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Preliminary communication

CONTRASTING HALOGENATING ACTION OF HALOGENOALKANES AND HALOGENS TOWARDS DIPHOSPHAZANE-BRIDGED DERIVATIVES OF IRON AND RUTHENIUM NONACARBONYL. CRYSTAL STRUCTURE OF $[Ru_2Cl_2(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$

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Summary

Dissolution of $[Fe_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (R = Me, Pr^i or Ph) and $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (R = Me or Pr^i) in CCl_4 leads to the rapid formation of $[Fe_2(\mu\text{-}Cl)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]Cl$ and $[Ru_2Cl_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$, respectively, with the latter isomerising in dichloromethane or chloroform solution to $[Ru_2(\mu\text{-}Cl)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]Cl$, which in turn decarbonylates to $[Ru_2(\mu\text{-}Cl)Cl(CO)_3\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$; the structure of $[Ru_2Cl_2(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ has been established X-ray crystallographically.

We have previously established that reaction of $[M_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (M = Fe, R = Me, Pr^i or Ph; M = Ru, R = Me or Pr^i) (I) with halogens involves the heterolytic fission of the halogen and the initial formation of the ionic pentacarbonyl $[M_2X(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ (X = Cl, Br or I) (II) which subsequently decarbonylates in solution to the tetracarbonyl species $[M_2(\mu\text{-}X)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (IV) [1,2]. While the iron tetraisopropoxy- and tetraphenoxy diphosphazane species $[Fe_2(\mu\text{-}X)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ (R = Pr^i or Ph) (IV, M = Fe) are inert to attack by halide ions, $[Fe_2(\mu\text{-}X)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]^+$ (IV, M = Fe) rearranges in the presence of X^- to the Michaelis–Arbuzov product $[Fe_2(\mu\text{-}X)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(O)(OMe)\}\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}]$ (V). The pentacarbonyl species, $[Fe_2X(CO)_5\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]^+$ (II, M = Fe) are also susceptible to Michaelis–Arbuzov rearrangement in the presence of halide ions producing $[Fe_2X(CO)_5\{\mu\text{-}(MeO)_2PN(Et)P(O)(OMe)\}\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}]$ (III) which readily loses carbon monoxide to afford $(Fe_2(\mu\text{-}X)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(O)(OMe)\}\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}]$ (V). On the other hand the ruthenium species $[Ru_2(\mu\text{-}X)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ (R = Me or Pr^i) (IV, M = Ru) are

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slowly substituted by halide ions to give the tricarbonyl compounds $[Ru_2(\mu\text{-}X)X(CO)_3\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (VI). Significantly there was no evidence for the formation of the neutral dihalide $[Ru_2X_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ in any of these reactions, summarised in Scheme 1.

We have now found that halogenoalkanes also readily halogenate $[M_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (M = Fe, R = Me, Pr^i or Ph; M = Ru, R = Me or Pr^i) (I) but by a very different pathway. Thus dissolution of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (R = Me or Pr^i) [3] in freshly distilled CCl_4 at ambient temperature leads to the rapid formation of a neutral compound characterised by routine methods as well as by X-ray crystallography * in the case of the tetramethoxydiphosphazane derivative, as the neutral dichloride $[Ru_2Cl_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (VII). The molecular stereochemistry of $[Ru_2Cl_2(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ is illustrated in Fig. 1. The two ruthenium atoms which are bridged by the two diphosphazane ligands *trans* disposed with respect to each other, adopt octahedral local geometries and are separated by a distance of 2.887(6) Å corresponding to a formal ruthenium–ruthenium bond. The two chlorine atoms are axially disposed while the four terminal carbonyl groups occupy equatorial positions. The two $RuP_2(CO)_2Cl$ units are slightly staggered with respect to each other which is reflected by the Ru(1)–P(1)–P(2)–Ru(2) torsion angle of 24.5°.

$[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (I, M = Ru) also reacts with dichloromethane and chloroform (vide infra) but at a much slower rate and as a consequence the carbon tetrachloride reaction could be monitored by means of ^{31}P NMR spectroscopy using CD_2Cl_2 as solvent. The formation of the ionic chloro-bridged derivative, $[Ru_2(\mu\text{-}Cl)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]Cl$ (II, M = Ru) as well as $[Ru_2Cl_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (VII) was observed but by also using infrared spectroscopy to monitor this reaction (in CH_2Cl_2) the former compound was established to be produced via the latter. Consistent with these observations $[Ru_2Cl_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ was found to be stable in non-polar solvents but to isomerise to $[Ru_2(\mu\text{-}Cl)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]Cl$ in CH_2Cl_2.

