

tionsablauf liegen aber zur Zeit noch nicht vor. Die Röntgenstrukturanalyse ermöglichte somit die Strukturaufklärung des nur in wenigen Kristallen gebildeten Nebenproduktes.

Die 1,3,4-Tri-*O*-acetyl-2-desoxy-2-fluor- α -D-xylopyranose weist im Kristall eine normale Sesselkonformation ${}^4C_1(D)$ auf. Das Fluor ist am C(2) äquatorial, die *O*-Acetylgruppe am C(1) axial gebunden. Es liegt somit die α -D-xylo-Konfiguration vor. Die Acetylgruppen nehmen eine Stellung ein wie sie auch bei anderen Zuckeracetaten gefunden wurden (Luger & Paulsen, 1974). Die C=O-Bindung der Acetylgruppen verläuft jeweils etwa parallel zur benachbarten C-H-Bindung des Rings. Die Bindungsabstände im Pyranosering (Tabelle 2) entsprechen den normalen Werten.

Es ist zu bemerken, dass der Abstand C(1)–O(6) mit 1,389 Å etwas kleiner ist als der von C(5)–O(6) mit 1,440 Å. Man könnte geneigt sein, hier einen 'Back-Donation-Effekt' zu vermuten, der bei axialer Gruppe an C(1) die C(1)–O(6)-Bindung verkürzt, was auch zur Verstärkung des anomeren Effektes führt. Die Daten sind jedoch etwas kritisch zu bewerten, da beim Tri-*O*-benzoyl- β -D-xylopyranosylbromid, bei dem ein derartiger Effekt vorhanden ist, die Abstandsdiﬀerenz der entsprechenden Bindungen mit 0,088 Å deutlich grösser ist (Luger, Durette & Paulsen, 1974). Messungen an D-Arabinose-tetraacetaten, bei denen die α - und β -Form vermessen wurden, zeigen, dass sowohl bei äquatorialer wie bei axialer Stellung des Substituenten am C(1) die C(1)–O(6)-Bindung etwas kleiner ist. Die Werte lauten: α -Form mit äquatorialer OAc-Gruppe C(1)–O(6) 1,409,

C(5)–O(6) 1,422 Å (James & Stevens, 1974a) und β -Form mit axialer OAc-Gruppe C(1)–O(6) 1,395, C(5)–O(6) 1,429 Å (James & Stevens, 1974b). Sicher sind noch weitere Abstandswerte in diesem Sinne zu vergleichen. Bei der untersuchten Verbindung dürfte die gefundene Abstandsdiﬀerenz aber schwerlich auf einen den anomeren Effekt verstärkenden 'Back-Donation-Effekt' zurückzuführen sein.

Literatur

- HALL, L. D. & MANVILLE, J. F. (1969). *Canad. J. Chem.* **47**, 19–30.
 HUTTNER, G. & SCHELLE, S. (1971). *MOLPLOT-Programm*. Technische Univ., München.
 JAMES, V. J. & STEVENS, J. D. (1974a). *Cryst. Struct. Commun.* **3**, 187–190.
 JAMES, V. J. & STEVENS, J. D. (1974b). *Cryst. Struct. Commun.* **3**, 19–22.
 KARLE, J. & HAUPTMAN, H. (1956). *Acta Cryst.* **9**, 635–651.
 KOTHE, G., LUGER, P. & PAULSEN, H. (1974). *Carbohydr. Res.* **37**, 283–292.
 LUGER, P., DURETTE, P. L. & PAULSEN, H. (1974). *Chem. Ber.* **107**, 2615–2625.
 LUGER, P., KOTHE, G. & PAULSEN, H. (1974). *Chem. Ber.* **107**, 2626–2634.
 LUGER, P. & PAULSEN, H. (1974). *Chem. Ber.* **107**, 1579–1589.
 LUNDT, K. & PEDERSEN, C. (1966). *Mikrochem. Acta*, S. 126–132.
 STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972). X-RAY system – version of June 1972. Tech. Rep. TR-192, Computer Science Center, Univ. of Maryland.

