Journal of Organometallic Chemistry, 303 (1986) 437–442
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

A VIBRATIONAL STUDY BY RAMAN SPECTROSCOPY OF SOME DINUCLEAR GOLD YLIDE COMPLEXES

ROBIN J.H. CLARK, JOANNE H. TOCHER

Christopher Ingold Laboratories, University College London, 20 Gordon Street, London WC1H 0AJ (Great Britain)

JOHN P. FACKLER Jr., R. NEIRA, H.H. MURRAY and H. KNACKEL

Laboratory for Molecular Structure and Bonding, Department of Chemistry, Texas A and M University, College Station, TX 77843 (U.S.A.)

(Received October 15th, 1985)

Summary

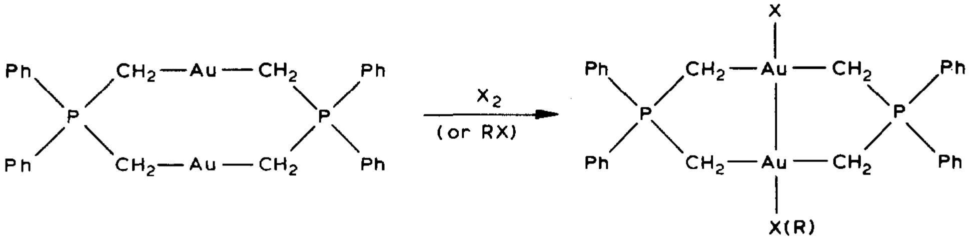
A vibrational study of the dinuclear gold ylide complexes $[Au(CH_2)_2PPh_2]_2$ and $[Au(CH_2)_2PPh_2]_2X_2$ ($X = Cl$, Br or I) has been undertaken by Raman spectroscopy. The non-bonding Au–Au interaction in the Au^I dimer, $[Au(CH_2)_2PPh_2]_2$, at 64 cm^{-1} shifts to higher wavenumber in the single-bonded Au^{II} halogen complexes, with bands at 162, 132 and 103 cm^{-1} for $X = Cl$, Br and I, respectively, being assigned to ν(Au–Au). The Au–X vibration was also identified. The general trends in Au–Au and Au–X stretching vibrations with changing halogen are compared with those for other dinuclear metal–metal bonded complexes, with a metal–metal bond order of one, and with those for mononuclear gold–halogen complexes.

Introduction

Gold has a strong tendency to form bonds to itself, as is testified by the facile decomposition of many gold complexes to metallic gold. Metal–metal bonds are also present in many complexes; for example [AuCN(CNMe)] contains linear gold(I) species, but there are also weak Au–Au bonds [1] leading to the formation of two-dimensional polymeric layers. The gold–gold distance is of the order of 3.6 Å. Where bridging occurs, a stronger Au–Au bond is formed, e.g. in the gold(I) dithiocarbamate $[(AuS_2CNPr_2)_2]$ a gold–gold distance of 2.76 Å is found [2] (compare metallic gold [3] for which the closest inter-nuclear distance is 2.884 Å). In such complexes the nature of the gold–gold interaction is not clearly understood, and it has been suggested that the short gold–gold contacts are simply due to packing effects in the solid.

0022-328X/86/$03.50

The dinuclear gold(I) phosphorus ylide complex $[Au(CH_2)_2PPh_2]_2$ [4] has been shown to be a reactive, coordinatively unsaturated, dimetal system, undergoing oxidative-addition reactions at the metal centres. The addition of halogens, pseudohalogens or alkyl halides leads to genuine d^9–d^9, Au^{II}–Au^{II} metal–metal single-bonded complexes [4-9], viz.



(X = Cl, Br, I or CN;
RX = CH_3Br, $(CH_2CN)Br$, etc.)

These complexes, therefore, present the opportunity of studying the extent of Au–Au interactions on going from a metal–metal bond order of zero to unity, and the way in which the Au–Au interactions change with change of axial halogen.

