Gold-197 Mössbauer and ^{31}P-{^{1}H} Nuclear Magnetic Resonance Spectroscopic Studies on Gold(I) Complexes with Tertiary Phosphines

Ali K. H. Al-Sa'ady, Charles A. McAuliffe, Karen Moss, R. V. (' Dick ') Parish,* and Roy Fields
Department of Chemistry, The University of Manchester Institute of Science and Technology, Manchester M60 1QD

Further studies on solutions of [AuXL] + L and [AuL_2]BPh_4 + L (X = Cl or I; L = tertiary phosphine) show that for L = $PBu^n{}_2Ph$ or $PPr^i{}_2Ph$, no more than three ligands can be co-ordinated to the gold atom, while for L = $PPr^n{}_2Ph$, PEt_2Ph, $PMePh_2$, or PMe_2Ph, four ligands can be co-ordinated. However, for L = PMe_2Ph the tris(ligand) complex is not observed. There is some evidence for association of the halide with [AuL_2]$^+$ for L = $PPr^n{}_2Ph$. Gold-197 Mössbauer data are reported for a range of complexes of types [AuXL] and [AuL_2]Y (X = Cl or I, Y = BPh_4 or ClO_4), which are consistent with values for related compounds. The former show the curious trend that the isomer shift and quadrupole splitting are lower for X = I than for X = Cl. The four-co-ordinate complexes [AuL_4]BPh_4 (L = PMe_2Ph or $PMePh_2$) follow previous trends, and the quadrupole splitting of [AuCl(PPh_3)$_3$] is consistent with the known distorted tetrahedral structure.

Previous studies in this laboratory have shown that in solution the formation of the complexes [AuL_n]$^+$ (n = 3 or 4; L= tertiary phosphine) is dependent on the cone angle of the ligand.[1] We now present data for the homologous series of ligands PR_2Ph (R = Me, Et, Pr^n, Pr^i, or Bu^n) which further exemplify these trends. Gold-197 Mössbauer spectroscopic data for some new two- and four-co-ordinate complexes of these ligands are also given.

Results and Discussion

Solution Studies.—Solutions of the complexes [AuClL] were treated with aliquots of the appropriate ligand. At room temperature, rapid exchange gave only single, average signals. At 180—200 K, well resolved spectra were obtained, showing the co-ordination chemical shifts (c.c.s.) listed in Table 1. The general trends are similar to those noted previously:[1] the c.c.s. values lie in the order [AuClL] < [AuL_2]$^+$ > [AuL_3]$^+$ > [AuL_4]$^+$.

The data for L = PMe_2Ph agree with those reported earlier,[2] except that the species with c.c.s. 23.2 p.p.m. is now assigned as the tetrakis(ligand) complex, [Au(PMe_2Ph)$_4$]$^+$. This assignment is supported by direct observation of a single resonance, at the same c.c.s., for [Au(PMe_2Ph)$_4$]BPh_4; there was no indication of dissociation. Addition of two or more molar equivalents of the ligand to a solution of [Au(PMe_2Ph)$_2$]BPh_4 gave only the resonances of [Au(PMe_2Ph)$_4$]$^+$ and the free ligand. In this system, the tris(ligand) complex is clearly unstable to disproportionation.

For L = $PPr^i{}_2Ph$ or $PBu^n{}_2Ph$, only three species could be detected. At Au : L = 1 : 2.5, two broad signals were obtained, one close to that of [AuL_2]$^+$, the other with lower c.c.s. The shape and slight shift of the spectra indicate some exchange even at 180 K. On raising Au : L to 1 : 3.5, the spectrum sharpened, showing the high-field signal and the free ligand. For these ligands, therefore, the tris complex is the highest formed. This behaviour is similar to that reported[1] for L = P(C_6H_{11})Ph_2. Correlations have been made between the maximum number of ligands bound to gold(I), palladium(0), or platinum(0) and the cone angle of the ligand.[1] The cone angle for $PPr^i{}_2Ph$ is slightly greater than that for P(C_6H_{11})Ph_2 (160 and 154° respectively).[3] According to Tolman,[3] however, ethyl, n-propyl, and n-butyl groups give the same contribution to the total cone angle, but the increased bulk of the n-butyl group is evident both here, for L = $PBu^n{}_2Ph$, and in our earlier study with L = $PBu^n{}_3$: no tetrakis complex could be detected in either case.

