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Preliminary communication

CLUSTER CHEMISTRY

XXIX*. PREPARATION OF CLUSTER COMPLEXES CONTAINING ARYLDIAZO LIGANDS: CRYSTAL STRUCTURE OF $[HRu_3(\mu\text{-}N_2C_6H_4)(\mu_3\text{-}PhAsCH_2AsPh_2)(CO)_8]$

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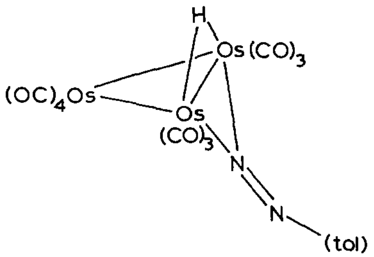
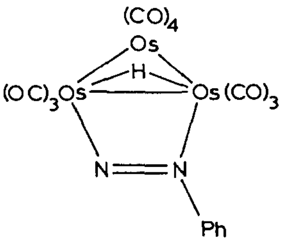
Summary

Hydrogenation of $[Ru_3(CO)_{10}(L_2)]$ (L_2 = dppm or dpam) affords $[HRu_3(\mu_3\text{-}PhECH_2EPh_2)(CO)_9]$ (E = P or As), which is deprotonated by $K[HBBu^s_3]$. Reactions of the anions with $[PhN_2][PF_6]$ give $[Ru_3(\mu\text{-}N_2Ph)(\mu_3\text{-}PhECH_2EPh_2)(CO)_9]$, which undergo facile cyclometallation reactions when heated, as revealed by an X-ray structure of the title complex.

Although extensive studies of mononuclear complexes containing nitrosyl (NO) or aryldiazo (ArN_2) ligands have shown the complementary nature of these two ligands [1], there are only two structurally characterised cluster complexes, $(\mu\text{-}H)Os_3(\mu\text{-}\eta^1\text{-}N{=}NC_6H_4Me\text{-}p)(CO)_{10}$ (I) [2] and $(\mu\text{-}H)Os_3(\mu\text{-}\eta^2\text{-}N{=}NPh)(CO)_{10}$ (II) [3], containing the ArN_2 ligands. Recently a reversible photochemical/thermal interconversion of the η^1- and η^2-ArN_2 ligands in



(I)



(II)

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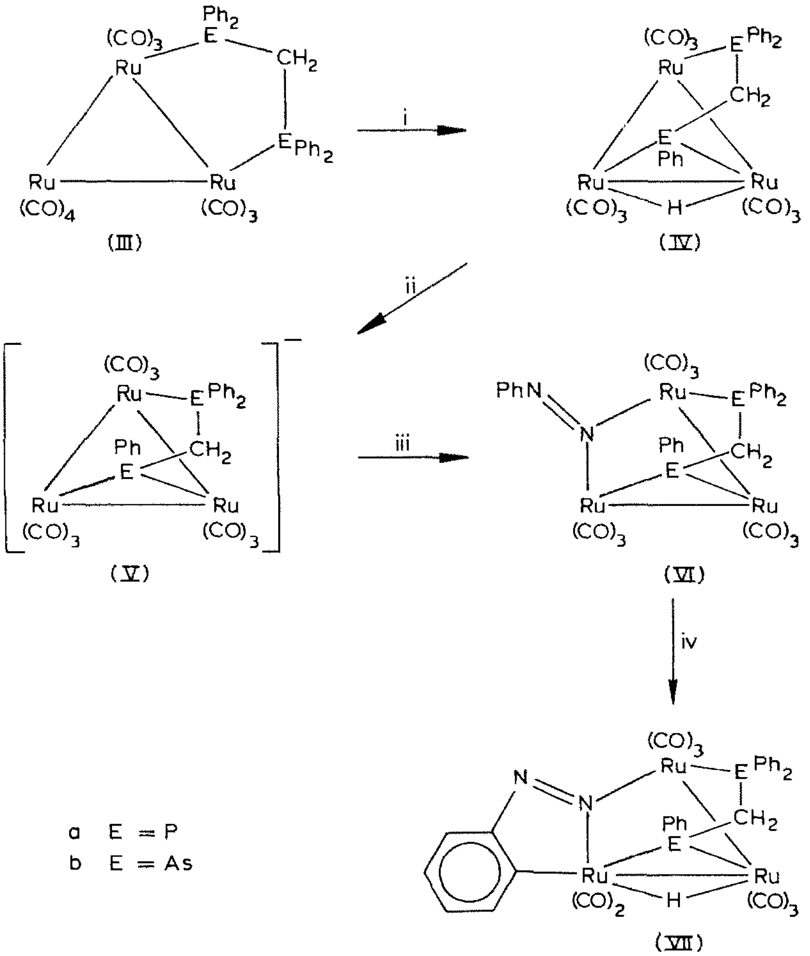
*For Part XXVIII, see ref. 12.

these two types of complex has been described [3]. Below we report the synthesis and characterisation of the first examples of ruthenium cluster complexes containing ArN_2 ligands, together with a facile cyclometallation reaction.