Despite the increasing interest in this area, not least due to the formation of stable Au^{II} species and their interesting oxidative-addition reductive-elimination chemistry [4], most investigations have focussed on X-ray diffraction and NMR [4,10] data. However, Raman spectroscopy is known to be an excellent method for obtaining information regarding the metal–metal stretching vibration of dinuclear metal–metal bonded species [11–13]. A previous study of the vibrational properties of dinuclear gold ylide complexes by Raman spectroscopy was limited largely to the use of 501.7 nm radiation [14]. In this study, we have employed excitation sources throughout the visible region in the examination of $[Au(CH_2)_2PPh_2]_2$ and the Au^{II} compounds $[Au(CH_2)_2PPh_2]_2X_2$ (X = Cl, Br or I) and the unsymmetrical $[Au(CH_2)_2PPh_2]_2(CH_2CN)Br$. The results of this study allow assignment of the Au–Au stretching vibration for a series of gold(II) phosphorus ylide dimers.

Experimental

Materials: Complexes were prepared at Texas A & M University and are reported elsewhere.

Instrumentation: Raman data were recorded with a Spex 14018 (Ramalog 6) double monochromator with 1800 line mm^{-1} Jobin-Yvon holographic gratings. Coherent Radiation models 170-4 argon and CR3000K and CR500K krypton ion lasers provided the exciting lines. Detection of the scattered radiation was by standard photon-counting techniques employing cooled RCAC31034 photomultipliers. All spectra were recorded at approximately 80 K using a Dewar assembly from samples of the complex dispersed in potassium halide discs.

Results and discussion

All spectra were recorded using a number of exciting lines in the visible region. The long term integrity of the Au^{II} complexes in solution is questionable, particu-

TABLE 1

WAVENUMBERS AND ASSIGNMENTS[a] OF THE BANDS OBTAINED FROM THE RAMAN SPECTRUM OF $[Au(CH_2)_2PPh_2]_2$

Wavenumber (cm^{-1})	Assignment
64	ν(Au–Au)[b]
79	ρ(C–Au–C)
104	metalloring vibration
136	metalloring vibration
215	ρ(Ph–P–Ph)
230	$\delta(CH_2–Au–CH_2)$
275	Ph, out-of-plane ring deformation
440	ν(p-Ph)
499	
587	ν(Au–C)
616	Ph, in-plane ring deformation
685	$\nu(P–CH_2)$
999	Ph, symmetric ring stretch
1023	in-plane C–H bend
1100	aromatic vibration

[a] Based upon assignments of Fackler and co-workers [14], and the following references: H. Schmidbaur and R. Franke, Inorg. Chim. Acta, 13 (1975) 85. S.K. Freeman, Applications of Laser Raman Spectroscopy, Wiley, New York, 1974. D.E.C. Corbridge, Topics in Phosphorus Chemistry, Interscience, New York, 6 (1969) 229. W.V. Sawodny, Z. Anorg. Allg. Chem., 304 (1960) 147. H. Halman, Spectrochim. Acta, 16 (1960) 407. K. Shobatake and K. Nakamoto, J. Am. Chem. Soc., 92 (1970) 3332. R.J. Puddephatt, The Chemistry of Gold, Elsevier, New York (1978). [b] In an earlier study (F.J. Farrell and T.G. Spiro, Inorg. Chem., 10 (1971) 1606) of the Raman spectrum of $[AuS_2CNR_2]_2$ ($R = C_4H_9$) a band at 185 cm^{-1} was attributed to ν(Au–Au), implying a significant Au–Au bond order. However, this assignment appears to be incorrect, the 185 cm^{-1} band being attributable to the symmetric Au–S–C bending mode (probably with some symmetric SCS bending contribution). From the present study, the Au–Au stretching vibration would be expected between 60 and 105 cm^{-1} for this compound.

larly for the RX adduct [4,10] where an equilibrium is quickly established between $[Au(CH_2)_2PPh_2]_2RX$ and the parent gold(I) dimer plus free RX. Accordingly, solid pellets were used exclusively, the appropriate potassium halide being used as a grinding agent to prevent possible halogen exchange.

