, although all isolated complexes were air stable.

Instrumentation: Perkin–Elmer 683 double-beam spectrophotometer (IR; calibrated with polystyrene and benzene); Bruker WP80 (^1H NMR at 80 MHz; internal reference $SiMe_4$).

Preparation of aryldiazo derivatives

(a) $Ru_3(\mu$-η^1-$N_2Ph)(\mu_3$-$PPhCH_2PPh_2)(CO)_9$ (3). A solution of $Ru_3(CO)_{10}$(dppm) (100 mg, 0.103 mmol) in thf (10 ml) was treated with $K[HBBu^s_3]$ (0.22 ml of a 0.5 *M* solution in thf, 0.11 mmol). After stirring at 25°C for 5 h, solid $[PhN_2][PF_6]$ (30 mg, 0.12 mmol) was added and the mixture stirred for 1 h. Evaporation and preparative TLC [light petroleum/acetone 95/5] gave six bands. Band 4, R_f 0.38, yellow, recrystallised from Et_2O/MeOH to give yellow crystals of $Ru_3(\mu$-$H)(\mu_3$-$PPhCH_2PPh_2)(CO)_9$ (**6**) (5 mg, 6%), identified by comparison of its IR ν(CO) spectrum with that of an authentic sample. Band 6, R_f 0.22, yellow, recrystallised from CH_2Cl_2/MeOH to give fine yellow needle-like crystals of $Ru_3(\mu$-η^1-$N_2Ph)(\mu_3$-$PPhCH_2PPh_2)(CO)_9$ (**3**) (77 mg, 77%), m.p. 141–144°C. [Found: C, 42.18; H, 1.94; N, 2.28; $C_{34}H_{22}N_2O_9P_2Ru_3$ calcd.: C, 42.20; H, 2.29; N, 2.89%]. Infrared (cyclohexane): ν(CO) 2079w, 2059vs, 2023s, 2006w, 1994m, 1973w, 1958m; ν(NN) 1575 cm^{-1}. ^1H NMR: δ ($CDCl_3$) 4.60 [dd, *J*(PH) 10.5 and 11.5 Hz, 2H, CH_2], 6.65–8.0 (m, 20H, Ph). The remaining bands were present in trace amounts only and were not identified.

(b) $Ru_3(\mu$-η^1-$N_2Ph)(\mu_3$-$AsPhCH_2AsPh_2)(CO)_9$ (4). The cluster anion was prepared by the above method using $Ru_3(CO)_{10}$(dpam) (300 mg, 0.284 mmol), thf (10 ml) and $K[HBBu^s_3]$ (0.60 ml of a 0.5 *M* solution in thf, 0.30 mmol). Solid $[PhN_2][PF_6]$ (75 mg, 0.30 mmol) was added and the mixture stirred for 10 min. Evaporation and preparative TLC [light petroleum/acetone 80/20] gave 2 bands. Band 1, R_f 0.50, yellow, recrystallised from Et_2O/MeOH to give a yellow powder of $Ru_3(\mu$-$H)(\mu_3$-$AsPhCH_2AsPh_2)(CO)_9$ (**7**) (10 mg, 4%), identified by comparison of its IR ν(CO) spectrum with that of an authentic sample. Band 2, R_f 0.40, yellow-orange, recrystallised from CH_2Cl_2/MeOH to give orange needle-like crystals of $Ru_3(\mu$-η^1-$N_2Ph)(\mu_3$-$AsPhCH_2AsPh_2)(CO)_9$ (**4**) (172 mg, 57%), m.p. 146–149°C (dec.). [Found: C, 38.79; H, 1.92; N, 2.64; $C_{34}H_{22}As_2N_2O_9Ru_3$ calcd.: C, 38.69; H, 2.10; N, 2.65%]. Infrared (cyclohexane): ν(CO) 2078m, 2058vs, 2023vs, 2002m, 1994m, 1979w, 1959m; ν(NN) 1576w cm^{-1}. ^1H NMR: δ ($CDCl_3$) 4.53 (s, 2H, CH_2), 6.65–7.8 (m, 20H, Ph).

(c) $Ru_3(\mu$-η^1-$N_2C_6H_3Cl_2$-2,4$)(\mu_3$-$PPhCH_2PPh_2)(CO)_9$ (5). This complex was obtained after preparative TLC [light petroleum/acetone 90/10] from a reaction using $Ru_3(CO)_{10}$(dppm) (200 mg, 0.207 mmol), thf (10 ml), $K[HBBu^s_3]$ (0.22 ml of a 0.5 *M* solution in thf, 0.21 mmol) and $[2,4\text{-}Cl_2C_6H_3N_2][BF_4]$, carried out as in (b) above. The yellow band with R_f 0.25 was recrystallised from CH_2Cl_2/MeOH to

give orange crystals of $Ru_3(\mu\text{-}\eta^1\text{-}N_2C_6H_3Cl_2\text{-}2,4)(\mu_3\text{-}PPhCH_2PPh_2)(CO)_9$ (**5**) (30 mg, 7%), m.p. > 150°C (dec.). [Found: C, 38.75; H, 1.85; N, 2.63; $C_{34}H_{20}Cl_2N_2O_9P_2Ru_3$ calcd.: C, 39.40; H, 1.94; N, 2.70%]. Infrared (cyclohexane): ν(CO) 2081m, 2059vs, 2026vs, 2013w, 2000(sh), 1998s, 1971w, 1961m cm^{-1}, ^{1}H NMR: δ ($CDCl_3$) 4.66 (m, 2H, CH_2), 6.60–8.20 (m, 18H, Ph and C_6H_3).

