339. *Metal–Metal Bonds. Part I. Compounds of Gold*(0) *with the Carbonyls of Manganese, Iron, and Cobalt.*

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Substances which contain metal-to-metal bonds are classified into four main types: metals, concentrated metal compounds, covalent compounds, and metal-donor compounds. The conditions favouring the formation of covalent M–M bonds are discussed, particular attention being paid to the electron configuration and effective electronegativity of the metal atom. The electronegativity of $d^{10}s^1$ atoms, *e.g.*, gold, is considered and the formal similarity of the latter with the halogens is emphasised. By using a general reaction between the compound $Ph_3P\rightarrow AuCl$ and salts of the $[Mn(CO)_5]^-$, $[Fe(CO)_4]^{2-}$, and $[Co(CO)_4]^-$ ions, the compounds $Ph_3P\rightarrow Au{-}Mn(CO)_5$, $(Ph_3P\rightarrow Au)_2Fe(CO)_4$ and $Ph_3P\rightarrow Au{-}Co(CO)_4$ have been prepared. The molecular weight, magnetic susceptibility, and infrared spectra have been investigated. The similarity of the manganese and iron compounds $Mn(CO)_5I$ and $Fe(CO)_4I_2$ is discussed.

The object of this investigation was the preparation of transition-metal complexes containing metal-to-metal bonds. Bonds of this type are, as pointed out by Pauling,[1] more common than is usually supposed. The strength of such a covalent bond between two atoms A and B is dependent [2] mainly on the overlap integral of the orbitals involved in bond formation, and the product of the effective electronegativities. Hence, it would appear that, in principle, the design of compounds containing metal-to-metal bonds is largely a matter of choosing metal atoms with the appropriate electron configuration to which are attached groups which make the (half-filled) orbital the right size for overlap.

An examination of the common substances containing metal-to-metal bonds suggests that they may be conveniently divided into four main classes as shown in Table 1.

Type I compounds will not be discussed here, beyond drawing attention to the fact that they represent one extreme type of metal-to-metal bond involving multicentre orbitals. In certain alloys, a change-over to a largely ionic structure is feasible in certain cases, see cæsium auride [3] below.

Type II compounds may be regarded as intermediate between metals and covalent halides. Thus, in compounds like $MoCl_2$, in which there occurs the $[Mo_6Cl_8]^{4+}$ ion, certain features of the metal are retained in the intranuclear Mo–Mo bonding. Examples of chain formation are provided by NbI_4[4] and MoI_3,[5] which involve the sharing of edges and faces of octahedra, respectively. Compounds of class IV are not common but do occur in certain d^8 complexes. These are frequently tetragonal rather than square co-ordinate [6] and sometimes polymerisation *via* metal–metal bonds involving a donor bond can occur. The low solubility of bisdimethylglyoximatonickel(II) arises from this phenomenon.[7]

Finally, type III compounds arise with certain metal atoms containing one electron

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[1] Pauling, *Chem. and Eng. News*, 1947, **25**, 2970, 3045.
[2] Mulliken, *J. Phys. Chem.*, 1952, **56**, 295.
[3] Spicer, Sommer, and White, *Phys. Rev.*, 1959, **115**, 57.
[4] Dahl and Wampler, *J. Amer. Chem. Soc.*, 1959, **81**, 3150.
[5] Lewis, Machin, Nyholm, Pauling, and Smith, *Chem. and Ind.*, 1960, 259.
[6] Harris and Livingstone, *Rev. of Pure and Applied Chem.*, 1962, **12**, 16.
[7] Godycki and Rundle, *Acta Cryst.*, 1953, **6**, 478; see also Rundle, *J. Phys. Chem.*, 1957, **61**, 45.

less than a closed shell or sub-shell.[8] Thus, in Hg_2Cl_2 the formal $6s^1$ mercury atom becomes $6s^2$ and in $Co_2(CO)_8$ the d^9 atom becomes d^{10} after metal–metal bond formation. The structure of $Co_2(CO)_8$ involves two bridging CO groups in addition to the Co–Co bond; this is in contrast to the structure of $Rh_2(CO)_8$ and $Ir_2(CO)_8$ in which bridging CO groups are not present.[9] In $Mn_2(CO)_{10}$ the formal d^7 configuration becomes d^8 whilst an example of the $d^5 \rightarrow d^6$ change occurs in $Cp(CO)_3Cr–Cr(CO)_3Cp$,[10] (Cp = cyclopentadienyl).

TABLE 1.

Types of substances containing metal-to-metal bonds.

