

Preliminary communication

Synthesis of three-, four-, and five-membered dimetalloheterocyclic compounds by reaction of the hydride $[\text{Ru}_2\text{H}(\text{CO})_5\{\mu\text{-(RO)}_2\text{PN}(\text{Et})\text{P}(\text{OR})_2\}_2][\text{PF}_6]$ ($\text{R} = \text{Me}$ or Pr^i) with unsaturated systems of the type $\text{X}\equiv\text{Y}$ and $\text{X}'=\text{Y}'=\text{Z}'$. Crystal structures of representative examples of the three types of products

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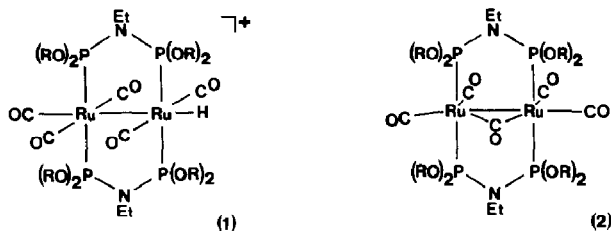
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Abstract

Reactions of $[\text{Ru}_2\text{H}(\text{CO})_5\{\mu\text{-(RO)}_2\text{PN}(\text{Et})\text{P}(\text{OR})_2\}_2][\text{PF}_6]$ ($\text{R} = \text{Me}$ or Pr^i) with unsaturated compounds such as alkynes, nitriles and carbon disulphide give three-, four-, or five-membered dimetalloheterocyclic species depending on the nature of the unsaturated system. The structures of $[\text{Ru}_2\{\mu\text{-}\eta^1\text{-N}(\text{CHPh})\}(\text{CO})_4\{\mu\text{-(Pr}^i\text{O)}_2\text{PN}(\text{Et})\text{P}(\text{OPr}^i)_2\}_2][\text{PF}_6]$, $[\text{Ru}_2\{\mu\text{-}\eta^2\text{-OC}(\text{CHCHPh})\}(\text{CO})_4\{\mu\text{-(Pr}^i\text{O)}_2\text{PN}(\text{Et})\text{P}(\text{OPr}^i)_2\}_2][\text{PF}_6]$ and $[\text{Ru}_2\{\mu\text{-}\eta^2\text{-PhNC}(\text{H})\text{S}\}(\text{CO})_4\{\mu\text{-(Pr}^i\text{O)}_2\text{PN}(\text{Et})\text{P}(\text{OPr}^i)_2\}_2][\text{PF}_6]$ have been determined by X-ray crystallography.

We have established previously that the hydrides $[\text{Ru}_2\text{H}(\text{CO})_5\{\mu\text{-(RO)}_2\text{PN}(\text{Et})\text{P}(\text{OR})_2\}_2][\text{A}]$ ($\text{R} = \text{Me}$ or Pr^i ; $\text{A} = \text{PF}_6$ or BF_4) (1,A), which are readily obtained by protonation of $[\text{Ru}_2(\mu\text{-CO})(\text{CO})_4\{\mu\text{-(RO)}_2\text{PN}(\text{Et})\text{P}(\text{OR})_2\}_2]$ (2), exist in two isomeric forms in solution and that the hydride ligand in both isomers of these species



is fluxional [1]. Furthermore, treatment of these hydride derivatives either with strong acids HX having conjugate bases with ligating properties or with strong acids

