618. *Metal–Metal Bonds. Part II.*[1] *Further Complexes containing Gold–Manganese Bonds*

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Further complexes containing gold–manganese bonds, LAu–Mn(CO)$_5$ [L = (PhO)$_3$P, (p-MeO·C$_6$H$_4$)$_3$P, (p-Me·C$_6$H$_4$)$_3$P, Ph$_3$As, and Ph$_3$Sb] and Ph$_3$PAu–Mn(CO)$_4$L′ [L′ = Ph$_3$P, (PhO)$_3$P, Ph$_3$As, and py], are described. Their infrared spectra in the carbonyl region have been assigned. For the complexes LAu–Mn(CO)$_5$ the force constants for the CO groups have been calculated on the basis of the Cotton model, and the results interpreted in terms of the effect of substitution on the metal–carbon π-bonding in the systems.

IN Part I of this Series,[1] a complex containing a gold–manganese bond, Ph$_3$PAu–Mn(CO)$_5$, was prepared by the following reaction:

$$\mathrm{Ph_3PAuCl + Na[Mn(CO)_5] \longrightarrow Ph_3PAu{-}Mn(CO)_5 + NaCl}$$

We have extended this study to test the more general application of this reaction, to study the influence on the infrared-active C–O stretching vibrations of changes in the ligand attached to gold, and to investigate the reactions of the typical compound Ph$_3$PAu–Mn(CO)$_5$ with a number of ligands.

The complexes LAuCl [L = (PhO)$_3$P, (p-MeO·C$_6$H$_4$)$_3$P, Ph$_3$As, and Ph$_3$Sb] react readily with the salt Na[Mn(CO)$_5$] in tetrahydrofuran to yield the products LAu–Mn(CO)$_5$, whose physical properties are listed in Table 1. Clearly, they are compounds containing gold–manganese bonds, being diamagnetic, non-electrolytes in nitrobenzene, and monomeric in benzene or acetone. Their general stability towards air and moisture is similar to that

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[1] Part I, E. Coffey, J. Lewis, and R. S. Nyholm, *J.*, 1964, 1741.

TABLE 1

	Complex	M. p. (decomp.)	Conductance in $PhNO_2$		Mol. wt. and solvent	
			Λ_M (ohm^{-1} cm.^{2})	Concn. (10^3M)	Found	Calc.
(I)	$(PhO)_3PAuMn(CO)_5$	68°	0·19	1·0	677 (benzene)	702
(II)	$(p\text{-}MeO{\cdot}C_6H_4)_3PAuMn(CO)_5$	132	0·18	5·45	739 (benzene)	744
(III)	$(p\text{-}Me{\cdot}C_6H_4)_3PAuMn(CO)_5$	179	0·22	1·4	661 (benzene)	696
(IV)	$Ph_3AsAuMn(CO)_5$	64	0·15	2·6	653 (benzene)	698
(V)	$Ph_3SbAuMn(CO)_5$	—	—	—	702 (benzene)	745
(VI)	$Ph_3PAuMn(CO)_4Ph_3P$	140	0·09	2·25	841 (benzene)	887
(VII)	$Ph_3PAuMn(CO)_4(PhO)_3P$	90	0·12	1·9	916 (benzene)	936
(VIII)	$Ph_3PAuMn(CO)_4Ph_3As$	135	0·13	0·97	903 (acetone)	932
(IX)	$Ph_3PAuMn(CO)_4py$	121	0·12	1·6	681 (benzene)	705

Compounds (I)—(V) are brown, (VI) is yellow-brown, and (VII)—(IX) are light brown