Type I: Metals —— Condensed state (various arrangements)

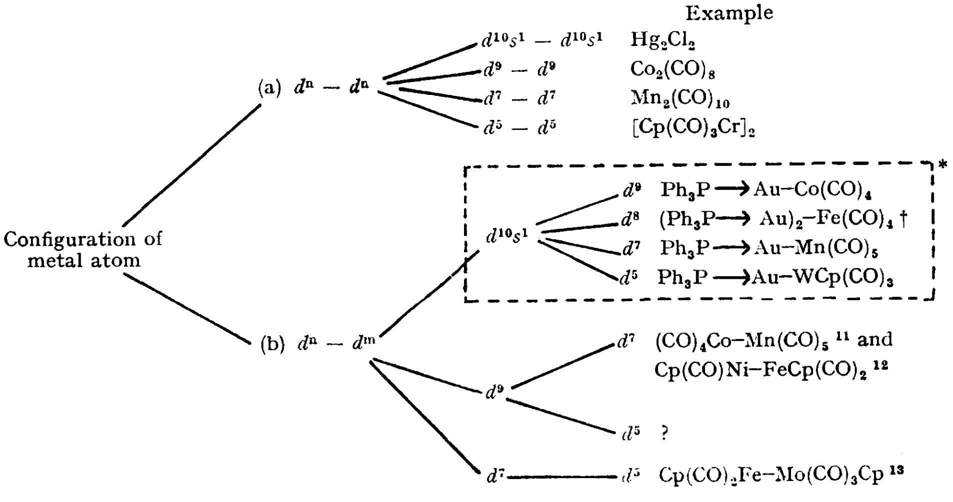
Type II: Concentrated metal compounds
- d', *e.g.*, $(NbI_4)_n$
- d^2, *e.g.*, $(MoO_2)_n$, $[Nb_6Cl_{12}]^{2+}$
- d^3, *e.g.*, $(MoI_3)_n$, $[W_3Cl_9]^{3-}$
- d^4, *e.g.*, $(MoCl_2)_n$, based on $[Mo_6Cl_8]^{4+}$ unit

Type III: Compounds containing single covalent M–M bonds
- Metals in vapour phase
  - (Can be monoatomic, *e.g.*, Hg(0))
  - Diatomic, *e.g.*, Cu_2, Li_2, etc.
- Metal atoms with *same* configuration, *e.g.*, $Mn_2(CO)_{10}$
- Metal atoms with *different* configuration, *e.g.*, $Hg(Mn(CO)_5)_2$

Type IV: Metal donor complexes, *e.g.*, Bisdimethylglyoximatonickel(II)

TABLE 2.

Covalent metal-to-metal bonds.



* Compounds in rectangle first reported in this paper. † Iron atom is regarded formally as having initially 2 unpaired electrons.

We can divide type III compounds into sub-classes according as the metal atoms have the same or different electron configurations as shown in Table 2.

Further sub-divisions of (*a*) emerge according as one changes: (i) the oxidation state

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[8] Nyholm, *Proc. Chem. Soc.*, 1961, 273.

[9] Dahl, Martell, and Wampler, *J. Amer. Chem. Soc.*, 1961, **83**, 1761.

[10] Wilson and Shoemaker, *J. Chem. Phys.*, 1957, **27**, 809.

[11] Pauson, personal communication, 1962.

[12] Tiley-Bassett, *Proc. Chem. Soc.*, 1960, 419.

[13] King, Treichel, and Stone, *Chem. and Ind.*, 1961, 747.

of the two atoms; thus, in the compound $(CO)_5Mn{-}Fe(CO)_2Cp$,[13] there is a d^7—d^7 arrangement with one Mn(0) and one Fe(+I) atom; and (ii) the nature of the attached metals. The compound $Cp(CO)_3Mo{-}W(CO)_3Cp$,[14] for example, involves the union of two different metal atoms in the same vertical column, both being d^5. It is noteworthy amongst the examples shown in Table 2 that most of the compounds so far prepared involve carbon monoxide as ligand, the metal being in a low oxidation state. One has to pass to $d^{10}s^1$ elements, *e.g.*, group IV, for the oxidation states +III to be observed; here the bonds are of the sp^3 type. Other examples include the newly prepared $d^{10}s^1$–d^n compounds of Ge(III).[15] The need to differentiate between oxidation state and valency should be mentioned. In $Ph_3Sn{-}SnPh_3$ the tin is quadrivalent but the oxidation state is +III. The situation is exactly analogous with the mercury atom in mercurous chloride.

It is clear that in most cases the metal atom reaches the nearest rare-gas configuration, or its equivalent. For the third transition series the $6s \rightarrow 6p$ separation is so large that a filled $6s^2$ sub-shell is often quite stable [cf. Hg(0) and two-co-ordinate Tl(III)]. This is reflected in the ionisation potentials for the sequence Au, $6s^1$, 9·22 ev.; Hg, $6s^2$, 10·43 ev.; Tl, $6s^26p^1$, 6·11 ev.[16] Electron affinities are also expected to be large for the $6s^1$ configuration. These data are scarce for transition elements; Edlen [17] has estimated electron affinities for the first two short periods and these show characteristic maxima corresponding to the completion of filled (ns^2, ns^2np^6) or half-filled (np^3) sub-shells. Estimated values [8] for Cu, Ag, and Au (2·0, 2·2, and 2·7 ev., respectively) may be too high by as much as 0·5 ev. but they still show the very high electron-attracting tendency of $d^{10}s^1$ neutral atoms. The electronegativity of gold is unusually high, the sum of the first ionisation potential and the electron affinity (~11·9 ev.) being not much less than that for iodine (13·6 ev.). It is tempting to regard gold as having similarities with the halogens and this is reflected in the properties of the 1 : 1 alloy of cæsium and gold. This has the CsCl structure; it involves a 42% contraction on formation from the metals and its resistivity at 20° (0·01 ohm cm.) is a thousand times that of cæsium ($21{\cdot}5 \times 10^{-6}$) or gold ($2{\cdot}4 \times 10^{-6}$).[3]

