## Some New Complexes containing Gold-Iron Bonds

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The preparation of the new complexes LAuFe(CO)<sub>3</sub>NO and Ph<sub>3</sub>PAuFe(CO)<sub>2</sub>(NO)L' is reported [L = (MeO)<sub>3</sub>P, Me<sub>3</sub>P, Ph(C<sub>6</sub>H<sub>11</sub>)<sub>2</sub>P, Ph<sub>2</sub>(C<sub>6</sub>H<sub>11</sub>)P, Ph<sub>3</sub>P, (p-ClC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>P, and (p-MeC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>P; L' = (PhO)<sub>3</sub>P, Ph<sub>3</sub>P, and PhEt<sub>2</sub>As]. It is suggested that they are isostructural with Ph<sub>3</sub>PAuCo(CO)<sub>4</sub> with an approximately linear L-Au-Fe-L' system, and trigonal bipyramidal co-ordination about the iron atom. The i.r. spectra of the compounds are consistent with this proposal. In donor solvents LAuFe(CO)<sub>3</sub>NO and Ph<sub>3</sub>PAuFe(CO)<sub>2</sub>(NO)P(OPh)<sub>3</sub> dissociate reversibly to the [Fe(CO)<sub>3</sub>NO]<sup>-</sup> and [Fe(CO)<sub>2</sub>(NO)P(OPh)<sub>3</sub>]<sup>-</sup> ions respectively. Similar behaviour has been observed for Ph<sub>3</sub>PAuFo(CO)<sub>4</sub> but not for Ph<sub>3</sub>PAuFe(CO)<sub>2</sub>(NO)PPh<sub>3</sub>, Ph<sub>3</sub>PAuFe(CO)<sub>2</sub>(NO)AsEt<sub>2</sub>Ph, or Ph<sub>3</sub>PAuFo(CO)<sub>3</sub>PPh<sub>3</sub>.

THE reaction of Ph<sub>3</sub>PAuCl with salts of the  $[Co(CO)_4]^$ ion gives Ph<sub>3</sub>PAuCo(CO)<sub>4</sub>,<sup>1</sup> which contains a goldcobalt bond.<sup>1,2</sup> The substituted derivatives Ph<sub>3</sub>PAu-(CO)<sub>3</sub>L' [L' = Ph<sub>3</sub>P, Bu<sup>n</sup><sub>3</sub>P, and (PhO)<sub>3</sub>P] have also been reported.<sup>3</sup>

Here, the isoelectronic compounds,  $LAuFe(CO)_3NO$ and  $Ph_3PAuFe(CO)_2(NO)L'$  are described  $[L = (MeO)_3P$ ,

<sup>1</sup> C. E. Coffey, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 1964, 1741.

Me<sub>3</sub>P, PhCy<sub>2</sub>P, Ph<sub>2</sub>CyP, Ph<sub>3</sub>P,  $(\notp$ -ClC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>P, and  $(\notp$ -MeC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>P where Cy = cyclohexyl; L' = (PhO)<sub>3</sub>P, Ph<sub>3</sub>P, and AsEt<sub>2</sub>Ph]. Their i.r. spectra and dissociation in donor solvents are reported, discussed, and compared with those of Ph<sub>3</sub>PAuCo(CO)<sub>4</sub> and Ph<sub>3</sub>PAuCo(CO)<sub>3</sub>PPh<sub>3</sub>.

## EXPERIMENTAL

The phosphines  $Me_3P$ ,  $PhCy_2P$ ,  $Ph_2CyP$ ,  $Ph_3P$ ,  $(p-ClC_6H_4)_3P$ , and  $(p-MeC_6H_4)_3P$  were converted into the

<sup>3</sup> L. M. Bower and M. H. B. Stiddard, J. Chem. Soc. (A), 1968, 706.

<sup>&</sup>lt;sup>2</sup> B. T. Kilbourn, T. L. Blundell, and H. M. Powell, Chem. Comm., 1965, 444; J. Chem. Soc. (A), 1971, 1685.

gold(I) complexes LAuCl by reaction with chloroauric acid in cold ethanol.<sup>4</sup> (MeO)<sub>3</sub>PAuCl was obtained by the addition of trichlorophosphine to chloroauric acid in ether. An oil was precipitated. The ether layer was removed, and the oil reacted with and then recrystallized from methanol. The preparations of Ph<sub>3</sub>PAuCo(CO)<sub>4</sub>,<sup>1</sup> Hg{Fe(CO)<sub>3</sub>-NO<sub>2,5,6</sub> and Hg{Fe(CO)<sub>2</sub>(NO)AsEt<sub>2</sub>Ph}<sub>2</sub> <sup>7</sup> have been described.