The principal vibrational modes associated with the gold(I) dimer $[Au(CH_2)_2PPh_2]_2$, as determined by Raman spectroscopy, and their assignments are listed in Table 1.

TABLE 2

GOLD–GOLD AND GOLD–HALOGEN STRETCHING FREQUENCIES (cm^{-1}) FOR $[Au(CH_2)_2PPh_2]_2X_2$

Compound	ν(Au–Au)	ν(Au–X)
$[Au(CH_2)_2PPh_2]_2Cl_2$	162 (ν_1)	293 (ν_2)
$[Au(CH_2)_2PPh_2]_2Br_2$	132 (ν_1)	220 (ν_2)
$[Au(CH_2)_2PPh_2]_2I_2$	103 (ν_2)	165 (ν_1), 329 ($2\nu_1$), 490 ($3\nu_1$)[a]

[a] Obtained by use of 514.5 and 496.5 nm radiation only, see text.

The complex exists as discrete dinuclear units with no intermolecular gold–gold interactions. Single crystal X-ray studies have shown that, upon oxidative-addition with halogen or alkyl halide, the 8-membered gold-ylide metalloring framework remains largely unaltered [4]. In the series of Au^{II} complexes examined similar bands to those appearing in the vibrational spectrum of the gold(I) dimer can be identified as being due to the metalloring and likewise assigned. We need, therefore, in discussing the $[Au(CH_2)_2PPh_2]_2X_2$ complexes, to consider only the X–Au–Au–X unit in detail. A considerable shortening of the intramolecular gold–gold distance is observed upon oxidative-addition, from approximately 3.0 Å in the gold(I) dimer to the region of 2.6 Å [4,9]. This decrease in Au–Au bond length is in keeping with the formation of a single metal–metal bond between the Au^{II}–Au^{II} centres. With this increase in bond order from zero to one, the Au–Au stretching vibration would be expected to be shifted to higher wavenumbers. This is indeed what is found in practice. Table 2 lists the vibrational band wavenumbers for the Au–Au and Au–X interactions for the $[Au(CH_2)_2PPh_2]_2X_2$ complexes (X = Cl, Br or I). These bands are by far the most intense in the spectral region examined (50–1500 cm^{-1}).

Only when X = I is there any change in the spectrum on changing the excitation line. The solid-state reflectance spectra [14] show strong features in the visible region

TABLE 3

COMPARISON OF SOME GOLD–HALOGEN STRETCHING VIBRATIONS (cm^{-1})

Complex	X = Cl	X = Br	X = I
$[Au(CH_2)_2PPh_2]_2X_2$	293	220	165
$[AuX_2]^-$	329	209	158[a]
$[Ph_3PAuX]$	329	229	187[b]
$[AuX_3Ph]$	341	204	153[c]
	289	182	162[d]

[a] Ref. 16. [b] Ref. 17. [c] Symmetric stretch of *trans*-AuX_2 grouping [18]. [d] *Trans* to Ph ligand [18].

TABLE 4

COMPARISON OF THE WAVENUMBERS OF METAL–METAL STRETCHING MODES FOR Au^{II} YLIDE, Hg^{II} HALIDE, AND Pt^{III} DIPHOSPHITE DIMERS

Complex	X	ν(M–M) (cm^{-1})
$[Au(CH_2)_2PPh_2]_2X_2$	Cl	162
	Br	132
	I	103
Hg_2X_2[a]	Cl	166
	Br	132
$K_4[Pt_2(pop)_4X_2]$[b]	Cl	158
	Br	133
	I	105

[a] Ref. 19. [b] Ref. 20, 22.