The role of formal charge is clearly important in deciding whether M–M bond formation occurs. In general, as the oxidation state rises, the tendency to form paramagnetic monomers rather than M–M bonds increases. Thus, for the sequence of d^9 atoms Fe(—I), Co(0), Ni(+I), Cu(+II) we note that the tendency to form paramagnetic derivatives increases as we pass towards copper. This can be physically pictured as involving a contraction of the *d* orbital, containing the unpaired electron, away from the bonding region. Indeed Cu(II) only forms M–M bonds in δ-bonded complexes, such as cupric acetate monohydrate [18] and similar derivatives. As the charge decreases one can visualise the orbital as becoming more spread out and more capable of bond formation, as in $[Fe_2(CO)_8]^{2-}$.

In descending a vertical triad in the transition series the orbitals become bigger and it is likely that overlap will increase. As pointed out above, for the smaller first-transition metals, both CO bridging and M–M bond formation occurs in certain carbonyls whereas CO bridging does not occur for the second two series. Thus, the observed CO stretching frequencies are, respectively, 2043, 2020, 1997, 1858, and 1826 cm.$^{-1}$ in $Fe_2(CO)_9$ and 2049, 2016, and 2000 cm.$^{-1}$ in $Ru_2(CO)_9$. In short, M–M bonding alone is sufficient to ensure the stability of the $Ru_3(CO)_{12}$ dimer.

We now consider the role of the attached ligands in deciding whether M–M bonds will be formed. Different ligands will clearly affect the formal charge on the metal, partly

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[14] Abel, Singh, and Wilkinson, *J.*, 1960, 1321.

[15] Seyferth, Hofmann, Burton, and Helling, *Inorganic Chemistry*, 1962, **1**, 227.

[16] Moore, " Atomic Energy Levels." U.S. Nat. Bur. Standards Circular No. 467, 1952, Vol. II; 1958, Vol. III.

[17] Edlen, *J. Chem. Phys.*, 1960, **33**, 98.

[18] Cotton and Wilkinson, *J. Amer. Chem. Soc.*, 1957, **79**, 752.

owing to their differing inductive effects and partly because of the ability of some to form d_π bonds.

Few data are available concerning the effect of substituents in manganese carbonyl upon the strength of the Mn–Mn bond. Compounds of empirical formula $L(CO)_4Mn$ (where L is a monodentate ligand) have been prepared; in some cases a coloured diamagnetic dimer is formed [*e.g.*, if L = $P(OPh)_3$, $P(OMe)_3$, $PPh(OPh)_2$, P(cyclohexyl)$_3$], and in others the nearly colourless paramagnetic monomer is produced (*e.g.*, if L = PPh_3, PEt_3, P(*p*-Tolyl)$_3$, $AsPh_3$, $SbPh_3$). The monomer formed can be regarded as a free radical, so a comparison with the corresponding behaviour of the free-radical forming atoms in the first two periods (*e.g.*, C, N, O, Cl) is useful. These atoms give rise to compounds of the type R_nX-XR_n, where R is an alkyl or aryl group, an oxygen atom, etc. Now the formation of the free radical $R_nX\cdot$ can be brought about, either by choosing R so as to stabilise the monomer, or so as to bring about destabilisation of the dimer.

The factors which appear to force the reaction $R_nX-XR_n \rightarrow 2R_nX\cdot$ to the right, are: (1) Groups favouring delocalisation of the unpaired electron. Thus the triphenymethyl radical is stabilised by structures of quinonoid type. In effect, one completes the octet of the central carbon atom, the electron spending most of its time at the *ortho*- and *para*-positions of the benzene rings. The placing of nitro-groups in the *para*-position enhances this stabilisation. (2) Contraction of the orbital containing the unpaired electron; *e.g.*, paramagnetic transition-metal ions in complexes contain unpaired electrons in *d* orbitals which have been drawn in, away from the bonding region. (3) Steric repulsion between the two R_nX groups. Thus the dissociation [19] of (α-naphthyl)CPh_2-CPh_2(α-naphthyl) (54%), and of *o*-Et·C_6H_4·CPh_2–CPh·C_6H_4·Et-*o* (82%), in 10% benzene solution, is much larger than in similar compounds where the steric effect is less (see also Ziegler [20]). (4) Repulsion between non-bonding electrons.[21] There are many compounds known of groups V, VI, and VII elements, for which lone-pair repulsion on adjacent atoms is postulated.[22] Evidence for this includes the low bond energy of molecular fluorine, the fact that the oxygen molecule is a diradical and the long nitrogen–nitrogen bond in hydrazine. Clearly, if one increased this repulsion sufficiently one might form a free radical; thus, Ingold [23] pointed out that dissociation of R_2N-NR_2 into free radicals was enhanced when R = *p*-$Me_2N\cdot C_6H_4$ or *p*-$MeO\cdot C_6H_4$ (as compared with R = Ph). The former two groups have the *opposite* effect when substituted in R_3C-CR_3 where there are no lone pairs on the carbon atom.