Results and discussion

The radical anion-catalysed reactions [4] between $[Ru_3(CO)_{12}]$ and dppm or dpam afford $[Ru_3(CO)_{10}(L_2)]$ (IIIa, L_2 = dppm; IIIb, L_2 = dpam; Scheme 1), which on hydrogenation (20 atm H_2, 80°C, 3 h) lose benzene to give the corresponding hydrido complexes (IVa, IVb) in high yields. (For IVa, ν(CO) (cyclohexane) 2084s, 2053vs, 2031vs, 2014m, 2001m, 1996m, 1990m, 1984m, 1964m(br) cm^{-1}; ^1H NMR: δ ($CDCl_3$) −16.65, t(br), J(HP) 10.8 Hz, RuH; for IVb, ν(CO) (cyclohexane) 2081s, 2052vs, 2029vs, 2009s, 1992s, 1972w, 1968m cm^{-1}; ^1H NMR: δ ($CDCl_3$) −16.35, s(br) RuH). Similar reactions have been described for $[Ru_3(CO)_8(L_2)_2]$ [5]. Treatment of (IVa,b) with $K[HBBu^s_3]$ in tetrahydrofuran solution rapidly affords the corresponding anions



SCHEME 1. Reagents i, $+H_2$, $-C_6H_6$; ii, $K[HBBu^s_3]$; iii, PhN_2^+; iv, 80°C/1 h.

$[Ru_3(\mu_3\text{-}PhECH_2EPh_2)(CO)_9]^-$ (Va, E = P; Vb, E = As), for which an interesting chemistry has been developed.

For example, the reactions between (Va,Vb) and $[PhN_2][PF_6]$ in tetrahydrofuran proceed readily at room temperature to give yellow-orange complexes (VIa,VIb) whose properties (for VIa, ν(CO) (cyclohexane) 2079w, 2059vs, 2023s, 2006w, 1994m, 1973w, 1958m; ν(NN) 1575w cm^{-1} ; ^{1}H NMR: δ ($CDCl_3$) 6.65—8.0, m, 20H, Ph; 4.60, dd, J(HP) 10.3, 11.7Hz, 2H, CH_2 ; for VIb, ν(CO) (cyclohexane) 2078m, 2058vs, 2023vs, 2002m, 1994m, 1979w, 1959m; ν(NN) 1576w cm^{-1} ; ^{1}H NMR: δ ($CDCl_3$) 6.65—7.8, m, 20H, Ph; 4.53, s, 2H, CH_2) indicate that they are the expected μ-N_2Ph complexes. Suitable crystals for X-ray studies have not yet been obtained, but facile isomerization of these complexes occurs on heating in cyclohexane for 1 h to give VIIa, VIIb) in high yields. (For VIIa, ν(CO) (cyclohexane) 2085s, 2055vs, 2036vs, 2024m, 2008s, 2002(sh), 1994s, 1980vs, 1962w, 1941w cm^{-1} ; ^{1}H NMR: δ ($CDCl_3$) 7.15—8.25, m, 19H, Ph + C_6H_4; 2.54, 12 lines, 2H, CH_2; —11.45, dd, J(HP) 2.6, 15.5 Hz, 1H, RuH; for VIIb, ν(CO) (cylohexane) 2084s, 2054vs, 2033vs, 2013w, 2007s, 1999m, 1996m, 1979s, 1958vw, 1940w cm^{-1} ; ^{1}H NMR: δ ($CDCl_3$) 7.10—8.20, m, 19H, Ph + C_6H_4; 2.66; AB quartet, J(AB) 12.9Hz, 2H, CH_2 ; —11.65, s, 1H, RuH). The presence of the metal-bonded hydrogen, together with the extended aromatic proton resonances, suggested that cyclometallation of the aryldiazo ligand had occurred, and this has been confirmed by a single-crystal X-ray study of VIIb.

Crystal data: $C_{33}H_{22}As_2N_2O_8Ru_3$, M = 1027.7, triclinic, space group $P\bar{1}$; a 10.846(2), b 12.084(4), c 15.884(4) Å, α 72.63(2), β 68.25(2), γ 68.07(2)°, U 1762.4 Å^3, D_m 1.94, D_c 1.94 g cm^{-3} for Z = 2, $F(000)$ = 992, λ(Mo-K_α) 0.7107 Å, μ(Mo-K_α) 31.29 cm^{-1}, T 23°C.

The ruthenium atoms were located by direct methods using the SHELX system of programmes [6]. Successive difference Fourier syntheses revealed the position of all non-hydrogen atoms and the hydride ligand. The phenyl rings were included as rigid groups, hydrogen atoms for the methylene group and the phenyl rings were given calculated positions and a common temperature factor. The structure was refined by blocked full-matrix least-squares techniques (with all non-hydrogen atoms and non-phenyl carbons anisotropic) to R = 0.028, R_w = 0.034 (for 3676 independent reflections with $I \geqslant 2.5\sigma(I)$, collected with $2.4 \leqslant 2\theta \leqslant 44°$ on an Enraf—Nonius CAD4 diffractometer)*.

