09.4-3 UNUSUAL SILVER(I) PHENOXYALKANDATES. By Graham Smith ${ }^{1}$, Colin H.L. Kennard ${ }^{2}$, Thomas C.W. Mak ${ }^{3}$, Wai-Hing Yip ${ }^{3}$ and Eric J. Q'Reilly, Departments of Chemistry, Queensland Institute of Technology ${ }^{1}$, University of Queensland ${ }^{2}$, Australia and The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong ${ }^{3}$.

The structures of three atypical silver(I) carboxylates have been determined using X-ray diffraction. The silver(I) complex with (2-chlorophenoxy)acetic acid, $\left[\left(\mathrm{Ag}_{2} \mathrm{~L} 2\right) \cdot \mathrm{AgClO}_{4}\right]_{n}, \quad(1), \quad\left(\mathrm{L}=2-\mathrm{Cl}-\mathrm{C}_{6} \mathrm{H}_{4} \cdot 0 \mathrm{OCH}_{2} \mathrm{CO}_{2}\right)$ comprises a basic bis-carboxylate dimer core similar to known silver(I) carboxylates but with a third linear silver and a carboxylate oxygen extending the dimer into a polymer structure. In addition, the perchlorate group is coordinated in one of the axial dimer sites.

(1)


In the isomorphous silver(I) complexes of the herbicides ( 2,4 -dichlorophenoxy) acetic acid (2,4-D) and (4-chloro-2-methylphenoxy) acetic acid (MCPA), [AgL] ${ }_{n}$, (2a, 2b), the zig-zag polymer structures comprise only linear $0-\mathrm{Ag}-0$ bonds via carboxylate oxygens.
09.4-4 COPPER(I) AND SILVER(I)-DIRHODIUM POLYHYDRIDES. By F. Bachechi, Istituto di Strutturistica Chimica, C.N.R., Area della Ricerca di Roma, Rome, Italy, and J. Ott, U. Statler and L. M. Venanzi, Laboratorium fur Anorganische Chemie, ETH-Z, Zurich, Switzerland.

The tripod-like tridentate ligand 1,1,1-tris(diphenylphosphinomethyl)ethane, triphos, has a specific geometry which only allows a facial coordination to a metal centre. The fragments (triphos)M can either activate a large variety of small molecules or stabilize groups of atoms which cannot exist by themselves or facilitate both polynuclear complex and hydrogen-bridge formation (L. Sacconi, F. Mani, Trans. Met. Chem. 1982, 8, 179). When $\left[\mathrm{RhH}_{3}\right.$ (triphos) $]$ is allowed to react with $\mathrm{Cu}^{+}$or $\mathrm{Ag}^{+}$ salts (molar ratio 2:1) the trinuclear hydrides [ $\mathrm{Rh}_{2} \mathrm{CuH}_{6}$ (triphos) $\left.)^{+}\right]^{+}$1, and $\left[\mathrm{Rh}_{2} \mathrm{AgH}_{6}(\text { triphos })_{2}\right]^{+}$, 2, are obtained. X-ray analyses of the $\left[\mathrm{CF}_{3} \mathrm{SO}_{3}\right]$ salts of $\underline{1}$ and $\underline{2}$ were undertaken. The two compounds are isomorphousand have a binary symmetry with an axis passing through the coinage metal. The crystal structures revealed linear trimetallic chains in which the triphos ligands adopt a staggered rotational conformation. The hydrides were not located by X-ray analysys, but the heavy donor atom arrangement suggests that the $\mathrm{Cu}^{+}$and $\mathrm{Ag}^{+}$centres, respectively in $\underline{1}$ and $\underline{2}$, interact with the six hydrides, which bridge the $M-M$ contacts, in a severely distorted octahedral configuration. Their structures will be discussed and compared with those of related iridium compounds containing monodentate phosphines.
09.4-5 PYRIDINE-BASE ADDUCTS OF GROUP (IB) metal (I) halides.
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Copper(I) and silver(I) halides form a variety of oligomeric and polymeric species when combined with nitrogen or phosphorus bases. For complexes of the ratio MX : base, l:1, the metal environment may be 2,3 or 4 coordinate; the coordination number decreasing in parallel with the increasing steric hindrance of the base.

$\begin{array}{lcccc}\text { 'Stair } & \text { Cube } & \text { "Split Stalr" } & \text { Dimer } & \text { Monomer } \\ \text { (4-coord- } & \text { (4-coord- } & \text { (3-coordinate) } & \begin{array}{l}\text { (3-coord- } \\ \text { (3-coord- } \\ \text { (nate) }\end{array} & \text { inate) }\end{array}$

Substitution in the 2- and 6- position of the pyridine bases allows a number of ligands with various steric profiles and functionalities to be obtained.

In this report, structures of CuX and $\mathrm{AgX}(\mathrm{X}=\mathrm{Cl}, \mathrm{Br}, \mathrm{I})$ with a variety of substituted pyridine bases characterize the diversity of structural types in this system and define the transitional forms between these various types.

| Base | CuCl | CuBr | CuI |
| :---: | :---: | :---: | :---: |
| Pyridine | Stair | Stair | Stair |
| $\begin{aligned} & \text { Diphenyl-2-pyridyl- } \\ & \text { methane } \end{aligned}$ | Cube | Cube | Cube |
| 2,6-Lutidine | Split <br> stair | $\begin{aligned} & \text { Split } \\ & \text { stair } \end{aligned}$ | Dimer |
| 2,4,6-Collidine | Ionic* | Split stair | Split stair |
| Acridine | Split <br> stair | Split stair | $\begin{aligned} & \text { Split } \\ & \text { stair } \end{aligned}$ |
| Octahydroacridine | Dimer | Dimer | Dimer |
| $\begin{aligned} & \text { Tetramethylpiper- } \\ & \text { dine } \end{aligned}$ | Monomer | Monomer | Dimer |

${ }^{*}\left[\mathrm{CuL}_{2}\right]^{+}\left[\mathrm{CuCl}_{2}\right]^{-}$