The following reactions were carried out at room temperature in dried and deoxygenated solvents under an atmosphere of nitrogen. The LAuFe(CO)<sub>s</sub>NO complexes were prepared by the addition of LAuCl (ca. 0.5 g) to a tetrahydrofuran solution of Na[Fe(CO),NO], prepared in situ by the reaction of  $Hg[Fe(CO)_3NO]_2$  (0.3-0.5 g) with sodium amalgam. The products were isolated by removal of the solvent from the reaction mixtures, and purified by recrystallization from pentane. Ph<sub>3</sub>PAuFe-(CO)<sub>2</sub>(NO)AsEt<sub>2</sub>Ph was prepared similarly using Hg[Fe-(CO)<sub>2</sub>(NO)AsEt<sub>2</sub>Ph]<sub>2</sub> in place of Hg[Fe(CO)<sub>3</sub>NO]<sub>2</sub>. Yields were 30-60%.

The complexes  $Ph_3PAuFe(CO)_2(NO)L'$  [L' = (PhO)<sub>3</sub>P, and Ph<sub>3</sub>P] were obtained by the reaction of Ph<sub>3</sub>PAuFe- $(CO)_3NO$  with an excess of the free ligand L' in benzene solution in the dark. Spectroscopic studies showed the reactions to be complete within 30 min. The products The frequencies and relative intensities of absorption bands which lie between 1600 and 2100  $cm^{-1}$  are given in the Table

## RESULTS AND DISCUSSION

The new LAuFe(CO)<sub>2</sub>(NO)L' derivatives  $[L = (MeO)_3$ -P, Me<sub>3</sub>P, PhCy<sub>2</sub>P, Ph<sub>2</sub>CyP, Ph<sub>3</sub>P,  $(p-ClC_6H_4)_3P$ , or  $(p-MeC_6H_4)_3P$  when L' = CO;  $L = Ph_3P$  when L' $= (PhO)_{3}P$  or  $Ph_{3}P$ ] contain gold-iron bonds. All are yellow to red crystalline solids which, with the exception of (MeO)<sub>3</sub>PAuFe(CO)<sub>3</sub>NO and Me<sub>3</sub>PAuFe- $(CO)_aNO$ , are stable in air at room temperature.

In solution, the complexes decompose more or less rapidly, and absorption bands due to  $L'Fe(CO)(NO)_2$ are soon detected in their i.r. spectra. This behaviour is typical of all compounds of the general type XFe-(CO)<sub>2</sub>(NO)L' which we have prepared.<sup>7,8</sup> It severely limits the accessible range of iron carbonyl nitrosyl complexes as compared with the isoelectronic cobalt carbonyl derivatives.

The reactions of both Ph<sub>3</sub>PAuFe(CO)<sub>3</sub>NO and Ph<sub>3</sub>-PAuCo(CO)<sub>4</sub> with Ph<sub>3</sub>P, to give Ph<sub>3</sub>PAuFe(CO)<sub>2</sub>(NO)-PPh<sub>3</sub> and Ph<sub>3</sub>PAuCo(CO)<sub>3</sub>PPh<sub>3</sub> respectively, are rapid.

Melting point, analytical data, and i.r. spectra of some gold compounds  $(1600-2100 \text{ cm}^{-1})$  with relative peak heights in parentheses