The reactions of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (I, M = Ru) with

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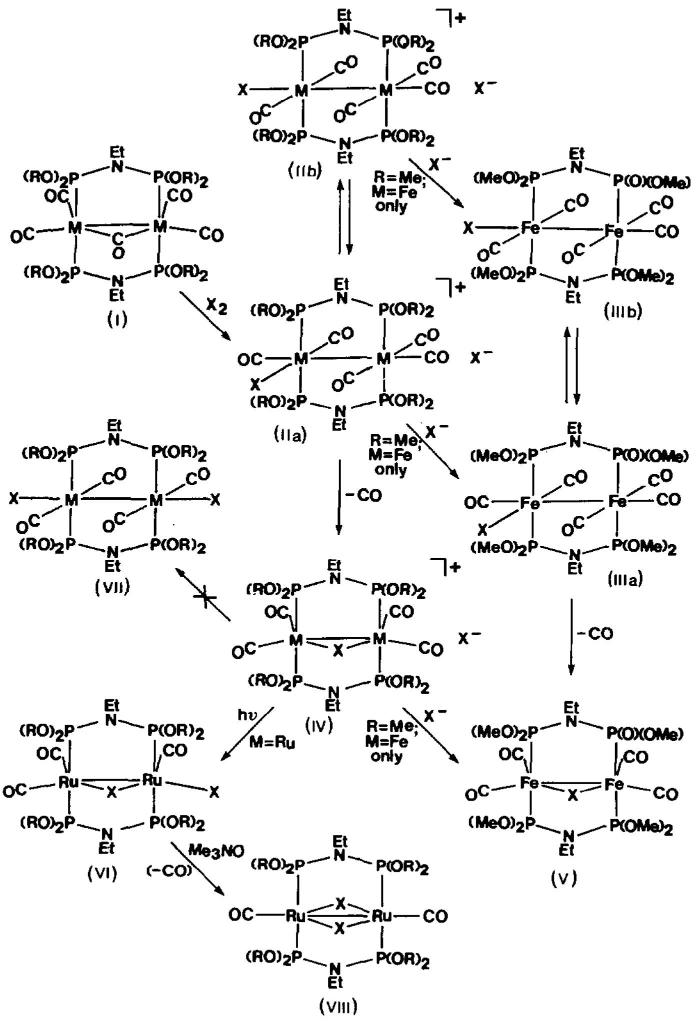
* *Crystal data*: $C_{16}H_{34}O_{12}N_2P_4Cl_2Ru_2$. $M = 843.38$, orthorhombic, *Cmca*, *a* 14.97(1), *b* 13.72(1), *c* 15.14(1) Å, *U* 3109.9 Å^3. D_c 1.80 g cm^{-3} for $Z = 4$, D_m 1.86 g cm^{-3}. $F(000) = 1688$, $\lambda(\text{Mo-}K_\alpha)$ 0.71069 Å, $\mu(\text{Mo-}K_\alpha)$ 13.70 cm^{-1}. 1215 reflections were measured on a Philips PW1100 diffractometer (N.P.R.L., C.S.I.R., Pretoria), 941 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 $R = 0.152$, with anisotropic thermal factors for the Ru, P and Cl atoms, and isotropic thermal factors for the remaining non-hydrogen atoms. The molecules are located on sites of $2/m$ symmetry but are disordered. The model of disorder used allows the local *m* [100] symmetry to be destroyed but necessarily preserves the *m* [100] symmetry for the crystal as a whole. Thus each individual molecule possesses a crystallographically imposed 2-fold axis but no mirror plane. Convergence was achieved with the final refinement and a final difference map was featureless with a maximum peak height of 2 e Å^{-3}.

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 (Great Britain). Any request should be accompanied by a full literature citation for this communication.



SCHEME 1

CH_2Cl_2 and $CHCl_3$ are not only slow but also very complex. For instance the reaction between $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ and CH_2Cl_2 gives, according to ^{31}P NMR spectroscopic evidence, at least four products, two major and two minor, with the two major ones exhibiting a singlet and a set of resonances with an AA′BB′ pattern respectively. The chemical shifts of these resonances are different from those observed for $[Ru_2Cl_2(CO)_4\{\mu\text{-}(MeO)_2PN(Et)\text{-}P(OMe)_2\}_2]$ (VII) and $[Ru_2(\mu\text{-}Cl)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]PF_6$ (IV, M = Ru) and for $[Ru_2(\mu\text{-}Cl)Cl(CO)_3\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ (VI) respectively while the frequencies of the C–O stretching peaks in the infrared spectrum of the reaction mixture are also different to those observed for the above three compounds. Attempts to separate and isolate the two major products proved unsuccessful owing to the slow formation of the eventual product of the reaction viz. $[Ru_2(\mu\text{-}Cl)\text{-}Cl(CO)_3\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ (VI).

