THE MOLECULAR STRUCTURE
OF METHYL(TRIMETHYLPHOSPHINE)GOLD(I)
BY GAS ELECTRON DIFFRACTION *

ARNE HAALAND *, JENS HOUGEN, HANS V. VOLDEN

Department of Chemistry, University of Oslo, P.O.Box 1033 Blindern, 0315 Oslo 3 (Norway)

and R.J. PUDDEPHATT

Department of Chemistry, University of Western Ontario, London, Western Ontario N6A 5B7 (Canada)

(Received October 9th, 1986)

Summary

The gas electron diffraction pattern of $(CH_3)AuP(CH_3)_3$ recorded with reservoir and nozzle temperatures of about 105°C is consistent with a molecular model of C_{3v} symmetry (i.e. bond angle CAuP 180°) and bond distances Au–P 228.0(5) and Au–C 203.4(12) pm.

The synthesis and characterization of the first organometallic derivatives of gold(I), a series of organogold complexes with tertiary phosphines, were reported by Calvin, Coates and Dixon in 1959 [1]. The IR spectrum of the simplest member of the series, MeAuPMe$_3$, was published in an article four years later [2]. The synthesis and properties were later described in more detail by Schmidbaur and Shiotani [3].

An X-ray diffraction investigation of MeAuPPh$_3$ confirmed the linear coordination of the gold atom and provided rough values for the Au–C and Au–P bond distances [4]. The infrared and Raman spectra of MeAuPMe$_3$ have been recorded and assigned, and a Urey-Bradley force field determined by normal coordinate analysis [5]. The two low energy peaks at 8.24 and 9.22 eV in the photoelectron spectra have been assigned to the Au–C and Au–P σ-bonding orbitals, respectively [6]. The bonding, and particularly the role of the formally occupied $5d_{z^2}$ orbital on Au, has been discussed on the basis of SCF-Xα-SW [6] and SCF-LCAO-MO calculations including relativistic effects [7].

Our reason for attempting to determine the gas phase structure of MeAuPMe$_3$ lies in our general interest in metal–C(alkyl) bond distances and their variation across or down the Periodic Table [8].

---

* Dedicated to Professor G.E. Coates on the occasion of his 70th birthday.

Experimental

MeAuPMe₃ (m.p. 70–71°C) was synthesized as described in Ref. 2.

The gas electron diffraction pattern was recorded on Balzers Eldigraph KDG-2 with a nozzle temperature of about 105°C. Exposures were made with nozzle-to-plate distances of about 50 and 25 cm. Six plates from each set were photometered and the scattering data processed by standard procedures. The molecular intensity curves obtained for each nozzle-to-plate distance were averaged but not connected. The curves extended from s 17.5 to 140 nm^{-1} with increment Δs 1.25 nm^{-1} (50 cm plates) and from s 42.5 to 200 nm^{-1} with increment Δs 2.50 nm^{-1} (25 cm plates).

The complex atomic scattering factors, $f'(s)$, of C, P and bonded H have been calculated from an analytical representation of the atomic potential [9] with a program written by Yates [10] and modified by T.G. Strand. The scattering factors of Au were interpolated to correct potential from the values of Bonham and Schäfer [11].

Structure analysis. Structure refinements were based on a molecular model of C_{3v} symmetry as shown in Fig. 1. The Me(Au) and Me(P) groups were assumed to be isostructural and to have C_{3v} symmetry with the C_3 axes coinciding with the C–P(Au) bonds. Me group orientations are indicated in Fig. 1.

Root-mean-square amplitudes of vibration (l) and shrinkage corrections were calculated from the published Urey-Bradley force-field [5], augmented by two methyl group torsional force constants by use of a program written by Hilderbrandt [12].

Six independent structure paramaters (the bond distances Au–P, Au–C, P–C and C–H(mean), and the valence angles Au–P–C and H–C–H were refined by least-squares calculations on the intensity data along with ten r.m.s. vibrational amplitudes. In Table 1 we list the best values obtained without shrinkage corrections. The
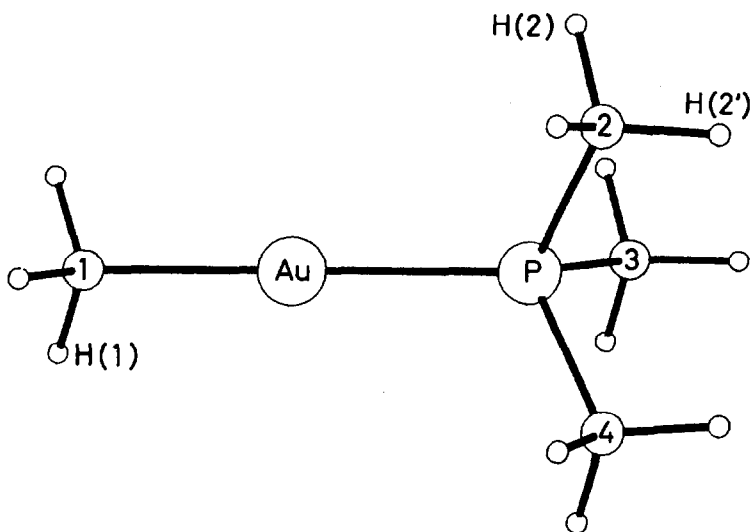

Fig. 1. Molecular model of CH₃AuP(CH₃)₂, C_{3v} symmetry.

