Heterobimetallic Cluster Cations from the Reactions of Diphosphazane-bridged Derivatives of $[Ru_2(CO)_9]$ with Metal-containing Electrophiles: Mechanism of the One-electron Oxidation of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ by Silver Salts

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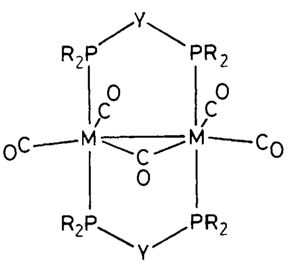
Reaction of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (R = Me or Pr^i) with $[AuCl(PPh_3)]$, $[Cu(MeCN)_4]^+$, and $HgCl_2$ gives cationic products in which the metal substrate is either co-ordinated terminally as in $[Ru_2(HgCl)(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ or in the bridging mode as in $[Ru_2\{\mu\text{-}Au(PPh_3)\}(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$, the structure of the latter being confirmed *X*-ray crystallographically; silver(I) salts similarly afford products of the type $[Ru_2(\mu\text{-}AgL)(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ (L = acetone, acetonitrile, *etc.*) but, for weakly co-ordinating ligands L, these species readily rearrange with the nature of the final product being dependent on L and the solvent employed; $[Ru_2(\mu\text{-}AgL)(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ is shown to be an intermediate in the one-electron oxidation of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$.

We have established[1] from cyclic voltammetric studies that while the one-electron oxidation of the diphosphorus ligand-bridged derivatives $[M_2(\mu\text{-}CO)(CO)_4(\mu\text{-}R_2PYPR_2)_2]$ (1) (M = Fe, Y = CH_2, R = Ph or Me; M = Fe, Y = NEt, R = OMe, OEt or OPr^i; M = Ru, Y = NEt, R = OPr^i) in acetone or benzonitrile is reversible, that of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ is irreversible with the one-electron oxidized product participating in some chemical process and the product thereof being immediately oxidized to $[Ru_2(CO)_5(\text{solvent})\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]^{2+}$. Further oxidation of $[M_2(\mu\text{-}CO)(CO)_4(\mu\text{-}R_2PYPR_2)_2]^+$ was shown to produce the dications which, apart from $[Fe_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}Ph_2PCH_2PPh_2)_2]^{2+}$ in acetone, are unstable, and react with the solvent to afford $[M_2(CO)_5(\text{solvent})(\mu\text{-}R_2PYPR_2)_2]^{2+}$ (2). The latter is potentially an excellent precursor for the synthesis of a wide range of di-iron and diruthenium derivatives and thus its synthesis by chemical means was investigated.



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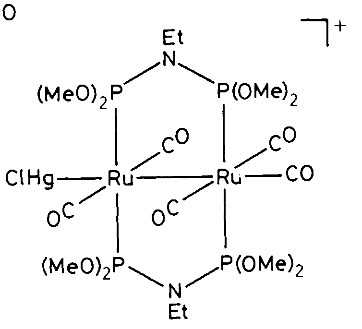

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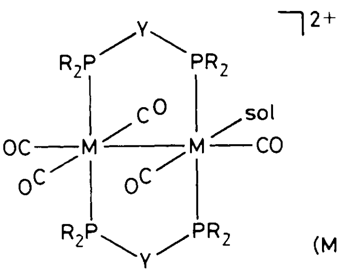

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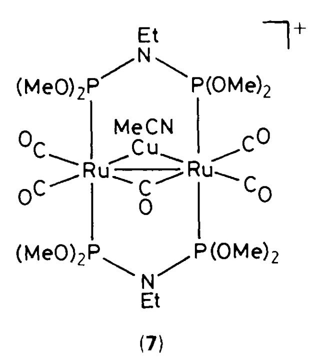

