Bis(4,5-dimethylimidazol-2-ylidene)gold(I) Chloride Hydrate: an Unexpected Product from the Reaction of Tris(4,5-dimethylimidazol-2-yl)phosphine and Tetrachloroauric Acid

By J. F. Britten, C. J. L. Lock* and Zhixian Wang

Laboratories for Inorganic Medicine, Departments of Chemistry and Pathology, McMaster University, ABB-266A, Hamilton, Ontario, Canada L8S 4M1

Abstract. [Au(C$_5$H$_8$N$_2$)$_2$]Cl.H$_2$O, M_r = 442.7, monoclinic, $P2_1/n$, a = 7.692 (2), b = 11.351 (2), c = 16.890 (3) Å, β = 97.98 (2)°, V = 1460.4 (5) Å^3, Z = 4, D_m = 2.01 (1), D_x = 2.013 Mg m^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, μ = 10.25 mm^{-1}, $F(000)$ = 840, T = 298 (1) K, R = 0.0350, wR = 0.0394 for 2581 unique reflections and 148 parameters. The Au atom is nearly rectilinearly bonded to C atoms from two imidazole rings. Part of the deviation of the C—Au—C angle [175.8 (2)°] from 180° is to allow the Au atoms in neighbouring cations to approach one another; Au$\cdots$Au$'$ = 3.372 (1) Å. The Au—C distances [2.012 (6) and 2.016 (6) Å] are similar to those in bis(1-benzylimidazolin-2-ylidene)gold(I) chloride (2.027 Å average) [Bonati, Burini & Pietroni (1989). *J. Organomet. Chem.* **375**, 147–160].

Introduction. Gold complexes are used in the treatment of rheumatoid arthritis. One of the drugs recently introduced, auranofin, contains a triethylphosphine group; we have been preparing other phosphine complexes for testing. When the ligand tris(4,5-dimethylimidazol-2-yl)phosphine was reacted with tetrachloroauric acid in methanol the title compound was obtained in low yield (14%),† instead of the expected phosphine gold(I) chloride complex. Crystals were obtained by evaporation of a 1:1 v/v methanol–water solution at 300 K.

Experimental. Density was measured by suspension in chloroform–bromoform mixture. The crystal chosen for diffraction was a colourless needle of dimensions 0.15 × 0.20 × 0.35 mm. Unit-cell parameters were determined by least-squares fit of positional parameters for 24 strong reflections with 20.6 < 2θ < 38.4°, on a Siemens $P4$ diffractometer with rotating anode and graphite-monochromated Mo $K\alpha$ radiation, at 298 (1) K. Intensities were measured for 2θ < 50° by ω–2θ-scan technique, with

$0 \le h \le 9$, $0 \le k \le 13$, $-20 \le l \le 19$, and scan speed 1.5–14.7° min^{-1} in 2θ. The total background time to scan ratio was 1:2. Three standard reflections ($0\bar{2}5$, 225, $1\bar{3}3$) measured every 100 reflections showed no instrument instability or crystal decay; R_{int} = 0.0065. 2941 reflections were measured. Profile analysis, Lp and empirical absorption corrections were made with the use of *SHELXTL-Plus* (Sheldrick, 1990) (μ = 10.25 mm^{-1}, transmission-factor range 0.019–0.057). Zonal reflections averaged to give 2581 independent reflections; R_{int} = 0.018. Reflections with $3\sigma_I \ge I \ge -3\sigma_I$ were treated by the method of French & Wilson (1978). The structure was solved by the Patterson method and all atoms, except two H atoms, were located from the difference maps. Anisotropic full-matrix least-squares refinement minimized $\sum w(|F_o| - |F_c|)^2$, $w = (\sigma_F^2 + 0.0010F_o)^{-1}$. Scale, secondary-extinction [x = 0.00025 (5)], positional and anisotropic temperature factors for non-H atoms were varied; 148 parameters. The H atoms on the water molecule were not found. Final R = 0.0350, wR = 0.0394, S = 0.89. Refinement ended when $(\Delta/\sigma)_{max}$ = 0.146. The final difference map revealed an electron density maximum of 1.40, and minimum of -0.83 e Å^{-3}, near the Au atom. Scattering factors were obtained from the program package (Sheldrick, 1990) on a VAX 3100 computer. Atomic positional parameters and U_{eq} values are given in Table 1.‡ Distances and angles are in Table 2. Best planes were calculated with the program *UTILITY* from the program suite *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989).

