

CARBONYL CHEMISTRY OF THE GROUP IB METALS

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I. INTRODUCTION

Currently, various aspects of the organometallic chemistry of the Group IB elements (copper, silver and gold) are being investigated in several laboratories. One area which has received relatively little attention is that concerned with complexes containing carbonyl groups attached to these metals. The early literature is scattered and confusing, and preparatory to our own work in this field, it was necessary to review the achievements of more than a century's endeavours.

II. PURE CARBONYLS

Many claims for the observation of copper carbonyl species have appeared in the literature, most being based on transport of copper metal from one site to another when heated in a stream of carbon monoxide at more or less elevated temperatures. With one possible exception, however, there has been no well-substantiated account of the isolation of a discrete binary carbonyl containing any of the Group IB elements.

According to contemporary ideas, the most likely formulations of carbonyl complexes of the Group IB elements, together with their hydrido derivatives, are illustrated in Table 1.

TABLE 1

Expected Group IB carbonyl species (Compared With Some Known Group VIII Complexes)

$\text{Fe}(\text{CO})_5$	$\text{Fe}_2(\text{CO})_9$	$\text{Fe}_3(\text{CO})_{12}$	$[\text{Fe}_4(\text{CO})_{13}]^{2-}$	$[\text{Fe}_6\text{C}(\text{CO})_{16}]^{2-}$
$[\text{Co}(\text{CO})_4]^-$	$\text{Co}_2(\text{CO})_8$	$[\text{Co}_3(\text{CO})_{10}]^-$	$\text{Co}_4(\text{CO})_{12}$	$\text{Co}_6(\text{CO})_{16}$
$\text{Ni}(\text{CO})_4$	$[\text{Ni}_2(\text{CO})_6]^{2-}$	$[\text{Ni}_3(\text{CO})_8]^{2-}$	$[\text{Ni}_4(\text{CO})_9]^{2-}$	
$\text{HM}(\text{CO})_3$	$\text{M}_2(\text{CO})_6$	$\text{H}_3\text{M}_3(\text{CO})_6$	$\text{M}_4(\text{CO})_8$	$\text{H}_6\text{M}_6(\text{CO})_6$

In addition, some known examples of complexes of similar types formed by elements of preceding Groups are also listed. The tendency for Group IB metals to form polynuclear aggregates with their lower-valent derivatives has been encountered previously in complexes such as $[\text{CuI}(\text{AsMe}_3)]_4$ ¹, $[\text{AgI}(\text{AsEt}_3)]_4$ ², $[\text{HCu}(\text{PPh}_3)]_6$ ³, $[\text{Cu}(m\text{-CF}_3\text{C}_6\text{H}_4)]_8$ ⁴, $[\text{Cu}(\text{C}_6\text{F}_5)]_4$ ⁴, $[\text{Au}_9[\text{P}(p\text{-MeC}_6\text{H}_4)_3]_8]\text{X}_3$ ⁵, and $[\text{Au}_{11}\text{X}_3(\text{PPh}_3)_7]$ ⁶.

The lack of stability of the simple carbonyls appears to reflect a lack of available back-bonding orbitals on the metal atom, resulting from the presence of a filled *d* shell. The available data concerning $\nu(\text{CO})$ frequencies of Group IB metal carbonyl derivatives (see below) show that these lie very close to the value for free carbon monoxide. The CO stretching force constants, $k(\text{CO})$, for the series $(\pi\text{-C}_5\text{H}_5)\text{M}(\text{CO})_n$ have been determined⁷, and also indicate that a decrease in transfer of electron density into the CO π^* orbitals from the metal occurs on moving to the right of the Periodic Table. On the other hand, there is no reluctance for these elements to accept σ donor electron density, a multitude of stable complexes being formed with the appropriate ligands.

Infrared evidence for the formation of discrete molecules of copper and silver carbonyls by cocondensation of the metal atoms with carbon monoxide at 20 K has been presented⁸. The resulting matrix shows two $\nu(\text{CO})$ peaks, which shift to a lower frequency when C^{18}O is used. However, these molecules are extremely labile, the infrared bands disappearing on photolysis (copper) or even in the infrared beam (silver).

Early reports

(i) *Copper*. The first account of the volatility of copper in gas streams containing carbon monoxide concerned copper transport during the oxidation of methanol to formaldehyde over heated copper oxides⁹. The deposition of $\text{Cu}(\text{OH})_2$ from methanol formed from CO and hydrogen on copper-containing catalysts was similarly explained in terms of hydrolysis of a supposed carbonyl¹⁰. Pospekhov¹¹ considered the possibility of formation of polymeric $[\text{Cu}(\text{CO})_3]_n$ or $\text{HCu}(\text{CO})_3$ compounds. However, painstaking studies by several workers, both of these and related reactions, failed to confirm the existence of any carbonyl species¹²⁻¹⁵. With Cu_2O , for instance, a purple-red mirror formed at 600°, but was shown to be some compound formed within the glass¹⁴; a report¹⁶ of a white sublimate (a supposed $[\text{Cu}(\text{CO})_3]_2$) formed in a similar reaction, was later ascribed to halogen-containing impurities¹⁷. The general concensus of opinion suggests that copper is transported in these systems by the formation of volatile copper(I) formates (or homologous salts), formed from traces of water or organic materials^{18,19}.

An amusing application of these reactions, however they occur, was the coating of bees with metal so that the minutest details of their anatomical structure were preserved²⁰. The idea of extension of this process to other organic materials²¹, and to larger animals, even human beings, perhaps can be thought to predate Goldfinger²².

The infrared spectra of CO adsorbed on copper films^{23,24} show $\nu(\text{CO})$ bands suggesting bonding to discrete atoms on the surface²⁵; use of Cu_2F_2 results in an increase in the stretching frequency²⁶.

(ii) *Silver*. The carbonyl chemistry of silver is completely undeveloped, no stable

carbonyl or carbonyl derivative having been reported. Many investigations have been directed towards binding CO onto silver atoms, and early accounts speak of failure²⁷. Russian workers have described the adsorption of CO on a silver mirror, the $\nu(\text{CO})$ frequencies suggesting a linear Ag-C-O combination²⁸. The formation of a silver carbonyl from silver atoms and CO in a matrix at 20 K has been described briefly⁸.