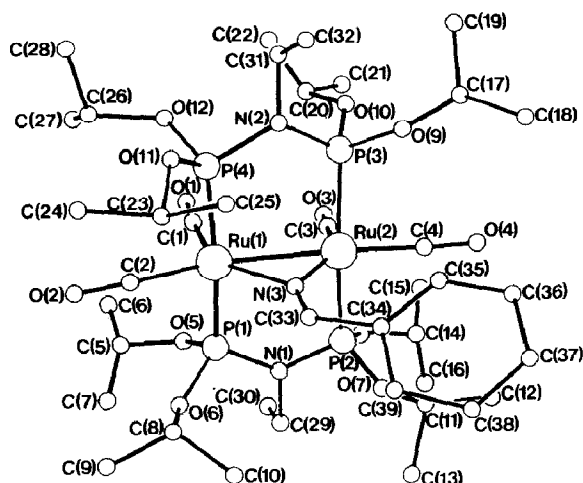
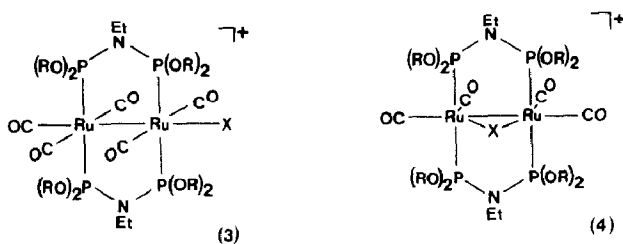


Fig. 1. The stereochemistry of $[\text{Ru}_2\{\mu\text{-}\eta^1\text{-N(CHPh)}\}(\text{CO})_4\{\mu\text{-(Pr}^i\text{O)}_2\text{PN(Et)P(OPr}^i)_2\}_2]^+$. Relevant interatomic distances: Ru(1)–Ru(2), 2.714(1); Ru(1)–P(1), 2.330(2); Ru(1)–P(4), 2.330(2); Ru(2)–P(2), 2.343(2); Ru(2)–P(3), 2.347(2); Ru(1)–N(3), 2.092(6); Ru(2)–N(3), 2.075(6); N(3)–C(33), 1.307(10) Å.

in the presence of appropriate anionic nucleophiles X^- has been found to lead to the formal replacement of the hydride ligand by the conjugate base or the anionic nucleophile to afford products of the type $[\text{Ru}_2\text{X}(\text{CO})_5\{\mu\text{-(RO)}_2\text{PN(Et)P(OR)}_2\}_2][\text{A}]$ (3,A) or of the type $[\text{Ru}_2(\mu\text{-X})(\text{CO})_4\{\mu\text{-(RO)}_2\text{PN(Et)P(OR)}_2\}_2][\text{A}]$ (4,A) [2]. We have now shown that these cationic hydrides are susceptible to attack



by unsaturated compounds of general formulae $\text{X}\equiv\text{Y}$ and $\text{X}'=\text{Y}'=\text{Z}'$ to give dimetallo-cyclic products and the results of this study are reported below.

Reaction of $[\text{Ru}_2\text{H}(\text{CO})_5\{\mu\text{-(RO)}_2\text{PN(Et)P(OR)}_2\}_2][\text{PF}_6]$ ($\text{R} = \text{Me}$ or Pr^i) with benzonitrile in 1,2-dichloroethane under reflux was found to lead to the quantitative formation of a product characterized as $[\text{Ru}_2\{\mu\text{-}\eta^1\text{-N(CHPh)}\}(\text{CO})_4\{\mu\text{-(RO)}_2\text{PN(Et)P(OR)}_2\}_2][\text{PF}_6]$, which results from the formal insertion of the unsaturated benzonitrile ligand into the ruthenium–hydrogen bond and subsequent decarbonylation. The structure of the tetraisopropoxy diphosphazane derivative has been established by X-ray crystallography and is illustrated in Fig. 1*. The cation adopts

* *Crystal data:* $\text{C}_{39}\text{H}_{72}\text{F}_6\text{N}_3\text{O}_{12}\text{P}_3\text{Ru}_2$, $M = 1246.0$, monoclinic, $P2_1/c$, a 11.512(2), b 24.954(5), c 20.479(4) Å, β 108.44(3)°, U 5581.0 Å³, D_c 1.48 g cm⁻³, $Z = 4$, Mo- K_α radiation, λ 0.71069 Å, μ 7.49 cm⁻¹. 8865 unique reflection intensities were measured on a Nonius CAD-4 diffractometer (N.C.R.L., Pretoria) in the range $2 \leq \theta \leq 23^\circ$, 7122 of which were classed as observed ($I > 3\sigma(I)$). The data were corrected for absorption using the empirical (χ scan) method and used in the solution and refinement [3] of the structure. Final $R = 0.072$, $R_w = 0.092$ for 334 parameters, maximum shift over e.s.d. in the last full-matrix least-squares cycle = 0.82, featureless final difference Fourier with maximum peak height = 1.1 eÅ⁻³. Tables of atomic coordinates and interatomic distances and angles have been deposited at the Cambridge Crystallographic Data Centre.