Cyclometallation reactions

(a) $Ru_3(\mu\text{-}H)(\mu\text{-}\eta^1,\eta^1\text{-}N_2C_6H_4)(\mu_3\text{-}PPhCH_2PPh_2)(CO)_8$ (8). A solution of $Ru_3(\mu\text{-}\eta^1\text{-}N_2Ph)(\mu_3\text{-}PPhCH_2PPh_2)(CO)_9$ (**3**) (30 mg, 0.031 mmol) was heated in refluxing cyclohexane (30 ml) for 1 h, after which time the reaction was adjudged complete (TLC). Evaporation and recrystallisation from CH_2Cl_2/MeOH gave large orange crystals of $Ru_3(\mu\text{-}H)(\mu\text{-}\eta^1,\eta^1\text{-}N_2C_6H_4)(\mu_3\text{-}PPhCH_2PPh_2)(CO)_8 \cdot 0.5CH_2Cl_2$ (**8**) (23 mg, 73%), m.p. 158–160°C (dec.). [Found: C, 41.11; H, 2.30; N, 2.83; $C_{35}H_{22}N_2O_8P_2Ru_3 \cdot 0.5CH_2Cl_2$ calcd.: C, 40.97; H, 2.36; N, 2.85%]. Infrared (cyclohexane): ν(CO) 2085s, 2055vs, 2036vs, 2024m, 2008s, 2002(sh), 1994s, 1980vs, 1962w, 1941w cm^{-1}. ^{1}H NMR: δ ($CDCl_3$) -11.45 [dd, *J*(PH) 2.5 and 15.5 Hz, 1H, RuH], 2.54 [AB(XY) pattern, 2H, CH_2], 7.15–8.25 (m, 19H, Ph and C_6H_4).

(b) $Ru_3(\mu\text{-}H)(\mu\text{-}\eta^1,\eta^1\text{-}N_2C_6H_4)(\mu_3\text{-}AsPhCH_2AsPh_2)(CO)_8$ (9). A similar reaction of $Ru_3(\mu\text{-}\eta^1\text{-}N_2Ph)(\mu_3\text{-}AsPhCH_2AsPh_2)(CO)_9$ (**4**) (80 mg, 0.076 mmol) afforded orange crystals (from CH_2Cl_2/MeOH) of $Ru_3(\mu\text{-}H)(\mu\text{-}\eta^1,\eta^1\text{-}N_2C_6H_4)(\mu_3\text{-}AsPhCH_2AsPh_2)(CO)_8$ (**9**) (67 mg, 86%), m.p. 158–161°C (dec.). [Found: C, 38.73; H, 1.92; N, 2.66; $C_{33}H_{22}As_2N_2O_8Ru_3$ calcd.: C, 38.57; H, 2.16; N, 2.73%]. Infrared (cyclohexane): ν(CO) 2084s, 2054vs, 2033vs, 2013w, 2007s, 1999m, 1996m, 1979s, 1958vs, 1940w cm^{-1}. ^{1}H NMR: δ ($CDCl_3$) -11.64 (s, 1H, RuH), 2.66 [AB quartet, *J*(AB) 12.9 Hz, 2H, CH_2], 7.10–8.20 (m, 19H, Ph and C_6H_4).

Crystallography

Crystal data. (**5**) $Ru_3(\mu_3\text{-}PPhCH_2PPh_2)(\mu\text{-}\eta^1\text{-}N{=}NC_6H_3Cl_2)(CO)_9 \equiv C_{34}H_{20}Cl_2N_2O_9P_2Ru_3$, $M = 1036.6$, Monoclinic, space group $P2_1/c$ ((C^5_{2h}, No. 14), *a* 11.94(1), *b* 28.69(1), *c* 12.306(8) Å, β 117.98(5)°, *U* 3721(4) Å^3. D_m 1.83(1), D_c ($Z = 4$) 1.85 g cm^{-3}. $F(000) = 2024$. Monochromatic Mo-K_α radiation, λ 0.7106$_9$ Å, μ_{Mo} 13.4 cm^{-1}, specimen: 0.35 × 0.27 × 0.15 mm. $A^{\star}_{\min,\max} = 1.18$, 1.38. $R = 0.035$, $R' = 0.029$.

Structure determination. A unique data set was measured to $2\theta_{\max}$ 50°, using a Syntex P$\bar{1}$ four-circle diffractometer in conventional $2\theta/\theta$ scan mode. 6503 independent reflections were obtained, 4739 with $I > 3\sigma(I)$ being considered 'observed' and used in the basically 9 × 9 block diagonal least-squares refinement after absorption correction and solution of the structure by vector methods. Anisotropic thermal parameters were refined for the nonhydrogen atoms; $(x, y, z, U_{iso})_H$ were constrained at idealized values. Residuals R, R' are quoted on $|F|$; statistical reflection weights were derived from $\sigma^2(I) = (\sigma^2(I_{diff}) + 0.0009\ \sigma^4(I_{diff}))$. Results are given in the Figures and Tables; atom labelling is shown in the Figures. Neutral complex scattering factors were employed; computation used the XTAL 83 program system implemented by S.R. Hall on a Perkin–Elmer 3240 computer.

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