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Structure and Bonding in Gold(I) Compounds. Part 2.† Mössbauer Spectrum of Linear Gold(I) Complexes

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Mössbauer data for a large number of gold(1) complexes are presented. From these data and previously published work it is concluded that: (i) the bonding involves only 6s and 6p orbitals; (ii) π acceptance by ligands from gold is negligible; (iii) the gold atom tends to concentrate s character in bonds to such ligands as phosphines and p character to such as chlorine and cyanide; and (iv) the bonding properties of a ligand may vary considerably. The difficulties that these conclusions bring to the classification of ligands and the correlation with n.q.r. data are discussed.

Two-FOLD linear co-ordination is one of the simplest geometries known for metal complexes, and gold(I) is unusual in forming a large number of such complexes. In this paper we report Mössbauer data for a large number of linear gold(I) complexes, which, taken together with previously published work,¹⁻³ and the n.q.r. data discussed in the previous paper,⁴ afford a considerable insight into the electronic structure of these complexes. The 77 keV ¹⁹⁷Au Mössbauer resonance is very sensitive to chemical environment,[‡] and the complexes studied show a wide variation in quadrupole splitting and isomer shift.¹⁻³

RESULTS AND DISCUSSION

The results and previously published data are given in Tables 1-3.

Two different bonding schemes have been proposed for gold(I) complexes. The Au⁺ ion is formally a $5d^{10}$ ion, and the simpler explanation supposes donation from the ligands into the empty 6s and $6p_z$ orbitals of the gold atom (the z axis being the ligand–gold–ligand axis). An alternative scheme,⁵ involving the formation of two sd_{z^2} hybrid orbitals (one empty, one occupied), supposes

† Part 1 is ref. 4.

‡ Throughout this paper: 1 eV $\approx 1.60 \times 10^{-19}$ J.

- ¹ H. D. Bartunik, W. Potzel, R. L. Mössbauer, and G. Kaindl, Z. Physik, 1970, **240**, 1.
- ² J. S. Charlton and D. I. Nichols, J. Chem. Soc. (A), 1970, 1484.
- ³ M. O. Faltens and D. A. Shirley, J. Chem. Phys., 1970, 53, 4249.

the occupied hybrid to lie in the xy plane, and donation to take place into the empty hybrid directed along the z axis. These two schemes predict different trends for the quadrupole splitting of the gold: the first predicts charge donation into the p_z orbital of a spherical d^{10} ion, giving a negative electric field gradient (e.f.g.) and an increasing quadrupole splitting with increasing σ -donor power of the ligands; the second, by its initial hybridisation, involves partial emptying of the d_{z^2} orbital giving a positive e.f.g. which may be reduced by σ donation from both ligands into the sd_{z^2} hybrid. The second model thus predicts that the quadrupole splitting will decrease with increasing σ -donor power of the ligands. In both models π acceptance can take place from the d_{xz} and d_{yz} orbitals.

The sign of the e.f.g. in K[Au(CN)₂] has recently been found to be negative by single-crystal methods,⁶ and confirmed by pressure studies,⁷ implying the 6s,6p model of binding to be correct. This is supported by the steady increase in quadrupole splitting, ΔE , as the σ -donor power of the ligands increases: e.g. [AuCl₂]⁻, ΔE 6.13; [AuCl(PPh₃)], ΔE 7.72; [AuMe(PPh₃)], ΔE 10.35 mm s⁻¹. The photoelectron spectrum of some isoelectronic and isostructural mercury(II) compounds shows little evidence

⁴ P. G. Jones and A. F. Williams, preceding paper.

L. E. Örgel and J. D. Dunitz, Adv. Inorg. Chem. Radiochem., 1970, 2, 1.
 H. Prosser, F. E. Wagner, G. Wortmann, and G. M. Kalvius,

H. Prosser, F. E. Wagner, G. Wortmann, and G. M. Kalvius,
 Hyperfine Interactions, 1975, 1, 25.
 ⁷ H. Prosser, G. Wortmann, W. B. Holzapfel, and K. Syassen,

⁷ H. Prosser, G. Wortmann, W. B. Holzapfel, and K. Syassen Z. Physik, 1976, **B24** 7.