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The diruthenium diphosphazane-bridged species $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ (1; M = Ru, Y = NEt, R = OMe)[2], an electron-rich derivative of $[Ru_2(CO)_9]$, was observed to react readily with silver(I) salts, one-electron oxidants, but the nature of the final product was found to be very dependent on the nature of the ligand co-ordinated to the silver(I) ion.† For instance, treatment of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ with an equimolar amount of $AgSbF_6$ in a weakly co-ordinating oxygen-donor solvent such as acetone leads to the precipitation of elemental silver and the formation of a half molar amount of $[Ru_2(CO)_5(\text{solvent})\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]^{2+}$ (2; M = Ru, Y = NEt, R = OMe).‡ On the other hand, reaction of this species with an equimolar amount of $AgSbF_6$ in MeCN or with an equimolar amount of $[Ag(\text{pyridine})_4]SbF_6$ in tetrahydrofuran (THF) gives a product characterized spectroscopically as $[Ru_2(\mu\text{-}AgL)(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]SbF_6$ (3,SbF_6), (L = MeCN or C_5H_5N).§ Significantly, solid $[Ru_2\{\mu\text{-}Ag(MeCN)\}(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]SbF_6$

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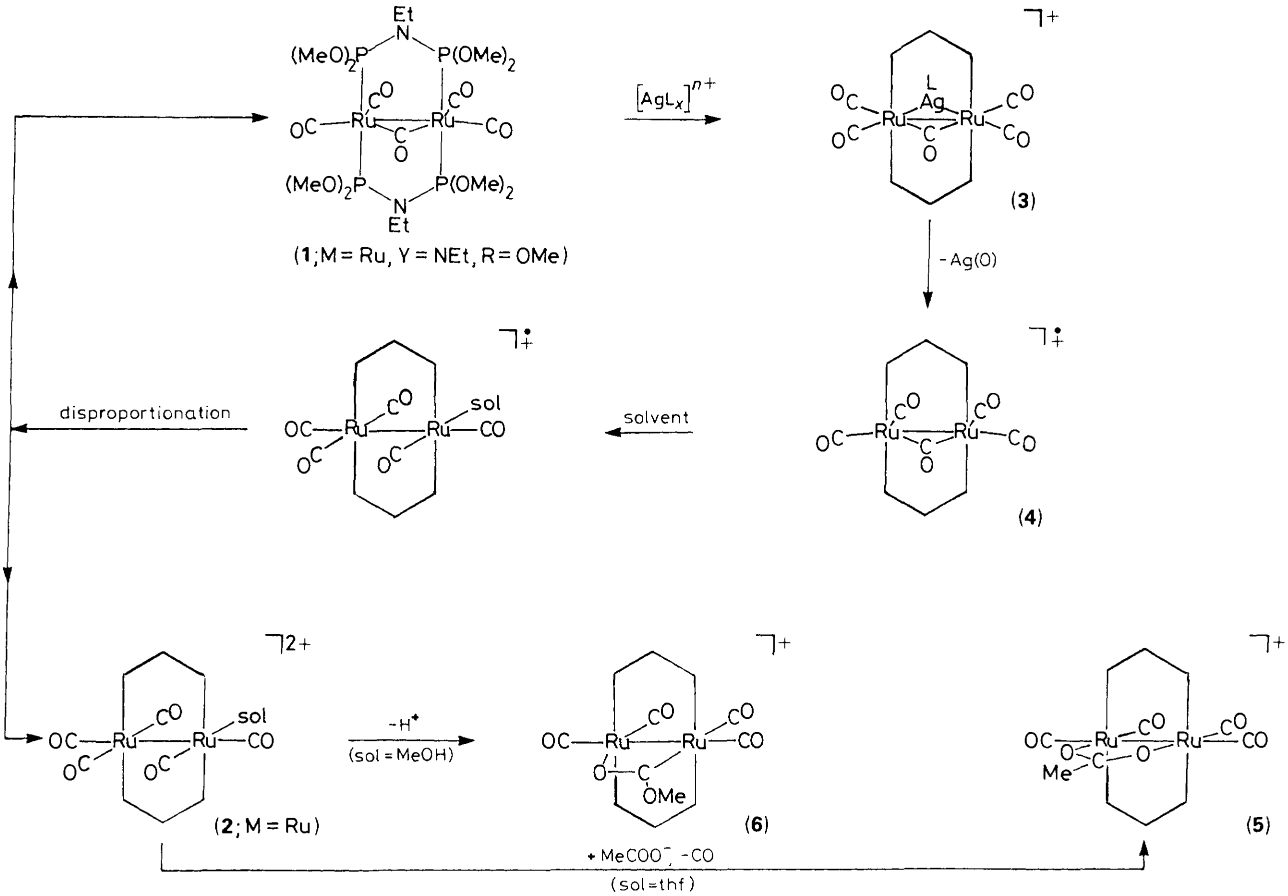
† The behaviour of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ towards Ag^I salts and other metal-containing electrophiles is essentially the same as that for $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$.