shown by $Ph_3PAu{-}Mn(CO)_5$, although the compounds containing Ph_3As and Ph_3Sb appear to be less stable. Their infrared spectra in the C–O stretching region are compared in Table 2 with those of structurally similar compounds. The local symmetry around the manganese must be nearly C_{4v}, so that in principle three infrared-active C–O stretching vibrations are expected ($2A_1 + E$). A B_1 mode, which also occurs, should be infrared-inactive, but it is possible that the symmetry of the molecule may be lowered sufficiently by the ligand on the gold atom to allow this vibration to become active, albeit weakly so. The observed spectra show one very strong band, and a weaker one at higher frequencies. In some spectra there is a shoulder on the high-frequency side of the strong band, whilst one shows a third band at lower frequencies. The strong band is readily assigned to the E vibration. If the symmetry is lower than C_{4v} then this vibration should not be degenerate; the shoulder on the strong band might be due to splitting of the two components, but we consider that this is unlikely, the separation of the shoulder from the main band being far too large. In order to assign the other bands in the spectra, and also to further our understanding of the π-bonding in these systems, we have carried out force-constant calculations using the models recently proposed by Cotton and Kraihenzel.[2] The results are favourable only on the assignment of the band above 2000 cm.$^{-1}$ to that A_1 mode involving mostly vibration of the four carbonyl groups *cis* to the gold atom, the shoulder on the E absorption as the B_1 vibration and the second A_1 frequency to be coincident with, and masked by, the E frequency. If the shoulder is assigned to the second A_1 vibration the stretching force-constant of the carbonyl group *trans* to the gold turns out to be greater than that of the *cis*-groups. In the case of the *p*-tolyl derivative, the only reasonable set of force constants is obtained when the two weaker bands are assigned to A_1 vibrations. The results of the force-constant calculations are shown in Table 3. The terminology is such that k_1 is the force constant of the CO group *trans* to the gold, k_2 that of the *cis*-groups, and k_i the generalised interaction constant. Several sets of answers may be obtained from the observed

TABLE 2

Infrared spectra (CO stretching vibrations, cm.$^{-1}$) of complexes $LAu{-}Mn(CO)_5$ in chloroform solution

Complex		A_1 (a)	A_1 (b)	B_1	E
(I)	See Table 1	2070ms	(1965)	1990sh	1965vs
(II)		2062ms	(1961)	2000sh	1961vs
(III)		2061ms	1913w	—	1992vs
(IV)		2062ms	(1961)	—	1961vs
(V)		2030ms	(1927)	—	1927vs
	$Mn(CO)_5Cl$ *	2148, 2138	2002, 1999	—	2063, 2054
	$Mn(CO)_5Br$ *	2144, 2133	2004, 2001	—	2056, 2050
	$Mn(CO)_5I$ *	2133, 2125	2005, 2003	—	2048, 2044
	$Mn_2(CO)_{10}$	2043, 2043	1982, 2012	—	2012 (A), 1982 (B)

* From Cotton and Kraihenzel (ref. 2).

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[2] F. A. Cotton and C. S. Kraihenzel, *J. Amer. Chem. Soc.*, 1962, **84**, 4432; C. S. Kraihenzel and F. A. Cotton, *Inorg. Chem.*, 1963, **2**, 533; F. A. Cotton, *ibid.*, 1964, **3**, 702.

TABLE 3

Force-constants of compounds $LMn(CO)_5$

Compound	k_1	k_2	k_i	ν_B (calc.)
$Ph_3PAuMn(CO)_5$	15·70	16·03	0·25	1994
$(PhO)_3P$	15·84	16·18	0·26	2000
$(p\text{-}Me{\cdot}C_6H_4)_3P$	14·90	16·45	0·18	2017
$(p\text{-}MeO{\cdot}C_6H_4)_3P$	15·71	16·04	0·25	1994
Ph_3As	15·71	16·04	0·25	1994
Ph_3Sb	15·18	15·50	0·25	1960
$ClMn(CO)_5$	16·30	17·66	0·23	2090
$Mn_2(CO)_{10}$ *	(A) 15·91	16·51	0·08	2021
	(B) 16·60, 16·28	16·10, 16·21	0·12, 0·17	1995, 2005

* See also ref. 3.

frequencies, but under the conditions that $k_1 < k_2$ and that $k_i > 0$, a unique set is obtained, and can be obtained only for the assignments given in Table 2 (see ref. 2). Decacarbonyldimanganese has been treated as two independent $Mn(CO)_5$ groups in C_{4v} symmetry, as the correlation with the D_{4d} symmetry of the dimer does not affect infrared activities.

Decacarbonyldimanganese is, however, a little difficult to deal with, as the mutual effect of one half of the molecule on the π-bonding in the other half of the molecule is unpredictable. We may assume that k_i is positive but not that $k_1 < k_2$; a definite assignment of the three strong bands is then not possible. However, as k_i is positive, at least one A_1 vibration must occur at a frequency higher than that of the E vibration, and so the E vibration can be assigned as the middle or the lowest peak [assignments (A) and (B) in Table 2]. The two A_1 vibrations are in any case too close for a realistic mechanical distinction to be made between them.[3]

Table 3 shows that, in the gold–manganese compounds, k_i is constant and higher than in the halides and parent carbonyl, thereby indicating a generally greater amount of π-bonding in these compounds. Values of k_1 and k_2 are low; there appears to be little difference between the arsine and phosphine derivatives, but the lower values for the stibine compound show that here the π-donation to carbon monoxide is stronger.