In applying these ideas to $Mn_2(CO)_{10}$ it is first noteworthy that the Mn–Mn bond appears to be unusually long; [24] we postulate that this is due, as in hydrazine, to repulsion between the non-bonding d_ϵ^6 sub-shells on the two manganese atoms. If so, one should be able to decrease further the Mn–Mn bond strength, leading to free-radical formation, by replacing one or more carbonyl groups by a ligand of poorer π-bond capacity. This releases d_ϵ electrons, which would, on flowing towards the Mn–Mn bond, increase repulsion between the two manganese atoms favouring dissociation. The tertiary phosphines which behave most like carbonyl are those in which the phosphorus atom is attached to electronegative groups, *e.g.*, PF_3, PCl_3, $MePCl_2$, etc. We find [25] that phosphorus trifluoride forms a coloured diamagnetic product with $Mn_2(CO)_{10}$ of the formula $PF_3\cdot(CO)_4Mn-Mn(CO)_4\cdot PF_3$. Similar behaviour is observed with phosphorus trichloride. We suggest that the main factor responsible for the destabilisation of $L(CO)_4Mn-Mn(CO)_4L$ by ligands of the type PPh_3 and PEt_3, etc., is that these ligands are poor *d* electron acceptors from the metals.

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[19] Waters, " The Chemistry of Free Radicals," Oxford Univ. Press, 2nd Edn., 1948.
[20] Ziegler, *Annalen*, 1942, 551, 127.
[21] See Pauling, " Nature of the Chemical Bond," Cornell Univ. Press, New York, 1960, 3rd Edn., p. 211.
[22] Walsh, *J.*, 1948, 398.
[23] Ingold, *Trans. Faraday Soc.*, 1934, **152**, 52.
[24] Dahl, Ishishi, and Rundle, *J. Chem. Phys.*, 1957, **26**, 1750.
[25] Kasenally and Nyholm, 1962, unpublished.

This suggests that the inductive effect due to the high electronegativity of the oxygen atom is more important than any oxygen-to-phosphorus π-bond contribution to the structure of the phosphine.[26]

To sum up, M–M bond formation is favoured by: (*a*) a metal atom having the required unpaired electron(s) available, as in the d^9 Co(0) atom, or capable of being made readily available by unpairing [as in Fe(0)]; (*b*) orbitals of the required energy, *i.e.*, able to overlap at distances comparable with ordinary bond lengths. This condition can be achieved by decreasing the formal charge on the metal atom, or by changing the effective electronegativity of the metal atom by attaching suitable ligands. The latter can affect the metal both by their different σ bonding abilities and by their capacities to accept d electrons.

The foregoing empirical correlation with electron configuration being used, an investigation of the preparation of M–M bonded complexes has been undertaken. We here confine attention to certain new compounds of a $d^{10}s^1$ atom of oxidation state zero (gold) with carbonyl anions of metals of the first transition series.

The formation of compounds containing metal-to-metal bonds by atoms with a $d^{10}s^1$ configuration is well known for many different oxidation states of the post-transition atoms. Table 3 shows typical examples of these substances and indicates where such compounds have not been prepared previously. In particular the paucity of derivatives having an oxidation state 0 for the atoms with a $d^{10}s^1$ configuration led to the present study of the complexes of gold (0). The Table 3 draws attention to certain interesting problems. First there is the absence of palladium and platinum derivatives corresponding to $[Ni_2(CO)_6]^{2-}$. Secondly, we note certain horizontal and vertical discontinuities; for example, whereas one can obtain a gold–gold bond in gold (Au_2) (in the gas phase), and a metal–metal bond in mercurous chloride, no Tl–Tl bond has been demonstrated with Tl(II); ($TlCl_2$ is, like $Ga[GaCl_4]$,[27] probably $Tl^+[TlCl_4]^-$); however, Pb(III) does form a Pb–Pb bond in its hexaphenyl derivative. In the oxidation state zero the bond energies[28] for Cu_2 (47 kcal. mole^{-1}), Ag_2 (39 kcal. mole^{-1}), and Au_2 (52 kcal. mole^{-1}) * pass through a minimum at the second row and this at least parallels the greater stability of the Hg–Hg bond as compared with zinc or cadmium. However, in the Ga, In, and Tl triad, a metal–metal bond has been reported[30] in the case of Ga(II)

TABLE 3.

Examples of compounds with metal–metal bonds containing $d^{10}s^1$ atoms.

