Acta Cryst. (1985). C**41**, 1174–1176

Structures of Two Gold(I) Complexes with Tricyclohexylphosphine: $[(Cy_3P)AuCl]$ and $[(Cy_3P)_2Au]^+.Cl^-$

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(*Received* 9 *October* 1984; *accepted* 12 *April* 1985)

Abstract. Chloro(tricyclohexylphosphine)gold(I), $C_{18}H_{33}AuClP$ (MONO), $M_r = 512{\cdot}86$, triclinic, $P\bar{1}$, $a = 9{\cdot}214\ (3)$, $b = 10{\cdot}147\ (3)$, $c = 10{\cdot}890\ (3)$ Å, $\alpha = 89{\cdot}25\ (2)$, $\beta = 80{\cdot}58\ (2)$,* $\gamma = 77{\cdot}41\ (2)°$, $V = 980{\cdot}0$ Å^3, $Z = 2$, $D_x = 1{\cdot}74$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 7{\cdot}7$ mm^{-1}, $F(000) = 504$, room temperature, final $R = [\sum(|F_o| - |F_c|)/\sum F_o] = 0{\cdot}056$ for 2935 unique reflections. Bis(tricyclohexylphosphine)gold(I) chloride, $C_{36}H_{66}AuP_2^+.Cl^-$ (BIS), $M_r = 793{\cdot}29$, monoclinic, $P2_1/c$, $a = 9{\cdot}504\ (2)$, $b = 17{\cdot}421\ (3)$, $c = 11{\cdot}607\ (2)$ Å, $\beta = 107{\cdot}82\ (2)°$, $V = 1829{\cdot}6$ Å^3, $Z = 2$, $D_x = 1{\cdot}44$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 4{\cdot}2$ mm^{-1}, $F(000) = 816$, room temperature, final $R = 0{\cdot}034$ for 2313 unique reflections. Both MONO and BIS adopt linear two-coordinate configurations typical of Au^I. The coordination in MONO is nearly linear, with a P—Au—Cl angle of 177·0 (2)° and Au—P and Au—Cl bond distances of 2·242 (4) and 2·279 (5) Å, respectively. In the BIS complex the Cl is ionic. The cation $[(Cy_3P)_2Au]^+$ is at a center of symmetry, so the two phosphines are staggered with exactly linear P—Au—P coordination and the P—Au distance is 2·321 (2) Å.

Introduction. Although gold(I) compounds with phosphine ligands usually form linear two-coordinate gold(I) complexes, several three- and four-coordinate gold(I) complexes have recently been reported with triphenylphosphine and with thiocyanato or chloro ligands. Thus, for $L = Ph_3P$, L_2AuSCN and L_2AuCl are three-coordinate (Muir, Muir & Arias, 1982; Baenziger, Dittemore & Doyle, 1974), while L_3AuSCN (Muir, Muir, Arias, Campana & Dwight, 1982; Muir, Muir, Arias, Jones & Sheldrick, 1984) and L_3AuCl (Jones, Sheldrick, Muir, Muir & Pulgar, 1982) are four-coordinate. On the other hand, for $L' = Cy_3P$, the tricyclohexylphosphine complexes $[L'_2Au]$SCN and $[L'_2Au]PF_6$ both form linear two-coordinate ionic structures (Muir, Muir & Lorca, 1980; Cooper, Dennis, Henrick & McPartlin, 1980). In an effort to obtain higher-coordinate complexes with Cy_3P, we attempted to prepare L'_3AuCl.

Experimental. Anhydrous tetrachloroauric acid was reduced to Au^I by reaction with 2,2′-thiodiethanol in EtOH, after which tricyclohexylphosphine was added stoichiometrically to precipitate MONO. The precipitate was then reacted with a fivefold excess of tricyclohexylphosphine, and the EtOH solution evaporated to yield colorless crystals with an elementary analysis of $C_{36}H_{66}P_2AuCl$ (BIS). Further examination of these crystals revealed a few with a different crystalline form, which might be the desired higher-coordinate complex. Subsequent structural analyses showed these to be a few crystals of MONO among the many crystals of BIS.