The *p*-tolyl derivative is anomalous in showing lower coupling than the other compounds, but apparently a strongly preferred back-donation to the *trans-* as opposed to the *cis*-carbonyl groups. There is no obvious explanation for this difference.

Heating of the complex $Ph_3PAu–Mn(CO)_5$ with the ligands (L′)Ph_3P, $(PhO)_3P$, Ph_3As, and py results in the ready formation of the substituted derivatives $Ph_3PAu–Mn(CO)_4L'$, whose properties are listed in Table 1. It has not proved possible to replace more than one carbonyl group, and identical phosphine and arsine derivatives have been prepared starting from the substituted carbonyl anions $[Mn(CO)_4L']^-$. The four carbonyl groups can be disposed around the manganese atom to produce local symmetries of C_{4v} or C_s, showing, respectively, two ($A_1 + E$) and four ($3A' + A''$) infrared-active C–O stretching

TABLE 4

Infrared-active C–O stretching bands (cm.$^{-1}$) of complexes $LAu–Mn(CO)_4L'$ in chloroform solution

Complex		Assignments			
		A' (a)	A' (b)	A' (c)	A''
(VI)	See Table 1	2000ms	1916sh	—	1894vs
(VII)		2016ms	1969sh	—	1923vs
(VIII)		2000ms	1916sh	—	1894vs
(IX)		2000ms	1908sh	—	1887vs
$Mn(CO)_4Ph_3PBr$ *		2100	2024	1962	2010
$Mn(CO)_4Ph_3AsI$ †		2092	—	1965	2016
$Mn(CO)_4Ph_3PCl$ †		2101	—	1965	2016

* See A. G. Osborne and M. H. B. Stiddard, *J.*, 1965, 700. † See R. J. Angelici and F. Basolo, *J. Amer. Chem. Soc.*, 1962, **84**, 2495.

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[3] N. Flitcroft, D. K. Huggins, H. D. Kaesz, *Inorg. Chem.*, 1964, **3**, 1123.

vibrations. Data presented in Table 4 obviously indicate that substitution has occurred *cis* to the metal–metal bond (C_s symmetry), although it is not possible to resolve the fourth band. Although it is not feasible to make assignments with complete assurance, the higher-energy vibration, A'(a), probably involves symmetric stretching of the pair of *trans*-carbonyl groups, and the very strong band almost certainly results from their antisymmetric stretching (A''). The spectra are closely allied to those of the complexes $Mn(CO)_4LX$, except that the bands occur at lower frequencies. Further, the positions of the bands are markedly dependent upon the substituting ligand and are consistent with the generally accepted π-acceptor properties of the latter. The carbonyl replacement reactions of the complex $Ph_3PAu{-}Mn(CO)_5$ show similarities to those of both decacarbonyldimanganese and the halogenocarbonyls. Comparisons are summarised in Table 5.

TABLE 5

Behaviour of complexes $LAu{-}Mn(CO)_5$, $Mn_2(CO)_{10}$, and $Mn(CO)_5X$ towards various ligands

Ligand	$LAu{-}Mn(CO)_5$	$(CO)_5Mn{-}Mn(CO)_5$	$Mn(CO)_5X)$
Phosphines and arsines	Monosubstitution *cis* to Au–Mn bond	Monosubstitution/Mn * *trans* to Mn–Mn bond	Monosubstitution † *cis* to Mn–X bond + Disubstitution § *cis* and *trans* to Mn–X band
Pyridine	Monosubstitution *cis* to Au–Mn bond	Disproportionation to $[Mn\ py_6][Mn(CO)_5]_2$ ‡	

* † See footnotes to Table 4. ‡ See W. Hieber and W. Schropp, *Z. Naturforsch.*, 1960, **15**b, 271. § See E. Abel and G. Wilkinson, *J.*, 1959, 1501.