Electron confign. of first atom	Electron confign. of second atom	Formal oxidation state of $d^{10}s^1$ atom(s)				
		−I	0	+I	+II	+III
$d^{10}s^1$	$d^{10}s^1$	$[Ni_2(CO)_6]^{2-}$	Au_2	ClHg–HgCl	$(–S–)_3Ga–Ga(–S–)_3$	$Ph_3Pb–PbPh_3$
	d^9	—	$Ph_3P\rightarrow Au–Co(CO)_4$ *		$(CH_3)_2Sn[Co(CO)_4]_2$	$Bu_3Sn–Co(CO)_4$
	d^8	—	$(Ph_3P\rightarrow Au)_2Fe(CO)_4$ *	$(CH_3Hg)_2Fe(CO)_4$	$Bu_2Sn=Fe(CO)_4$	$(Bu_3Sn)_2Fe(CO)_4$
	d^7	—	$Ph_3P\rightarrow Au–Mn(CO)_5$ *	—	$Me_2Sn[Mn(CO)_5]_2$	$Ph_3Ge–Mn(CO)_5$
	d^5	—	$Ph_3P\rightarrow Au–W(CO)_3Cp$ *	—	—	—

* Reported in this investigation.

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* Mass spectrometry gives Cu_2, 45·5 kcal. mole^{-1}; Ag_2 37·6 kcal.; Au_2, 51·5 kcal. mole^{-1}.[29]

[26] Pidcock, Richards, and Venanzi, *Proc. Chem. Soc.*, 1962, 184.

[27] Garton and Powell, *J. Inorg. and Nuclear Chem.*, 1957, **4**, 84.

[28] Cottrell, " The Strengths of Chemical Bonds," Butterworths, London, 1958, 2nd Edn., p. 270.

[29] Ackerman, Stafford, and Drowart, *J. Chem. Phys.*, 1960, **33**, 1784.

[30] Hahn and Frank, *Z. anorg. Chem.*, 1958, **278**, 340.

in Ga_2S_2. The carbon-like atoms Ge(III), Sn(III), and Pb(III) all give rise to metal–metal bonds readily but no case of a metal–metal bond between the atoms As(IV), Sb(IV), or Bi(IV) has been definitely established. [The diamagnetism [31] of K_2SbCl_6 is attributed, as with that of $TlCl_2$, to a mixture of two oxidation states (III and V).] Finally, comment is called for on the point that $d^{10}s^1$ atoms clearly form metal–metal bonds much more readily than do the atoms containing unpaired *d*-electrons. The reason for this appears to be the same as that which explains their reluctance to form free radicals, namely, that the unpaired electron is in an orbital which is in the bonding region and readily overlaps a similar orbital, or that containing an unpaired electron on another atom.

The Reactions of $Ph_3P{\rightarrow}AuCl$ *with Various Carbonyl Anions.*—The general reaction studied is of the type $xPh_3P{\rightarrow}AuCl + Na_x[M(CO)_y]^{x-} \rightarrow (Ph_3P{\rightarrow}Au)_xM(CO)_y + xNaCl$. If one treats a solution of sodium pentacarbonyl manganate in tetrahydrofuran with triphenylphosphineaurous chloride one can isolate a pale brown product after treating the solution with water. On recrystallisation, the compound $Ph_3P{\rightarrow}AuMn(CO)_5$ is obtained as pale brown air-stable crystals. The complex is diamagnetic, monomeric in benzene, and a non-electrolyte in nitrobenzene. It is decomposed by mineral acids and mild oxidising agents.

When treated with hydrogen chloride double decomposition occurs to give a mixture of $HMn(CO)_5$ and $Ph_3P{\rightarrow}AuCl$. The reaction with iodine yields initially, as one might expect, a mixture of $Mn(CO)_5I$ and $Ph_3P{\rightarrow}AuI$. The addition of excess of iodine gives a conducting solution; although the expected product $Ph_3P{\rightarrow}AuI_3$ should be a non-electrolyte, Mann and Purdie [32] showed that this compound is unstable. The nature of the decomposition products giving rise to the electrical conductivity were not investigated.

Disodium tetracarbonyl ferrate also reacts readily with $Ph_3P{\rightarrow}AuCl$ to yield the compound $(Ph_3P{\rightarrow}Au)_2Fe(CO)_4$ as pale yellow crystals. The complex is readily soluble in inorganic solvents in which it is monomeric. It is a nonelectrolyte in nitrobenzene. The infrared spectrum in chloroform shows bands at 2004, 1934, and 1894 cm.$^{-1}$ which can be attributed to C–O stretching modes; it is of interest to note that the complex $Fe(CO)_4I_2$ shows bands at 2071, 2091, and 2136 cm.$^{-1}$ in chloroform. The similarity of this spectrum to that of $Fe(CO)_4(Au{\leftarrow}PPh_3)_2$ points strongly to a *cis*-arrangement of the two $(Ph_3P{\rightarrow}Au)$ groups. In short, the $Ph_3P{\rightarrow}Au$ group is behaving as a pseudohalogen so far as the $>Fe(CO)_4$ group is concerned. As expected, treatment with hydrogen chloride yields $Ph_3P{\rightarrow}AuCl$ and the carbonyl hydride, whilst iodine gives $Ph_3P{\rightarrow}AuI$ and $Fe(CO)_4I_2$.

Finally, on treating a solution of $[CoPy_6][Co(CO)_4]_2$ in tetrahydrofuran with $Ph_3P{\rightarrow}AuCl$ we obtained pale brown crystals of the compound $Ph_3P{\rightarrow}AuCo(CO)_4$. This

TABLE 4.