		Found (%)			Reqd. (%)				(20)				
Compound «	M.p. (°C) b	Ċ	ъ	N	C	$\tilde{H}$	N	$\nu(NO)$			ν(CO)		
(MeO),PAuFe(CO),NO	50 - 51(d)	14.6	$2 \cdot 0$	2.5	14.7	1.9	2.8	1752 (6.8)	1939 (10)		1973 (5.6)		2036 (9.0)
Me <sub>s</sub> PAuFe(CO) <sub>s</sub> NO	86—88(d)	15.8	1.8	2.9	16.2	$2 \cdot 0$	$3 \cdot 1$	1745 (8·9 <sup>-</sup>	)1930 (8.3)		1963 (3·5)		2031(`10)
PhČy <sub>2</sub> PAuFe(ĆŎ) <sub>3</sub> NO	113 - 115(d)	38.8	4.4	$2 \cdot 2$	39.4	$4 \cdot 2$	$2 \cdot 2$	1742 (6.9)	1924 (7.3)		1960 (3.0)		2030 (10)
Ph <sub>2</sub> CyPAuFe(CO) <sub>2</sub> NO	129—130(d)	39.3	3.4	1.9	39.7	3.3	$2 \cdot 2$	1744 (6.0)	1927 (7.0)		1961 (3·4)		2032 (10)
Ph <sub>3</sub> PAuFe(CO) <sub>3</sub> NO	98—99(d)	<b>4</b> 0·1	$2 \cdot 4$	1.9	40.1	$2 \cdot 4$	$2 \cdot 2$	1745 (6·9)	<b>1929</b> (7·0)		1964 (3·0)		2031 (10)
(p-ClC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> PAuFe- (CO) <sub>2</sub> NO	123—124(d)	$35 \cdot 2$	1.8	1.7	<b>35</b> ·4	1.6	1.9	1749 (5.7)	1931 (6.7)		1967 (2.6)		2035 (10)
(p-MeC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> PAuFe- (CO) <sub>2</sub> NO	125—127(d)	42.5	3.1	1.8	<b>42</b> ·6	3.1	$2 \cdot 1$	1744 (7.1)	<b>1928</b> (7·1)		<b>1962</b> (3·0)		2030 (10)
$Ph_{3}PAuFe(CO)_{2}(NO)-$ P(OPh),	dec. 102	50.3	3.5	1.5	$50 \cdot 2$	3.3	1.5	•1717 (8·6)		1897 (10)		<b>1960 (3·1)</b>	
Ph <sub>3</sub> PAuFe(CO) <sub>2</sub> (NO)- PPh <sub>2</sub>	dec. 80	52.7	3∙6	1.6	$52 \cdot 9$	$3 \cdot 5$	1.6	¢ 1694 (8·8)		1877 (10)		1941 (2.9)	
Ph <sub>3</sub> PAuFe(CO) <sub>2</sub> (NO)- AsEt.Ph	96—98(d)	<b>44</b> ·9	3.9	1.5	<b>44</b> ·4	<b>3</b> ·7	1.7	• 1692 (7·7)		1871 (10)		1937 (2·9)	
Ph,PAuCo(CO),	113-115	<b>41</b> ·7	$2 \cdot 4$		<b>41</b> .5	$2 \cdot 4$			1957 (10)		1988 (5.4)		2055 (9.3)
Ph,PAuCo(CO),PPh,	dec. 159	<b>54</b> ·4	3.7		5 <b>4</b> ·3	3.5		С	( )	1902 (sh)	. ,	1914 (10)	

<sup>a</sup> Cy = cyclohexyl. <sup>b</sup> Measured in sealed tubes, dec. = decomposes without melting; (d) = melts with decomposition. <sup>e</sup> Measured in carbon disulphide solution, the others in heptane.

were isolated by removal of the solvent, and the residue recrystallized from benzene-hexane mixtures; yields were 80% for  $L' = Ph_3P$  and 55% for  $(PhO)_3P$ . Similar reactions with  $L' = Ph_2MeP$  or  $Et_3P$  gave unidentified products which did not contain nitrosyl groups, and Ph<sub>2</sub>MeAs did not react under these conditions.

The reaction between Ph<sub>3</sub>P and Ph<sub>3</sub>PAuCo(CO)<sub>4</sub> was carried out as described for Ph<sub>3</sub>P and Ph<sub>3</sub>PAuFe(CO)<sub>3</sub>NO. It proceeded with equal rapidity.

Melting points and analyses for the complexes are summarised in the Table.

I.r. spectra were obtained as described previously.<sup>7</sup>

4 A. Levi-Malvano, Atti. Accad. naz. Lincei Rend. Classe Sci. fiz. mat. nat., 1908, 17, 857.

<sup>5</sup> W. Hieber and H. Beutner, Z. anorg. Chem., 1963, 320, 101. <sup>6</sup> R. B. King, 'Organometallic Syntheses,' Academic Press, New York, 1965, vol. 1, p. 165.
<sup>7</sup> M. Casey and A. R. Manning, J. Chem. Soc. (A), 1970, 2258.

This compares with the relative inertness of Ph<sub>3</sub>SnFe-(CO)<sub>3</sub>NO,<sup>8</sup> Ph<sub>3</sub>SnCo(CO)<sub>4</sub>, and Ph<sub>3</sub>PAuMn(CO)<sub>5</sub><sup>9</sup> where CO substitution may be effected only by more vigorous reaction conditions (cf. ref. 10).