EXPERIMENTAL

Compounds LAuCl.—Those compounds where L = Ph_3P, Ph_3As, $(p\text{-}Me{\cdot}C_6H_4)_3P$, and $(p\text{-}MeO{\cdot}C_6H_4)_3P$ were prepared according to the method of Levi-Malvano.[4] Others were made as follows.

Chloro(triphenylphosphite)gold(I).—To a solution of chloroauric acid (1·0 g.) in ether (15 ml.) was added, dropwise, trichlorophosphine until the colour of the solution was discharged. Excess of triphenyl phosphite was added, the solvent slowly evaporated, and the white crystalline *product* (1·4 g.) recrystallised from methanol (Found: C, 39·7; H, 2·6; P, 5·8. $C_{18}H_{15}AuClO_3P$ requires C, 39·8; H, 2·8; P, 5·7).

Chloro(triphenylstibine)gold(I).—To a solution of gold(I) chloride (0·5 g.) in ethanol (15 ml.) containing lithium chloride a saturated solution of triphenylstibine in ethanol was added dropwise until the colour of the solution was discharged. The unstable *product*, which separated, was filtered off under nitrogen and used immediately. It decomposes readily to metallic gold and could not be analysed.

Compounds $LAu{-}Mn(CO)_5$.—With the exceptions noted below, these *substances* were prepared exactly as described for $Ph_3PAu{-}Mn(CO)_5$. Slight, but important, variations are as follows. *Compound* $Ph_3AsAu{-}Mn(CO)_5$ was isolated by removing tetrahydrofuran under reduced pressure and recrystallising the residue from light petroleum under nitrogen. *Compound* $Ph_3SbAu{-}Mn(CO)_5$ was isolated by partially removing tetrahydrofuran and precipitating the product with pentane.

Compounds $Ph_3Au{-}Mn(CO)_4L'$.—(*a*) [L′ = Ph_3P, $(PhO)_3P$, Ph_3As, and py]. The complex $Ph_3PAu{-}Mn(CO)_5$ (0·65 g.) and an excess of the ligand (*ca.* 3 equiv.) were heated in a sealed and evacuated tube for 4 hr. at 120°. The *product* (30% yield) was separated from decomposed materials by dissolution in a minimum volume of benzene and reprecipitation with light petroleum.

(*b*) [L′ = Ph_3P, $(PhO)_3P$, and Ph_3As]. To a solution of Ph_3PAuCl (0·5 g.) in tetrahydrofuran (15 ml.) the salt $Na[Mn(CO)_4L']$ [5] (1 equiv.) in the same solvent (25 ml.) was added. After stirring for 15 min., the solution was added to water (100 ml.) and set aside overnight at 0°. The crystals of the *product* which separated (80% yield) were recrystallised from benzene–light petroleum or ethanol–water.

Metal Analyses.—Gold contents were determined by dissolving the complex (0·2 g.) in aqua regia and precipitating the metal with hydrazine. Manganese was determined by the bismuthate method.

[4] A. Levi-Malvano, *Atti Accad. naz. Lincei*, 1908, **17**, 857.

[5] W. Hieber, G. Faulhaber, and F. Theubert, *Z. Naturforsch.*, 1960, **15**b, 326.

	Found (%)					Required (%)				
Complex	C	H	P/N	Au	Mn	C	H	P/N	Au	Mn
(I)	39·2	2·3	4·6	27·75	—	39·3	3·1	4·4	28·0	—
(II)	42·1	3·0	4·5	—	6·9	41·9	2·8	4·2	—	7·3
(III)	44·7	3·3	—	28·0	—	44·8	3·0	4·45	28·3	—
(IV)	40·05	2·2	—	28·0	7·35	39·5	2·1	—	28·2	7·85
(V)	36·12	1·85	—	25·9	—	37·1	2·0	—	26·4	—
(VI)	54·1	3·4	6·9	22·0	—	54·05	3·4	7·0	22·2	—
(VII)	51·1	3·4	6·55	20·6	—	51·3	3·2	6·6	21·1	—
(VIII)	51·0	3·2	3·0	21·0	—	51·5	3·2	3·3	21·1	—
(IX)	45·4	2·7	4·1/1·7	27·8	—	46·0	2·8	4·4/2·0	27·95	—

We are indebted to the Ethyl Corporation for gifts of decacarbonyldimanganese, to E. I. du Pont de Nemours Limited for a maintenance grant to A. S. K., and to the D.S.I.R. for a grant to A. R. M.

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[*Received, December* 11*th*, 1964.]