Rectangular plates, 0·15 × 0·15 × 0·06 mm for MONO, trapezoidal plates, 0·3 × 0·2 × 0·15 mm for BIS, Stoe diffractometer, profile-fitted intensities (Clegg, 1981), monochromated Mo $K\alpha$, $2\theta_{max} = 50°$, room-temperature lattice parameters from least squares for 32 (MONO), 36 reflections (BIS) (both in range $20 \le 2\theta \le 24°$). MONO: $+h\pm k\pm l$ with $h \le 10$, $|k| \le 12$, $|l| \le 12$, plus some $-h$ equivalents; 3 standard reflections, *ca* 6% decay corrected for; total reflections 3913, R_{int} 0·039; 3432 unique reflections, 2935 with $F > 4\sigma(F)$; BIS: $-h+k\pm l$ with $|h| \le 11$, $k \le 20$, $|l| \le 13$; 3 standards, no decay; because of pseudo A centering, some equivalents of the weak reflection class with $h+$ were also collected; total reflections 3781, R_{int} 0·024; 3209 unique reflections, 2313 with $F > 3\sigma(F)$. Absorption corrections from ψ scans, transmission factors 0·50 to 0·86 (MONO) and 0·41 to 0·46 (BIS). Both structures solved with *SHELXTL* (Sheldrick, 1978), heavy-atom and Fourier

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* Part of this paper was presented at the American Crystallographic Association as Abstract PB22, *ACA Abstracts Ser.* 2, Vol. 11 (1982), at which time the MONO β parameter was incorrectly listed as 89·25°.

0108-2701/85/081174-03$01.50

Table 1. *Atom coordinates* ($\times 10^4$) *and isotropic temperature factors* ($\text{Å}^2 \times 10^3$)

	MONO				BIS			
	x	y	z	U or U_{eq}*	x	y	z	U or U_{eq}*
Au(1)	3854 (1)	−355 (1)	2780 (1)	47 (1)*	5000	5000	0	30 (1)*
P	4130 (3)	1781 (3)	2871 (2)	38 (1)*	5309 (1)	4985 (1)	2062 (1)	28 (1)*
C(11)	3308 (11)	2488 (10)	4440 (9)	41 (2)	3520 (5)	5090 (3)	2356 (4)	31 (1)
C(12)	1677 (13)	2355 (12)	4801 (10)	51 (3)	2715 (6)	5830 (3)	1819 (5)	41 (1)
C(13)	1034 (17)	2821 (14)	6132 (12)	72 (4)	1284 (6)	5918 (3)	2162 (5)	48 (2)
C(14)	1226 (14)	4204 (12)	6390 (11)	58 (3)	266 (7)	5234 (3)	1713 (5)	47 (2)
C(15)	2783 (15)	4359 (14)	6055 (12)	70 (4)	1040 (6)	4478 (4)	2153 (5)	53 (2)
C(16)	3416 (15)	3939 (12)	4698 (11)	61 (3)	2499 (6)	4402 (3)	1877 (5)	43 (2)
C(21)	3123 (11)	2857 (10)	1758 (9)	40 (2)	6053 (6)	4042 (3)	2685 (4)	29 (1)
C(22)	3616 (13)	4210 (11)	1456 (10)	50 (3)	6231 (6)	3946 (3)	4041 (5)	42 (2)
C(23)	2618 (15)	5062 (12)	663 (11)	61 (3)	6726 (6)	3130 (3)	4435 (6)	51 (2)
C(24)	2552 (16)	4356 (13)	−521 (12)	70 (4)	8167 (7)	2937 (4)	4183 (5)	54 (2)
C(25)	2104 (16)	3009 (14)	−254 (13)	73 (4)	8009 (7)	3035 (3)	2846 (5)	53 (2)
C(26)	3126 (15)	2086 (13)	540 (11)	62 (3)	7488 (6)	3849 (3)	2416 (5)	43 (2)
C(31)	6120 (12)	1906 (11)	2614 (9)	45 (2)	6595 (6)	5729 (3)	2921 (5)	31 (1)
C(32)	6911 (14)	1349 (13)	1318 (11)	63 (3)	6247 (6)	6017 (3)	4061 (5)	41 (2)
C(33)	8585 (17)	1444 (15)	1124 (14)	78 (4)	7366 (7)	6609 (3)	4734 (5)	47 (2)
C(34)	9360 (20)	752 (17)	2180 (14)	91 (5)	7469 (7)	7278 (4)	3940 (5)	56 (2)
C(35)	8583 (17)	1249 (16)	3417 (13)	81 (4)	7852 (7)	7000 (4)	2823 (6)	59 (2)
C(36)	6919 (15)	1204 (13)	3603 (12)	64 (3)	6721 (7)	6406 (3)	2112 (5)	45 (2)
Cl	3468 (5)	−2498 (3)	2767 (4)	87 (2)*	0	0	0	61 (1)*