(iii) *Gold*. The adsorption of CO on gold films is indicated by a $\nu(\text{CO})$ band at 2174 cm^{-1} ²⁸; no other work appears to have been recorded.

III. COMPLEXES CONTAINING CARBON MONOXIDE

Well-defined complexes of the Group IB metals containing carbon monoxide are sufficiently rare and diversified to justify individual discussion. At present they are largely confined to copper, only two gold derivatives being known.

(i) *Cu(CO)Cl*. Finely divided Cu_2Cl_2 absorbs CO under 100 atm pressure at room temperature to give a 1/1 adduct. Small amounts of moisture accelerate the reaction²⁹. Other authors have noted that the complex cannot be formed at atmospheric pressure^{30,31}. This complex has also been noted as a by-product in carbonylations of rhenium chlorides (ReCl_5 or K_2ReCl_6), or of iron or nickel chlorides, in the presence of finely divided copper³². According to its method of preparation, the complex forms a voluminous white powder, or white crystals, stable in a CO atmosphere. In air, CO is rapidly evolved, and decarbonylation is complete at 60° ; CO pressures at various temperatures are: 34.1 (-10°), 67 (0°), 129 (10°), 235 mm (20°)³³.

(ii) *Cu(CO)Cl · 2H₂O*. The absorption of CO by a solution of Cu_2Cl_2 in hydrochloric acid to give a 1/1 adduct was first noticed over a hundred years ago, although the product was not isolated³⁴. First details of the preparation were reported in 1899³⁰. Passage of CO into the solution at 0° gives a white flaky crystalline deposit. It can also be obtained from neutral or weakly ammoniacal media^{31,35,36}. The complex readily loses CO unless kept in an atmosphere of the gas, with decomposition pressures of 145 (10°) and 320 mm (20°)³⁷. It rapidly turns green in the presence of moisture, and rapid evolution of CO results on treatment with concentrated mineral acids, sodium hydroxide, or ethanol. It is thought to be a true carbonyl halide, probably $[\text{CuCl}(\text{CO})(\text{H}_2\text{O})_2]$, although earlier it was considered to be ionic, containing the $[\text{Cu}(\text{CO})]^+$ cation³⁸.

(iii) *2CuCl · CO · 2H₂O*. A compound of this composition was reported as pearl leaflets, formed by passing CO through a cold saturated solution of Cu_2Cl_2 in hydrochloric acid³⁹. However, it is now thought to have been wrongly identified, and actually to be the 1/1 adduct described above.

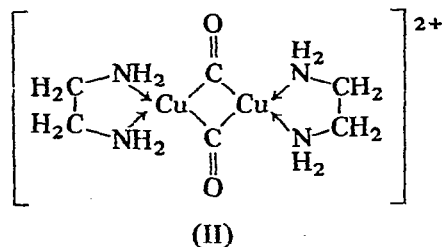
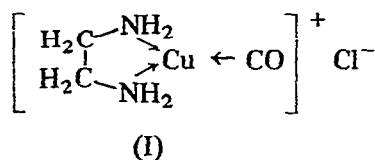
(iv) *Cu(CO)Br*. Anhydrous Cu_2Br_2 reacts very slowly with CO (100 atm, 1 week) to form $\text{Cu}(\text{CO})\text{Br}$ as a voluminous powder, considerably less stable than the chloride²⁹. The dissociation pressures are: 253 (-10°), 447 (0°), 773 (10°), 1269 mm (20°)³³. It has also been noted in the products from the carbonylation of rhenium, iron or nickel bromides in the presence of copper powder³².

(v) $\text{Cu}(\text{CO})\text{CN}$. This complex is apparently formed in solution on passing CO into a suspension of $\text{CuCN} \cdot \text{NH}_3$ in liquid ammonia at -78° . At -33° the $\text{CuCN} \cdot \text{NH}_3$ complex is reprecipitated with evolution of one CO per copper atom⁴⁰.

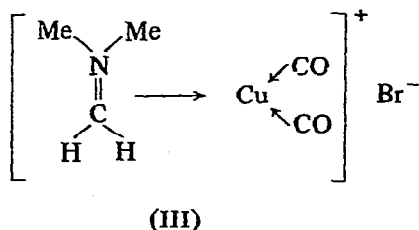
(vi) $\text{Cu}_2\text{SO}_4 \cdot 2\text{CO} \cdot \text{H}_2\text{O}$. Small white efflorescent crystals separate from a reaction between CO and a mixture of finely divided copper and copper(II) sulphate solution at low temperatures⁴¹. The complex is very air-sensitive, readily decomposing to CO, copper and CuSO_4 .

(vii) $\text{Cu}(\text{CO})(\text{CF}_3\text{CO}_2)$. The first well-characterised stable copper carbonyl complex other than the halides was reported in 1969⁴², being obtained from a solution of Cu_2O in trifluoroacetic acid in the presence of CO. White crystals of the adduct $\text{Cu}(\text{CO})(\text{CF}_3\text{CO}_2) \cdot \text{CF}_3\text{CO}_2\text{H}$ are initially formed, but the molecule of acid can be pumped off. Continued evacuation also removes the CO, affording copper(I) trifluoroacetate. The carbonyl complex is extremely sensitive to oxygen, however.

(viii) $[\text{Cu}(\text{en})(\text{CO})]\text{Cl}$ and $[(\text{en})\text{Cu}(\text{CO})_2\text{Cu}(\text{en})]\text{Cl}_2$. 1,2-Diaminoethane (en) reacts with $\text{Cu}(\text{CO})\text{Cl}$ at 0° with displacement of CO; at -30° , however, white $[\text{Cu}(\text{en})(\text{CO})]\text{Cl}$ (I) is formed⁴³. In methanol, the complex behaves as a 1/1 electrolyte. A second white complex of the same empirical formula is a 1/2 electrolyte, and has $\nu(\text{CO})$ bands in the bridging carbonyl region. Consequently it is suggested to contain the $[(\text{en})\text{Cu}(\text{CO})_2\text{Cu}(\text{en})]^{2+}$ cation (II). In solution, an equilibrium between the two complexes obtains, the former predominating above -30° . The proposed structure (II) resembles that of the palladium complex $[(\text{phen})\text{Pd}(\text{CO})_2\text{Pd}(\text{phen})]^{44}$.

