Synthesis and Crystal Structure of Cyano(trimethylphosphine)gold(I)

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The crystal structure of $[AuCN\{P(CH_3)_3\}]$, $M_r = 299.063$, has been determined at room temperature from single-crystal X-ray intensity data. The space group is triclinic, $P\bar{1}$, with $a = 9.031(2)$, $b = 9.481(2)$, $c = 13.990(4)$ Å, $\alpha = 76.03(1)$, $\beta = 79.64(2)$, $\gamma = 75.61(2)°$, $V = 1116.8(3)$ Å^3, $Z = 6$, $D_x = 2.67$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.7107 Å, $\mu = 19.81$ mm^{-1} and $F(000) = 134$. The refinement for the positional and thermal parameters, carried out by full matrix least-squares calculations, converged to $R = 0.055$ and $R_w = 0.069$ for 2415 reflections with $I > 3\sigma(I)$.

There are three $[AuCN\{P(CH_3)_3\}]$ complexes in the asymmetric unit with P–Au–C angles close to linear, between 178.4 and 178.8°. The complexes are stacked along ***a*** in a staggered conformation so that an infinite zig-zag-shaped array of gold atoms is formed. Within a chain the angles Au–Au–Au are between 138 and 140° and the Au–Au distances between 3.24 and 3.32 Å. Since there are no ligand bridges between the gold atoms, the fairly short gold–gold distances indicate weak metal–metal bonding. It is thus justified to formulate the compound as $[AuCN\{P(CH_3)_3\}]_\infty$. There are only van der Waals interactions between the chains.

Gold(I) readily forms crystalline complexes of the composition AuXY, where X = Cl, Br, I and Y is a sulfide. For X = Cl or Br and Y = dibenzylsulfide[1] (DBS) or tetrahydrothiophene[2] (THT), the crystals contain infinite chains of virtually linear complexes XAuY, joined by Au–Au bonds. The two DBS compounds are, moreover, isostructural, and so are the corresponding THT compounds. The Au–Au distances do not vary much, only between 3.29 and 3.35 Å, indicating a fairly weak metal–metal bond of much the same strength in all the compounds. The iodide AuI(THT) has, on the other hand, a very different structure,[3] composed of alternating linear cations $Au(THT)_2^+$ and linear anions AuI_2^-, joined by quite strong metal–metal bonds. The Au–Au distances are 2.97–2.98 Å, i.e. only about 0.1 Å longer than in gold metal. An isostructural compound is formed by tetrahydroselenophene,[2] with Au–Au bonds of much the same strength, bond length 2.99–3.00 Å.

An important aim of the present investigation is to find the conditions for the formation of such arrays of gold atoms in crystal structures. To this end it might be fruitful to look into the consequences of an exchange of sulfide for phosphine.

Compounds AuXY where Y is the aromatic triphenylphosphine are generally simple monomers in the crystalline state.[4–7] This applies not only to the halides but also[5,7] to X = SCN or CN. If X is the extremely soft ligand 2-phenylethynyl a dimer is formed, however.[8] With the aliphatic trimethylphosphine, even the less soft iodide causes a dimeric complex to be formed.[6] A further interesting combination would evidently be that of an aliphatic phosphine and the very soft cyanide ligand.

The structure of such a complex, viz. cyano(triethylphosphine)gold(I) has been investigated and reported to be a monomer.[9] The analogous trimethylphosphine complex has now been prepared, and its structure solved. In connection with this, the geometric structure of the triethylphosphine complex has been recalculated from the published atomic coordinates. Both complexes have chain structures, with Au–Au distances similar to those quoted above for the chloro and bromo sulfides, as will be further discussed below.

Secondary and, even more, primary phosphines are generally stronger donors than the tertiary ones. It might therefore be postulated that such phosphines provoke chain or, at least, pair formation even with less soft ligands X than CN or I. Recent investigations show that this is indeed the case, as is evident from the comparison presented below.