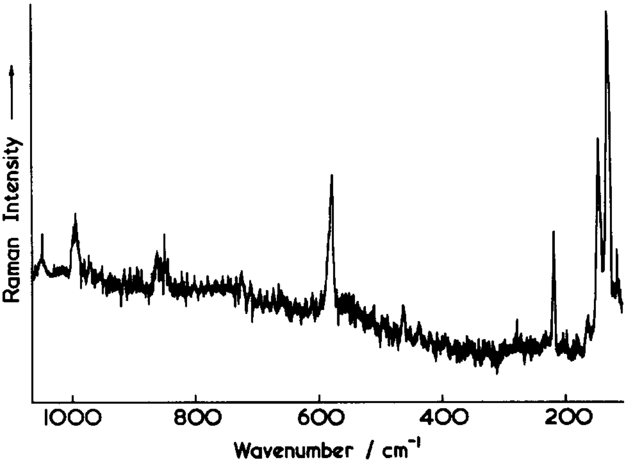


Fig. 1. Raman spectrum of $[Au(CH_2)_2PPh_2]_2Br_2$ at 80 K recorded with excitation at 514.5 nm.

only for $[Au(CH_2)_2PPh_2]_2I_2$. When X = Cl, no such features are observed, for X = Br, only a weak shoulder is observed at 490 nm, but for X = I two broad bands are detected with approximate λ_{max} values of 570 and 485 nm. That at 485 nm has been assigned to a $1b_{2u} \rightarrow 2b_{2u}$ transition [15], i.e. to one from an orbital which is antibonding in Au–Au and bonding in Au–I interactions, to one which is antibonding in Au–Au and Au–I interactions. As the excitation line falls within the 485 nm band, i.e. when 514.5 or 496.5 nm radiation is employed, a progression in ν_1, the Au–I stretching mode is observed (to $3\nu_1$), consistent with the expected increase in the Au–I bond length on excitation.

As X is changed from Cl to Br to I, the vibrational frequency of the Au–X stretching mode decreases. This behaviour is also observed for a series of unrelated Au^I and Au^{III} monomeric complexes, compared in Table 3 [16–18]. As will be observed, not only does the general trend in Au–X stretching frequencies agree with the Au^I and Au^{III} data as the halogen is varied, but the actual values obtained are also of similar magnitude.

The band assigned to the ν(Au–Au) stretching mode decreases in wavenumber in the order X = Cl > Br > I. This is also the order of increasing Au–Au bond length [4,14]. The decrease in the metal–metal stretching frequency found for the $[Au(CH_2)_2PPh_2]_2X_2$ complexes with changing halogen is in good agreement with the trend found for singly-bonded dimetallic systems, such as Hg_2X_2 [19] and, more relevantly, the Pt^{III} diphosphite compounds $K_4[Pt_2(pop)_4X_2]$ (pop = $P_2O_5H_2^{2-}$) [20–22] (X = Cl, Br, or I) (Table 4). The Pt^{III} diphosphite complexes exhibit a similar chemistry to the gold(II) ylides, also being prepared by the oxidative addition of halogen or alkyl halides to a binuclear platinum(II) tetrakis(diphosphite) ion, $[Pt_2(pop)_4]^{4-}$. A change in the Pt–Pt bond order from zero to one is achieved upon oxidative addition with a shortening of the bond length from 2.925 to 2.695 Å, where X = Cl [20] and to 2.723 Å where X = Br [23].

The vibrational spectrum of $[Au(CH_2)_2PPh_2]_2(CH_2CN)Br$ was also recorded. The assignment of the Au–Au and Au–Br stretching modes is not so straightforward in this case, no clearly dominating bands being present in the 90–250 cm^{-1} region.

However, we can tentatively assign bands at 116 and 172 cm^{-1} to the ν(Au–Au) and ν(Au–Br) modes, respectively. Further work in the area of the Au^{II} RX oxidative addition products is necessary to confirm these assignments.