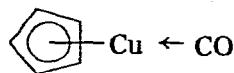


(ix) $[\text{CuCl}(\text{Me}_2\text{N}=\text{CH}_2)(\text{CO})]\text{Br}$. Although not isolated, evidence for a complex of structure (III) has been presented⁴⁵. As with diaminoethane, CO is liberated on reacting $\text{Cu}(\text{CO})\text{Cl}$ with dimethylaminomethylene bromide. However, the product absorbs CO at



-40° to give a pale yellow 1/1 adduct, stable below -15° ; above this temperature, CO is liberated. A second complex, $\text{Cu}_2(\text{CO})(\text{Me}_2\text{N}=\text{CH}_2)\text{Cl}_2\text{Br}$, which dissociates quantitatively at 0° , is formed from $\text{Cu}(\text{CO})\text{Cl}$ and $[\text{Cu}(\text{Me}_2\text{N}=\text{CH}_2)\text{Cl}]\text{Br}$.

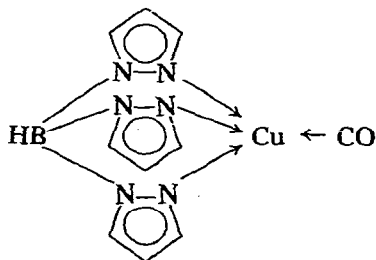
(x) $(\pi\text{-C}_5\text{H}_5)\text{Cu}(\text{CO})$. A slow reaction between finely divided Cu_2Cl_2 and thallium cyclopentadienide in the presence of CO affords a colourless solution of $(\pi\text{-C}_5\text{H}_5)\text{Cu}(\text{CO})$ (IV), which is volatile in vacuo, but could not be completely separated from pentane⁷. The



(IV)

carbonyl is characterised by a single $\nu(\text{CO})$ band at 2093 cm^{-1} , and a singlet in the $^1\text{H NMR}$ at τ 4.3 (C_5H_5 protons). It is thermally quite unstable, and deposits a yellow-orange solid; with phosphines, CO is evolved, with formation of $(\pi\text{-C}_5\text{H}_5)\text{Cu}(\text{PR}_3)$ derivatives.

(xi) $[\text{HB}(\text{pz})_3]\text{Cu}(\text{CO})$. A stable copper carbonyl derivative can be obtained by the immediate reaction between Cu_2Cl_2 and potassium hydrotripyrzolyborate⁴⁶ in the presence of CO. The complex is an air-stable white crystalline solid (V). It is very soluble in light petroleum, the solutions being somewhat air-sensitive, and slowly turning green. On heating, decarbonylation occurs at $165\text{--}167^{\circ}$ to give $\text{Cu}_2[\text{HB}(\text{pz})_3]_2$, which then slowly disproportionates to copper metal and the copper(II) derivative, $\text{Cu}[\text{HB}(\text{pz})_3]_2$.



(V)

The decarbonylation reaction is reversible in solution. Reactions with other ligands, e.g. phosphines, arsines, isocyanides, etc., rapidly give complexes of the type $[\text{HB}(\text{pz})_3]\text{CuL}$, with evolution of CO ⁴⁷. An analogous complex containing the hydrotris(3,5-dimethylpyrazolyl)borate anion has also been obtained. This complex decomposes at 186° , and has a considerably lower $\nu(\text{CO})$ frequency⁴⁷.

(xii) $\text{Au}(\text{CO})\text{Cl}$. A small amount of $\text{Au}(\text{CO})\text{Cl}$ was first obtained⁴⁸ by passing CO over gold(I) or -(III) chloride between $50\text{--}120^{\circ}$, and in up to 20% yield by using a fast gas stream at 110° . The best preparation consists in passing dry CO through a suspension of AuCl in benzene at room temperature; addition of light petroleum precipitates the pure product in 95% yield⁴⁹. The complex forms white laminar crystals, often with a mother-of-pearl

appearance, which sublime in a stream of CO. In vacuum, CO is lost, leaving pure AuCl. Water causes immediate evolution of CO, with separation of metallic gold, although it appears to be soluble without decomposition in glacial acetic acid.

Several reactions have been studied⁴⁹. Generally a ligand L, e.g. pyridine reacts to displace CO, forming LAuCl. With Grignard reagents, RMgX, CO is liberated, gold deposited, and high yields of the radical combination products, R₂, are obtained.

(xiii) *Au(CO)Br*. Only a small amount of crystalline material, presumably Au(CO)Br, was obtained by passing CO over AuBr₃ at 100°^{48,49}. No reaction was found with AuI.

Haemocyanin adduct

Haemocyanin is the blue copper-containing protein with an oxygen-transport function, which is found in mollusc and arthropod haemolymph. It decolourises in the presence of CO, but the colour is restored when exposed to air⁵⁰. In 1934, the proportion of bound CO was first determined as one molecule per two copper atoms. The CO is liberated by potassium cyanide, and the relative affinities of haemocyanin for oxygen and CO are in the ratio 20/1⁵¹. Several possible structures for the adduct have been discussed⁵²⁻⁵⁴, but only recently the infrared spectrum has been examined. A single broad $\nu(\text{CO})$ band at 2063 cm⁻¹ suggests that the CO is bonded to only one of the two copper atoms. Equilibration of oxyhaemocyanin with CO results in rapid deoxygenation, with concomitant disappearance of a band at 348 nm⁵⁵.