* Equivalent isotropic U calculated from anisotropic U. $U_{eq} = (U_{11} + U_{22} + U_{33})/3$.

methods; isotropic then anisotropic refinement on F of Au, Cl and P, H by riding model [C—H 0·96 Å, H—C—H 109·5°, U(H) = 1·2 U(C)]. MONO: $wR = 0{\cdot}058$, $w^{-1} = \sigma^2(F) + 0{\cdot}0007\,F^2$; difference syntheses showed no densities above 1·0 e Å^{-3} except one of 4·5 e Å^{-3} at a position related to the gold atom, which may be a minor twin component undetected on Weissenberg photo, residual absorption errors or fractionally occupied alternative gold site; max. Δ/σ −0·008. BIS: $wR = 0{\cdot}030$, $w^{-1} = \sigma^2(F) + 0{\cdot}00005F^2$, no difference peak above 0·5 e Å^{-3}; max. $\Delta/\sigma = 0{\cdot}025$. Scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. The atomic coordinates and equivalent isotropic temperature factors are listed in Table 1, and principal bond lengths and angles are listed in Table 2.*

The conformations of the title compounds and the numbering of the atoms are shown in Fig. 1. Both MONO and BIS adopt the two-coordinate linear geometry typical of Au^{I} complexes: MONO is nearly linear, with a P—Au—Cl angle of 177·0 (2)°, compared to 179·6 (8)° for analogous Ph_3PAuCl (Baenziger, Bennett & Soboroff, 1976); Au—Cl is 2·279 (5) for MONO, 2·279 (3) for Ph_3PAuCl; Au—P 2·242 (4) for MONO, 2·235 (3) for Ph_3PAuCl. A larger difference is observed in the average P—C distance, which is 1·842 (4) Å for MONO, but only 1·820 (22) Å for the less bulky Ph_3PAuCl.

Table 2. *Bond lengths* (Å) *and angles* (°)

	MONO	BIS		MONO	BIS
Au(1)—P	2·242 (4)	2·321 (2)	Au(1)—Cl	2·279 (5)	
P—C(11)	1·838 (10)	1·843 (7)	P—C(21)	1·848 (11)	1·846 (6)
P—C(31)	1·840 (13)	1·849 (6)			
P—Au(1)—Cl	177·0 (2)		Au(1)—P—C(11)	108·7 (5)	110·9 (3)
Au(1)—P—C(21)	111·7 (5)	109·0 (3)	Au(1)—P—C(31)	112·8 (4)	113·7 (3)
C(11)—P—C(21)	107·2 (5)	106·3 (3)	C(11)—P—C(31)	106·5 (6)	109·0 (4)
C(21)—P—C(31)	109·6 (6)	107·6 (3)			

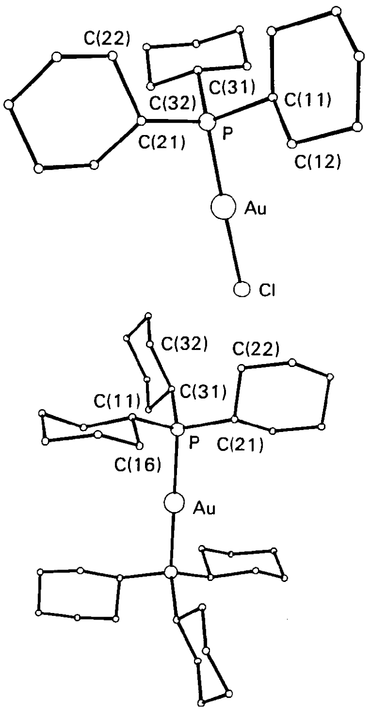

Fig. 1. The $(Cy_3P)AuCl$ molecule and $[(Cy_3P)_2Au]^+$ cation, and their atom-labeling schemes.