Conclusions

The present study of the vibrational spectra of gold ylide complexes leads to the assignment of a band at 64 cm^{-1} to a weak Au–Au interaction in the Au^{I} dimer, with a formal metal–metal bond order of zero, and to the detection of its shift to increased vibrational wavenumber upon oxidative addition with halogen. These Au^{II}–Au^{II} complexes, with a bond order of one, show a similar structural and vibrational dependence on halogen as found with other binuclear systems with a bond order of one. This and the similarities between both the trend and magnitude of Au–X stretching vibrations in the dinuclear gold ylide complexes and monomeric gold halogen complexes help to confirm the assignments.

Further work in this area, particularly regarding the RX oxidative-addition products, should provide vibrational evidence for the amplification of the structural *trans* effect [4] for dinuclear gold(II) species.

Acknowledgements

The Petroleum Research Fund administered by the American Chemical Society has supported R. Neira. J.P.F. thanks the National Science Foundation NSF CHE 8408414 and the Welch Foundation for funding, and J.H.T. thanks the SERC for support.

References

1 S. Esperas, Acta Chem. Scand. Ser. A., A30 (1976) 527.
2 S. Åkerstrom, Ark. Kemi., 14 (1959) 387.
3 R. Hesse and P. Jennische, Acta Chem. Scand., 26 (1972) 3855.
4 J.D. Basil, H.H. Murray, J.P. Fackler Jr., J. Tocher, A.M. Mazany, B. Trzcinska-Bancroft, H. Knachel, D. Dudis, T.J. Delord and D. Marler, J. Am. Chem. Soc., in press.
5 H. Schmidbaur, Acc. Chem. Res., 8 (1975) 62.
6 H. Schmidbaur, J.R. Mandl, A. Frank and G. Huttner, Chem. Ber., 109 (1976) 466.
7 H. Schmidbaur, Angew. Chem. Int. Ed. Engl., 15 (1976) 728.
8 H. Schmidbaur, A. Wohlleben. F.E. Wagner. D.F. van der Vondel, and G.P. van der Kelen, Chem. Ber., 110 (1977) 2758.
9 H.H. Murray, A.M. Mazany and J.P. Fackler Jr., Organometallics, 4 (1985) 154.
10 J.P. Fackler Jr., J.D. Basil and H.H. Murray, Organometallics, 3 (1984) 821.
11 F.A. Cotton and R.A. Walton, Multiple Bonds Between Metal Atoms, John Wiley and Sons, New York, 1982.
12 R.J.H. Clark and B. Stewart, Structure and Bonding, 36 (1979) 1.
13 R.J.H. Clark and R.E. Hester (Eds.), Advances in Infrared and Raman Spectroscopy, Heyden, London, Vol. 1, 1975, pp. 143–172.
14 R. del Pilar Neira, PhD Thesis, Case Western Reserve University, 1984.
15 J.P. Fackler Jr. and J.D. Basil, A.C.S. Symp. Ser., 211 (1983) 201.
16 P. Braunstein and R.J.H. Clark, J. Chem. Soc., Dalton Trans., (1973) 1845.
17 D.R. Williamson and M.C. Baird, J. Inorg. Nucl. Chem., 34 (1972) 3393.
18 P. Braunstein and R.J.H. Clark, Inorg. Chem., 13 (1974) 2224.
19 H.M. Gager, J. Lewis and M.J. Ware, J. Chem. Soc., Chem. Commun., 17 (1966) 617.
20 C.M. Che, W.P. Schaefer, H.B. Gray, M.K. Dickson, P. Stein and D.M. Roundhill, J. Am. Chem. Soc., 104 (1982) 4253.
21 P. Stein, M.K. Dickson and D.M. Roundhill, J. Am. Chem. Soc., 105 (1983) 3489.
22 R.J.H. Clark and M. Kurmoo, Inorg. Chem., 24 (1985) 4420.
23 R.J.H. Clark, M. Kurmoo, H.M. Dawes and M.B. Hursthouse, Inorg. Chem., in press.