

993. Metal-Metal Bonds. Part V.¹ Complexes Containing Copper- and Silver-Metal Linkages

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Using the triarsines, 1,1,1-tris(dimethylarsinomethyl)ethane and bis-(*o*-dimethylarsinophenyl)methylarsine, complexes of the type (Triars)-M-Mn(CO)₅, [(Triars)M]₂Fe(CO)₄, and (Triars)M-Co(CO)₄ (M = Cu and Ag) have been prepared by reaction of the tri(tertiary arsine) complexes of copper(I) and silver(I) with the carbonyl anions [Mn(CO)₅]⁻, [Fe(CO)₄]²⁻, and [Co(CO)₄]⁻ in tetrahydrofuran. Physical data are consistent with the proposed formulations. The infrared spectra in the C-O stretching region correlate with the electronegativity of the copper and silver atoms.

In Parts I and II^{2,3} of this Series, complexes containing gold-manganese, gold-iron, and gold-cobalt bonds were described. Also, the stability of such compounds as Ph₃PAu-Mn(CO)₅ was interpreted in terms of the relatively high electronegativity of the gold atom. This is discussed further below. Copper and silver atoms also have a high electronegativity (though lower than that of gold), so it might be expected that the formation of similar compounds containing copper or silver would be feasible. It is noteworthy that in such compounds as Ph₃PAu-Mn(CO)₅ the stereochemistry and co-ordination number of the gold atom are those found in conventional complexes of gold(I), *e.g.*, Ph₃PAuCl. Thus, it can be argued that, in complexes containing copper- or silver-metal bonds, the co-ordination number of the former metal atoms should be ideally 4, as in their univalent complexes. In order to satisfy this criterion, the following tri(tertiary arsines) have been used: 1,1,1-tris(dimethylarsinomethyl)ethane (*v*-Triars) and bis-(*o*-dimethylarsinophenyl)-methylarsine (*o*-Triars). Both readily form tetrahedral complexes of the general type (Triars)MX on reaction with copper(I) and silver(I) halides in ethanol. The reactions of these triarsine complexes with the carbonyl anions Mn(CO)₅⁻, Fe(CO)₄²⁻, and Co(CO)₄⁻ have been investigated.

The copper complexes (*v*-Triars)CuBr and (*o*-Triars)CuBr react with one equivalent of sodium pentacarbonylmanganate(-I) in tetrahydrofuran to give (*v*-Triars)Cu-Mn(CO)₅ and (*o*-Triars)Cu-Mn(CO)₅, respectively. These are diamagnetic, non-electrolytes in nitrobenzene, and monomeric in benzene or dichloromethane (see Table 1). Similar experiments starting with the complex (*v*-Triars)AgBr produced a compound too unstable to isolate. However, using the other triarsine complex, a stable product (*o*-Triars)-Ag-Mn(CO)₅ was isolated. Similarly, reaction of the complexes (*o*-Triars)CuBr and (*o*-Triars)AgBr with the appropriate amounts of the carbonyl salts Na₂[Fe(CO)₄] and Na[Co(CO)₄] led to the expected complexes containing bonds from copper or silver to iron and cobalt (see Table 1).

In Table 1 are listed the infrared spectra in the C-O stretching region. The local symmetry of the Mn(CO)₅ group in the complexes must be C_{4v}, leading to three infrared-active C-O stretching vibrations (2A₁ + E). Two bands only are observed, and it is likely that the A₁ vibration involving the unique carbonyl group *trans* to copper or silver is accidentally degenerate with the E vibration.³ The infrared-active C-O stretching vibrations occur at lower frequencies than in the gold-manganese compounds,³ and, by use of the simplified secular equations of Cotton and Kraihanzel,⁴ calculated C-O stretching force constants are compared in Table 2 with those of structurally related compounds.

The infrared spectra of the complexes [(*o*-Triars)M]₂Fe(CO)₄ and (*o*-Triars)M-Co(CO)₄ are typical of tetracarbonyl complexes with C_{2v} and C_{3v} symmetry, respectively.