TABLE 2

$\nu(\text{CO})$ Bands in Group IA-carbonyls

System	$\nu(\text{CO})$ (cm ⁻¹)	Solvent	Ref.
Cu-CO condensate, 20 K	1989, 1975		8
Cu-CO (surface adsorption)	2120		25
	2095		26
Cu ₂ F ₂ -CO (adsorbed)	2146		26
CuCl(CO)	2069	pyridine	55
	2112	water	55
CuCl(CO)	2090	MeOH	43
Cu(CF ₃ CO ₂) (CO)	2155	nujol	42
[Cu(en) (CO)] Cl	2080	MeOH	43
[Cu ₂ (en) ₂ (CO) ₂] Cl ₂	1905	MeOH	43
[CuCl(CO)(Me ₂ N=CH ₂)] Br	2080	THF mull, -60°	45
(π -C ₆ H ₅)Cu(CO)	2093	petrol	7
[HB(pz) ₃] Cu(CO)	2083	cyclohexane	47
[HB(3,5-Me ₂ pz) ₃] Cu(CO)	2066	cyclohexane	47
Haemocyanin-CO adduct	2063	water	55
Ag-CO (surface adsorption)	2182		28
Ag-CO condensate, 20 K	1968, 1939		8
Au-CO (surface adsorption)	2174		28
Au(CO)Cl	2080		

Infrared studies. As is well-known, studies of the infrared spectra of metal carbonyl complexes, especially in the $\nu(\text{CO})$ region, enable much information to be obtained concerning the bonding, and particularly the back-bonding, characteristics of the M-C-O system. Table 2 lists the reported $\nu(\text{CO})$ bands for CO attached to copper, silver or gold in a variety of environments. Typical metal carbonyls show bands in the 2000 cm^{-1} region (for terminal CO groups), while free CO shows $\nu(\text{CO})$ at 2143 cm^{-1} . It can be seen that the amount of back-bonding in copper carbonyl species is small, resulting in high $\nu(\text{CO})$ values; in some cases, frequencies higher than that characteristic of free CO have been reported.

IV. CARBON MONOXIDE ABSORPTION BY SOLUTION OF COPPER COMPOUNDS

It has long been known that copper(I) halides in complexing solvents avidly absorb CO, to the extent of one molecule of CO per atom of copper. As described above, the complex $\text{CuCl} \cdot \text{CO} \cdot 2\text{H}_2\text{O}$ may be isolated under some conditions. Detailed investigations into the effect of temperature, pressure, concentration, and solvent have failed to reveal any other than 1/1 adducts⁵⁶. The ease of absorption of CO is strongly dependent on the nature of the halogen, and these properties have been related to heats of formation of the copper(I) halides. The complexes are generally very sensitive to oxygen, and competitive uptake of oxygen and CO results in rapid oxidation to copper(II) complexes. Electrolysis of CO-containing ammoniacal solutions results in deposition of copper at the cathode, with evolution of carbon monoxide. In contrast, hydrochloric acid solutions liberate CO at the anode. These results accord with the formation of complex cations and anions, respectively⁵⁷.

Older work. The 1/1 adduct was first obtained by Leblanc³⁴, and confirmed by Berthelot⁵⁸. Acidic or ammoniacal solutions were used in gas analysis. The reactions were investigated by Drehschmidt⁵⁹, then by Winkler⁶⁰, who found that the gas was only loosely bonded, and easily replaced. Hempel⁶¹ found ammoniacal solutions to be preferable. A variety of other measurements were recorded, largely at the end of the nineteenth century⁶²⁻⁶⁴.

Aqueous suspensions. Only slow absorption of CO occurs with suspensions of Cu_2Cl_2 in water, with formation of crystalline $\text{CuCl} \cdot \text{CO} \cdot 2\text{H}_2\text{O}$ ^{30,31}. Increasing amounts of water lead to partial hydrolysis, which can be reversed by addition of hydrochloric acid. The chloride is superior to the bromide, iodide, cyanide, or thiocyanate⁵⁶. The application of this reaction to technical separation of CO from various gas mixtures has been discussed^{36,65}.

Solutions containing hydrochloric acid. The absorption of CO by solutions of Cu_2Cl_2 in hydrochloric acid depends on concentration (best with $\text{CuCl}/\text{HCl}=1/9$), pressure, and is increased on lowering the temperature³¹. The reaction is catalysed by 1-2% SnCl_2 ⁶⁶, or by addition of PdCl_2 ⁶⁷. In practice, a mixture of CuSO_4 , NaCl, and copper in concentrated hydrochloric acid has been used^{36,68}. In gas analysis, absorption by these acidic solutions is never complete; if a large amount of CO has to be removed, 80% can be absorbed in $\text{HCl-Cu}_2\text{Cl}_2$ solutions, and the remainder in ammoniacal solution⁶⁹⁻⁷¹. The solutions may be regenerated by simple heating, or by passage of air through them. In the latter case, reduction with copper, SO_2 , or SnCl_2 is necessary^{72,73}.

Ammoniacal solutions. In dilute ($\frac{1}{30}N$) ammonia solutions, the very slow absorption of CO by Cu_2Cl_2 is accompanied by separation of crystalline solid. With higher concentrations ($2N$), the formation of copper-ammine-carbonyl complexes is noted³¹. Up to 96% of the theoretical amount of CO is absorbed by Cu_2Cl_2 in 12.5% aqueous ammonia⁵⁶. Addition of ammonium chloride improves the ease of absorption⁶⁶, and several recipes for suitable solutions for industrial use, or for gas analysis, are available^{36,68,74}. Ammoniacal copper(I) chloride solutions are used extensively for the purification of industrial gases⁷⁵⁻⁷⁸, and have been since the nineteenth century⁷⁹.

Solutions in organic bases. A variety of alternative solvents for Cu_2Cl_2 have been examined, the most successful being ethanolamine and pyridine. Use of the former results in rapid absorption of large volumes of CO. However, none of these alternatives offers any economic advantage over the more commonly used solutions described above³⁶. In aniline, toluidine, or piperidine, 1/1 adducts can be formed, but the theoretical limit is seldom reached, absorption being very slow^{30,31,80}.

Alkali salt solutions. The absorption of CO by Cu_2Cl_2 -KCl solution is less than in hydrochloric acid, and is complete when 42.5% of the theoretical amount has been absorbed⁵⁶. In aqueous ammonium chloride, absorption is good, but this solution is too corrosive for technical use⁸¹. Addition of SnCl_2 gives a noticeable improvement⁶⁸, and best results were obtained with the ratio $\text{Cu}_2\text{Cl}_2/\text{NH}_4\text{Cl} = 1/8$. Other mixtures have incorporated NaCl, MgCl_2 , $\text{KCl} \cdot \text{MgCl}_2$, and cold saturated $(\text{NH}_4)_2\text{SO}_4$ ^{31,82,83}.

