Preparation and Structures of the $Me_4N[M^1\{M^2(CO)_3(\pi\text{-}C_5H_5)\}_2]$ Salts ($M^1 = Cu^I$ or Ag^I; M^2 = Mo or W)

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Summary The i.r. spectra of the new $Me_4N[M^1\{M^2(CO)_3(\pi\text{-}C_5H_5\}_2]$ salts ($M^1 = Cu^I$ or Ag^I, M^2 = Mo or W) imply that the M^2–Ag–M^2 bonding is linear, and that the $[(\pi\text{-}C_5H_5)M^2(CO)_3]^-$ ligands are, at best, poor π-acceptors.

THE crystalline $Me_4N[M^1\{M^2(CO)_3(\pi\text{-}C_5H_5)\}_2]$ salts ($M^1 = Cu^I$ or Ag^I, M^2 = Mo or W) may be isolated from aqueous diglyme solutions of $Na[M^2(CO)_3(\pi\text{-}C_5H_5)]$ and copper(I) chloride or silver(I) nitrate (mol ratio 2:1) by the addition of aqueous $[Me_4N]Cl$ solution. Whilst the copper compounds are yellow, those of silver are colourless. All are quite stable in the solid state, but are readily oxidised in solution.

The i.r. spectra of the silver derivatives are similar to those of the well-known $Hg[M^2(CO)_3(\pi\text{-}C_5H_5)]_2$ compounds in the C–O stretching region,[1] but with the expected shifts of absorption bands to lower frequencies; $Me_4N[Ag\{Mo(CO)_3(\pi\text{-}C_5H_5)\}_2]$ ν_{CO} (THF) 1790 (sh), 1811 (10), 1828 (10), 1917 (9·8), 1932 (5·6) (cm^{-1} with relative peak heights in parentheses). This suggests that the complex anions are non-centrosymmetric but have linear M^2–Ag–M^2 systems. The spectra of the copper compounds are somewhat different but it is not clear if this is due to gross structural differences. As silver(I) tends to form four-co-ordinate complexes with π-bonding ligands and linear two-co-ordinate derivatives with non-π-bonding ligands,[2] these observations imply that the $\{(\pi\text{-}C_5H_5)M(CO)_3\}^-$ ions are, at best, weak π-acceptor ligands.

All previously known compounds containing silver(I)–transition-metal bonds have been of the type, *e.g.* $L_3AgCo(CO)_4$,[3,4] where the three other ligands L are phosphines or arsines which are π-acceptors. The $[Ag\{M(CO)_3(\pi\text{-}C_5H_5)\}_2]^-$ ions are the first reported examples of linear, two-co-ordinate silver(I)–transition-metal compounds.

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