TABLE 1

INTERATOMIC DISTANCES (r_a), r.m.s. VIBRATIONAL AMPLITUDES (l(ED)) AND VALENCE ANGLES OF MeAuPMe$_3$ DETERMINED BY GED (Estimated standard deviations in parentheses in units of the last digit. Vibrational amplitudes (l(FF)) calculated from an approximate molecular force field)

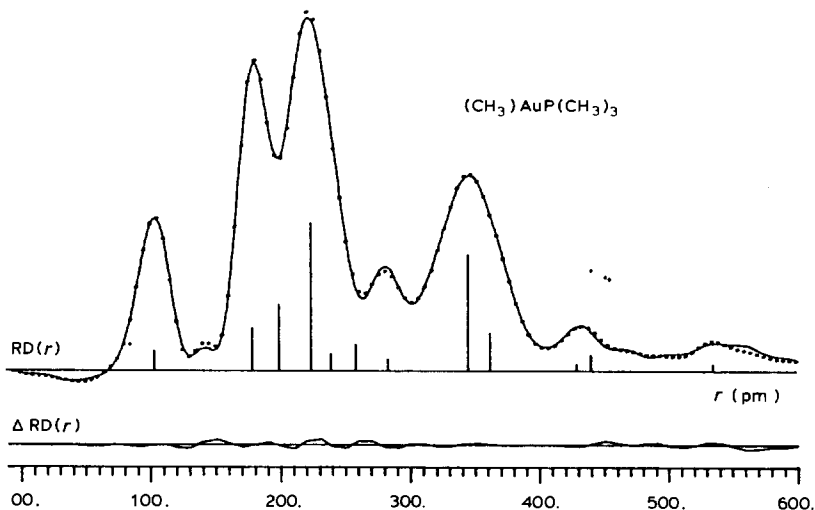|	r_a (pm)	l(ED) (pm)	l(FF) (pm)
Bond distances			
Au–P	228.0(5)	6.0(20)	5.7
Au–C	203.4(12)	6.3(30)	6.0
P–C	182.9(6)	6.7(10)	5.3
C–H [a]	107.8(4)	6.4(10)	7.9
Nonbonded distances			
Au$\cdots$C(2)	347.9(10)	13.6(7)	11.1
Au$\cdots$H(1)	262(3)	(12.8)	12.8
Au$\cdots$H(2)	365(4)	27(3)	21.5
Au$\cdots$H(2′)	442(2)	14(5)	12.5
P$\cdots$C(1)	431(3)	8(2)	8.7
P$\cdots$H(2)	243(4)	(11.4)	11.4
C(2)$\cdots$C(3)	287(3)	9(1)	10.2
C(1)$\cdots$C(2)	536(3)	29(4)	15.7
Valence angles ($^\circ$)			
P–Au–C	(180)		
Au–P–C	115.2(3)		
C–P–C	103.2(3)		
H–C–H	108(3)		

[a] Mean values.

Fig. 2. Above: Dots; experimental radial distribution (RD) curve, line; calculated RD curve for best model. Major interatomic distances indicated by bars of height approximately proportional to the area under the corresponding peak. Below: difference curve. Artificial damping constant $k = 20$ pm^2.

quoted estimated standard deviations have been expanded to include the added uncertainty due to data correlation and possible scale errors.

Refinements with shrinkage corrections yielded a slightly poorer fit ($R = \Sigma(I_{obs} - I_{calc})^2/I_{obs}^2 = 5.31$ vs. 5.18). The best values thus obtained differed from those in Table 1 by less than one half of the quoted e.s.d.

Experimental and calculated radial distribution curves are compared in Fig. 2.

Discussion

The Au–C bond distance obtained in this study of MeAuPMe$_3$, 203.3(12) pm, is in agreement with that of the dicyclopropylketone complex I, 206.5(5) pm by X-ray
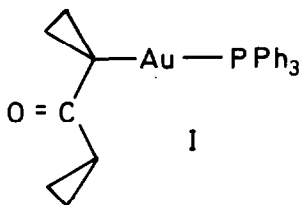
diffraction [13], though it is not in agreement with the rather inaccurate Au–C bond distance in MeAuPPh$_3$, 212.4(28) pm [4].