Use of other copper compounds

(i) *Copper(I) bromide.* In ammoniacal solution absorption is as good as the chloride; in hydrobromic acid, only small amounts of CO are absorbed^{31,36,56}. The best results were obtained using aqueous $\text{KBr} \cdot \text{Cu}_2\text{Br}_2$, which took up 52% of the theoretical amount⁵⁶.

(ii) *Copper(I) iodide.* This compound gives the poorest results for any copper halide, only 4% of the theoretical amount of CO being absorbed in 25% aqueous hydriodic acid. In no case has any well-defined complex been indicated, and the overall affinity for CO is $\text{Cu}_2\text{I}_2 \ll \text{Cu}_2\text{Br}_2 < \text{Cu}_2\text{Cl}_2$ ^{29,31,36,56}.

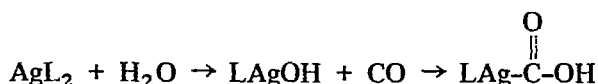
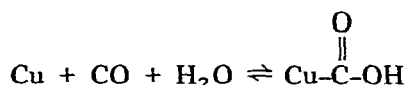
(iii) *Copper(I) sulphate.* Slow absorption of CO by a solution of CuSO_4 containing finely divided copper eventually results in decolourisation, with formation of a copper(I) complex⁴¹. Up to one mole of CO per mole of copper compound can be absorbed by a solution of copper(I) oxide in concentrated sulphuric acid; on heating the gas is released, though above 80° it is mixed with SO_2 formed by a redox reaction⁸⁴. A mixture of Cu_2O and β -naphthol in 95% sulphuric acid has an excellent absorptive capacity, and is claimed to be superior to ammoniacal Cu_2Cl_2 in gas analysis^{85,86}.

(iv) *Miscellaneous compounds.* Solutions of other copper compounds absorb CO. The carbonate tends to deposit copper, even in the presence of ammonium carbonate⁸⁷. In ammoniacal solution, the complexes are unstable to potassium cyanide, although long

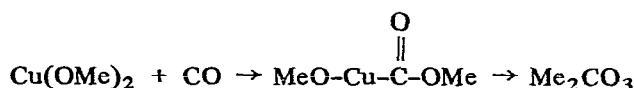
passage of CO results in the formation of a stable complex, containing one CO per copper atom⁸⁸. A variety of organic salts have been examined, and the best results seem to be obtained using ammoniacal copper formates⁸⁹ or lactates⁸¹.

V. ORGANIC SYNTHESSES USING CARBON MONOXIDE IN THE PRESENCE OF COPPER COMPOUNDS

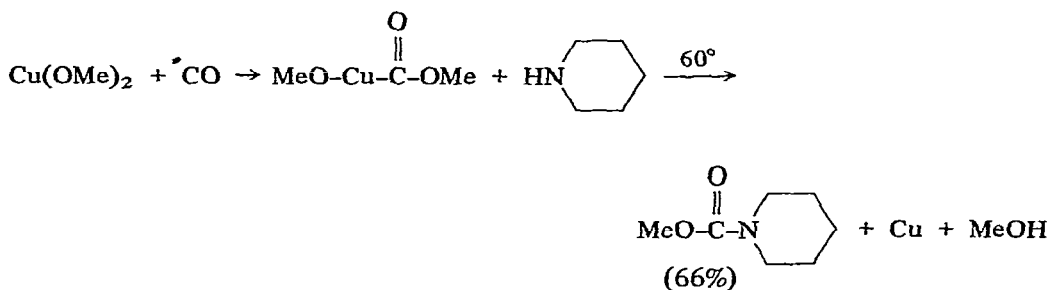
Carbonyl complexes were originally implicated in the oxidation of CO by molecular oxygen, catalysed by copper(II)⁹⁰, and in the reduction of silver amine complexes by CO⁹¹. Currently an insertion mechanism is favoured, the rate-determining step being the formation of carboxylic acid derivatives:



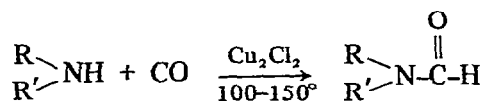
A similar insertion into copper-alkoxyl bonds is suggested^{92,93} as the mechanism for the formation of dimethyl carbonate by carbonylation of copper(II) methoxide in pyridine:



In the presence of an amine, e.g. piperidine, a urethane is formed:

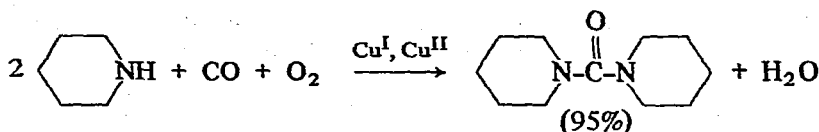


Previously, the copper-catalysed carbonylation of amines to *N*-alkylformamides had been described⁹⁴:



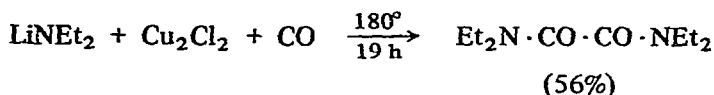
(R,R' = Me, 85; Et, 48; (CH₂)₅, 93; R = H, R' = n-Bu, 20; allyl, 15%)

This reaction contrasts with other transition-metal catalysts which usually afford the corresponding urea derivative. At room temperature and atmospheric pressure, urea derivatives are formed in good yield in the presence of oxygen⁹⁵:



A detailed examination of the variables led to the suggestion of a mechanism involving coordination of CO to the metal, giving an intermediate [detected by appearance of $\nu(\text{CO})$ at 2060 cm^{-1}] to which the amine migrated, followed by dissociation to the radical RNCO^\cdot .