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2,2'-Bipyridyltriphenylphosphinegold(I) Hexafluorophosphate

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Abstract. [(C₁₀N₂H₈)Au{P(C₆H₅)₃}] [PF₆], triclinic, $P\bar{1}$; $a=11.025(1)$, $b=11.248(1)$, $c=12.045(2)$ Å, $\alpha=81.63(1)$, $\beta=71.98(1)$, $\gamma=72.57(1)^\circ$; $Z=2$, $D_o=1.85$, $D_c=1.87$ g cm⁻³. The Au atom is in a highly distorted threefold planar coordination, with an asymmetrically bonded bidentate bipyridyl ligand [Au–N, 2.166(2), 2.406(2) Å] and a triphenylphosphine ligand [Au–P, 2.212(1) Å] producing widely differing P–Au–N angles [157.1(1), 130.4(1)°].

Introduction. Initial cell dimensions were determined from precession photographs (Mo $K\alpha$ radiation). There were no systematic absences; the centrosymmetric space group $P\bar{1}$ was indicated by the statistical distribution of E values, and confirmed by successful structure refinement.

A thin plate 0.4 × 0.4 × 0.04 mm (dominant faces {010}) was sealed in a Lindemann glass tube and mounted on a Hilger–Watts Y290 four-circle diffractometer, with c misaligned slightly from the spindle (φ) axis. Cell parameters and the orientation matrix were refined by least squares from 12 reflexions ($2\theta > 37^\circ$) (Busing & Levy, 1967). Intensities were collected for all unique reflexions with $2\theta \leq 55^\circ$ (Mo $K\alpha$ radiation, Zr filter, $\lambda=0.71069$ Å, θ – 2θ scan mode, 2s count at each of 80 steps of 0.01° in θ , background counts of 40s at each end of the scan). Three standard reflexions showed <1% intensity decay during the collection; linear decay functions were calculated and applied. Absorption corrections were applied by a Gaussian integration method (Sheldrick, 1975) ($\mu=59.71$ cm⁻¹, 512 grid points, transmission factors ranging from

<0.4. An analysis of the variance (Hamilton, 1974) showed the weighting scheme to be consistent. Atomic parameters are shown in Table 1.*

Discussion. The compound (Fig. 1) was prepared from Ph_3PAuCl , bipyridyl and AgPF_6 in dichloromethane solution (Mays, 1975); an alternative method has been reported (Uson, Languna & Sanjoaquin, 1974). The structure was determined in order to distinguish between a trigonal planar coordination, which is rare in Au^I reported structures (Guggenberger, 1974; Baenziger, Dittmore & Doyle, 1974) and a linear twofold coordination such as is commonly observed, e.g. in $\text{Ph}_3\text{PAuSSCNEt}_2$ (Wijnhoven, Bosman & Beurskens, 1972), where the potentially bidentate dithiocarbamate ligand is coordinated to Au through only one S atom. The coordination is found to be intermediate between the two extremes.

Unconstrained bond lengths and angles are shown in Fig. 2. The coordination is close to planar, the Au atom lying 0.10 Å out of the plane of the three coordinating atoms. The binding of the bidentate bipyridyl ligand is highly asymmetric, and the Au–P length is comparable to that in two- rather than three-coordinate Au^I complexes [comprehensive lists are given by Guggenberger (1974) and Baenziger *et al.* (1974)]. A remarkably similar coordination geometry has been observed in $[(\text{bipy})\text{HgMe}]^+$ (Canty, Marker & Gatehouse, 1975). The two rings of the bipyridyl ligand are essentially planar (r.m.s. deviations from least-squares planes are 0.010 and 0.015 Å), but the coordinated ligand is subject to distortions such as have been observed and discussed for other bipyridyl metal complexes (Clegg & Wheatley, 1974) [angle of twist about C(5)–C(6) $\sim 7^\circ$; the Au–N bonds are inclined at 8 and 2.2° to the two rings].