Discussion. The expected product from the reaction of tris(4,5-dimethylimidazol-2-yl)phosphine

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‡ The complete details of the preparation, as well as lists of structure factors, anisotropic temperature factors, H-atom positions, best planes and dihedral angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55130 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: BR0015]

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* To whom correspondence should be addressed.

† See deposition footnote.

Table 1. *Atomic coordinates* ($\times$ 10^4) *and equivalent isotropic displacement coefficients* (Å^2 $\times$ 10^3)

Equivalent isotropic U is defined as one third of the trace of the orthogonalized U_{ij} tensor.

|	x	y	z	U_{eq}
Au	482.2 (3)	967.3 (2)	4304.8 (1)	52 (1)
N(1)	$-$1228 (7)	$-$974 (4)	3230 (3)	55 (2)
C(2)	209 (8)	$-$389 (5)	3531 (3)	51 (2)
N(3)	1496 (8)	$-$874 (4)	3166 (3)	63 (2)
C(4)	870 (9)	$-$1784 (6)	2663 (4)	61 (2)
C(5)	$-$869 (8)	$-$1847 (5)	2690 (3)	55 (2)
C(1)	2006 (12)	$-$2458 (8)	2192 (5)	94 (4)
C(3)	$-$2288 (10)	$-$2625 (7)	2273 (4)	79 (3)
N(1a)	2306 (7)	2975 (5)	5250 (3)	53 (2)
C(2a)	833 (8)	2394 (5)	5020 (3)	61 (2)
N(3a)	$-$371 (7)	2990 (5)	5351 (3)	61 (2)
C(4a)	385 (10)	3941 (6)	5799 (4)	64 (2)
C(5a)	2054 (11)	3938 (6)	5730 (4)	69 (3)
C(1a)	$-$700 (12)	4759 (7)	6239 (5)	93 (3)
C(3a)	3554 (12)	4731 (8)	6046 (4)	99 (4)
Cl(1)*	5840 (3)	2016 (2)	4885 (1)	71 (1)
O(1)*	5840 (3)	2016 (2)	4885 (1)	71 (1)
Cl(2)*	5300 (4)	$-$263 (3)	3719 (2)	81 (1)
O(2)*	5300 (7)	$-$263 (3)	3719 (2)	81 (1)

* A disordered Cl$^-$ ion and H$_2$O molecule were refined on these sites with a 50% occupancy for each.

Table 2. *Interatomic distances* (Å) *and angles* (°) *and hydrogen-bonded distances* (Å)

Au—C(2)	2.012 (6)	Au—C(2a)	2.016 (6)
Au⋯Au'	3.372 (1)	N(1)—C(2)	1.328 (7)
N(1)—C(5)	1.400 (8)	C(2)—N(3)	1.353 (9)
N(3)—C(4)	1.381 (8)	C(4)—C(5)	1.347 (9)
C(4)—C(1)	1.48 (1)	C(5)—C(3)	1.50 (1)
N(1a)—C(2a)	1.322 (8)	N(1a)—C(5a)	1.390 (9)
C(2a)—N(3a)	1.331 (8)	N(3a)—C(4a)	1.398 (8)
C(4a)—C(5a)	1.31 (1)	C(4a)—C(1a)	1.51 (1)
C(5a)—C(3a)	1.50 (1)	Au⋯Cl(2),O(2)	4.210 (6)
Au⋯Cl(2),O(2)	4.204 (6)		