¹ Part IV, R. S. Nyholm and K. Vrieze, preceding Paper.

² C. E. Coffey, J. Lewis, and R. S. Nyholm, *J.*, 1964, 1741.

³ A. S. Kasentially, J. Lewis, A. R. Manning, J. R. Miller, R. S. Nyholm, and M. H. B. Stiddard, *J.*, 1965, 3407.

⁴ F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, 1962, **84**, 4432.

TABLE 1
 Physical properties of the complexes

Compound *	Colour	M. p.	Molecular weight †			Conductance in PhNO ₂		C-O stretch (cm. ⁻¹) in CHCl ₃
			Concn. (M)	Found	Reqd.	Λ _M (ohm ⁻¹ cm. ²)	Concn. (× 10 ³)	
(<i>ν</i> -Triars)Cu-Mn(CO) ₅	Light brown	200°	0.050	618 ‡	642	0.08	0.92	2010s, 1891vs
(<i>o</i> -Triars)Cu-Mn(CO) ₅	Light brown	140	0.030	734	710	0.07	1.2	2033s, 1919vs
(<i>o</i> -Triars)Ag-Mn(CO) ₅	Light brown	84	0.035	770	754	0.07	1.0	2037s, 1919vs
(<i>o</i> -Triars)Cu-Co(CO) ₄	Pale yellow	171	0.040	697	686	0.09	1.5	2033s, 1945sh, 1919s
(<i>o</i> -Triars)Ag-Co(CO) ₄	Pale yellow	105	0.042	778	730	0.07	1.0	2037s, 1953sh, 1923s
[(<i>o</i> -Triars)Cu] ₂ Fe(CO) ₄	Yellow-brown	107	0.025	1131	1198	0.1	0.96	1942s, 1876sh, 1852vs §
[(<i>o</i> -Triars)Ag] ₂ Fe(CO) ₄	Yellow	95	0.025	1210	1287	0.09	0.86	1957s, 1883sh, 1862vs §

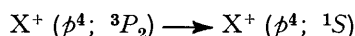
* All are diamagnetic in the solid state at 23°. † Determined osmometrically in benzene. ‡ In dichloromethane. § In Nujol.

TABLE 2

Complex	C-O stretching force constants* (mdyne Å ⁻¹)			Complex	<i>k</i> ₁	<i>k</i> ₂	<i>k</i> _i
	<i>k</i> ₁	<i>k</i> ₂	<i>k</i> _i				
I-Mn(CO) ₅	16.33	17.41	0.22	(<i>o</i> -Triars)Ag-Mn(CO) ₅	15.06	15.43	0.28
Ph ₃ PAu-Mn(CO) ₅	15.70	16.03	0.25	(<i>o</i> -Triars)Cu-Mn(CO) ₅	15.05	15.39	0.26

* *k*₁ and *k*₂ refer, respectively, to carbonyl groups *trans* and *cis* to the metal-metal bond; *k*₂ is a general interaction constant.

In attempting to make a correlation between the electronegativity of the atom L (= Cl, Br, I, Cu, Ag, or Au) and the infrared-active C-O stretching vibration in complexes containing the group L-Mn(CO)₅, the first problem is to decide upon values for the electronegativities of the halogen and of the Group IB metal atoms. We consider that, for our purposes, the tendency of the formally positive halogen (or metal) atom to acquire a pair of electrons is the important quantity. For hydrogen, copper, silver, or gold this is conveniently measured (as originally proposed by Mulliken) by adding together the first ionisation potential and the electron affinity. For the halogens, however, this is less satisfactory because there is a change in the multiplicity in going from X⁺ to X⁻; thus, Cl⁺ is a triplet whereas Cl⁻ is a singlet state. Hence, we have estimated electronegativities for the halogens which include the promotion energy for the process.