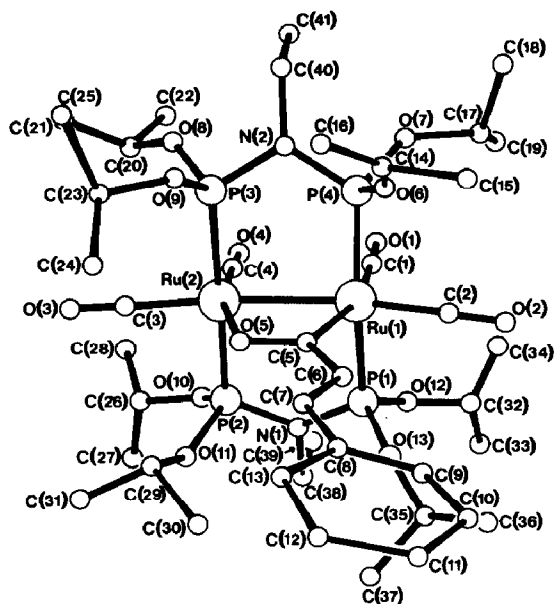


Fig. 2. The stereochemistry of $[\text{Ru}_2\{\mu\text{-}\eta^2\text{-OC}(\text{CHCHPh})\}(\text{CO})_4\{\mu\text{-(Pr}^i\text{O)}_2\text{PN}(\text{Et})\text{P}(\text{OPr}^i)_2\}_2]^+$. Relevant interatomic distances: Ru(1)–Ru(2), 2.781(1); Ru(1)–P(1), 2.311(3); Ru(1)–P(4), 2.318(3); Ru(2)–P(2), 2.337(3); Ru(2)–P(3), 2.333(3); Ru(2)–O(5), 2.121(6); Ru(1)–C(5), 2.091(9); C(5)–O(5), 1.246(11); C(5)–C(6), 1.451(14); C(6)–C(7), 1.368(15) Å.

an eclipsed configuration with the two ruthenium atoms linked by a formal metal–metal bond (Ru(1)–Ru(2) 2.714(1) Å) and bridged by an azavinylidene and two diphosphazane ligands. The azavinylidene group coordinates solely through the nitrogen atom giving rise to a three-membered dimetalloheterocyclic ring. A related trinuclear product, $[\text{Ru}_3(\mu\text{-H})\{\mu\text{-N}(\text{CHPh})\}(\text{CO})_{10}]$, has been made previously by treatment of $[\text{Ru}_3(\text{CO})_{12}]$ with PhCN in the presence of acetic acid [4] or by reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with benzonitrile in ligroin at 130 °C under an atmosphere of hydrogen [5].

Phenylacetylene, isoelectronic with benzonitrile, was also found to react readily with $[\text{Ru}_2\text{H}(\text{CO})_5\{\mu\text{-(RO)}_2\text{PN}(\text{Et})\text{P}(\text{OR})_2\}_2][\text{PF}_6]$ in refluxing thf, but to give a structurally different type of product, $[\text{Ru}_2\{\mu\text{-}\eta^2\text{-OC}(\text{CHCHPh})\}(\text{CO})_4\{\mu\text{-(RO)}_2\text{PN}(\text{Et})\text{P}(\text{OR})_2\}_2][\text{PF}_6]$. On the basis of the structure established by X-ray crystallography for the compound isolated from the reaction involving the tetraiso-propoxydiphosphazane derivative, it is apparent that while the phenylacetylene, like benzonitrile, formally inserts into the ruthenium–hydrogen bond in these compounds, the resulting terminal styryl group, in contrast to the azavinylidene ligand, preferentially migrates to a coordinated carbonyl ligand rather than displace such a ligand. The stereochemistry of $[\text{Ru}_2\{\mu\text{-}\eta^2\text{-OC}(\text{CHCHPh})\}(\text{CO})_4\{\mu\text{-(Pr}^i\text{O)}_2\text{PN}(\text{Et})\text{P}(\text{OPr}^i)_2\}_2]^+$ is illustrated in Fig. 2*. This cation also adopts an eclipsed config-