C(2)—Au—C(2a)	175.8 (2)	C(2)—Au—Au'	86.6 (2)
C(2a)—Au—Au'	97.5 (2)	C(2)—N(1)—C(5)	111.9 (5)
Au—C(2)—N(1)	129.6 (5)	Au—C(2)—N(3)	126.1 (4)
N(1)—C(2)—N(3)	104.2 (5)	C(2)—N(3)—C(4)	111.7 (5)
N(3)—C(4)—C(5)	106.4 (6)	N(3)—C(4)—C(1)	122.6 (6)
C(5)—C(4)—C(1)	131.0 (6)	N(1)—C(5)—C(4)	105.7 (5)
N(1)—C(5)—C(3)	121.7 (6)	C(4)—C(5)—C(3)	132.6 (6)
C(2a)—N(1a)—C(5a)	112.4 (6)	Au—C(2a)—N(1a)	128.0 (5)
Au—C(2a)—N(3a)	128.1 (4)	N(1a)—C(2a)—N(3a)	104.0 (5)
C(2a)—N(3a)—C(4a)	111.0 (6)	N(3a)—C(4a)—C(5a)	106.8 (6)
N(3a)—C(4a)—C(1a)	121.6 (7)	C(5a)—C(4a)—C(1a)	131.5 (7)
N(1a)—C(5a)—C(4a)	105.8 (6)	N(1a)—C(5a)—C(3a)	121.1 (7)
C(4a)—C(5a)—C(3a)	133.1 (7)		

Hydrogen bonds

N(1)⋯O(2),Cl(2)	3.014 (8)	N(3a)⋯Cl(1),O(1)	3.114 (8)
O(2),Cl(2)⋯Cl(1),O(1)	3.296 (8)	Cl(2),O(2)⋯Cl(1),O(1)	3.242 (8)
N(3)⋯Cl(2),O(2)	3.026 (8)	N(1a)⋯Cl(1),O(1)	3.069 (8)

Ball *et al.* (1984) suggested a mechanism which involved oxidation of the phosphine, followed by protonation of the sp^2 N atom of an imidazole group and subsequent C—P bond cleavage and elimination of imidazole. Clearly such a mechanism could apply in this case. The acid solution will cause protonation of substituted imidazole and Au^{III} is capable of oxidizing the phosphine; indeed it was planned to use excess phosphine as the reducing agent. Ball *et al.* (1984) did not address the nature of the eliminated group, implying that it is imidazole (*d*). We suggest that the mechanism is (only part of the molecule shown):

(a)   (b)   (c)   (d)
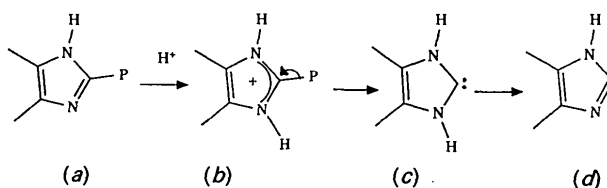
It appears that the carbene, (*c*), lasts sufficiently long to react with Au^I. It is not clear whether it is necessary for the phosphine to bind an Au atom to hold it near to the leaving carbene, nor whether Au is a catalyst in the process, a role assigned to Zn by Ball *et al.* (1984) in their studies of the cleavage of imidazole from tris(imidazol-2-yl)phosphine.