Mössbauer data for [AuClL] complexes (at liquid-helium temperature)

	•••••P	oravaro	/		
	Sa	ΔE	Г		
Ligand L		mm s ⁻¹		$\chi^{2 b}$	Ref.
Cl-d	1.72	6.13	2.28	396 (390)	
SPh ₂	1.91	6.40	1.87	749 (380)	
$NH(C_{6}H_{11})_{2}$	2.13	6.48	2.00	402 (390)	
PPh ₃ S	2.23	6.37	2.42	403 (390)	
C ₅ H ₅ N	2.29	6.75	3.34	467 (390)	
	2.88	6.4		· · ·	2
SMe ₂	2.44	6.42			2
$C_{8}H_{14}$	2.49	6.31	2.29	425 (390)	
PCl ₃ ^g	2.98	6.60	2.51	363 (389)	
CO	3.06	7.35	2.99	424 (390)	
AsPh ₃	3.10	7.10	1.84	171 (241)	h
	3.10	7.00		()	2
p-MeOC ₆ H ₄ NC	3.30	7.90	2.19	362 (390)	
C ₆ H ₁₁ NC	3.59	8.27	2.09	427 (389)	
PMePh ₂	3.70	7.15	2.05	408 (390)	
PEta	3.79	7.18	1.80	385 (389)	
P(OMe) ₃	3.81	7.06	2.60	482 (390)	
P(OPh) ₃	3.92	7.64	2.16	431 (390)	
PMe ₂ Ph	4.04	7.03	2.51	418 (390)	
PPh ₃	4.05	7.52	2.06	181 (241)	h
-	4.14	7.47		()	2
PhNC	4.10	9.05	3.5	358 (388) ^f	
$P(C_{6}F_{5})Ph_{2}$	4.11	7.87			1
$C(NHC_{6}H_{4}OMe-p)$,	4.22	8.06	2.02	401 (389)	-
$P(C_6H_{11})_3$	4.43	7.59	3.05	502 (391)	
				``'	

For Tables 1–3, errors are ± 0.1 mm s⁻¹ unless otherwise stated.

^a Isomer shift relative to gold metal. ^b The number of degrees of freedom is given in parentheses. ^c Data marked *k* or unreferenced are from this work. ^d [AsPh₄]⁺ counter cation. Bad fit is due to an instrumental error affecting the baseline; the absorption peaks were well fitted. J Poor spectrum; error $\pm 0.2 \text{ mm s}^{-1}$. $^{\circ}X$ -Ray structure shows linear LAuCl: G. J. Arai, Rec. Trav. chim., 1962, **81**, 307 (PCl₃); N. C. Baenziger, W. E. Bennett, and D. M. Soboroff, Acta Cryst., 1976, **B32**, 962 (PPh₃). ^h Data obtained at P.C.M.U., Harwell.

TABLE 2

Mössbauer data for [AuL(PPh₃)]⁺ complexes (at liquid-helium temperature)

	8 "	ΔE	Г		
Ligand L	·	mm s ⁻¹	χ^{2b}	Ref.	
SCN]-	2.28	8.53	2.20	275 (241)	d
I-	2.42	8.3		· · ·	2
$[Au(PPh_3)Fe(CO)_4]^-$	3.68	7.37	2.20	226(241)	d
PPh ₃ O ^e	3.80	6.49	2.40	425 (389)	
Br-	3.94	7.40		. ,	2
$C_{6}H_{4}Me-p$	3.96	7.43	2.12	196 (241)	d
CI-	4.05	7.53	2.06	181 (241)	d
PPh ₃ S ^e	4.25	8.02	2.32	400 (390)	
SMe ₂ ^e	4.44	8.20	2.24	414 (392)	
CO ₂ Me] ⁻	4.48	7.6			2
N ₃]-	4.48	8.4			2
C ₅ H ₅ N ^e	4.55	8.50	2.79	458 (390)	
C ₅ H ₁₀ NH ^e	4.64	8.75	2.17	419 (390) ^J	r
AsPh ₃	4.75	9.16	2.77	701 (349)	
PPh ₃ ^e	5.06	9.43	2.67	413 (392)	
CN]-9	5.08	10.5			2
$C_5H_4Fe(C_5H_5)$] ⁻	6.03	10.22	2.02	226 (241)	d
Me ^{- h}	6.11	10.35		. ,	2