The Au–P bond distances obtained in the three studies, 228.0(5), 228.1(1) [13] and 227.9(8) pm [4] respectively, are indistinguishable. The Au–P bond distance in ClAuPMe$_3$ is, however, significantly shorter, 223.5(3) pm [14]: Similar shortening of electron donor acceptor bonds when alkyl groups on the acceptor atom are replaced by electronegative Cl atoms is well documented for complexes of Main Group metals [15,16].

The P–C bond distance in the complex, 182.9(6) pm, is shorter – though not significantly shorter – than that in free PMe$_3$ [17], 184.6(3) pm, and the C–P–C angle in the complex, 103.1(3)°, is significantly larger than that in free PMe$_3$ [17], 98.6(3)°. Both changes are in the direction predicted by the Valence Shell Electron Pair Repulsion model.

What would be the Au–C bond distance in base-free monomeric MeAu? Since coordination of electron donors to Main Group metal alkyls generally appears to increase M–C bond distances, the Au–C bond distance in MeAu should be shorter than in the complex, i.e. shorter than 203 pm. Another estimate is obtained by adding the Au–H bond distance of the diatomic molecule AuH [18], 152.4 pm, to a typical C (sp^3)–C(sp^3) bond distance of 153 pm and subtract a typical C(sp^3)–H bond distance of 110 pm to yield Au–C 195 pm.

In any case the Au–C bond distance in MeAu is significantly shorter than the Hg–C bond distance in Me$_2$Hg, 208.3(2) by GED [19]. The anomalously small bonding radius of Au compound to its nearest neighbours in the Periodic Table has been ascribed to relativistic effects [20,21].

References

1 G. Calvin, G.E. Coates and P.S. Dixon, Chem. Ind. (London), (1959) 1628.
2 G.E. Coates and C. Parkin, J. Chem. Soc., (1963) 421.
3 H. Schmidbaur and A. Shiotani, Chem. Ber., 104 (1971) 2821.
4 P.G. Gavens, J.J. Guy, M.J. Mays and G.M. Sheldrick, Acta Cryst. B, 33 (1977) 137.
5 C.F. Shaw and R.S. Tobias, Inorg. Chem., 12 (1973) 965.
6 G.M. Bancroft, T. Chan, R.J. Puddephatt and J.S. Tse, Inorg. Chem., 21 (1982) 2946.
7 R.L. Dekock, E.J. Baerends, P.M. Boerrigter and R. Hengelmolen, J. Am. Chem. Soc., 106 (1984) 3387.
8 A. Haaland, J. Mol. Struct., 97 (1983) 115.
9 T.G. Strand and R.A. Bonham, J. Chem. Phys., 40 (1964) 1686.
10 A.C. Yates, Comput. Phys. Commun., 2 (1971) 175.
11 R.A. Bonham and L. Schäfer in J.A. Ibers and W.C. Hamilton (Eds.), International Tables for X-ray Crystallography, Vol. IV, Kynoch Press, Birmingham, 1974.
12 R.L. Hilderbrandt and J.D. Wieser, J. Chem. Phys., 55 (1971) 4648.
13 E.G. Perevalova, I.G. Bolesov, Yu.T. Struchkov, I.F. Leschova, Ye.S. Kalyuzhnaya, T.I. Voyevodskaya, Yu.L. Slovokhotov and K.I. Grandberg, J. Organomet. Chem., 286 (1985) 129.
14 N.C. Baenziger, W.E. Bennett and D.M. Soboroff, Acta Cryst. B, 32 (1976) 962.
15 A. Haaland, Organometallic Compounds Studied by Gas-Phase Electron Diffraction, Top. Curr. Chem., 53 (1975) 1.
16 A. Haaland in I. Hargittai (Ed.), The Molecular Structures of Organometallic Compounds of Main Group Elements Determined by Gas Electron Diffraction, in Stereochemical Applications of Gas-Phase Electron Diffraction, VCH Publishers, Deerfield Beach, Fla., in press.
17 L.S. Bartell and L.O. Brockway, J. Chem. Phys., 32 (1960) 512.
18 K.P. Huber and G. Herzberg, Molecular Spectra and Molecular Structure, Vol. IV, Constants of Diatomic Molecules, Van Nostrand, New York, 1979.
19 K. Kashiwabara, S. Konaka, T. Iijima and M. Kimura, Bull. Chem. Soc. Japan, 46 (1973) 407.
20 P. Pyyköö and J.-P. Desclaux, Acc. Chem. Res., 12 (1979) 267.
21 K.S. Pitzer Acc. Chem. Res., 12 (1979) 271.