The title gold–carbene complex is very stable, and is similar in structure to bis(1-benzylimidazol-2-ylidene)gold(I) chloride (Bonati, Burini & Petroni, 1989). Corresponding angles agree very closely, both within and between compounds. Internally, equivalent bond lengths agree well: the largest difference is between C(4)—C(5) and C(4a)—C(5a) at 2.8σ. The picture of the carbene at (*c*) is only roughly accurate. The olefinic bonds, C(4)—C(5), C(4a)—C(5a), (average 1.329 Å) are consistent with C=C distances (1.337 Å). There is delocalization of the carbene electron density, however. Thus the average distance for N(1)—C(2), N(1a)—C(2a), N(3)—C(2) and N(3a)—C(2a), 1.334 (5) Å, is closer to that of a C=N bond rather than a single bond (1.29 *vs* 1.47 Å) (Pauling, 1960), and even the average distance for N(1)—C(5), N(1a)—C(5a), N(3)—C(4) and N(3a)—C(4a), 1.392 (5) Å, is shorter than a C—N
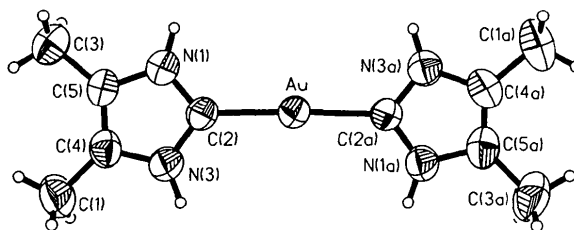
(tdmip) was (tdmip)AuCl, with the ligand bound to Au through the P atom. We have obtained similar compounds previously (Lock & Turner, 1987). The formation of the carbene (the cation is shown in Fig. 1) involves the cleavage of at least one of the imidazole groups from the phosphine and reaction of the carbene with Au. Such cleavage has been established previously in the presence of a metal (Ball, Brown & Cocho, 1984) and for a free ligand (Howard-Lock, Lock, Penny & Turner, 1989) when tris(imidazol-2-yl)phosphine was converted to a bis(imidazol-2-yl)phosphinic acid. In this previous work the fate of the cleaved imidazole was not established.

Fig. 1. The cation [(C$_5$H$_8$N$_2$)$_2$Au]$^+$ showing the atom numbering.

bond. As a consequence, the Au—C bond does not have much multiple-bond character. The average Au—C distance, 2.014 (6) Å, is not much shorter than Au^{III}—CH_3 bonds (Canty, Michin, Healy & White, 1982; Stein, Fackler, Paparizos & Chen, 1981) or than the formal Au—C single bonds in $[Au(C_6F_5)_2]^-$ (Usón, Laguna, Vicente, Garcia, Jones & Sheldrick, 1981). The distances are longer than other formal Au—C single bonds in 'BuNC—Au—Cl (Eggleston, Chodosh, Webb & Davis, 1986) and C_6F_5—$Au(C_5H_7NS)$ (Raubenheimer, Scott, Roos & Otte, 1990). They are as long as (Baukova, Slovokhotov & Struchkov, 1981; Schubert, Ackermann & Aumann, 1982) or longer than distances observed in compounds where a single carbene is bound to an Au atom (Raubenheimer, Scott, Roos & Otte, 1990; Bonati, Burini & Pietroni, 1991), suggesting that the carbene has a strong *trans* influence.

Because of the large errors involved in the structure determination by Bonati *et al.* (1989), one cannot say that there are significant differences based on a bond for bond comparison, particuarly within the imidazole rings. The average values do differ, however, and in a manner which is systematic. Thus ⟨C(4)—C(5), C(4a)—C(5a)⟩ in our compounds is shorter by 0.034 Å, ⟨N(1)—C(5), N(1a)—C(5a),

N(3)—C(4), N(3a)—C(4a)⟩ is longer by 0.033 Å and ⟨N(1)—C(2), N(1a)—C(2a), N(3)—C(2), N(3a)—C(2a)⟩ is shorter by 0.017 Å.

The molecule is essentially planar, unlike previous structures where the dihedral angle between the imidazole rings was quite large (Bonati *et al.*, 1989), but this could be caused by the packing. Here the cations are arranged so that they are eclipsed (Fig. 2), whereas in the previous structure adjacent cations had their long axes nearly at 90° to each other. The cations are bent slightly at the Au atom [C(2)—Au—C(2a) = 175.8 (2)°, Fig. 2(b)] to allow an Au···Au' interaction [3.372 (1) Å] and to minimize methyl group repulsive interactions. These latter interactions appear to cause the cations not to lie exactly one over the other [Fig. 2(a)].