In three cases, the iodo-complexes [AuIL] were examined (L = PMe_2Ph, $PPr^n{}_2Ph$, or $PPr^i{}_2Ph$). These gave resonances 4—5 p.p.m. to low field of the corresponding chloro-complexes; such shielding effects are common in transition-metal complexes. On addition of the ligand, small differences (0.6—4.5 p.p.m.) were found between the c.c.s. of the iodo- and chloro-complexes and of the bis(ligand) complexes [AuL_2]BPh_4. It is difficult to assess the significance of such small shifts but, given the general reproducibility of *ca.* ±0.3 p.p.m., differences of more than about 1 p.p.m. are probably significant. Thus, for L = PMe_2Ph, the three shifts are indistinguishable, but for L = $PPr^n{}_2Ph$ they lie in the order I^- < Cl^- < $BPh_4{}^-$. This may indicate some association of the halide ions with the cation, towards the formation of the three-co-ordinate complex [$AuXL_2$], which is greater for X = I than for X = Cl. Consistently, for the bulkier ligand $PPr^i{}_2Ph$, the chloride and iodide bis(ligand) systems have the same c.c.s.

In mixtures of [AuClL] and [AuIL] (L = PMe_2Ph or $PPr^i{}_2Ph$), a single averaged signal was seen at ambient temperature which resolved into separate components characteristic of the individual complexes at 200 K. Presumably, associative exchange occurs by intramolecular co-ordination of the halide ligands.

Gold-197 Mössbauer Spectra.—New data are reported in Table 2. The two-co-ordinate complexes are unexceptional apart from the three pairs [AuXL] with X = Cl or I, L = PMe_2Ph, $PPr^n{}_2Ph$, or $PPr^i{}_2Ph$. In these cases, the iodide has the smaller isomer shift (i.s.) and quadrupole splitting (q.s.). Similar trends are found for L = PPh_3 and for [AuX_2]$^-$ and AuX (Table 2).[4-8] In every case, the difference is barely greater than the experimental error, but all show the same behaviour. This is unexpected, since gold(I) is ' soft ' and would be expected to form a more covalent bond with iodide than with chloride, *i.e.* the Mössbauer parameters show the opposite trend to that expected. This is at present inexplicable.

The data for [Au{$Ph_2P(CH_2)_2O(CH_2)_2O(CH_2)_2PPh_2$}]$BPh_4$ are similar to those of other bis(phosphine) complexes,

Table 1. Phosphorus-31 co-ordination chemical shifts ($\delta_{\mathrm{complex}} - \delta_{\mathrm{ligand}}$)/p.p.m. for [AuXL] + L (X = Cl or I) and $[\mathrm{AuL_2}]\mathrm{X}$ + L (X = $\mathrm{BPh_4}$)

L	X	[AuXL]	$[\mathrm{AuL_2}]^+$	$[\mathrm{AuL_3}]^+$	$[\mathrm{AuL_4}]^+$	δ_{ligand} [a]	Cone angle/°
$\mathrm{PMe_2Ph}$	Cl	48.6	62.8		23.2	−45.8	122
	I	52.7	62.0		23.4		
	$\mathrm{BPh_4}$ [b]		63.1		22.9		
	$\mathrm{BPh_4}$ [c]				23.1		
	Cl + I [d]	48.0, 52.3					
$\mathrm{PEt_2Ph}$	Cl	55.0	64.2	56.6	8.0	−18.1	136
$\mathrm{PPr^n{}_2Ph}$	Cl	54.4	63.3	58.1	19.6	−25.4	136
	I	59.6	61.0				
	$\mathrm{BPh_4}$		65.5				
$\mathrm{PPr^i{}_2Ph}$	Cl	51.8	60.7	52.2		6.8	155
	I	56.9	60.1	51.9			
	Cl + I [d]	54.3, 57.1		52.9			
$\mathrm{PBu^n{}_2Ph}$	Cl	56.8	76.2	67.8		−26.2	136
$\mathrm{PMePh_2}$	$\mathrm{BPh_4}$	54.5			22.8	−38.5	136

[a] In p.p.m. downfield from 85% $\mathrm{H_3PO_4}$. [b] Starting from $[\mathrm{Au(PMe_2Ph)_2}]\mathrm{BPh_4}$. [c] Starting from $[\mathrm{Au(PMe_2Ph)_4}]\mathrm{BPh_4}$. [d] A mixture of $[\mathrm{AuCl(PPr^i{}_2Ph)}]$ and $[\mathrm{AuI(PPr^i{}_2Ph)}]$.