" and b as in Table 1. " Data marked d or unreferenced are from this work. " Data obtained at P.C.M.U., Harwell. " $[PF_6]^-$ counter anion. " Bad fit due to instrumental error affecting the baseline, absorption peaks were well fitted. " X-Ray structure shows linear co-ordination: P. L. Bellon, M. Manassero, and M. Sansoni *Bicerca Sci* 1959 **39** 173. M. Manassero, and M. Sansoni, *Ricerca Sci.*, 1959, **39**, 173. * X-Ray structure of the chloride salt shows linear co-ordination; the chloride has similar Mössbauer parameters (see following paper).

of bonding by the $5d_{z^2}$ orbital.⁸ We cannot completely discount slight participation of the $5d_{z^2}$ orbital in the bonding, but the Mössbauer data suggest it to be greatly inferior to the participation of the $6p_z$ orbital and we shall neglect it in the following discussion. The 'ligandfield ' splitting of the 5d orbitals in $[NBu_4][Au(CN)_2]$ has been estimated as only 3 000-5 000 cm⁻¹ giving further support for our assumptions.9 If the 6s,6p scheme is followed, then increasing σ donation by a ligand into the 6s orbital will increase the value of $|\psi(0)|^2$, and hence the isomer shift, δ , of the gold atom ($\delta R/R$ is positive for

TABLE 3

Mössbauer data for $[AuL_2]^+$ and miscellaneous complexes (at liquid-helium temperature)

	8 a	ΔE	Г		
Ligand L		mm s ⁻¹		$x^{2 b}$	Ref.
C1- d	1.72	6.13	2.28	396 (390)	
PPh ₃ S ^e	2.46	6.82	2.21	426 (390)	
$[N_3]^{-d}$	2.61	6.84			1
etu ^{e, f}	2.77	7.49	2.27	400 (390)	-
C ₅ H ₅ N ^e	3.19	7.32	2.95	517 (390)	g
SMe ₂ ^{e,h}	3.43	7.56	2.80	426 (392)	
AsPh ₃ ^e	3.98	8.45	2.20	505 (390)	g
C ₅ H ₁₀ NH ^e	4.04	7.88	2.49	422 (389)	
[ČN]- <i>i</i>	4.30	10.12		()	1
PMePh2 e, j	4.75	9.69	2.12	183 (190)	
PPh3 e	5.06	9.43	2.67	413 (392)	
PEta	5.40	10.18	2.35	364 (390)	
$P(C_{6}H_{11})_{3}^{c}$	5.44	10.37	2.29	382 (388)	
PMe2Ph	5.48	10.15	2.28	434 (388)	
	Miscell	aneous c	omplexe	s	
[Au(PEt _a)(SMe _a)]+ e	4.46	8.48	2.10	364 (388)	
$[Au{P(C_6H_{11})_3}(SCN)]$	4.52	8.22	1.92	211 (241)	k

" and b as in Table 1. " Data marked k or unreferenced are from this work. d [AsPh₄]⁺ counter cation. e [PF₆]⁻ counter ion. ${}^{f}X$ -Ray structure of the chloride salt shows linear coordination; the chloride has similar Mössbauer parameters (see following paper). "Bad fit due to an instrumental error affecting the baseline; the absorption peaks were well fitted. ^h Poor spectrum; error ± 0.2 mm s⁻¹. ⁱ K⁺ counter cation. X-Ray structure shows linear co-ordination: A. Rosenzweig and D. T. Cromer, Acta Cryst., 1959, 12, 709. JX-Ray structure shows linear co-ordination; J. J. Guy, P. G. Jones, and G. M. Sheldrick, Acta Cryst., 1976, B32, 1937. * Data measured at P.C.M.U., Harwell.

 $^{197}\mathrm{Au}),$ at the same time as the e.f.g. is increased by σ donation into the $6p_z$. A plot of isomer shift against quadrupole splitting is roughly linear confirming our assumptions; this relation was first noted by Faltens and Shirley 3 for AuX compounds, but is equally valid for the large number of [AuLL']⁺ complexes discussed here. No deviation from the plot is noted for positively or negatively charged complexes, implying lattice effects to be unimportant.