* Crystal data: $\text{C}_{41}\text{H}_{73}\text{N}_2\text{F}_6\text{O}_{13}\text{P}_5\text{Ru}_2$, $M = 1272.2$, monoclinic, space group $P2_1/c$, a 17.394(1), b 12.551(2), c 27.044(3) Å, β 95.119(8)°, U 5881.01 Å³, D_c 1.437 g cm⁻³, $Z = 4$, Mo- K_α radiation, λ 0.71069 Å, μ 7.15 cm⁻¹. Nonius CAD-4 diffractometer, 6775 unique absorption corrected reflections with $(I > 3\sigma(I))$ in the range $2 \leq \theta \leq 23^\circ$. Structure solved from a Patterson synthesis and successive Fourier maps and refined to $R = 0.059$ (622 parameters). Tables of atomic coordinates and interatomic distances and angles have been deposited at the Cambridge Crystallographic Data Centre.

uration, and again the two ruthenium atoms are linked by a metal–metal bond (Ru(1)–Ru(2) 2.781(1) Å) as well as being bridged by two diphosphazane ligands. The salient structural feature of this cation is the presence of a four-membered dimetalloheterocyclic ring comprising the two ruthenium atoms and a carbonyl group, with a styryl group bonded to the ring carbon atom. A related compound, $[\text{Ru}_2\{\mu\text{-OC}(\text{CMeCMe}(\eta^2\text{-CMeCHMe}))\}\{\mu\text{-OC}(\text{NMe}_2)\}(\text{CO})_5]$, was previously isolated from the reaction of $[\text{Ru}_3(\mu\text{-H})\{\mu\text{-OC}(\text{NMe}_2)\}(\text{CO})_{10}]$ with dimethylacetylene [6].

The phenyldiazonium cation, PhN_2^+ , is also isoelectronic with benzonitrile and although its hexafluorophosphate salt was observed to react with $[\text{Ru}_2\text{H}(\text{CO})_5\{\mu\text{-(RO)}_2\text{PN}(\text{Et})\text{P}(\text{OR})_2\}_2][\text{PF}_6]$ in 1,2-dichloroethane under reflux (no reaction occurred at room temperature) the product was shown to be monocationic. On the other hand a dicationic species, $[\text{Ru}_2(\text{N}_2\text{HPh})(\text{CO})_5\{\mu\text{-(RO)}_2\text{PN}(\text{Et})\text{P}(\text{OR})_2\}_2][\text{PF}_6]_2$, is readily formed by treatment of $[\text{Ru}_2(\mu\text{-CO})(\text{CO})_4\{\mu\text{-(RO)}_2\text{PN}(\text{Et})\text{P}(\text{OR})_2\}_2]$ with $[\text{PhN}_2][\text{PF}_6]$ in methanol at room temperature [7].