Table 2. Gold-197 Mössbauer and far-i.r. spectroscopic data for gold(I) complexes

Complex	i.s.[a]/mm $\mathrm{s^{-1}}$	q.s./mm $\mathrm{s^{-1}}$	ν(Au−X)/$\mathrm{cm^{-1}}$	ν(Au−P)/$\mathrm{cm^{-1}}$	Ref.
$[\mathrm{AuCl(PMe_2Ph)}]$ [b]	3.95	7.10	316	373	5, 6
$[\mathrm{AuI(PMe_2Ph)}]$	3.67	6.91	164	362	
$[\mathrm{AuCl(PEt_2Ph)}]$	4.25	7.49	328	355	
$[\mathrm{AuCl(PPr^n{}_2Ph)}]$	4.09	7.47	321		
$[\mathrm{AuI(PPr^n{}_2Ph)}]$	3.65	6.95	168		
$[\mathrm{AuCl(PPr^i{}_2Ph)}]$	4.01	7.45	324	381	
$[\mathrm{AuI(PPr^i{}_2Ph)}]$	3.83	7.25	175		
$[\mathrm{AuCl(PPh_3)}]$ [b]	4.07	7.45			4—6
$[\mathrm{AuI(PPh_3)}]$ [b]	4.02	7.36			1, 6
$[\mathrm{Au(PMe_2Ph)_2}]\mathrm{BPh_4}$	5.05	9.49			
$[\mathrm{Au(PMe_2Ph)_2}]\mathrm{ClO_4}$	5.32	9.79			
$[\mathrm{Au(PPr^i{}_2Ph)_2}]\mathrm{BPh_4}$	5.36	9.97			
$[\mathrm{Au(PMe_2Ph)_4}]\mathrm{BPh_4}$	1.98	0.00			
$[\mathrm{Au(PMePh_2)_4}]\mathrm{BPh_4}$	1.19	0.00			
$[\mathrm{Au(PMePh_2)_4}]\mathrm{ClO_4}$	1.48	0.00			1
$[\mathrm{Au(PPh_3)_4}]\mathrm{ClO_4}$	−0.17	0.00			9
$[\mathrm{Au(AsPh_3)_4}]\mathrm{ClO_4}$	−0.39	0.00			1
$[\mathrm{Au(pdma)_2}][\mathrm{Au(C_6F_5)_2}]$ [c,d]	0.8	1.1			10
$[\mathrm{Au(SbPh_3)_4}][\mathrm{Au(C_6F_5)_2}]$ [c]	1.11	0.00			10
$[\mathrm{AuCl(PPh_3)_3}]$	1.18	4.38			
$[\mathrm{Au(SnCl_3)(PPh_3)_3}]$	1.64	3.57			12
AuCl [b]	−0.16	4.56			*e*
AuI [b]	−0.06	3.94			*e*
$[\mathrm{AuCl_2}]^-$ [b]	1.84	6.28			7, 8
$[\mathrm{AuI_2}]^-$ [b]	1.74	5.75			7, 8

[a] Relative to gold foil. [b] Average values given. [c] Data for cation only. [d] pdma = *o*-phenylenebis(dimethylarsine). [e] M. O. Faltens and D. A. Shirley, *J. Chem. Phys.*, 1970, **53**, 4249; H. D. Bartunik, W. Potzel, R. L. Mössbauer, and G. Kaindl, *Z. Phys.*, 1970, **240**, 1.

indicating linear two-co-ordination for the gold atom.[1,7,9] The Mössbauer data do not distinguish between a chelated monomer, a ring dimer, or a polymeric form for the cation. However, preliminary mass spectrometric data suggest a dimeric formulation.