Other related reactions include the carbonylation of lithium dialkylamide-copper(I) chloride mixtures to oxamides⁹⁶:



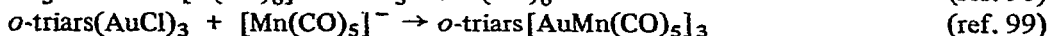
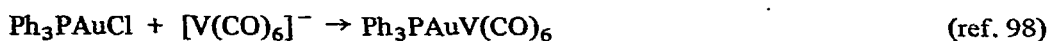
and the silver acetate-catalysed carbonylation of dialkylamines to oxamides, together with small amounts of formamides and acetamides, presumably via an intermediate such as AgCONEt_2 ⁹⁷.

VI. OTHER GROUP IB METAL COMPLEXES CONTAINING CARBONYL GROUPS

Several other complexes containing a Group IB metal linked to another metal carbonyl fragment are known. These complexes contain covalent metal-metal bonds. However, in none of these derivatives has carbonyl group transfer to the Group IB element occurred.

Known complexes are summarised in Table 3. They have been prepared by a variety of reactions, including

(i) Metathesis between a metal carbonyl anion and suitable halogen-containing Group IB complexes:



(ii) Reaction between a metal carbonyl hydride and a Group IB complex:



(iii) Elimination of Me_3SnCl in reactions of trimethyltin-transition metal carbonyl derivatives with Group IB complexes:



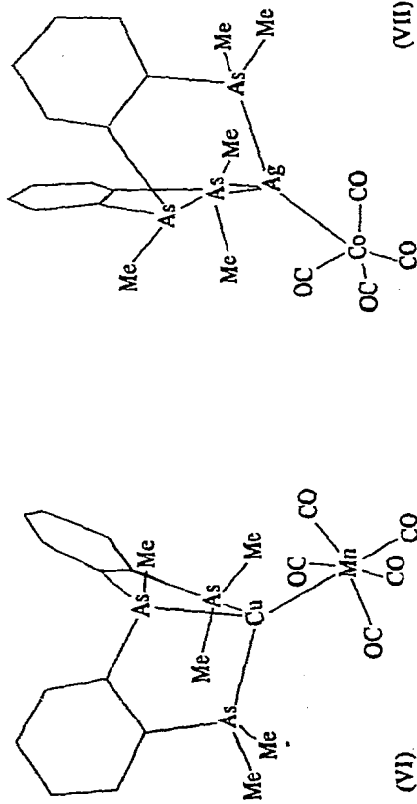
(iv) Oxidative addition reactions of the Group IB complex:



As found for the simple carbonyl derivatives, the silver complexes are the least stable. Few reactions have been studied; halogens or hydrohalic acids generally react to give the Group IB halide complex. Exchange of carbonyl groups has been studied with $\text{Ph}_3\text{PAuCo}(\text{CO})_4$.

TABLE 3
Other carbonyl complexes containing Group IB metals (for footnotes see p. 222)

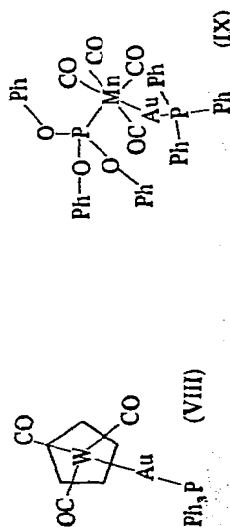
Complex ^a	Colour	M.p.	$\nu(\text{CO})$ (cm ⁻¹)	Solvent	Ref.
(<i>o</i> -triars)CuV(CO) ₆	Light yellow		2020m, 1925m, 1885(sh), 1858s	C ₆ H ₁₂	98
(<i>o</i> -triars)CuMo(CO) ₃ (C ₅ H ₇)	Pale yellow	187 (dec.)	1914s, 1811s, 1779s	CHCl ₃	100
(<i>o</i> -triars)CuW(CO) ₃ (C ₅ H ₇)	Pale yellow	185 (dec.)	1905s, 1803s, 1770s	CHCl ₃	100
(<i>p</i> -triars)CuMn(CO) ₅	Yellow brown	200	2010s, 1891vs	CHCl ₃	99, 104
(<i>o</i> -triars)CuMn(CO) ₅ (VI)	Light brown	140	2033s, 1919vs, 2033.3, 1927.4(br)	CHCl ₃	104
[(<i>o</i> -triars)Cu] ₂ Fe(CO) ₄	Yellow brown	107	1942s, 1876(sh), 1852vs	C ₆ H ₆	106
(<i>o</i> -triars)CuCo(CO) ₄	Pale yellow	171	2033s, 1945(sh), 1919s, 2027.5, 1951.2, 1912.1	Nujol	104
Ph ₃ PCuRh(CO)Cl ₁ (PPh ₃) ₃	Green-yellow	182 (dec.)	1977s	hexane	106
Ph ₃ PCuIr(CO)Cl ₁ (PPh ₃) ₂	Pale green	156 (dec.)	2038s	Nujol	105
(<i>o</i> -triars)AgV(CO) ₆	Orange	—		Nujol	105
(<i>o</i> -triars)AgMn(CO) ₅	Light brown	84	2037s, 1919vs, 2036.7, 1925.0	CHCl ₃	104
[(<i>o</i> -triars)Ag] ₂ Fe(CO) ₄	Yellow	95	1957s, 1883(sh), 1862	C ₆ H ₆	106
(<i>o</i> -triars)AgCo(CO) ₄ (VII)	Pale yellow	105	2037s, 1953(sh), 1923s, 2031.5, 1954.6, 1917.6	Nujol	104
				CHCl ₃	104
				hexane	106



(Table continued)