Complex	M. p.	Colour	Mol. conductivity in $PhNO_2$: $PhNO_2$ Λ_M	Mol. conductivity in $PhNO_2$: Concn. $\times 10M^{-3}$	Infra-red bands due to CO stretching (cm.$^{-1}$)
$Ph_3P{\rightarrow}Au{-}Mn(CO)_5$	151° (decomp.)	Pale brown	0·1	11·	2062ms, 1961vs (in CCl_4)
$(Ph_3P{\rightarrow}Au)_2Fe(CO)_4$	150° (decomp.)	Pale yellow	0·01	0·25	2004ms, 1934s,* 1894s* (in CCl_4)
$Ph_3P{\rightarrow}AuCo(CO_4)$	112—114°	Very pale brown	0·1	1·0	2054s, 1988s, 1957s and broad (in CS_2)
For comparison					
$[Mn(CO)_5I]$					2123, 2043, 2006 (in $CHCl_3$)
$[Fe(CO)_4I_2]^0$					2136, 2091, 2071 (in $CHCl_3$)

* Not resolved in chloroform.

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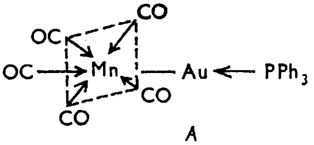
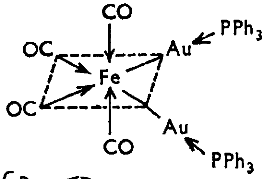
[31] Elliott, *J. Chem. Phys.*, 1934, **2**, 298.
[32] Mann and Purdie, *J.*, 1940, 1235.

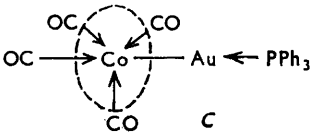
also is monomeric and a nonelectrolyte in nitrobenzene. This complex reacts with hydrogen chloride to yield the expected $Ph_3P{\rightarrow}AuCl$ and decomposition products of $HCo(CO)_4$. Similarly, iodine yields $Ph_3P{\rightarrow}AuI$ and some unstable carbonyl iodides of cobalt. On the basis of the molecular weight data, the molecular conductivity in nitrobenzene and the infrared spectra, the structures suggested for the three compounds are shown in A, B, and C.



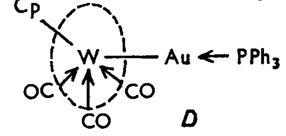
A



B



C



D

The properties of the complexes are summarised in Table 4. It is clear that the $Ph_3{\rightarrow}Au$ group may be regarded either as a unipositive group or as a uninegative anion. Discussion of this point at present is rather semantic and we prefer to regard these compounds at least formally as involving two metal atoms both having an oxidation state of zero.

In so far as average C–O stretching frequencies are meaningful, the values of these for the sequence, $Br_2Fe(CO)_4$ (mean 2116 cm.$^{-1}$), $I_2Fe(CO)_4$ (mean 2099 cm.$^{-1}$), $(Ph_3P{\rightarrow}Au)_2Fe(CO)_4$ (mean 1944 cm.$^{-1}$), and the $[Fe(CO)_4]^{2-}$ ion (mean 1788 cm.$^{-1}$) suggest that the $Ph_3P{\rightarrow}Au$ group has an effective electronegativity notably less than that of iodine. The stereochemistry of the $[Fe(CO)_4]^{2-}$ ion is, of course, different from that of the $X_2Fe(CO)_4$ compounds and hence C–O stretching frequencies are not comparable; but it is given to indicate the big change in C–O frequency in passing to a purely ionic compound. This is in accord with the electronegativity as measured by the sum of the electron affinity and the first ionisation potential; for the halogens and gold, these are Cl 16·7 ev., Br 15·3 ev., I 13·6 ev., and Au 11·9 ev. The effective electronegativity of gold will clearly be affected by the group used instead of triphenylphosphine and we are now examining the way in which the C–O stretching frequency varies with different ligands.

Similar conclusions emerge from a comparison of the mean C–O stretching frequencies for $ClMn(CO)_5$ (2064 cm.$^{-1}$), $BrMn(CO)_5$ (2061 cm.$^{-1}$), $IMn(CO)_5$ (2057 cm.$^{-1}$), and $Ph_3P{\rightarrow}Au{-}Mn(CO)_5$ (2012 cm.$^{-1}$). All that can be said of the cobalt complexes is that the order $Ph_3P{\rightarrow}Au{-}Co(CO)_4$ (2000 cm.$^{-1}$) > $[Co(CO)_4]^-$ (1901 cm.$^{-1}$) is preserved. One of our objectives is to try to prepare a compound of the type Ligand→Au–Au→Ligand. It is of great interest also to replace the gold atom in these compounds by copper and silver. The tendency for these metals to form four-co-ordinate univalent complexes (*e.g.*, $[CuI{\cdot}Et_3As]_4$ and $[AgI{\cdot}Et_3As]_4$ as compared with two-co-ordinate monomeric $[Et_3As{\rightarrow}AuI]^0$ suggests that monomeric four-co-ordinate complexes of the type $(Ligand)_3CuI$ will need to be used. Work in this direction is currently in progress.