An Additive Model.—The possibility of deriving a set of partial centre shifts (p.c.s.s) and partial quadrupole splitting (p.q.s.) parameters for the prediction of the isomer shifts and quadrupole splittings of other compounds is well established for low-spin iron(II) ¹⁰ and for tin(IV) compounds.¹¹ It is possible to derive similar

⁸ P. Burroughs, S. Evans, A. Hamnett, A. F. Orchard, and N. V. Richardson, J.C.S. Chem. Comm., 1974, 921.
⁹ W. R. Mason, J. Amer. Chem. Soc., 1976, 98, 5182.
¹⁰ G. M. Bancroft and E. T. Libbey, J.C.S. Dalton, 1973, 2103.
¹¹ M. G. Clark, A. G. Maddock, and R. H. Platt, J.C.S. Dalton,

1972, 281.

values for ligands bonded to Au^T: for example, from $[AuCl_2]^-$ (ΔE 6.13 mm s⁻¹), p.q.s.(Cl⁻) = 1.53 mm s⁻¹. It is necessary to choose an arbitrary zero for the p.c.s. scale, and we may take p.c.s.(Cl⁻) = 0, giving p.c.s.-(PPh₃) = 2.36 mm s⁻¹ and so on.

It is possible to derive partial Mössbauer parameters from any of Tables 1, 2, or 3; the values obtained vary quite considerably according to the table used, throwing great doubts on the validity of the additive model. Using values taken from Table 3 (where the two ligands



FIGURE 1 Gold-197 Mössbauer spectrum of [Au(PPh₃S)₂][PF₆]

present are the same), the root-mean-square differences observed and calculated values are (for 16 complexes) 0.42 mm s⁻¹ (chemical shift) and 0.51 mm s⁻¹ (quadrupole splitting). Given the greater absolute magnitude of the ¹⁹⁷Au chemical shifts and quadrupole splittings compared with results for ⁵⁷Fe and ¹¹⁹Sn, this represents reasonable agreement by the standards of the additive model, and is a great deal better than the results for octahedral iridium(III) complexes.¹² However, the large range of chemical shifts and quadrupole splittings shown by these gold(I) complexes enables us to identify systematic failings in the additive model. Thus it is noticed that p.c.s. and p.q.s. values derived from Table 1 ([AuClL] complexes) overestimate the chemical shift, and underestimate the quadrupole splitting, while the reverse is true for those values derived from Table 2 {[AuL- (PPh_3)]⁺ complexes}. There are three possible causes of this breakdown of the model: (a) extensive π bonding breaking down the localisation; (b) a decrease in ligand strength as the *trans* ligand increases in strength; and (c) variable hybridisation of the gold atom.

 π -Bonding Effects.—There is no evidence that π bonding plays any great part in the bonding of these complexes. If the $5d_{z^2}$ orbital is taken to be too low in energy to make a significant contribution to bonding, then it is not unreasonable to assume that the $5d_{xz}$ and

 $5d_{yz}$ orbitals are also non-bonding. Further support for this comes from a p.c.s.-p.q.s. plot (Figure 2). The p.c.s. and p.q.s. values may be related to the ligand bonding properties: σ donation will increase the occupation of the 6s and $6p_z$ orbitals, increasing the p.c.s. by the first, and the p.q.s. by the second. (Any screening of the 6s by the $6p_z$ will be at most a secondary effect.*) π Acceptance by the ligand will deplete the $5d_{xz}$ and $5d_{yz}$ orbital populations, and will increase the p.c.s. (by reducing screening), and decrease the p.q.s. (by depletion of charge along the z axis). We thus arrive at: p.c.s. $\infty(\sigma + \pi)$; p.q.s. $\infty(\sigma - \pi)$. A plot of p.c.s. against p.q.s. values (Figure 2) would thus be expected to show σ donors on a straight line and π acceptors just above it. In fact, most ligands lie close to the line, the phosphines slightly above it, but ligands generally thought to be strong π acceptors such as CO and the isocyanides lie below the line, contrary to the model found to work well for Fe^{II}.¹⁰

Generally, the effects of π bonding would be expected to be shown up by rather low quadrupole splittings for a given isomer shift, but this is not found even with ligands which might be expected to show strong acceptance (such



FIGURE 2 Partial centre shift plotted against partial quadrupole splitting. The values were derived from [AuClL] data to give the maximum number of points. The line is a least-squares fit; p.c.s.(Cl⁻) was taken to be zero. R = Aryl

as cyclo-octene, PCl₃, and CO). Mössbauer spectroscopy gives no evidence for extensive π bonding in these complexes, and this is supported by the high CO stretching frequency of [Au(CO)Cl] (2 158 cm⁻¹).¹⁴

Decrease in Donor Strength of the Ligand.—The possible variation of ligand strength is shown by the n.q.r. results in the previous paper,⁴ where the amount of charge donated by the chloride ligand decreases as the *trans*

^{*} For iodine the screening of the 5s orbital by the 5p is ca. $7\%.^{13}$ A theoretical estimate of the effect for gold is $5\%.^{1}$

 $^{^{12}}$ A. F. Williams, G. C. H. Jones, and A. G. Maddock, J.C.S. Dalton, 1975, 1592.