TABLE 3--continued

Complex ^d	Colour	M.p.	$\nu(\text{CO})$ (cm ⁻¹)	Solvent	Ref.
$\text{Ph}_3\text{PAuV}(\text{CO})_6$	Orange-yellow	(dec.) 134-136	2042vs, 1988m, 1958m, 1922s, 1888(sh), 1870m 2040s, 1980s, 1900(sh), 1863vs(br)	C_6H_{12} Nujol	98, 120
$\text{Ph}_3\text{PAuV}(\text{CO})_2\text{PPh}_3$	Orange	(dec.) 145-150	1995s, 1924m, 1885vs, 1875(sh), 1819s, 1993s, 1928(sh), 1915s, 1880vs, 1792vs	C_6H_{12} Nujol	120
$\text{Ph}_3\text{PAuNb}(\text{CO})_6$	Red-orange	(dec.) 125	2055vs, 1992m, 1964m, 1930s, 1900(sh), 1870(sh) 2050s, 1988s, 1879vs(br)	C_6H_{12} Nujol	120
$\text{Ph}_3\text{PAuNb}(\text{CO})_2\text{PPh}_3$	Red-orange	(dec.) 150	2014s, 1938s, 1896vs, 1879(sh), 1829s	C_6H_{12} Nujol	120
$\text{Ph}_3\text{PAuTa}(\text{CO})_6$	Orange-red	(dec.) 120	2005s, 1945(sh), 1924s, 1889vs(br), 1800vs 2055vs, 1985m, 1955m, 1920s, 1900(sh)	C_6H_{12} Nujol	120
$\text{Ph}_3\text{PAuTa}(\text{CO})_2\text{PPh}_3$	Orange-red	(dec.) 160	2050s, 1975s, 1895vs(br)	C_6H_{12} Nujol	120
$\text{Ph}_3\text{PAuCr}(\text{CO})_3(\text{C}_2\text{H}_5)$	Pale yellow	155-160 (dec.)	2005s, 1928s, 1886vs, 1876(sh), 1829s 2002s, 1930(sh), 1915s, 1880vs(br), 1802vs 1946s, 1863(sh), 1837s	C_6H_{12} Nujol hexane	100
$\text{Ph}_3\text{PAuMo}(\text{CO})_3(\text{C}_2\text{H}_5)$	Pale yellow	168-170 (dec.)	1957s, 1873(sh), 1848s	hexane	100
$(\text{C}_6\text{H}_{11})_3\text{PAuMo}(\text{CO})_3(\text{C}_2\text{H}_5)$	Pale yellow	222-228 (dec.)	1948s, 1860(sh), 1836s	hexane	100
$(\text{PhO})_3\text{PAuMo}(\text{CO})_3(\text{C}_2\text{H}_5)$	Pale yellow	75-78	1965s, 1885(sh), 1859s	hexane	100
$\text{Ph}_3\text{PAuW}(\text{CO})_3(\text{C}_2\text{H}_5)$ (VIII)	Pale yellow	201-203 (dec.)	1952s, 1866(sh), 1845s	hexane	100, 107
$\text{Ph}_3\text{PAuMn}(\text{CO})_5$	Pale brown	151 (dec.)	2059m, 1959s. 2062ms, 1961vs 2063.0, 1964.2	C_6H_{12} CHCl_3 , CCl_4 hexane	101 107, 109 106
$\text{Ph}_3\text{PAuMn}(\text{CO})_4\text{py}$	Brown	121 (dec.)	2000ms, 1908(sh), 1887vs	CHCl_3	108
$\text{Ph}_3\text{PAuMn}(\text{CO})_4\text{PPh}_2\text{-n}_3$	Brown	140 (dec.)	1999.5, 1923.2, 1907.6(sh), 1899.9, 1891.4	C_6H_6	106
$\text{Ph}_3\text{PAuMn}(\text{CO})_4\text{PPh}_3$	Brown	90 (dec.)	2000ms, 1916(sh), 1894vs 1999.1, 1925.7, 1902.1, 1891.3 2016ms, 1969(sh), 1923vs 2024.2, 2020.2(sh), 1941.5	CHCl_3 C_6H_6 CHCl_3 C_6H_6	108 106 108 106

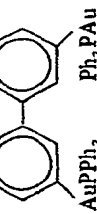


$\text{Ph}_3\text{PAuMn}(\text{CO})_4\text{AsPh}_3$	Brown	135 (dec.)	2000ms, 1916(sh), 1894vs	CHCl_3	108
$(p\text{-tol})_3\text{PAuMn}(\text{CO})_5$	Brown	179 (dec.)	2061ms, 1992vs, 1913w 2061.5, 1961.5	CHCl_3 hexane	108, 109 106
$(p\text{-MeOC}_6\text{H}_4)_3\text{PAuMn}(\text{CO})_5$	Brown	132 (dec.)	2062ms, 2000(sh), 1961vs	CHCl_3	108, 109
$(\text{PhO})_3\text{PAuMn}(\text{CO})_5$	Brown	68 (dec.)	2070ms, 1990(sh), 1965vs 2066.9, 1968.0	CHCl_3 hexane	108, 109 106
$(\text{PhO})_3\text{PAuMn}(\text{CO})_4\text{PPh}_3$			2004.3, 1931.0, 1913.2, 1902.2	C_6H_6	106
$(\text{C}_6\text{H}_{11})_3\text{PAuMn}(\text{CO})_5$			2058.6, 1957.3	hexane	106
$(\text{C}_6\text{H}_{11})_3\text{PAuMn}(\text{CO})_4\text{PPh}_3$	Brown	64 (dec.)	1996.9, 1919.6, 1895.5, 1883.6	C_6H_6	106
$\text{Ph}_3\text{AsAuMn}(\text{CO})_5$	Brown	64 (dec.)	2062ms, 1990(sh), 1961vs	CHCl_3	108, 109
$\text{Ph}_3\text{SbAuMn}(\text{CO})_5$	Brown	dec.	2030ms, 1927vs	CHCl_3	108, 109 99
$(p\text{-triars})[\text{AuMn}(\text{CO})_5]_3$					
$\text{Ph}_3\text{PAuRe}(\text{CO})_5$			2078.0, 1975.6, 1967.6	hexane	106
$\text{cis}(\text{-Ph}_3\text{PAu})_2\text{Fe}(\text{CO})_4$	Pale yellow	150 (dec.)	2004ms, 1934s, 1894s	CCl_4	107
$(m\text{-dpAu})_2\text{Fe}(\text{CO})_4$	Yellow	172	2010, 1940, 1899	nujol	110
$\text{Ph}_3\text{PAuFe}(\text{CO})_3\text{NO}$	Orange	98-99 (dec.)	2031vs, 1964m, 1929s; 1745s ^c	heptane	121
$\text{Ph}_2(\text{C}_6\text{H}_{11})_2\text{PAuFe}(\text{CO})_3\text{NO}$	Orange	129-130 (dec.)	2032vs, 1961m, 1927s; 1744s ^c	heptane	121
$\text{Ph}(\text{C}_6\text{H}_{11})_2\text{PAuFe}(\text{CO})_3\text{NO}$	Orange	113-115 (dec.)	2030vs, 1960m, 1924s; 1742s ^c	heptane	121
$(p\text{-MeC}_6\text{H}_4)_3\text{PAuFe}(\text{CO})_3\text{NO}$	Orange	125-127 (dec.)	2030vs, 1962m, 1928s; 1744s ^c	heptane	121
$(p\text{-ClC}_6\text{H}_4)_3\text{PAuFe}(\text{CO})_3\text{NO}$	Orange	123-124 (dec.)	2035vs, 1967m, 1931s; 1749s ^c	heptane	121
$\text{Me}_3\text{PAuFe}(\text{CO})_3\text{NO}$	Orange	86-88 (dec.)	2031vs, 1963m, 1930vs; 1745s ^c	heptane	121
$(\text{MeO})_3\text{PAuFe}(\text{CO})_3\text{NO}$	Orange	50-51 (dec.)	2036vs, 1973m, 1939vs; 1752m ^c	heptane	121
$\text{Ph}_3\text{PAuFe}(\text{CO})_2(\text{NO})\text{PPh}_3$	Orange	(dec.) 80	1941m, 1877vs; 1694s ^c	CS_2	121
$\text{Ph}_3\text{PAuFe}(\text{CO})_2(\text{NO})\text{P}(\text{OPh})_3$	Orange	(dec.) 102	1960m, 1897vs; 1717s ^c	CS_2	121
$\text{Ph}_3\text{PAuFe}(\text{CO})_2(\text{NO})\text{AsE}(\text{Ph})_2$	Orange	96-98 (dec.)	1937m, 1817vs; 1692s ^c	CS_2	121
$\text{cis}(\text{-Ph}_3\text{PAu})_2\text{Ru}(\text{CO})_4$					111
$\text{cis-Ph}_3\text{PAuRu}(\text{CO})_4\text{SiMe}_3$	Bronze	106-107	2059m, 1996s, 1989(sh), 1970s	C_6H_{12}	112
$\text{Ph}_3\text{Au}[\text{Os}(\text{CO})_4]_3\text{Cl}(\text{X})$		168	2098m, 2046s, 2016(sh), 2011s, 1984m, 1979(sh), 1967m	C_6H_{12}	102

