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Preliminary communication

HALOGENATION AND STEPWISE DECARBONYLATION OF DIPHOSPHAZANE-BRIDGED DERIVATIVES OF IRON AND RUTHENIUM NONACARBONYL. CRYSTAL STRUCTURES OF $[Fe_2I(CO)_5\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2][PF_6]$ AND $[Ru_2(\mu\text{-}I)I(CO)_3\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$

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Summary

Treatment of $[M_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (M = Fe or Ru; R = Me, Pr^i or Ph) with halogens gives $[M_2X(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]X$ (X = Cl, Br or I) which can be readily decarbonylated to $[M_2(\mu\text{-}X)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]X$ (M = Fe or Ru), $[M_2(\mu\text{-}X)X(CO)_3\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (M = Ru) and $[M_2(\mu\text{-}X)_2(CO)_2\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (M = Ru) under appropriate reaction conditions; the structures of $[Fe_2I(CO)_5\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]PF_6$ and $[Ru_2(\mu\text{-}I)I(CO)_3\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ have been established X-ray crystallographically.

We have previously established that $[Fe_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (R = Me, Pr^i or Ph) (I; M = Fe) [1] is very susceptible to electrophilic attack and reacts readily with equimolar quantities of chlorine, bromine or iodine to produce $[Fe_2(\mu\text{-}X)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]X$ (X = Cl, Br or I) (II; M = Fe) in which the halogen as well as the two diphosphazane ligands bridge the two iron atoms [2]. By monitoring these reactions by means of infrared and ^{31}P NMR spectroscopy we have now found that an intermediate product is initially formed and that this intermediate rapidly converts to the tetracarbonyl species $[Fe_2(\mu\text{-}X)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ in solution, with the rate of conversion increasing along the series R = Me $\ll$ Pr^i < Ph and to a smaller extent along the series X = Cl < Br < I. The three more stable tetramethoxydiphosphazane intermediates could be isolated as the hexafluorophosphate salts and were characterised as the

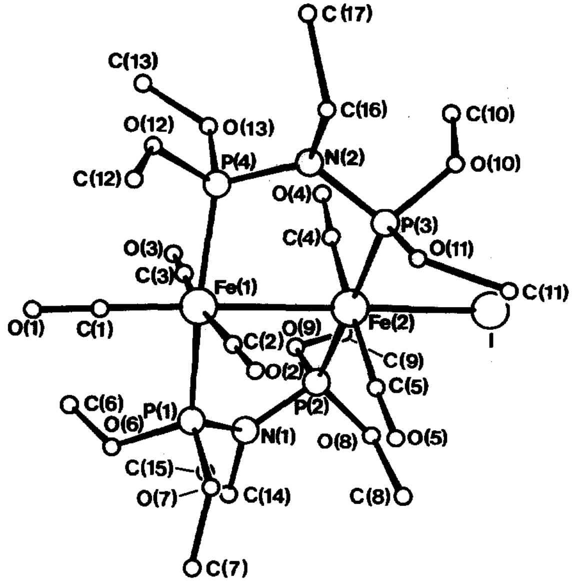
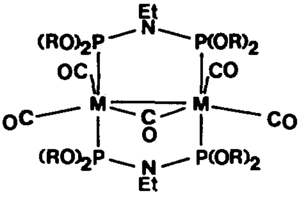
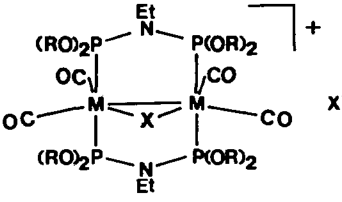


Fig. 1. The molecular stereochemistry of $[Fe_2I(CO)_5\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]PF_6$. Relevant inter-atomic distances: Fe(1)–Fe(2), 2.787(3); Fe(2)–I, 2.667(2); Fe(1)–P(1), 2.197(4); Fe(1)–P(4); 2.206(4); Fe(2)–P(2), 2.217(5); Fe(2)–P(3), 2.225(5); Fe(1)–C(1), 1.74(2); Fe(1)–C(2), 1.79(2); Fe(1)–C(3), 1.77(2); Fe(2)–C(4), 1.78(2); Fe(2)–C(5), 179(2) Å.