‡ All new compounds, apart from $[Ru_2(\mu\text{-}AgL)(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]SbF_6$ (L = MeCN or C_5H_5N) which could not be isolated pure, were characterized by analytical, as well as by spectroscopic means. The latter was identified by means of i.r. and n.m.r. spectroscopy only.

§ $[Ru_2\{\mu\text{-}Ag(C_5H_5N)\}(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]SbF_6$: ν(C–O): 2029sh, 1995vs, 1954m, and 1722m cm^{-1}; ^{31}P: 150.2 d, $^2J(^{107,109}Ag\text{–}P) = 13.6$ Hz.



Scheme 1

was established to degrade to elemental silver and an intense purple, very oxygen-sensitive species, presumed to be the one-electron oxidation product, $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]SbF_6$ (**4**, SbF_6), on heating to 50—70 °C *in vacuo*. This compound was observed to disproportionate spontaneously to the solvento species (**2**, SbF_6; M = Ru, Y = NEt, R = OMe) and the parent (**1**; M = Ru, Y = NEt, R = OMe) on dissolution in weakly co-ordinating polar solvents such as acetone or benzonitrile. $[Ru_2\{\mu\text{-}Ag(C_5H_5N)\}(\mu\text{-}CO)(CO)_4\{\mu(MeO)_2PN(Et)P\text{-}(OMe)_2\}_2]SbF_6$ is thermodynamically more stable than the silver–acetonitrile adduct but interestingly, while $[Ru_2\{\mu\text{-}Ag(MeCN)\}(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]SbF_6$ slowly disproportionates to $[Ru_2(CO)_5(MeCN)\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2](SbF_6)_2$ and $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ in acetonitrile, the silver–pyridine adduct degrades solely back to the parent compound (**1**; M = Ru, Y = NEt, R = OMe) on heating in pyridine. A solvent dependence is observed for the reaction of (**1**; M = Ru, Y = NEt, R = OMe) with an equimolar amount of silver acetate. The acetate-bridged species $[Ru_2\{\mu\text{-}O_2C(Me)\}\text{-}(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]^+$ (**5**) is produced in non-protic THF, whereas a product, identified *X*-ray crystallographically as its isomer *viz.* $[Ru_2\{\mu\text{-}OC(OMe)\}(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]^+$ (**6**),[3] is formed in methanol.

Although all attempts to obtain single crystals of the silver–acetonitrile and the silver–pyridine adducts (**3**, SbF_6) suitable for an *X*-ray diffraction study proved unsuccessful, it was possible to confirm the stereochemistry of these species through a crystal structure determination on the related gold–triphenylphosphine derivative $[Ru_2\{\mu\text{-}Au(PPh_3)\}(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]SbF_6$, synthesized by treatment of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ with an equimolar amount of $[AuCl(PPh_3)]$ followed by addition of $AgSbF_6$ to the reaction mixture containing the ionic product. This determination[¶] has established that the latter is symmetrical with the two ruthenium atoms separated by a distance of 2.883(1) Å, being bridged by a carbonyl and the $AuPPh_3$ moiety as well as by the two diphosphazane ligands (Figure 1). An interesting feature of the structure is the close approach of two of the carbonyl groups, CO(1) and CO(4), to the gold atom [Au–C(1) 2.57(1), Ru(1)–C(1) 1.95(1); Au–C(4) 2.50(1), Ru(2)–C(4) 1.94(1) Å] which could be interpreted in terms of their functioning as semi-bridging carbonyls.[4]

$[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ is in fact susceptible to attack by a wide range of metal-containing electrophiles and with $[Cu(MeCN)_4]^+$ and $HgCl_2$ for instance affords $[Ru_2\{\mu\text{-}Cu(MeCN)\}(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]^+$ (**7**) and $[Ru_2(HgCl)(CO)_5\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]^+$ (**8**) respectively. In the former the CuNCMe moiety bridges the two ruthenium atoms while in the latter the HgCl group is terminally co-ordinated.