Experimental

The compound was obtained by a procedure analogous to that used previously for the corresponding iodide,[6] i.e. by treating an ethanolic solution of the chloride with sodium cyanide.[10] The pale yellow product was recrystallized from

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Table 1. Positional and isotropic thermal parameters for the non-hydrogen atoms with e.s.d.s in parentheses.

Atom	*x/a*	*y/b*	*z/c*	$U_{iso}/10^{-2}$ Å^2 [a]
Au1	0.10251(11)	0.27466(10)	0.19529(7)	4.36(3)
Au2	0.43709(11)	0.19349(10)	0.28464(7)	4.47(4)
Au3	0.80337(11)	0.12366(10)	0.21011(6)	4.47(4)
P1	0.2051(7)	0.2147(8)	0.0462(5)	5.0(2)
P2	0.4215(7)	0.4292(7)	0.3031(5)	4.6(2)
P3	0.8681(7)	−0.0638(7)	0.3418(4)	4.4(2)
C1	0.013(3)	0.323(2)	0.329(2)	4.2(8)
C2	0.454(3)	−0.021(3)	0.272(2)	5.6(1.0)
C3	0.750(4)	0.285(3)	0.092(2)	5.7(1.2)
N1	−0.030(3)	0.347(3)	0.400(2)	7.4(1.1)
N2	0.461(3)	−0.124(3)	0.264(2)	9.2(1.4)
N3	0.721(3)	0.367(4)	0.035(2)	10.6(1.8)
C11	0.201(3)	0.023(3)	0.042(3)	8.8(1.5)
C12	0.413(2)	0.214(3)	0.010(2)	5.9(1.1)
C13	0.118(3)	0.321(3)	−0.062(2)	6.2(1.1)
C21	0.325(4)	0.465(3)	0.421(2)	7.2(1.2)
C22	0.608(3)	0.482(3)	0.293(3)	7.3(1.3)
C23	0.319(4)	0.571(3)	0.209(2)	7.4(1.3)
C31	0.738(3)	−0.035(4)	0.455(2)	7.6(1.3)
C32	0.859(3)	−0.247(2)	0.326(2)	7.0(1.2)
C33	1.060(3)	−0.080(3)	0.372(2)	5.3(0.9)

[a] U_{iso} has been calculated from the average of the anisotropic temperature factors.

chloroform, yielding colourless crystals. That this method also works in the case of cyanide had been confirmed by Dr. Goggin in a personal communication.

A single crystal with the dimensions 0.184 × 0.04 × 0.088 mm was used for data collection at room temperature on a CAD-4 diffractometer employing graphite-monochromatized Mo$K\alpha$ radiation ($\bar{\lambda}$ = 0.7107 Å). Laue class $\bar{1}$ and no systematic extinctions are consistent with the space groups $P1$ and $P\bar{1}$. Unit-cell dimensions were determined by least-squares calculations from 50 θ-angles measured on the diffractometer as $\theta_{hkl} = (\omega_{hkl} - \omega_{\bar{h}\bar{k}\bar{l}})/2$; a = 9.031(2), b = 9.481(2), c = 13.990(4) Å, α = 76.03(1), β = 79.64(2), γ = 75.61(2)°, V = 1116.8(3) Å^3 and Z = 6. The intensities of 4178 reflections in one hemisphere (3.0 < θ < 25.0°) were measured with ω–2θ scan (Δω = 0.7° + 0.5° tan θ). The scan interval was extended by 25 % at both ends for the background measurements. The ratio $\sigma(I)/I$ requested in a scan was 0.03 and the maximum recording time was 180 s. The variation in three standard reflections was <8 %. I and $\sigma(I)$ were corrected for Lorentz, polarisation and absorption effects (μ = 19.81 mm^{-1}, transmission factors 0.184–0.342). Only the 2415 reflections with $I > 3\sigma(I)$ were used in the calculations. The structure was solved by Patterson and difference Fourier methods assuming the centrosymmetric space group $P\bar{1}$. In the final cycles of full-matrix least-squares with all atoms anisotropically refined the weights were calculated from eqn. (1).