Carbon disulphide and phenylisothiocyanate, both of which belong to a class of unsaturated compounds of the type $\text{X}=\text{C}=\text{Y}$ (heterocumulenes), were also found to react readily with $[\text{Ru}_2\text{H}(\text{CO})_5\{\mu\text{-(RO)}_2\text{PN}(\text{Et})\text{P}(\text{OR})_2\}_2][\text{PF}_6]$ in 1,2-dichloroethane under reflux to give $[\text{Ru}_2\{\mu\text{-}\eta^2\text{-SC}(\text{H})\text{S}\}(\text{CO})_4\{\mu\text{-(RO)}_2\text{PN}(\text{Et})\text{P}(\text{OR})_2\}_2][\text{PF}_6]$ and $[\text{Ru}_2\{\mu\text{-}\eta^2\text{-PhNC}(\text{H})\text{S}\}(\text{CO})_4\{\mu\text{-(RO)}_2\text{PN}(\text{Et})\text{P}(\text{OR})_2\}_2][\text{PF}_6]$ respectively. Migration of the hydride ligand, in these cases to the carbon atom of the coordinated carbon disulphide or phenylisothiocyanate, also occurs in the formation of these ionic products but, in contrast to $[\text{Ru}_2\{\mu\text{-}\eta^2\text{-N}(\text{CHPh})\}(\text{CO})_4\{\mu\text{-(RO)}_2\text{PN}(\text{Et})\text{P}(\text{OR})_2\}_2]^+$, as shown by X-ray crystallography, the cations of these species contain five-membered dimetalloheterocyclic rings. The stereochemistry of $[\text{Ru}_2\{\mu\text{-}$

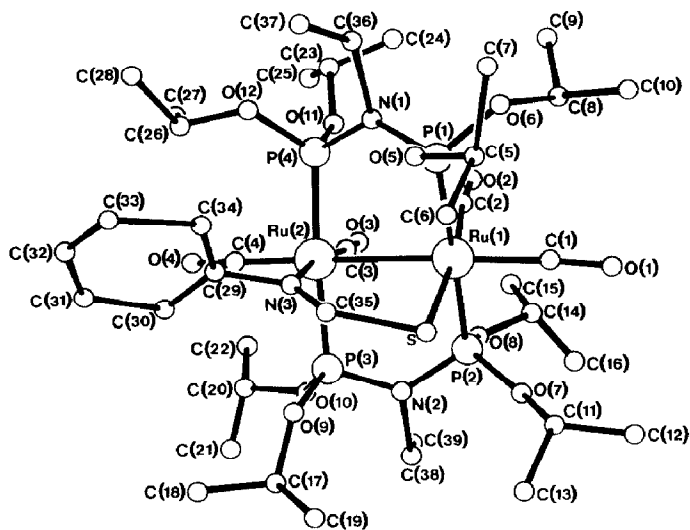
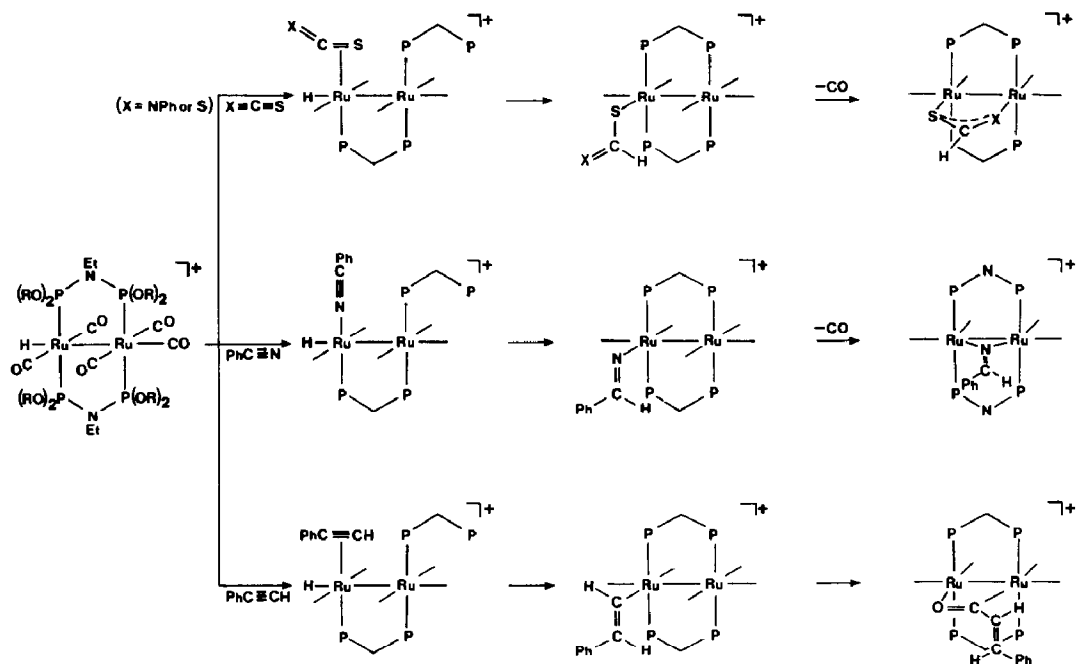