pentacarbonyl compounds $[Fe_2X(CO)_5\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]PF_6$. An X-ray crystal structure determination on $[Fe_2I(CO)_5\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]PF_6$ * revealed that the compound has the structure illustrated in Fig. 1. Salient features of this structure are that the compound adopts a staggered configuration with the extent of the stagger reflected by the P–Fe–Fe–P torsion angles {P(1)–Fe(1)–Fe(2)–P(2) 27.9°; P(4)–Fe(1)–Fe(2)–P(3) 29.3°} and that the iodine atom is axially disposed.



(I)



(II)

While the tetraisopropoxy- and tetraphenoxydiphosphazane species $[Fe_2X(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]X$ were observed to convert solely to $[Fe_2(\mu\text{-}$

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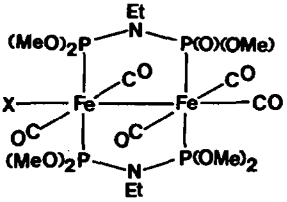
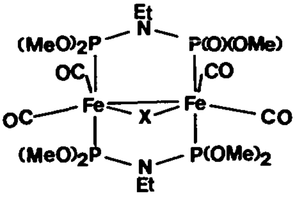
* *Crystal data*: $C_{17}H_{34}O_{13}N_2P_5IF_6Fe_2$. $M = 981.96$, orthorhombic, space group *Pbca*, *a* 20.233(9), *b* 15.545(7), *c* 22.218(9) Å, *U* 6988Å^3 D_c 1.87 g cm^{-3} for $Z = 8$, D_m 1.86 g cm^{-3}. $F(000) = 3904$, λ(Mo-K_α) 0.71069 Å, μ(Mo-K_α) 21.05 cm^{-1}. 4138 reflections were measured on a Philips PW1100 diffractometer (N.P.R.L., C.S.I.R., Pretoria), 3121 of which were classed as observed ($I > 3\sigma(I)$). Data were corrected for Lorentz and polarisation effects but not for absorption. The structure was solved by standard Patterson and Fourier methods and refined by full-matrix least-squares methods to $R = 0.080$ with the Fe, I and P atoms being assigned anisotropic temperature factors and the remaining atoms individual isotropic temperature factors.

X)(CO)$_4${μ-(RO)$_2$PN(Et)P(OR)$_2$}$_2$]X (II; M = Fe) in solution, the decarbonylation of the tetramethoxydiphosphazane derivatives [Fe$_2$X(CO)$_5${μ-(MeO)$_2$PN(Et)P-(OMe)$_2$}$_2$]X was found to be much more complex owing to accompanying Michaelis–Arbuzov rearrangements. In particular [Fe$_2$X(CO)$_5${μ-(MeO)$_2$PN(Et)P(O)-(OMe)}{μ-(MeO)$_2$PN(Et)P(OMe)$_2$}] (III) was found to form concurrently with [Fe$_2$(μ-X)(CO)$_4${μ-(MeO)$_2$PN(Et)P(OMe)$_2$}$_2$]X (II; M = Fe, R = Me) with both products degrading to [Fe$_2$(μ-X)(CO)$_4${μ-(MeO)$_2$PN(Et)P(O)(OMe)}{μ-(MeO)$_2$PN(Et)P(OMe)$_2$}] (IV) [2] in solution through decarbonylation and Michaelis–Arbuzov rearrangement respectively.

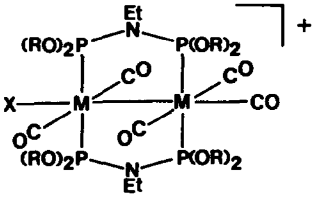


(III)

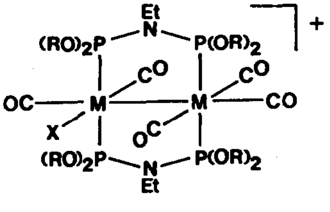


(IV)