$$w^{-1} = \sigma^2(|F_o|) + (0.055|F_o|)^2 + 3.0 \quad (1)$$

The function minimized was $\Sigma w(|F_o| - |F_c|)^2$. The final R-values were R = 0.055 and R_w = 0.069. A δR-plot re-

Table 2. Selected bond distances (in Å) and angles (in °).[a]

Coordination geometry around the gold atoms					
Au3^{i}–Au1	3.312(1)	Au3^{i}–Au1–Au2	139.21(4)		
Au1–Au2	3.320(2)	Au1–Au2–Au3	140.10(4)		
Au2–Au3	3.236(2)	Au2–Au3–Au1^{ii}	138.12(4)		
Au1–P1	2.268(6)	P1–Au1–C1	178.8(7)		
Au2–P2	2.279(6)	P2–Au2–C2	178.4(8)		
Au3–P3	2.277(6)	P3–Au3–C3	178.5(8)		
Au1–C1	2.02(2)				
Au2–C2	2.06(3)				
Au3–C3	2.00(3)				
Geometry of the cyanide groups					
C1–N1	1.06(3)	Au1–C1–N1	178(2)		
C2–N2	0.99(4)	Au2–C2–N2	179(3)		
C3–N3	0.99(5)	Au3–C3–N3	178(3)		
Geometry of the trimethylphosphine molecules					
P1–C11	1.84(3)	C11–P1–C12	101(1)	Au1–P1–C11	113(1)
P1–C12	1.85(2)	C11–O1–C13	103(1)	Au1–P1–C12	115(1)
P1–C13	1.79(3)	C12–P1–C13	104(1)	Au1–P1–C13	118(1)
P2–C21	1.79(3)	C21–P2–C22	104(1)	Au2–P2–C21	113(1)
P2–C22	1.84(3)	C21–P2–C23	106(1)	Au2–P2–C22	115(1)
P2–C23	1.84(3)	C22–P2–C23	104(1)	Au2–P2–C23	112(1)
P3–C31	1.83(3)	C31–P3–C32	105(1)	Au3–P3–C31	111(1)
P3–C32	1.83(2)	C31–P3–C33	105(1)	Au3–P3–C32	114(1)
P3–C33	1.82(2)	C32–P3–C33	107(1)	Au3–P3–C33	114(1)

[a] Symmetry codes: $^{i}x - 1, y, z$; $^{ii}x + 1, y, z$.

sulted in a straight line with slope 1.04 and intercept −0.07. Scattering factors with corrections for anomalous dispersion were taken from Ref. 11. Tables of $|F_o|$, $\sigma(|F_o|)$ and $|F_c|$ are available on request from the authors. The computer programs used are those compiled and amended by Lundgren.[12] Final atomic parameters are given in Table 1 and selected bond distances and angles in Table 2.

Description and discussion of the structure

The asymmetric unit contains three virtually linear neutral complexes, $[AuCN\{P(CH_3)_3\}]$; the P–Au–C angles are in the range 178.4–178.8°. The complexes are stacked along ***a*** in a staggered conformation so that an infinite zig-zag-shaped array of gold atoms is formed (Fig. 1). The angles Au–Au–Au are in the range 138–140° and the Au–Au distances are 3.24–3.32 Å. The chains are thus considerably more bent than in the sulfide and selenide complexes quoted above, where the Au–Au–Au angles are all around 160°. As to the Au–Au bond lengths, they are slightly shorter than in the DBS and THT chloro and bromo complexes. On the other hand, they are much longer than in the iodo complexes $[AuI(THT)]_\infty$ and $[AuI(THSe)]_\infty$. Somewhat unexpectedly, the chains found by the recalculation of the triethylphosphine complex have much the same Au–Au bond length, viz. 3.36 Å, and Au–Au–Au angle, 168°, as in the chloro and bromo sulfide complexes. Au–Au distances around 3.3 Å certainly indicate only weak interactions; it nevertheless seems appropriate to characterize these complexes as infinite metal–metal bonded structures. Among the phosphines, only the aliphatic ones seem able to provoke the formation of chain structures and moreover only in combination with the very soft cyanide ligand. With iodide, metal–metal bond formation in conjunction with an aliphatic phosphine stops with the dimer.