The two complexes $[\mathrm{AuL_4}]\mathrm{BPh_4}$ (L = $\mathrm{PMePh_2}$ or $\mathrm{PMe_2Ph}$) fit well with the four-co-ordinate phosphine complexes reported earlier.[1,9–11] The zero q.s. unambiguously demonstrates tetrahedral geometry, and the i.s. increases in the expected order: L = $\mathrm{PPh_3}$ < $\mathrm{PMePh_2}$ < $\mathrm{PMe_2Ph}$. The lower-symmetry complex $[\mathrm{AuCl(PPh_3)_3}]$ shows a low i.s. consistent with the known four-co-ordinate configuration of the cation,[11] and a small q.s. The latter is comparable with that of $[\mathrm{Au(SnCl_3)(PPh_3)_3}]$,[12] and arises from the same cause, *viz.* the difference in electron density between the bonds to the three phosphine ligands and that to the fourth ligand. Using the point-charge approach described earlier,[1] with partial quadrupole splitting values of −3.56 mm $\mathrm{s^{-1}}$ for $\mathrm{PPh_3}$ (ref. 4) and −2.02 mm $\mathrm{s^{-1}}$ for $\mathrm{Cl^-}$ (ref. 4), the calculated q.s. for $[\mathrm{AuCl(PPh_3)_3}]$ is 3.08 mm $\mathrm{s^{-1}}$. The observed value is rather larger (4.38 mm $\mathrm{s^{-1}}$), which is consistent with the known increase in P−Au−P bond angles from the tetrahedral value.[11]

Experimental

Phosphorus-31 n.m.r. spectra and gold-197 Mössbauer spectra were obtained as described previously.[1] The tertiary phosphines and their gold complexes were obtained by standard methods.

Acknowledgements

We are indebted to Professor C. E. Johnson for the loan of a $^{196}\mathrm{Pt}$ Mössbauer source, Mr. C. Evans for the n.m.r. measurements, Miss J. A. Sandbank for a sample of $[Au\{Ph_2P(CH_2)_2O(CH_2)_2O(CH_2)_2PPh_2\}]BPh_4$, Johnson Matthey Research Laboratories for the loan of gold salts, and the S.E.R.C. and the Iraq Government for financial support.

References

1 R. V. Parish, O. Parry, and C. A. McAuliffe, *J. Chem. Soc., Dalton Trans.*, 1981, 2098.
2 C. B. Colburn, W. E. Hill, C. A. McAuliffe, and R. V. Parish, *J. Chem. Soc., Chem. Commun.*, 1979, 218.
3 C. A. Tolman, *Chem. Rev.*, 1977, **77**, 313.
4 J. S. Charlton and D. I. Nichols, *J. Chem. Soc. A*, 1970, 1484.
5 C. A. McAuliffe, R. V. Parish, and P. D. Randall, *J. Chem. Soc., Dalton Trans.*, 1977, 1426.
6 F. A. Vollenbroek, P. C. P. Bouten, J. M. Trooster, J. P. van den Berg, and J. J. Bour, *Inorg. Chem.*, 1978, **17**, 1345.
7 P. G. Jones, A. G. Maddock, M. J. Mays, M. M. Muir, and A. F. Williams, *J. Chem. Soc., Dalton Trans.*, 1977, 1434.
8 M. P. A. Viegers, Ph.D. Thesis, University of Nijmegen, The Netherlands, 1976.
9 R. V. Parish and J. D. Rush, *Chem. Phys. Lett.*, 1979, **63**, 37.
10 K. Moss, R. V. Parish, A. Laguna, M. Laguna, and R. Usón, *J. Chem. Soc., Dalton Trans.*, 1983, 2071.
11 P. G. Jones, G. M. Sheldrick, J. A. Muir, M. M. Muir, and L. B. Pulgar, *J. Chem. Soc., Dalton Trans.*, 1982, 2123.
12 G. C. H. Jones, P. G. Jones, A. G. Maddock, M. J. Mays, P. A. Vergnano, and A. F. Williams, *J. Chem. Soc., Dalton Trans.*, 1977, 1440.

Received 22nd *June* 1983; *Paper* 3/1059