The bridged diruthenium derivatives [Ru$_2$(μ-CO)(CO)$_4$){μ-(RO)$_2$PN(Et)P-(OR)$_2$}$_2$] (R = Me or Pr^i) (I; M = Ru) [1] also react readily with halogens but in contrast to [Fe$_2$X(CO)$_5${μ-(RO)$_2$PN(Et)P(OR)$_2$}$_2$]$^+$, the ruthenium pentacarbonyl species, [Ru$_2$X(CO)$_5${μ-(RO)$_2$PN(Et)P(OR)$_2$}$_2$]$^+$ (X = Cl, Br or I), decarbonylate much more slowly to the corresponding tetracarbonyl species, viz. [Ru$_2$(μ-X)(CO)$_4${μ-(RO)$_2$PN(Et)P(OR)$_2$}$_2$]$^+$ with the rate of decarbonylation again increasing along the series R = Me $\ll$ Pr^i and along the series X = Cl < Br < I *. The pentacarbonyl species, [M$_2$X(CO)$_5${μ-(RO)$_2$PN(Et)P(OR)$_2$}$_2$]$^+$ (M = Fe or Ru) can exist in two isomeric forms (Va and Vb) and significantly the room temperature ^{31}P NMR spectrum of [Ru$_2$I(CO)$_5${μ-(MeO)$_2$PN(Et)P(OMe)$_2$}$_2$]PF$_6$ was found to contain two sets of resonances, each typical of AA′BB′ patterns, which is indicative of this compound being present in both isomeric forms in solution **. This is also in contrast to the iron pentacarbonyl derivatives which occur as a single isomer in solution, either Va or Vb (M = Fe).



(Va)



(Vb)

The tetracarbonyl species [Ru$_2$(μ-X)(CO)$_4${μ-(RO)$_2$PN(Et)P(OR)$_2$}$_2$] (II, M = Ru), readily converted to and characterised as the hexafluorophosphate salts, react

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* The decarbonylation is readily accelerated in polar, coordinating solvents such as dimethyl sulphoxide and acetone or under thermal or photochemical conditions.

** The ^{31}P NMR spectrum of [Ru$_2$I(CO)$_5${μ-(MeO)$_2$PN(Et)P(OMe)$_2$}$_2$]PF$_6$ at −60 °C contains essentially a single set of resonances with an AA′BB′ pattern which suggests that only the more stable isomer, presumably Va (M = Ru, R = Me) with an axially disposed iodine, is present in solution at low temperatures.

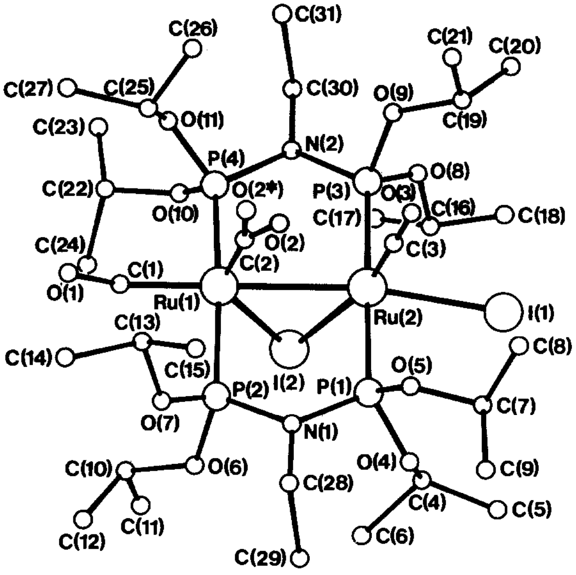

Fig. 2. The molecular stereochemistry of $[Ru_2(\mu\text{-}I)I(CO)_3\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ (O(2) is disordered between two alternative positions, see text). Relevant interatomic distances: Ru(1)–Ru(2), 2.794(1); Ru(1)–I(2), 2.724(1); Ru(2)–I(2), 2.767(1); Ru(2)–I(1), 2.732(1); Ru(1)–P(2), 2.325(4); Ru(1)–P(4); 2.333(4); Ru(2)–P(1), 2.327(4); Ru(2)–P(3), 2.339(4); Ru(1)–C(1), 1.89(2); Ru(1)–C(2), 1.82(2); Ru(2)–C(3), 1.79(2) Å.