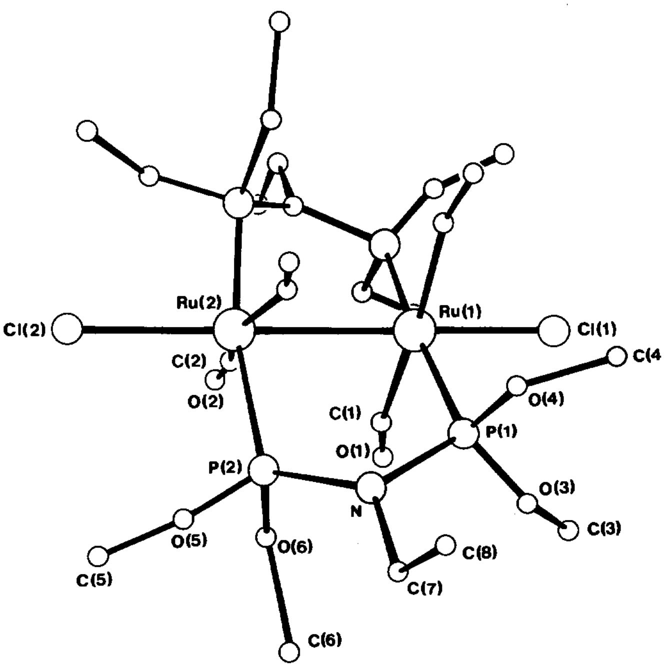


Fig. 1. The molecular stereochemistry of $[Ru_2Cl_2(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$. The molecule possesses a crystallographically imposed 2-fold axis (see text). Relevant interatomic distances (Å): Ru(1)–Ru(2), 2.887(6); Ru(1)–Cl(1), 2.32(5); Ru(2)–Cl(2), 2.32(5); Ru(1)–P(1), 2.34(2); Ru(2)–P(2), 2.31(1); Ru(1)–C(1), 2.14(7); Ru(2)–C(2), 1.91(10).

Carbon tetrachloride also reacts rapidly with the iron complexes $[Fe_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ ($R = Me$, Pr^i or Ph) (I, $M = Fe$) but in these cases the ionic species $[Fe_2(\mu\text{-}Cl)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]Cl$ (II, $M = Fe$) and not the neutral dichloride $[Fe_2Cl_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ were found to be the only isolable products. Dichloromethane and chloroform were shown to form the same products but at much slower rates than those for the corresponding CCl_4 reactions.

A number of aspects of these chlorination reactions warrant particular comment: (i) The ionic pentacarbonyl derivatives $[M_2Cl(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]Cl$ ($M = Fe$ or Ru) (II) could not be detected in any of the reactions of $[Fe_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ and $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ with CCl_4; (ii) The rate of formation of $[Ru_2Cl_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ in CCl_4 is considerably faster than the rate of decarbonylation of $[Ru_2Cl(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ to the ionic tetracarbonyl $[Ru_2(\mu\text{-}Cl)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ for the corresponding diphosphazane ligand; (iii) Chlorination of $[Fe_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ by CCl_4 does not take place in the dark; (iv) Carbonyl compounds such as $COCl_2$ and Cl_2CCO were identified in the reaction mixtures; (v) The rate of reaction of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ with CCl_4 is very dependent on the nature of R. For $R = Pr^i$, the reaction occurs spontaneously on dissolution of the parent pentacarbonyl in CCl_4 at 25°C whereas for $R = Me$ the reaction occurs ca. 100–1000 times slower under the same conditions.

The above observations are interpreted in terms of the chlorination of $[M_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (M = Fe or Ru) by chloroalkanes and in particular by carbon tetrachloride, occurring via a radical pathway, in contrast to that by chlorine. Although the various steps for this pathway have not been totally elucidated at this stage; it is apparent that one of them involves the radical assisted dissociation of carbon monoxide involving the formation of the oxidation products $COCl_2$, etc.

Carbon tetrabromide is an effective bromination agent for $[M_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (M = Fe or Ru) but in contrast to CCl_4 requires initiation by soft ultraviolet light. Furthermore $[Ru_2Br(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ is a product of this reaction even when freshly sublimed CBr_4 is used indicating that the mechanism of bromination is analogous to that of Br_2.

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