Finally, although it is not a derivative of a first-row transition metal, one of us (C. E. C.) has prepared in the Du Pont Laboratories a $d^{10}s^1$–d^5 complex, *viz.* $Cp(CO)_3W{-}Au{\leftarrow}PPh_3$. This was obtained in a similar manner to the other complexes. It is monomeric, a nonelectrolyte in nitrobenzene, and melts at 202—205°. A possible structure for this tungsten–gold complex is shown in *D*.

[*Note added in proof.* Complexes of the type $\text{Triarsine} \overset{\curvearrowright}{\underset{\curvearrowleft}{\rightarrow}} Cu{-}Mn(CO)_5$ and the silver analogue have now been isolated. Triarsine is $CH_3{\cdot}C(CH_2{\cdot}AsMe_2)_3$.]

EXPERIMENTAL

Triphenylphosphinegold–Pentacarbonylmanganese.—A solution of $NaMn(CO)_5$ (5×10^{-3}M) in tetrahydrofuran[33] (50 ml.) was filtered (under nitrogen) into a solution of Ph_3PAuCl[34] (5×10^{-3}M) in tetrahydrofuran (50 ml.). The mixture was kept at room temperature for 15 min., water (200 ml.) added, and the resulting suspension kept at 0° for 12 hr. The brown product was collected and crystallised from acetone–water and then from ethanol–water yielding very pale brown crystals (80%), m. p. 151° (decomp.) (Found: C, 42·1; H, 2·2; Au, 30·1%; *M*, ebullioscopic in benzene (3%), 680. $C_{23}H_{15}O_5AuMnP$ requires C, 42·2; H, 2·3; Au, 30·1%; *M*, 654).

The complex is very soluble in chloroform and benzene, less soluble in hexane and methanol, and insoluble in water. It is stable toward air, light, and water, but is decomposed by mineral acid and mild oxidising agents. The complex is diamagnetic (χ_M -250×10^{-6}) and virtually a non-conductor in nitrobenzene.

Bis(triphenylphosphinegold)–Tetracarbonyliron.—The tetracarbonyliron(-II) anion was produced by the following modification of a published method.[35] Pentacarbonyliron (1 ml.) was added to sodium borohydride (0·5 g.) in " diglyme " (30 ml.). When gas evolution ceased, methanol (10 ml.) was added to decompose excess of the borohydride. After gas evolution had ceased, Ph_3PAuCl (2 g.) in tetrahydrofuran was added. The resulting solution was kept at room temperature for 15 min. and then methanol (50 ml.) was added, followed by enough water to initiate crystallisation of the product. After cooling the solution for 12 hr. at 0°, the product was collected and washed with methanol giving pale yellow crystals (80%). After recrystallisation from acetone–water the compound decomposed at about 150° and evolved gas near 200° (Found: C, 44·4; H, 2·9; Au, 35·8%; *M*, cryoscopic in benzene (2·5%), 970. $C_{40}H_{30}O_4Au_2FeP_4$ requires C, 44·2; H, 2·8; Au, 36·3%; *M*, 1086). The complex was very soluble in chloroform and benzene, nearly insoluble in methanol and ethanol, and insoluble in water. The solid was stable toward air, light, and water but solutions underwent slow aerial oxidation. It was decomposed by mineral acids and by mild oxidising agents. The complex was diamagnetic (χ_M -590×10^{-6}) and virtually a non-conductor in nitrobenzene.

Triphenylphosphinegold–Tetracarbonylcobalt.—A solution containing the $[Co(CO)_4]^-$ ion was prepared by dissolving $Co_2(CO)_8$ (0·15 g.) {equivalent to $5·9 \times 10^{-4}$ mole of $[Co(CO)_4]^-$, *via* the reaction $3[Co(CO)_4]_2 + 12\ C_5H_5N \longrightarrow [Co(C_5H_5N)_5]^{2+}[Co(CO)_4]_2^- + 8CO$} in tetrahydrofuran (15 ml.) containing pyridine (0·5 ml.). When gas evolution ceased, the solution was treated with a solution of Ph_3PAuCl (0·274 g.) in tetrahydrofuran (25 ml.). The solution was kept at room temperature for 1 hr., then water (100 ml.) added, and the mixture kept at 0° for 24 hr. A mixture of sludge and crystalline product was recovered by filtration and extracted with acetone. Addition of water to the acetone extract gave a product which was crystallised from methanol yielding very pale brown crystals (60%), m. p. 112—114° (decomp.) (Found: C, 42·1; H, 2·55%; *M*, cryoscopic in benzene (2·7%), 530. $C_{22}H_{15}O_4AuCoP$ requires C, 41·9; H, 2·4%; *M*, 630). The complex was very soluble in benzene and chloroform, less soluble in methanol, and insoluble in water. The crystalline solid was stable toward air, light, and water. Solutions of the complex were slowly decomposed by air, immediately decomposed by acids and oxidising agents, and partially decomposed at about 80°. The complex was dimagnetic ($\chi_M = -320 \times 10^{-6}$) and virtually a non-conductor in nitrobenzene.