further with excess halide ions to give the neutral tricarbonyl derivatives $[Ru_2(\mu\text{-}X)X(CO)_3\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$. Significantly, although this decarbonylation process is a very slow one neither the neutral tetracarbonyl dihalides $[Ru_2X_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ nor Michaelis–Arbuzov products in those reactions involving $[Ru_2(\mu\text{-}X)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]X$, could be detected. Decarbonylation is achieved much more readily by heating or irradiation of solutions of $[Ru_2(\mu\text{-}X)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]X$ in THF with ultraviolet light or, alternatively, by eluting a solution of the compound through a silica column. The molecular geometry of $[Ru_2(\mu\text{-}I)I(CO)_3\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ has been established X-ray crystallographically * and is illustrated in Fig. 2. The structure is related to those of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ [1] and $[Fe_2(\mu\text{-}Br)(CO)_4\{\mu\text{-}(PhO)_2PN(Et)P(OPh)_2\}_2]PF_6$ [2] with the bridging and terminal iodines, the three carbonyl groups and the two ruthenium atoms being in a plane orthogonal to a plane containing the phosphorus atoms of the two diphosphazane ligands as well as the two ruthenium atoms. The equatorial carbonyl

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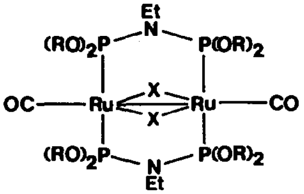
* *Crystal data*: $C_{31}H_{66}N_2O_{11}P_4Ru_2I_2$. $M = 1222.7$, monoclinic, space group Pn, a 11.557(4), b 13.095(3), c 16.263(3) Å, β 100.43(2)°, U 2420.5 Å^3. D_c 1.68g cm^{-3} for $Z = 2$. $F(000) = 1216$, λ(Mo-K_α) 0.71073 Å, μ(Mo-K_α) 19.1 cm^{-1}. 4139 reflections were measured on a Nonius CAD-4 diffractometer (N.C.R.L., C.S.I.R., Pretoria), 3896 of which were classed as observed ($I > 3\sigma(I)$). Data were corrected empirically for absorption as well as for Lorentz and polarisation effects. The structure was solved by standard Patterson and Fourier methods and refined by full-matrix least-squares methods to $R = 0.046$ with the Ru and I atoms being assigned anisotropic temperature factors, and the others averaged isotropic temperature factors.

coordinated to the ruthenium atom bonded to the axial carbonyl is disordered with the crystallographic refinement favouring neither of two discrete alternative positions for the oxygen atom such that two conformations must be assumed to occur with equal probability in the crystal. Alternative positions for the carbon of this carbonyl were not resolved but the comparatively high temperature factor refined for it is consistent with two closely spaced alternative positions. Significantly the disposition of this equatorial carbonyl is such that it could be considered as semi-bridging {Ru(2)–Ru(1)–C(2) 74.4(7)°, Ru(1)–C(2) 1.82(2) Å, Ru(2)–C(2) 2.89(2) Å} and, moreover, one of the two positions for the oxygen atom allows for a weak interaction between this oxygen and the second ruthenium atom {Ru(1)–C(2)–O(2) 145(2)°, Ru(2)–O(2) 2.81(2) Å}. Another striking structural feature is the different orientations of the two equatorial carbonyl groups. Comparison of the two angles Ru(2)–Ru(1)–C(2) {74.4(7)°} and Ru(1)–Ru(2)–C(3) {107.2(5)°} shows that while CO(2) is drawn towards Ru(2), CO(3) points outward. The net result is a more regular arrangement around Ru(2) compared to Ru(1).

Treatment of $[Ru_2(\mu\text{-}X)X(CO)_3\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ with trimethylamine oxide in acetone at 60°C was found to lead to further decarbonylation to produce the dicarbonyl species $[Ru_2(\mu\text{-}X)_2(CO)_2\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (VI) which on the basis of the infrared and ^{31}P NMR spectroscopic evidence has a symmetrical structure with both halogens bridging.



(VI)

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