¹³ N. N. Greenwood and T. C. Gibb, 'Mössbauer Spectroscopy,' Chapman and Hall, London, 1971, ch. 15.

¹⁴ D. B. Dell'Amico and F. Calderazzo, *Gazzetta*, 1973, 103, 1099.

ligand increases in strength. This phenomenon will clearly prejudice the accuracy of the additive model, but would affect quadrupole splitting and isomer shift equally, causing both to fall below calculated values when both ligands present are strong. This would



FIGURE 3 Plots of quadrupole splitting against isomer shift for (a) [AuClL] and (b) $[AuL(PPh_3)]^+$ showing the very different gradients of the regression lines

explain why p.c.s. values derived from [AuClL] overestimate the isomer shift when L is *trans* to a strong ligand such as PPh₃; it does not explain why the p.q.s. values derived from [AuClL] systematically *underestimate* the quadrupole splittings in these complexes. While the variation in strength of a given ligand is one factor in the failure of the additive model, it is clearly not the only factor involved.

¹⁵ H. A. Bent, Chem. Rev., 1961, 61, 275.

Variable Hybridisation of the Gold Atom.-It was mentioned above that a plot of δ against ΔE should be approximately linear; if separate plots for [AuClL] and $[AuL(PPh_3)]^+$ are drawn (Figure 3) a considerable difference in the gradients is found. For $[AuL(PPh_2)]^+$ the quadrupole splitting rises much more steeply with δ than for [AuClL]. This seems to imply that the effect of changing L in $[AuL(PPh_{a})]^{+}$ is to change the occupation of the $6p_z$ orbital rather than the 6s, while for [AuClL] it is the occupation of the 6s which changes more. This is in complete accord with Bent's rule 15 that the maximum s character is found in the bond to the least electronegative element: for [AuL(PPh₃)]⁺ the phosphine bonds strongly to the gold 6s orbital and the Au-L bond has mainly $6p_z$ character; thus the quadrupole splitting is more affected than the isomer shift on

TABLE 4

Gold-phosphorus bond-length data (Å)

Complex	trans-Ligand	Au-P	Ref.
[AuCl(PPh ₃)]	C1	2.335(3)	a
$[Au(C_{6}F_{5})(PPh_{3})]$	$C_{6}F_{5}$	2.27 (1)	ь
[Au(CN)(PPh ₃)]	CŇ	2.27 (1)	С
[AuMe(PPh _a)]	Me	2.279(8)	d
$[Au(PMePh_2)_2][PF_6]$	$PMePh_{2}$	2.316(4)	е
$[Au{P(C_{6}H_{11})_{3}}_{2}][SCN]$	$P(C_{6}H_{11})_{3}$	2.30(1)	f
		2.31(1)	-

^a Linear LAuCl: G. J. Arai, Rec. Trav. chim., 1962, **81**, 307 (PCl₃); N. C. Baenziger, W. E. Bennett, and D. M. Soboroff, Acta Cryst., 1976, **B32**, 962 (PPh₃). ^b R. W. Baker and P. J. Pauling, J.C.S. Dalton, 1972, 2264. ^e Linear co-ordination: P. L. Bellon, M. Manassero, and M. Sansoni, Ricerca Sci., 1959, **39**, 173. ^e X-Ray structure shows linear co-ordination; P. D. Gavens, J. J. Guy, M. J. Mays, and G. M. Sheldrick, Acta Cryst., 1977, **B32**, 137. ^e Linear co-ordination: J. J. Guy, P. G. Jones, and G. M. Sheldrick, Acta Cryst., 1976, **B32**, 1937. ^f Two co-ordinate: J. A. Muir and M. M. Muir, unpublished work.

changing L. The tendency of phosphorus to bond with s orbitals has also been noted in ³¹P n.m.r. studies.¹⁶