The molecular structure of VIIb is shown in Fig. 1, which also contains important bond distances and angles. The μ_3-$PhAsCH_2AsPh_2$ ligand, which is similar to that found in $[H_2Ru_3(\mu_3\text{-}PhAsCH_2AsPh_2)_2(CO)_6]$ [5], sits on one side of a somewhat enlarged Ru_3 triangle, two edges of which (Ru(1)—Ru(2) 2.903(1), Ru(2)—Ru(3) 3.055(1) Å; the latter is bridged by both the arsenido and hydride ligands) are bonding. The third edge (Ru(1)—Ru(3) 3.547(1) Å) is lengthened by the presence of the 3e-donor $C_6H_4N_2$ ligand. The separation may be compared with that found in $[Ru_3(\mu\text{-}NO)_2(CO)_{10}]$ (3.15 Å) [7]. In contrast with I, in which the ArN_2 ligand has been added to

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*The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

the Os=Os double bond in $H_2Os_3(CO)_{10}$, and which thus contains an Os—Os single bond (2.823(1) Å), there is essentially no bonding interaction between Ru(1) and Ru(3) in VIIb. The N(1)—N(2) separation (1.267(8) Å) is consistent with the presence of an N=N double bond, and is similar to those found in I (1.238(18) Å) and II (1.20(4) Å). The two atoms Ru(1) and Ru(3) are bridged by N(1) (Ru(1)—N(1) 2.092(5), Ru(3)—N(1) 2.065(7) Å; cf. Os—N distances of 2.036(11), 2.056(11) Å in I). The structural determination confirms that the ArN_2 ligand is cyclometallated, the phenyl ring on N(2) also being attached to Ru(3) by a conventional Ru—C bond (Ru(3)—C(46) 2.083(4) Å); there is no interaction of the C_6H_4 group with either of the other two metal atoms.

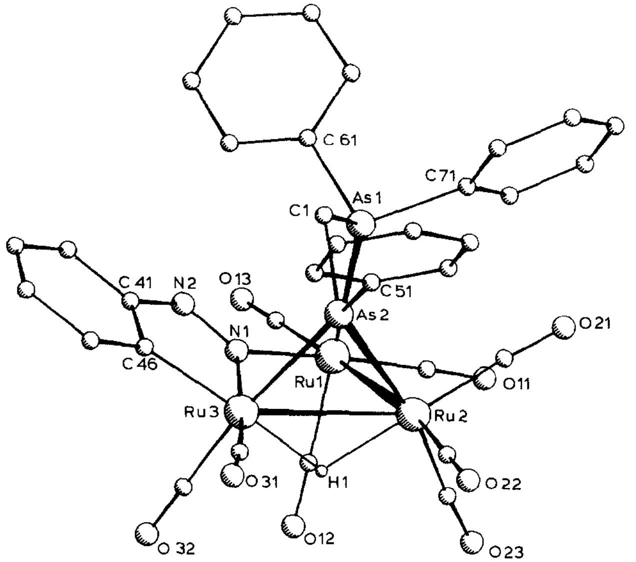

Fig. 1. PLUTO plot of the structure of $[HRu_3(CO)_8(\mu\text{-}C_6H_4N_2)(\mu_3\text{-}PhAsCH_2AsPh_2)]$ VIIb. Important bond distances and angles: Ru(1)—Ru(2) 2.903(1), Ru(2)—Ru(3) 3.055(1), Ru(1)—Ru(3) 3.547(1), Ru(1)—As(1) 2.498(1), Ru(2)—As(2) 2.456(1), Ru(3)—As(2) 2.437(1), Ru(3)—C(46) 2.083(4), Ru(1)—N(1) 2.092(5), Ru(3)—N(1) 2.065(7), N(1)—N(2) 1.267(8) Å; Ru(2)—As(2)—Ru(3) 77.3(1), Ru(1)—N(1)—Ru(3) 118.6(3), Ru(1)—N(1)—N(2) 121.2(5), Ru(3)—N(1)—N(2) 119.7(5), N(1)—Ru(3)—C(46) 77.4(2), N(1)—N(2)—C(41) 112.6(7), C(41)—C(46)—Ru(3) 109.6(3)°.

Cyclometallation of the aryldiazo ligand has occurred by oxidative addition of the *ortho*-C—H bond to Ru(3), the hydrogen taking up a position bridging Ru(3) and Ru(2). Although metallation of arenes is not unusual on cluster complexes, the reaction usually proceeds by cleavage of the functional group(s) or *ortho*-C—H bond(s) to give μ_3-C_6H_4 ligands [8]; this occurs even in reactions between arenes and $[Os_3(CO)_{10}(NCMe)_2]$ [9]. Our reaction contrasts with that found in the osmium series, and is characteristic of phenylazo-containing ligands (such as azobenzenes) on mononuclear complexes [10]. Indeed, azobenzenes react with some ruthenium cluster complexes to give mononuclear cyclometallated derivatives [11]; in the present instance, the μ_3-$PhECH_2PPh_2$ ligand prevents cluster degradation.

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