(Table continued)

TABLE 3—continued

Complex ^a	Colour	M.p.	$\nu(\text{CO})$ (cm ⁻¹)	Solvent	Ref.
$\text{Ph}_3\text{PAuCo}(\text{CO})_4$ (X)	Pale brown	112–114	2053s, 1983m, 1954s(br), 2054s, 1988s, 1957s 2055.0, 1986.4, 1956.0	C_6H_{12} CS_2 hexane	101, 121 107 106
$\text{Ph}_3\text{PAuCo}(\text{CO})_3\text{PBu-n}_3$			1985.3, 1914 -1918v(br)	CHCl_3 , C_6H_6	106
$\text{Ph}_3\text{PAuCo}(\text{CO})_3\text{PPh}_3$	Red-orange	159 (dec.)	1983.7	CHCl_3	106, 121
$\text{Ph}_3\text{PAuCo}(\text{CO})_3\text{P}(\text{OPh})_3$			2017.3, 1917.2	CHCl_3 , C_6H_6	106
$(\text{C}_6\text{H}_{11})_2\text{PAuCo}(\text{CO})_4$			2052.5, 1983.1, 1952.4	hexane	106
$\text{Ph}_3\text{PAuIr}(\text{CO})_3\text{PPh}_3$	White		1990w, 1930vs		113
$\text{Ph}_3\text{PAuIr}(\text{CO})_3(\text{PPh}_3)_2$					105



^a Ligands: *o*-triars = $\text{MeAs}(\text{C}_6\text{H}_4\text{AsMe}_2\text{-o})_3$, *p*-triars = $\text{MeC}(\text{CH}_2\text{AsMe}_2)_3$, *m*-*dp*Au₂ =

^b Shown to be the known oxygen adduct, $(\text{PPh}_3\text{P})_2\text{Ir}(\text{CO})\text{Cl}(\text{O}_2)$: see ref. 114.
^c $\nu(\text{NO})$.

where only three CO groups seem to exchange, with an approximately second-order rate¹⁰³. No exchange occurs with $\text{Ph}_3\text{PAuMn}(\text{CO})_5$, although the iodide $\text{Mn}(\text{CO})_5\text{I}$ does under the same conditions. Nyholm has considered that the Ph_3PAu group has a similar electronegativity to that of I, and studies of $\nu(\text{CO})$ spectra and force constant calculations appear to bear out this conclusion.

The first complexes of this type to be reported were $\text{Cu}_2(\text{NH}_3)_2\text{Fe}(\text{CO})_4$, $(\text{bipy})\text{AgCo}(\text{CO})_4$, and $(\text{phen})\text{Ag}_2\text{Fe}(\text{CO})_4$, which were made in 1938¹¹⁵. The structures of these compounds remain unknown. More recently, since the investigations of Nyholm and his colleagues, the structures of some of the complexes mentioned in Table 3 have been determined. Of interest are the transition metal–Group IB metal bond lengths, which are summarised in Table 4.

TABLE 4

Structures of some transition metal–Group IB metal complexes

Complex			Bond lengths (Å)	Ref.
$(o\text{-triars})\text{CuMn}(\text{CO})_5$	(VI)	Cu–Mn	2.56(1)	116
$(o\text{-triars})\text{AgCo}(\text{CO})_4$	(VII)	Ag–Co	2.66(1)	119
$\text{Ph}_3\text{PAuW}(\text{CO})_5(\text{C}_5\text{H}_5)$	(VIII)	Au–W	2.698(3)	118
$\text{cis-Ph}_3\text{PAuMn}(\text{CO})_4\text{P}(\text{OPh})_3$	(IX)	Au–Mn	2.57(1)	117
$\text{Ph}_3\text{PAuCo}(\text{CO})_4$	(X)	Au–Co	2.50(1)	116, 119

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