There is thus a variation in the hybridisation of the gold atom. The systematic failings of the additive model can all be explained if this is taken into account. Chlorine is the most electronegative ligand with which we are concerned here, and is the least strongly bonded with the 6s orbital. In complexes of the type [AuClL] the ligand L will tend to bond more with the 6s than the 6ϕ orbital than is normal, and consequently will have a higher p.c.s. and lower p.q.s. than would normally be expected, as was remarked above. It should be noted that this differential hybridisation is a much smaller effect than that produced by the change of ligand: even if triphenylphosphine shows a greater tendency to bond with the 6s orbital than chlorine, it is still a much stronger donor into the $6\phi_z$ orbital.

Such bond-length data as are available (Table 4) tend to confirm this interpretation: there is an appreciable lengthening of the Au-P bond as the strength of the *trans* ligand increases. It is not possible to distinguish the effects of (i) the weakening of ligand strength as the

¹⁶ J. F. Nixon and A. Pidcock, Ann. Rev. N.M.R. Spectroscopy, 1969, 2, 345.

trans influence increases, and (ii) the rehybridisation. However, the increase in Au-P length from [AuMe-(PPh₃)] to the two bis(phosphine) complexes is probably a hybridisation effect (less *s* character implying a longer bond ^{15,17}) as there is no great change in *trans*-ligand strength.

Ligand Strengths.—As mentioned above, it is not possible to discuss the finer differences between ligands, but one or two general points stand out.

(1) σ -Donor power. The methyl and cyanide groups are the strongest σ donors, and appear to be much stronger donors than the p-tolyl or σ -bonded ferrocenyl moieties. The carbene complex falls between these two sets of organic ligands. Of the neutral donors, the phosphines and phosphites appear to be strongest, as expected for a class B metal. This contrasts with iron(II) complexes, where CO and the isocyanides are the strongest ligands. Their relative weakness for Au^I may be due regression line of δ against ΔE . We suspect this to be due to a non-linear geometry in these complexes (see following paper) but a structural determination is necessary to resolve this.

Correlation with ³⁵Cl N.Q.R. Data for [AuClL] Complexes. —There is no close correlation between ¹⁹⁷Au Mössbauer data discussed here and the chlorine n.q.r. data discussed earlier.⁴ The chlorine n.q.r. signal decreases in energy as the *trans* ligand donates an increasing amount of charge to the gold atom. The Mössbauer data reflect not only this effect, but also the rehybridisation of the metal-ligand bonds. Both techniques suggest phosphines to be the strongest neutral ligands, but otherwise only roughly follow each others' trends.

The temperature variation of the n.q.r. frequency correlates well with the π -bonding powers of the *trans* ligand, yet the Mössbauer data suggest no significant π interactions affecting the gold atom. Two possible

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Yields and analytical data (%)

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	Analysis								
	Calc.			Found					
Complex ·	C	Н	N	P	C	н	N	P	Yield
[AuCl(SPh ₂)]	34.4	2.4			35.0	2.5			76
[AuCl{NH(CeH11)}]	34.8	5.6	3.4		34.9	5.5	3.4		91
Au(PPh _a)(PPh _a O)[[PF _a]	49.0	3.4			48.2	3.5			85
[Au(PPh ₃)(PPh ₃ S)][PF ₆]	48.1	3.4			47.1	3.5			89
Au (PPha) (SMea) [PF6]	36.1	3.2			35.0	3.3			96
$[Au(C_5H_5N)(PPh_3)][PF_6]$	40.4	3.0	2.1	9.1	40.1	3.2	2.2	9.1	53
[Au(NHČ ₅ H ₁₀)(PPh ₃)][PF ₆]	40.1	3.8	2.0	9.0	40.3	3.9	1.9	8.9	74
[Au(AsPh _a)(PPh _a)][PF ₆]	47.5	3.3			47.7	3.5			90
[Au(PPh ₃ S) ₂][PF ₆]	46.5	3.3			46.3	3.3			91
[Au(etu)][PF6]	13.2	2.2	10.3		13.2	2.1	10.2		63
Au(C,H,N),[PF,]	24.0	2.0	5.6		24.7	2.1	6.2		78
Au (SMe ₂), [PF ₄]	10.3	2.6			10.4	2.6			28
[Au(AsPh ₃) ₃][PF ₆]	45.3	3.2			45.1	3.3			98
[Au(PMePh,),][PF,]	42.1	3.5			42.2	3.6			76
[Au(PPh,),][PF,]	50.2	3.5			49.7	3.5			85
Au (PEta),][PFa]	24.9	5.2		16.1	25.5	5.0		15.9	57
$[Au \{P(C_{e}H_{1})_{a}\}_{a}][PF_{e}]$	47.9	7.4			48.7	7.3			71
[Au(PMe,Ph),][PF,]	31.1	3.6			31.3	3.6			76
$[Au(PEt_3)(SMe_2)][PF_6]$	18.4	4.1		11.9	18.3	4.0		12.4	81