The above results involving silver(I) ions can be readily explained in terms of the reaction pathway illustrated in

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[¶] *Crystal data*: $C_{35}H_{49}AuF_6N_2O_{13}P_5Ru_2Sb$, M = 1497.02, monoclinic, space group $P2_1/c$, a = 13.481(2), b = 20.723(3), c = 18.440(3) Å, β = 99.90(1)°, U = 5074.66 Å^3, D_m = 1.937 g cm^{-3}, D_c = 1.957 g cm^{-3}, Z = 4, Mo-K_α radiation, λ = 0.71069 Å, μ = 42.17 cm^{-1}. Nonius CAD4 diffractometer, 7933 unique reflections in the range $3 \leqslant 2\theta \leqslant 46°$. Structure solved from a Patterson synthesis and successive Fourier maps and refined to R = 0.0618 (386 parameters). Atomic co-ordinates, interatomic distances and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

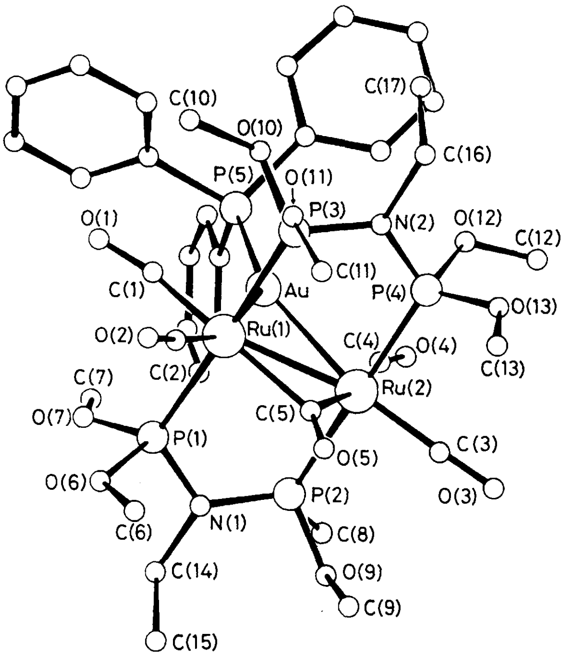

Figure 1. The stereochemistry of $[Ru_2\{\mu\text{-}Au(PPh_3)\}(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]^+$. Relevant interatomic distances: Ru(1)–Ru(2), 2.883(1); Au–Ru(1), 2.749(1); Au–Ru(2), 2.741(1); Ru(1)–P(1), 2.331(3); Ru(1)–P(3), 2.321(3); Ru(2)–P(2), 2.328(3); Ru(2)–P(4), 2.320(3); Au–P(5), 2.328(3) Å.

Scheme 1 and provide unequivocal evidence that the one-electron oxidation of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$, and presumably related dinuclear compounds bridged by diphosphorus ligands, by silver salts occurs *via* an inner sphere mechanism. Silver(I) salts are used extensively in inorganic and organometallic chemistry as one-electron oxidants, (*e.g.* ref. 5), while an increasing number of compounds formed by the addition of silver(I) complexes across a metal–metal bond in dinuclear and metal cluster derivatives or across a face of a metal cluster have been reported of late.[6—13] However, this is the first detailed study to provide tangible evidence that one-electron oxidation of polynuclear derivatives by silver(I) salts occurs *via* inner sphere intermediates in which the silver has added across an edge or a face of the metal atom framework and, apart from an investigation of the reactions of AgY salts with $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_{4-n}(CNMe)_n]$ complexes by Manning *et al.*,[14] this is the first to establish that the nature of the final product of this type of reaction can be very dependent on the nature of the ligand co-ordinated to the silver.

The authors express their sincere thanks to the Foundation for Research Development of the South African Council for Scientific and Industrial Research and the Universities of Natal and Durban-Westville for financial support, Johnson Matthey Limited for the loan of ruthenium salts, and Dr. P. H. van Rooyen of the N.C.R.L., C.S.I.R., Pretoria for the intensity data collection.

Received, 10th May 1989; Com. 9/01955C

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