The angle Au–C–N is, as expected, close to linear in both the aromatic and the aliphatic phosphine complexes. Also the Au–C bond lengths are, within experimental error, much the same.

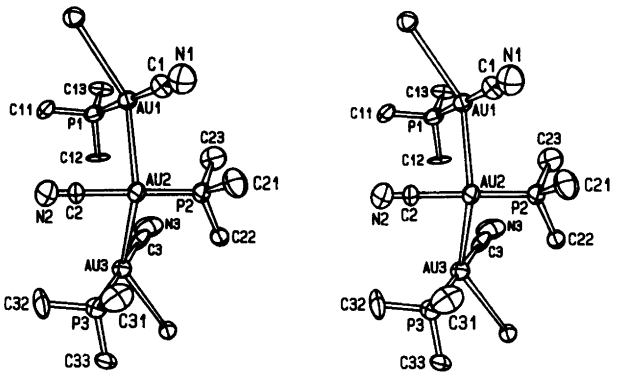

Fig. 1. A stereoscopic view of the coordination around the three crystallographically independent gold(I) atoms.

As might be surmised, dimers and chains are more readily formed in conjunction with the softer secondary and primary phosphines. In combination with secondary *o*-tolylphosphine, the chloride already form pairs,[13] admittedly with a fairly long distance Au–Au = 3.56 Å. Pairs are also formed in the diphenylphosphine gold(I) bromide,[14] with Au–Au = 3.256 Å; the shorter distance is certainly in the main due to the increase in softness on going from Cl to Br. In the primary 2,4,6-tributylphenylphosphine, the bulky organic group should make an aggregation of AuYX difficult; pairs are still formed with X = Cl, however, with an Au–Au distance = 3.440 Å.[15] The combination of 2-methylphenylphosphine and X = Br, finally, results in a chain structure.[16] Most interestingly, two Au–Au distances appear: a short one, 3.097 Å, and a long one, 3.380 Å; i.e. the same feature as in the present compound $[AuCN(PMe_3)]_\infty$, although in a much more marked degree.

Evidently, metal–metal bonds are formed more readily, the softer the ligands X *and* Y.

The Au–P bond lengths are, as expected, much the same in $[AuCN(PMe_3)]_\infty$ and $[AuCN(PEt_3)]_\infty$ (Table 3). In this table the Au–P bond lengths of a number of other phosphine complexes of interest are also listed. For the aromatic phosphine complexes the Au–P bonds seem to be longer, and hence weaker, as the donor strength of the other ligand, X, increases, i.e. in the sequence Cl < Br,SCN,I < CN, as might indeed be expected. No significant difference in bond length seems to exist between aromatic and aliphatic phosphine complexes, however. One might *per se* expect a shorter bond for the aliphatic species which are the stronger donors. This effect is wholly offset, however, by the dimer and chain formation taking

Table 3. Au–P bond distances in two-coordinated gold(I) complexes with phosphine ligands.

Compound	d_{Au-P}/Å	Ref.
$[AuCl(PH_2\{Bu_3Ph\})]_2$	2.242(2)	15
$[AuBr(PH_2\{MePh\})]_\infty$	2.244(2)	16
$[AuCl(PH\{Bu^n\}_2)]$	2.230(2)	13
$[AuBr(PHPh_2)]_2$	2.225(4)	14
$[AuCl(PPh_3)]$	2.235(3)	4
$[AuBr(PPh_3)]$	2.252(6)	5
$[AuI(PPh_3)]$	2.254(5)	5
$[AuI(PPh_3)]$	2.249(2)	6
$[AuSCN(PPh_3)]$	2.252(7)	5
$[AuCN(PPh_3)]$	2.278(2)	7
$[AuMe(PPh_3)]$	2.279(8)	17
$[Au(PPh_3)_2][TCNQ]$	2.286(3)	18
$[Au(PPh_3)_2][PF_6]$	2.312(4)	19
$[Au(PMePh_2)_2][PF_6]$	2.316(4)	20
$[AuI(PMe_3)]_2$	2.256(3)	6
$[AuCN(PMe_3)]_\infty$	2.268(6)	This work
$[AuCNPMe_3)]_\infty$	2.277(6)	This work
$[AuCN(PMe_3)]_\infty$	2.279(6)	This work
$[AuCN(PEt_3)]_\infty$	2.288(5)	9