to the absence of any π acceptance weakening their σ -donor powers.

(2) Tendency to s or p bonding. A qualitative measure of the tendency to s or p bonding may be obtained for certain ligands. The complex K[Au(CN)₂] has a lower isomer shift but a larger quadrupole splitting than [Au(PPh₃)₂][PF₆] implying the cyanide ion to be a stronger donor into the $6p_z$ orbital than PPh₃, while PPh₃ donates more strongly into the 6s. Similar reasoning, or the deviation from the p.c.s.-p.q.s. plot, suggests that the isocyanides and carbon monoxide are '*p*-type' ligands, while the sulphur and nitrogen ligands studied show no strong preference.

Finally we notice that the two complexes $[AuI(PPh_3)]$ and $[Au(PPh_3)(SCN)]$ have abnormally low isomer shifts and high quadrupole splittings: there is no obvious reason for this, and the related complex $[Au\{P(C_6H_{11})_3\}$ -(SCN)] has Mössbauer parameters much closer to the

 17 C. A. Coulson, 'Valence,' Oxford University Press, 1961, ch. 8.

solutions to this problem are: (i) the fallacy of the temperature-coefficient argument; and $(ii) \pi$ donation by the chlorine to the *trans* ligand involving no substantial transfer of charge to the gold. We feel inclined to accept the second solution which provides another reason for the relatively poor correlation of ν_{Cl} with the Mössbauer data, but it is difficult to estimate the sensitivity of $\partial \nu / \partial T$ to this form of π bonding.

Conclusions.—The combined Mössbauer and n.q.r. data show: (1) a change in the donor powers of a ligand dependent on the other ligands bonded to the central metal atom; (2) a variation in the hybridisation of the central metal atom which tends to concentrate more or less s character in particular metal-ligand bonds. The latter observation is in agreement with Syrkin's theory of the trans influence ¹⁸ which assigned more s character to the bond with a ligand with a high trans influence.

¹⁸ Y. Y. Syrkin, Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk, 1948, 69; T. G. Appleton, H. C. Clark, and L. E. Manzer, Co-ordination Chem. Rev., 1975, 10, 335.

Although the two effects mentioned above are smaller in magnitude than the most extreme changes in ligand possible (for example from chloride to phosphine), they are sufficiently large to swamp the finer differences between similar ligands (such as phosphines and phosphites). The classification of ligands seems to depend on: (a) the property being measured (e.g. ³⁵Cl n.q.r. data cf. Mössbauer data); (b) the other ligands present (e.g. as shown by the failure of additive models); and (c) the central metal atom (e.g. the variation of n.q.r.results from Pt^{II} to Au^I; the different p.c.s.-p.q.s. values found for Fe^{II}, Ir^{III}, and Au^I). These problems appear to be particularly important in gold(I) chemistry.

EXPERIMENTAL

Source of Complexes.—The complexes [Au(CO)Cl],14 $[Au\{C(NHC_6H_4OMe-p)_2\}Cl],^{19}$ $[Au(C_8H_{14})Cl],^{20}$ $[Au(PPh_3)-$ (SCN)],²¹ [Au{P(C₆H₁₁)₃}(SCN)],²² [{Au(PPh₃)}₂Fe(CO)₄],²³ $[Au(C_{6}H_{4}Me-p)(PPh_{3})],^{24}$ $[(H_{4}C_{5})Fe(C_{5}H_{4})Au(PPh_{3})],^{25}$ [Au- $Cl(PMe_2Ph)]$,²⁶ [AuCl(PMePh₂)],²⁶ and [Au(C₅H₁₀NH)₂]- $[PF_6]^{27}$ were made by literature methods. The complexes [AuClL] were prepared as described in ref. 4 together with the following variations.