By taking an arbitrary standard that the electronegativity of hydrogen is 2.10, comparative values for the relevant electronegativities are presented in Table 3. By use of these values, a possible relationship between electronegativity and (i) individual C-O

 TABLE 3
 Atom electronegativities

Element	F	Cl	Br	I	H	Au	Cu	Ag
Pauling	4.0	3.0	2.8	2.5	2.1	—	—	—
Mulliken	3.91	3.00	2.76	2.56	2.28	1.78	1.36	1.36
Pritchard and Skinner	3.9	3.0	2.8	2.5	2.1	2.1	1.7	1.7
This Paper	3.85	2.95	2.70	2.56	2.10	1.66	1.31	1.25

stretching frequencies, (ii) mean C-O stretching frequencies (average of three values, $2A_1 + E$) is presented in Figure 1; Figure 2 shows the C-O stretching force constants. Although no quantitative relationship is suggested, the main trend which is observed is that the effective positive charge on the manganese atom (as reflected by the C-O stretching frequencies and force constants) is related to the electronegativity of the ligand atom

attached. This trend clearly supports the accepted view that electronegativities decrease in the order $I > Au > Ag \sim Cu$.

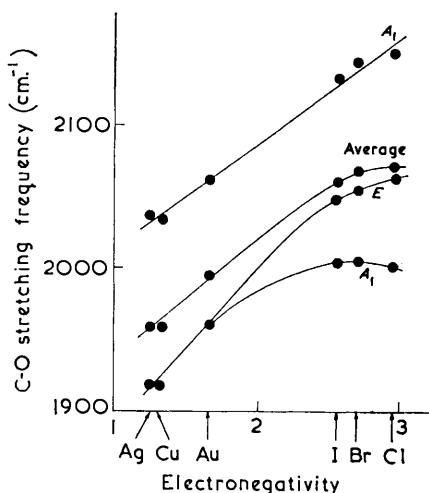


FIGURE 1

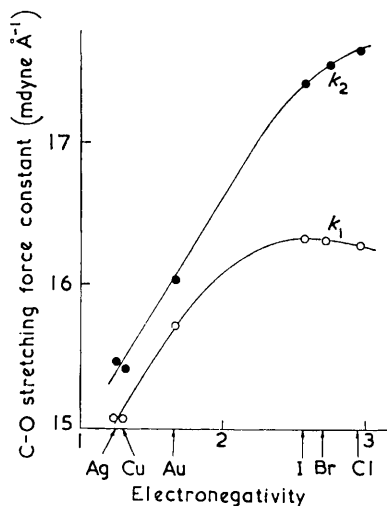


FIGURE 2

EXPERIMENTAL

1,1,1-Tris(dimethylarsinomethyl)ethanecopperpentacarbonylmanganese.—To a suspension of the complex (*ν*-Triars)CuBr (0.53 g.) in tetrahydrofuran (50 ml.) was added one equivalent of the salt Na[Mn(CO)₅] [prepared by reduction of Mn₂(CO)₁₀ (0.20 g.) with 3% sodium amalgam] in tetrahydrofuran (50 ml.). The mixture was stirred for 30 min. under nitrogen. Solvent was partially removed under reduced pressure and the *product* (0.42 g.), which was precipitated on addition of light petroleum, was purified by use of a dichloromethane–light petroleum mixture and dried *in vacuo* (Found: C, 30.2; H, 4.5; As, 34.7; Cu, 9.7; Mn, 8.2. C₁₆H₂₇As₃CuMnO₅ requires C, 29.9; H, 4.2; As, 35.0; Cu, 9.9; Mn, 8.5%). The compound, together with those following, is reasonably stable to air and moisture. It is soluble in most organic solvents, but tends to react with those containing halogen.

*Bis-(*o*-dimethylarsinophenyl)methylarsinocopperpentacarbonylmanganese*.—To a solution of the complex (*o*-Triars)CuBr (0.60 g.) in tetrahydrofuran (50 ml.) was added one equivalent of the salt Na[Mn(CO)₅] in the same solvent (50 ml.). The solution was heated under nitrogen for 3 min. at 100° and allowed to stand at room temperature for 3 hr. The solution was added to oxygen-free water (200 ml.) and kept overnight at 0°. The *product* (0.48 g.), which separated was recrystallised from acetone–water and dried *in vacuo* (Found: C, 37.4; H, 3.4; As, 31.7; Cu, 8.9. C₂₂H₂₃As₃CuMnO₅ requires C, 37.2; H, 3.2; As, 31.6; Cu, 8.9%).