Fig. 3. The stereochemistry of $[\text{Ru}_2\{\mu\text{-}\eta^2\text{-PhNC}(\text{H})\text{S}\}(\text{CO})_4\{\mu\text{-(Pr}^1\text{O)}_2\text{PN}(\text{Et})\text{P}(\text{OPr}^1)_2\}_2]^+$. Relevant interatomic distances: Ru(1)–Ru(2), 2.858(1); Ru(1)–P(1), 2.355(2); Ru(1)–P(2), 2.345(2); Ru(2)–P(3), 2.351(2); Ru(2)–P(4), 2.359(2); Ru(1)–S, 2.431(2); Ru(2)–N(3), 2.161(5); S–C(35), 1.719(8); N(3)–C(35), 1.282(10) Å.



Scheme 1

$\eta^2\text{-PhNC(H)S}\{\text{CO}\}_4\{\mu\text{-(Pr}^i\text{O)}_2\text{PN(Et)P(OPr}^i)_2\}_2\}^+$ is illustrated in Figure 3*. The surprising feature of the structure of this cation is that it adopts a staggered conformation (in contrast to that in $[\text{Ru}_2\{\mu\text{-OB(F)OH}\}\{\text{CO}\}_4\{\mu\text{-(MeO)}_2\text{PN(Et)P(OMe)}_2\}_2\}^+$ [2]) such that the RuNCSRu ring is puckered. This puckering is interpreted in terms of localized π -orbital overlap involving the carbon and nitrogen ring atoms, as opposed to delocalized π -orbital overlap involving the carbon, nitrogen, and sulphur ring atoms. The ring C–N {1.28(1) Å} and C–S {1.719(8) Å} distances are consistent with this interpretation. Corresponding triosmium compounds have been isolated from the reactions of $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}]$ with CS_2 and PhNCS , respectively [8,9].

A possible mechanism for the formation of these three-, four-, and five-membered dimetalloheterocyclic species is illustrated in Scheme 1. We suggest that the initial step involves the partial dissociation of one of the diphosphazane ligands from the complex and the concomitant coordination of the unsaturated reactant. Migration of the hydride ligand to the latter results in the formation of a σ -bonded moiety, which reacts further in one of two ways to afford the final product; the first

* *Crystal data:* $\text{C}_{39}\text{H}_{72}\text{N}_3\text{F}_6\text{O}_{12}\text{P}_5\text{SRu}_2$, $M = 1278.1$, triclinic, $P\bar{1}$, a 11.823(1), b 14.242(1), c 17.852(1) Å, α 97.520(6), β 98.815(5), γ 101.323(5)°, U 2872.0 Å³, D_c 1.44 g cm⁻³, $Z = 2$, Mo- K_α radiation, λ 0.71069 Å, μ 6.87 cm⁻¹. 5539 unique reflection intensities were measured on a Nonius CAD-4 diffractometer in the range $2 \leq \theta \leq 23^\circ$, 5113 of which were classed as observed ($I > 3\sigma(I)$). These data were corrected for absorption using the empirical (χ scan) method and used in the solution and refinement [3] of the structure. Final $R = 0.060$, $R_w = 0.082$ for 220 parameters, maximum shift over e.s.d. in the last full-matrix least square cycle = 0.28, featureless final difference Fourier with maximum peak height = 0.6 eÅ⁻³. Tables of atomic coordinates and interatomic distances and angles have been deposited at the Cambridge Crystallographic Data Centre.

way involves its migration to the carbon of an adjacent carbonyl, and the second the displacement of a carbonyl ligand.

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