 $[AuCl{NH(C_6H_{11})_2}]$. Dicyclohexylamine (2 cm³) was added to a solution of [AuCl(SMe₂)] (1.0 g) in chloroform (75 cm³). The solution was concentrated in vacuo, and addition of diethyl ether followed by refrigeration gave grey-white crystals which were washed with diethyl ether and dried in vacuo (yield 1.28 g, 91%)

[AuCl(SPh₂)]. The complex [Au(CO)Cl] (0.75 g) was added to a solution of excess of SPh₂ in dichloromethane. The solution was filtered, evaporated in vacuo, and the residue was recrystallised from dichloromethane-diethyl ether to give light brown crystals (0.92 g, 76%).

[AuL(PPh₃)][PF₆] and [AuL₂][PF₆]. The following general method was used. 28 $\,$ A 10% excess of Ag[PF_6] in a few millilitres of dichloromethane was added to a solution of an equimolar mixture of $[AuCl(PPh_3)]$ {for $[AuL(PPh_3)]^+$ } or [AuClL] (for $[AuL_2]^+$) and L. The AgCl was filtered off, the solution concentrated in vacuo, and the product was crystallised by addition of diethyl ether and refrigeration. For

¹⁹ F. Bonati and G. Minghetti, J. Organometallic Chem., 1973, 59, 403. ²⁰ R. Hüttel, H. Reinheimer, and H. Dietl, Chem. Ber., 1966,

99, 462.

²¹ N. J. DeStefano and J. L. Burmeister, Inorg. Chem., 1971, 10, 998.

²² J. Bailey, J. Inorg. Nuclear Chem., 1973, **35**, 1921

²³ E. Coffey, J. Lewis, and R. S. Nyholm, J. Chem. Soc., 1964, 1741.

²⁴ E. G. Perevalova, T. V. Bankora, K. I. Grandberg, and A. N. Nesmeyanov, Doklady Akad. Nauk S.S.S.R., 1972, 206, 1355.

 $[Au(C_5H_5N)(PPh_3)][PF_6]$, acetone was used as solvent and n-pentane as a precipitant. For [Au(PEt₃)(SMe₂)][PF₆], $[AuCl(PEt_3)]$ was treated with SMe₂ and Ag[PF₆] and npentane was used as a precipitant.

 $[Au(etu)_2][PF_6]$. The complex $[Au(etu)_2]Cl \cdot H_2O$ (etu = ethylenethiourea)²⁹ (0.25 g) was dissolved in water-ethanol (7:3) and the stoicheometric amount (0.09 g) of $[NH_4]$ - $[PF_6]$ in water was added. The resulting solution was allowed to stand over P_4O_{10} in a vacuum desiccator for several days, when the product appeared as white needles (0.19 g,63%). Concentrated aqueous solutions of the reagents immediately gave the product as a white powder in 85%yield.

The complexes $[AuLL'][PF_6]$ may be distinguished from equal mixtures of $[AuL_2]^+$ and $[AuL'_2]^+$ salts by their Mössbauer or ³¹P n.m.r. spectra. Phosphorus-31 n.m.r. spectra have in fact shown the existence of such mixtures when L and L' are different phosphines.²⁸ All the complexes gave satisfactory analytical data (Table 5). Many are unstable over a period of days at room temperature, giving a purple colouration due to the formation of gold metal.

Mössbauer Measurements.—All the spectra were recorded on a constant-acceleration spectrometer with source and absorber at liquid-helium temperature. The source was ¹⁹⁷Pt in platinum metal produced by neutron irradiation of a natural platinum foil in a flux of 10^{13} n cm⁻² s⁻¹ for 48 h at the HERALD reactor, Aldermaston. The 77 keV y-rays were detected with a Ge(Li) detector enabling resolution from the X-rays. Absorptions, using $ca. 100 \text{ mg cm}^{-2}$ of gold in the samples, were between 1 and 4%. The spectra were fitted with Lorentzian lineshapes using the leastsquares fitting program of Stone; 30 the linewidths and areas of the quadrupole doublets were constrained to be equal (relaxing this constraint had no effect on line positions). Only [AuCl(PCl₃)] showed any asymmetry of intensity in the doublets. A few of the Mössbauer measurements were repeated, and agreed with the previous results within experimental error.

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