*Bis-(*o*-dimethylarsinophenyl)methylarsinesilverpentacarbonylmanganese*.—To a solution of the complex (*o*-Triars)AgBr (0.66 g.) in tetrahydrofuran (35 ml.) was added one equivalent of the salt Na[Mn(CO)₅] in the same solvent (30 ml.). Treatment similar to that of the corresponding copper complexes yielded the *product* (0.52 g.) (Found: C, 35.2; H, 3.2; Ag, 14.1; As, 29.6. C₂₂H₂₃AgAs₃MnO₅ requires C, 35.0; H, 3.1; Ag, 14.3; As, 29.8%).

*Bis-(*o*-dimethylarsinophenyl)methylarsinocoppertetracarbonylcobalt*.—To a solution of the complex (*o*-Triars)CuBr in tetrahydrofuran (100 ml.) was added one equivalent of the salt Na[Co(CO)₄] [prepared by reduction of Co₂(CO)₈ (0.17 g.) with 3% sodium amalgam] in the same solvent (40 ml.). The solution was warmed at 40° for 1 hr. and added to oxygen-free water (150 ml.). The *product* (0.35 g.), which separated after 24 hr. at 0°, was recrystallised from methanol and dried *in vacuo* (Found: C, 36.6; H, 3.3; As 32.2; Co, 8.3; Cu, 9.15. C₂₁H₂₃As₃CoCuO₄ requires C, 36.7; H, 3.3; As, 32.7; Co, 8.5; Cu, 9.2%).

*Bis-(*o*-dimethylarsinophenyl)methylarsinesilvertetracarbonylcobalt*.—To a solution of the complex (*o*-Triars)AgBr in tetrahydrofuran (100 ml.) was added one equivalent of the salt Na[Co(CO)₄] in the same solvent (40 ml.). Similar treatment yielded the *product* (0.31 g.)

(Found: C, 34.6; H, 3.2; Ag, 14.8; As, 31.1. $C_{21}H_{23}AgAs_3CoO_4$ requires C, 34.5; H, 3.1; Ag, 14.7; As, 30.7%).

Bis-[bis-(*o*-dimethylarsinophenyl)methylarsinecopper]tetracarbonyliron.—To a solution of sodium borohydride (0.25 g.) in diglyme (30 ml.) was added pentacarbonyliron (0.3 ml.). On completion of the reduction, methanol (10 ml.) was added, followed by the complex (*o*-Triars)CuBr (0.60 g.) in tetrahydrofuran (50 ml.). The solution was warmed at 40° for 30 min. Methanol (50 ml.) was added, and sufficient water to initiate separation of the product. The solution was set aside at 0° for 18 hr. to complete the separation of the *compound* (0.41 g.), which was recrystallised from acetone–water and dried *in vacuo* (Found: C, 37.9; H, 3.7; As, 37.4; Cu, 10.3. $C_{38}H_{46}As_6Cu_2FeO_4$ requires C, 38.0; H, 3.8; As, 37.5; Cu, 10.6%).

Bis-[bis-(*o*-dimethylarsinophenyl)methylarsinesilver]tetracarbonyliron.—To a solution of the salt $Na_2[Fe(CO)_4]$, prepared by the described procedure, was added the complex (*o*-Triars)-AgBr (0.64 g.) in tetrahydrofuran (50 ml.). Similar treatment yielded the *product* (0.36 g.) (Found: C, 35.2; H, 3.5; Ag, 16.6; As, 34.7. $C_{38}H_{46}Ag_2As_6FeO_4$ requires C, 35.4; H, 3.5; Ag, 16.7; As, 35.0%).

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