The i.r. spectra of the LAuFe(CO)<sub>3</sub>NO and Ph<sub>3</sub>AuFe-(CO)<sub>2</sub>(NO)L' compounds between 1600 and 2000 cm<sup>-1</sup> (see Table) are similar to those of the corresponding Ph<sub>3</sub>SnFe(CO)<sub>2</sub>(NO)L',<sup>8</sup> although absorption bands due to the  $\nu(CO)$  and  $\nu(NO)$  vibrations have much lower frequencies for the gold complexes. The spectra are consistent with molecular structures similar to that

 <sup>&</sup>lt;sup>6</sup> M. Casey and A. R. Manning, J. Chem. Soc. (A), 1971, 256.
 <sup>9</sup> A. S. Kasenally, J. Lewis, A. R. Manning, J. R. Miller, R. S. Nyholm, and M. H. B. Stiddard, J. Chem. Soc., 1965, 3407.
 <sup>10</sup> S. Breitschaft and F. Basolo, J. Amer. Chem. Soc., 1966, 88, 2000. 2702.

found for  $Ph_3PAuCo(CO)_4^2$  with approximately linear P-Au-Fe-L' systems and a trigonal bipyramidal distribution of ligands about the iron atoms.<sup>8</sup>

When  $LAuFe(CO)_3NO [L = (MeO)_3P, Me_3P, PhCy_2P]$  $Ph_2CyP$ ,  $Ph_3P$ ,  $(p-ClC_6H_4)_3P$ , or  $(p-MeC_6H_4)_3P$ ] are dissolved in donor solvents, absorption bands due to the  $[Fe(CO)_3NO]^-$  ion are observed at 1648, 1884, and 1986 cm<sup>-1</sup> (acetonitrile solution).<sup>7,8</sup> Similarly,  $[Co(CO)_{4}]^{-}$ . Although  $Ph_3PAuCo(CO)_4$  ionizes to Ph<sub>3</sub>PAuFe(CO)<sub>2</sub>(NO)PPh<sub>3</sub>, Ph<sub>3</sub>PAuFe(CO)<sub>2</sub>(NO)AsEt<sub>2</sub>-Ph, and Ph<sub>3</sub>PAuCo(CO)<sub>3</sub>PPh<sub>3</sub> show no evidence for this type of behaviour, there are three absorption bands in the i.r. spectrum of acetonitrile solutions of Ph<sub>3</sub>PAuFe(CO)<sub>2</sub>(NO)P(OPh)<sub>3</sub> at 1628, 1855, and 1930 cm<sup>-1</sup> whose frequencies and relative intensities suggest that they are due to the  $[Fe(CO)_2(NO)P(OPh)_3]^-$  ion. These ionizations are reversible, and presumably lead to [LAu]<sup>+</sup> as the counter-ions.

Many complexes containing metal-metal bonds, M-M', dissociate in donor solvents to  $[M]^+$  and  $[M']^-$  ions where M and M' contain main group and transition-metal atoms respectively,<sup>7,8,11</sup> *e.g.*  $M = Ph_3Sn$  and

<sup>11</sup> J. M. Burlitch, J. Amer. Chem. Soc., 1969, 91, 4562.

 $M' = Fe(CO)_3NO.^8$  However, the observations reported here describe the first reversible ionic dissociation of a bond between two transition metals. Furthermore, the ionization of Ph<sub>3</sub>PAuFe(CO)<sub>2</sub>(NO)P(OPh)<sub>3</sub> is the first example of such behaviour on the part of a XFe-(CO)<sub>2</sub>(NO)PR<sub>3</sub> complex which we have observed. Normally it is suppressed on replacement of a CO group in XFe(CO)<sub>3</sub>NO derivatives by a phosphine or phosphite ligand.<sup>7,8</sup>

The gold-metal bond in Ph<sub>3</sub>PAuFe(CO)<sub>3</sub>NO ionizes more readily than does that in Ph<sub>3</sub>PAuCo(CO)<sub>4</sub>. The former dissociates completely in acetonitrile, whilst the latter dissociates partially in this solvent and completely in dimethyl sulphoxide solution. Furthermore, we have found that the [Fe(CO)<sub>3</sub>NO]<sup>-</sup> ion fails to react with many transition-metal halide complexes such as  $(\pi$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>Cl which readily undergo halide ion replacements on treatment with [Co(CO)<sub>4</sub>]<sup>-.12,13</sup> This suggests that although the two anions are isoelectronic [Co(CO)<sub>4</sub>]<sup>-</sup> is a stronger nucleophile than [Fe(CO)<sub>3</sub>NO]<sup>-</sup>.

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<sup>12</sup> K. K. Joshi and P. L. Pauson, Z. Naturforsch., 1962, 17b, 565.
 <sup>13</sup> A. R. Manning, J. Chem. Soc. (A), 1971, 2321.