The deviations from 120° of the bond angles at Au in $(\text{Ph}_3\text{P})_2\text{AuCl}$ have been attributed to steric factors (Baenziger *et al.*, 1974). The distortion is accompanied, however, by a shortening of the Au–P bonds relative to $[(\text{Ph}_3\text{P})_3\text{Au}]^+$ (Guggenberger, 1974) and a notably long Au–Cl bond. This represents a distortion away from trigonal planar towards twofold linear coordination, which is even stronger in $[(\text{bipy})\text{Au}(\text{PPh}_3)]^+$ and almost complete in $(\text{PPh}_3)\text{AuSSCNEt}_2$ (Wijnhoven *et al.*, 1972): the trends in bond lengths and angles, allowing for the different ligands involved, are consistent in the series of four complexes (Fig. 3). This distortion of trigonal coordination illustrates the principles already applied by Orgel (1958) to distorted octahedral and tetrahedral coordination of d^{10} ions such as Au^I and Hg^{II} , and is an example of a second-order Jahn–Teller effect (Jørgensen, 1962). A similar tendency

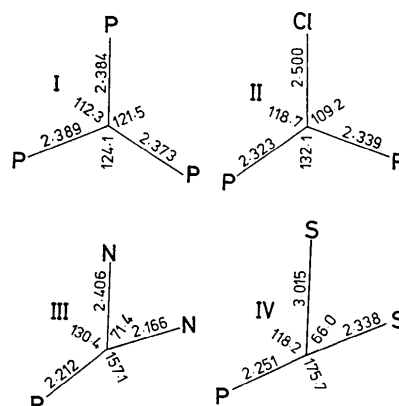


Fig. 3. Coordination of Au in Au^I complexes. (I) $[(\text{Ph}_3\text{P})_3\text{Au}]^+$; (II) $(\text{Ph}_3\text{P})_2\text{AuCl}$; (III) $[(\text{bipy})\text{AuPPh}_3]^+$; (IV) $(\text{Ph}_3\text{P})\text{AuSSCNEt}_2$.

towards linear twofold coordination has been observed in pentacoordinate d^{10} complexes (Epstein & Bernal, 1971; Clegg, Greenhalgh & Straughan, 1975) and may be similarly explained.

References

- BAENZIGER, N. C., DITTMORE, K. M. & DOYLE, J. R. (1974). *Inorg. Chem.* **13**, 805–811.
- BUSING, W. R. & LEVY, H. A. (1967). *Acta Cryst.* **22**, 457–464.
- CANTY, A. J., MARKER, A. & GATEHOUSE, B. M. (1975). *J. Organomet. Chem.* **88**, C31–C34.
- CHURCHILL, M. R. (1973). *Inorg. Chem.* **12**, 1213–1214.
- CLEGG, W. (1976). *Inorg. Chem.* **15**. In the press.
- CLEGG, W., GREENHALGH, D. A. & STRAUGHAN, B. P. (1975). *J. Chem. Soc. Dalton*, pp. 2591–2593.
- CLEGG, W. & WHEATLEY, P. J. (1974). *J. Chem. Soc. Dalton*, pp. 511–517.
- CROMER, D. T. & IBERS, J. A. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 149–150. Birmingham: Kynoch Press.
- CROMER, D. T. & WABER, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 99–102. Birmingham: Kynoch Press.
- DOMENICANO, A. & VACIAGO, A. (1975). *Acta Cryst.* **B31**, 2553–2554.
- EPSTEIN, E. F. & BERNAL, I. (1971). *J. Chem. Soc. (A)*, pp. 3628–3631.
- GUGGENBERGER, L. J. (1974). *J. Organomet. Chem.* **81**, 271–280.
- HAMILTON, W. C. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 293–294. Birmingham: Kynoch Press.
- JØRGENSEN, C. K. (1962). *Orbitals in Atoms and Molecules*, pp. 77–79. London: Academic Press.
- MAYS, M. J. (1975). Private communication.
- ORGE, L. E. (1958). *J. Chem. Soc.* pp. 4186–4190.
- SHELDRICK, G. M. (1975). *SHELX: Program for Crystal Structure Determination*, Univ. Chemical Laboratory, Lensfield Road, Cambridge, England.
- USON, R., LANGUNA, A. & SANJOAQUIN, J. L. (1974). *J. Organomet. Chem.* **80**, 147–154.
- WIJNHOVEN, J. G., BOSMAN, W. P. J. H. & BEURSKENS, P. T. (1972). *J. Cryst. Mol. Struct.* **2**, 7–15.

* A list of structure factors and a table of H atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31816 (37 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.