Action of Hydrochloric Acid on Triphenylphosphinegold–Pentacarbonylmanganese.—A hot solution of the complex (0·1709 g.), methanol (10 ml.), and acetone (5 ml.) was treated with 10N-hydrochloric acid (0·3 ml.) and boiled for 5 min. The characteristic odour of $HMn(CO)_5$ was observed. The solution was cooled and treated with methanol (10 ml.), and the resulting off-white crystals filtered off and washed with methanol. The filtrate was treated with water (10 ml.) and cooled overnight at 0° to produce a second small crop of crystals, which were collected, washed well with methanol, and added to the first. After being dried in a vacuum the product weighed 0·128 g. (99·9%), contained gold and chlorine, and had an infrared spectrum superimposable with that of authentic Ph_3PAuCl.

Addition of Hydrochloric Acid to Triphenylphosphinegold–Tetracarbonyliron.—A boiling solution of the complex (0·181 g.) in acetone (15 ml.) was treated with 10N-hydrochloric acid

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[33] Hieber and Wagner, *Z. Naturforsch.*, 1957, **12*b***, 478.
[34] Levi-Malvano, *Atti accad. Lincei*, 1908, **17**, 857.
[35] Haworth and Huff, *J. Inorg. and Nuclear Chem.*, 1961, **17**, 184.

(0·1 ml.) and boiled for 5 min. More hydrochloric acid (0·05 ml.) was added and the solution again boiled for 5 min. An excess of water (~30 ml.) was added to the solution, which was kept at 0° for 2 hr. The off-white crystalline product was filtered off and washed well with water and then with 1 : 1 ethanol : water and finally vacuum-dried giving a pale grey, crystalline solid (0·163 g., 98·7%) containing gold and chlorine and having an infrared spectrum identical with that of authentic Ph_3PAuCl.

Addition of Hydrochloric Acid to Triphenylphosphinegold–Tetracarbonylcobalt.—This gave a mixture containing decomposition products and some Ph_3PAuCl.

Action of Iodine on Triphenylphosphinegold–Pentacarbonylmanganese.—Conductometric titration of the complex in 1,2-dimethoxyethane with 0·01M-iodine in methanol showed that the first mol. of iodine gave a yellow solution containing non-conductors only. A second mol. of iodine gave rise to a strong electrolyte and additional iodine had no effect on the conductance of the solution. The solution obtained by addition of one mol. of iodine was concentrated, and excess of methanol was added to produce white needles of $(C_6H_5)_3PAuI$, identified by comparison with an authentic sample.

In a separate experiment, one mol. of iodine was added to a chloroform solution of the complex and an infrared spectrum of the solution was obtained. Three bands were observed in the 5 mμ region which were identical with those given by an authentic sample of $IMn(CO)_5$. Addition of a second mol. of iodine produced no change in this region of the infrared spectrum, showing that $IMn(CO)_5$ was unchanged and that the rise in conductance was due to a gold compound, presumably Ph_3PAuI_3 or its decomposition product.[32] This was confirmed by titrating Ph_3PAuI in 1,2-dimethoxyethane with iodine in methanol and observing a similar increase in conductance.

Action of Iodine on Bis(triphenylphosphinegold)–Tetracarbonyliron.—Conductometric titration of this complex was performed as described above. The first 1·1—1·2 mol. of iodine (the end point was not sharp) gave a non-conducting solution and $(C_6H_5)_3PAuI$ was isolated from the solution. Further addition of iodine gave a conducting solution. $(C_6H_5)_3PAuI$ was again found in the solution resulting from the addition of 1·1 mol. of iodine.

In a separate experiment, a solution of iodine in chloroform was added to the solution of the complex in chloroform, and the infrared spectrum of the resulting solution was recorded. After the addition of one mol. of iodine the major bands (accounting for 95% of the intensity) in the 5 mμ region were identical with those given by an authentic sample of pentacarbonyliron. A second mol. of iodine removed the pentacarbonyliron bands completely and gave bands at 2070, 2090, and 2136 $cm.^{-1}$, characteristic of di-iodotetracarbonyliron in chloroform.[36]

Addition of Iodine to Triphenylphosphinegold–Tetracarbonylcobalt.—Conductometric titration of this complex was performed as described above. The first 0·5 mol. of iodine gave a non-conducting solution [the conductance rose upon the addition of iodine and then slowly (about 1 min.) dropped back to an equilibrium value]. Further addition of iodine gave a conducting solution. $(C_6H_5)_3PAuI$ was isolated from the solution obtained by the addition of 0·5 mol. of iodine to the complex.

A solution of iodine in chloroform was added to a solution of the complex in chloroform, and the infrared spectra of the resulting solution were recorded. After the addition of 0·5 mol. of iodine, the spectrum was very complicated and could not be satisfactorily assigned. Bands were observed at 1837, 1872, 1905, 1953, 1980, 2023, 2043, and 2070 $cm.^{-1}$. The green solution was unstable and decomposed with the evolution of a gas and the precipitation of a sludge. Addition of 1·5 mol. of iodine gave a dark green solution which rapidly changed to a green-blue solution with evolution of gas. No bands were observed in the spectrum which could be attributed to a C–O stretch of a metal carbonyl.

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[36] Barraclough, Lewis, and Nyholm, *J.*, 1961, 2582.