place with the aliphatic phosphines, which leads to a higher coordination number around Au and hence to a lengthening of the bonds.[19,21,22] That other factors, such as packing forces, could also be of influence is illustrated by the difference in Au–P distance between the two salts of the cation complex $Au(PPh_3)_2^+$ (Table 3).

The Au–P distances involving primary and secondary phosphines do not differ very much from those found for tertiary ones (Table 3). As might be expected, they are all on the lower side.

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References

1. Strähle, J., Hiller, W. and Conzelmann, W. *Z. Naturforsch., Teil B 39* (1984) 538.
2. Ahrland, S., Dreisch, K., Norén, B. and Oskarsson, Å. *To be published.*
3. Ahrland, S., Norén, B. and Oskarsson, Å. *Inorg. Chem. 24* (1985) 1330.
4. Baenziger, N. C., Bennett, W. E. and Soboroff, D. M. *Acta Crystallogr., Sect. B 32* (1976) 962.
5. Barron, P. F., Engelhardt, L. M., Healy, P. C., Oddy, J. and White, A. H. *Aust. J. Chem. 40* (1987) 1545.
6. Ahrland, S., Dreisch, K., Norén, B. and Oskarsson, Å. *Acta Chem. Scand., Ser. A 41* (1987) 173.
7. Jones, P. and Lautner, J. *Acta Crystallogr., Sect. C 44* (1988) 2091.
8. Bruce, M. I. and Duffy, D. N. *Aust. J. Chem. 39* (1986) 1697.
9. Hormann, A., Shaw, C., Bennet, D. and Reiff, W. *Inorg. Chem. 25* (1986) 3953.
10. Duddell, D. A., Goggin, P. L., Goodfellow, R. J., Norton, M. G. and Smith, J. G. *J. Chem. Soc. A* (1970) 545.
11. *International Tables for X-Ray Crystallography,* The Kynoch Press, Birmingham 1974, Vol. IV.
12. Lundgren, J. O. *Crystallographic Computer Programs,* Report No. UUIC-B13-4-05, University of Uppsala, Uppsala, Sweden 1982.
13. Schmidbaur, H., Weidenhiller, G., Aly, A. M. M., Steigelmann, O. and Müller, G. *Z. Naturforsch., Teil B 44* (1989) 1503.
14. Dyson, D. B., Parish, R. V., McAuliffe, C. A., Pritchard, R. G., Fields, R. and Beagley, B. *J. Chem. Soc., Dalton Trans.* (1989) 907.
15. Schmidbaur, H., Weidenhiller, G., Steigelmann, O. and Müller, G. *Chem. Ber. 123* (1990) 285.
16. Schmidbaur, H., Weidenhiller, G., Steigelmann, O. and Müller, G. *Z. Naturforsch., Teil B 45* (1990) 747.
17. Gavens, P. D., Guy, J. J., Mays, M. J. and Sheldrick, G. M. *Acta Crystallogr., Sect. B 33* (1977) 137.
18. Baenziger, N. C., Dittemore, K. M. and Doyle, J. R. *Inorg. Chem. 13* (1974) 805, *cf.* also Ref. 15.
19. Muir, J., Muir, M., Arias, S., Jones, P. G. and Sheldrick, G. M. *Inorg. Chim. Acta 81* (1984) 169.
20. Guy, J. J., Jones, P. G. and Sheldrick, G. M. *Acta Crystallogr., Sect. B 32* (1976) 1937.
21. Melnik, M. and Parish, R. V. *Coord. Chem. Rev. 70* (1986) 157.
22. Ahrland, S., Nilsson, K., Persson, I., Yuchi, A. and Penner-Hahn, J. E. *Inorg. Chem. 28* (1989) 1833.

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