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* Lists of structure factors, anisotropic thermal factors and H coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42164 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The BIS complex is exactly linear with staggered tricyclohexylphosphine groups, as required by the location of the cation on a center of symmetry. This contrasts with the analogous complexes with SCN$^-$ (Muir, Muir & Lorca, 1980) and PF$_6^-$ (Cooper, Dennis, Henrick & McPartlin, 1980), which have nearly eclipsed tricyclohexylphosphine groups, and for which the P—Au—P angles are 177·2 (4) and 178·0 (2)°, respectively. Au—P bond lengths and their deviations are 2·321 (2), 2·306 (15) and 2·325 (1) Å, respectively, for the BIS, SCN$^-$ and PF$_6^-$ complexes.

Both of the title compounds resulted from our attempt to prepare a higher-coordinate complex with Cy$_3$P, specifically, L'_3AuCl. We find, however, that although two-, three-, or four-coordinate complexes can be prepared with $L' =$ Ph$_3$P, only linear two-coordinate complexes can be prepared with $L' =$ Cy$_3$P. This difference between Cy$_3$P and Ph$_3$P could be attributed to either steric or electronic effects. Since the ligand cone angles are not that different (170 *vs* 145°: Tolman, 1977), the effect may well be largely electronic. The phenyl group, through resonance, may better maintain optimum electronic density on the P and Au, even when additional groups are added. The cyclohexyl group, however, has only inductive effects with which to adjust electronic density in the complex.

This research has been supported in part by grant RR-8102 from the Division of Research Resources, US National Institutes of Health.

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Acta Cryst. (1985). C**41**, 1176–1179

Structure of a Binuclear Manganese(II) Complex: 1,1,1,1,1,2-Hexaaqua-*μ*-(*o*-phenylenediaminetetraacetato-O^1:N,N',O^2,O^3,O^4,O^5)-dimanganese(II), [Mn$_2$(C$_{14}$H$_{12}$N$_2$O$_8$)(H$_2$O)$_6$]

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(*Received* 25 *February* 1985; *accepted* 17 *April* 1985)

Abstract. $M_r = 554{\cdot}24$, triclinic, $P\bar{1}$, $a = 9{\cdot}893$ (1), $b = 11{\cdot}543$ (1), $c = 9{\cdot}844$ (1) Å, $\alpha = 98{\cdot}71$ (1), $\beta = 104{\cdot}59$ (1), $\gamma = 97{\cdot}70$ (1)°, $V = 1057{\cdot}9$ (2) Å^3, $Z = 2$, $D_m = 1{\cdot}744$, $D_x = 1{\cdot}741$ g cm^{-3}, λ(Cu $K\alpha$) = 1·5417 Å, $\mu = 102{\cdot}23$ cm^{-1}, $F(000) = 568$, $T = 293$ K. Final $R = 0{\cdot}048$ for 3335 observed reflections. The title compound is a binuclear manganese(II) complex bridged by a carboxylate oxygen of the aminopolycarboxylic acid. The chelated manganese(II) ion is coordinated to a water molecule and is heptacoordinate, whereas the other metal ion is octahedrally surrounded by six oxygen atoms.

Introduction. In an attempt to improve the complexing ability of aminopolycarboxylic acids such as ethylenediaminetetraacetic acid (H$_4$edta), substitution of the phenylene group for the ethylenic backbone has been proved to reduce the protonation constants of nitrogen donor atoms drastically, and to modify the formation constant for a series of transition-metal ions (Grimes, Huggard & Wilford, 1963; Nakasuka, Kunimatsu, Matsumura & Tanaka, 1985). The electron-withdrawing effect of the benzene ring apparently causes these changes in complexation of this type of new ligand, *o*-phenylenediamine-*N,N,N',N'*-tetraacetic acid (H$_4$phdta), and the planar configuration of the N—C—C—N moiety is expected to modify the mode of

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