The packing is shown in Fig. 3. The cations within the pairs are related by the inversion centres at $\frac{1}{2},\frac{1}{2},0$ and $0,0,\frac{1}{2}$. These pairs are stacked along the **b** direction at $x = \frac{1}{2}$, $z = 0$ and $x = 0$, $z = \frac{1}{2}$, with the long axes of the molecules roughly parallel to the *bc* plane. The first set of cations are tilted roughly 50° to the *ac* plane and are thus about 80° to the second set of cations, which are tilted in the opposite directions. Within the stacks there are π–π interactions between one pair of cations and the next pair. Between the first set of cations and the second set of cations, around $z = \frac{1}{4},\frac{3}{4}$, there are van der Waals interactions between the methyl groups and the rings. In the **a** direction a pair of cations is bound to the next translationally equivalent pair by hydrogen bonds through pairs of Cl(1),O(1) and Cl(2),O(2) atoms.
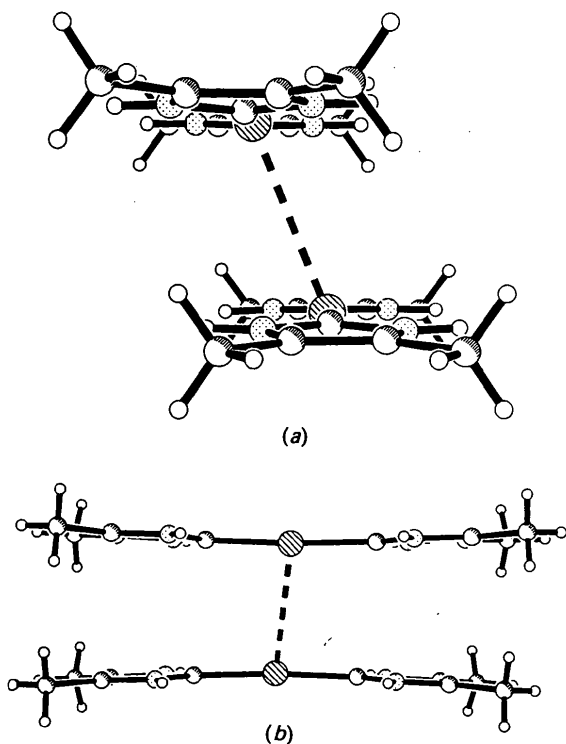

(*a*)

(*b*)

Fig. 2. Views of pairs of cations showing the gold–gold interaction: (*a*) along the long molecular axis; (*b*) at right angles to the long molecular axis.
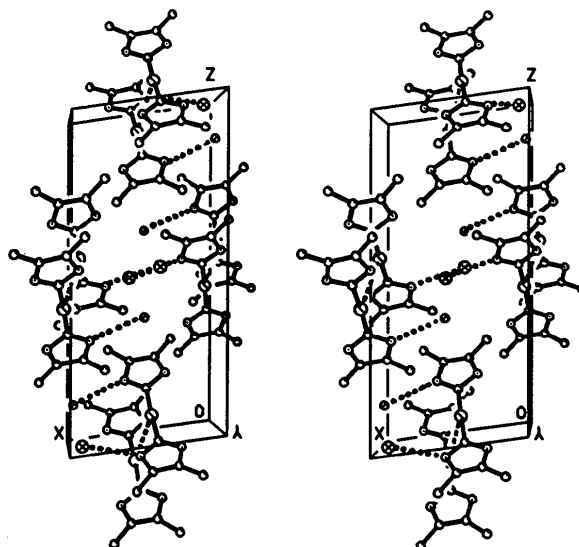

Fig. 3. The packing of $[(C_5H_8N_2)_2Au]^+.Cl^-.H_2O$ within the unit cell. **a*** and **c** are parallel to the bottom and sides of the page and the view is down **b**. Hydrogen bonds are represented by dotted lines.

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Structure of Trimethylplatinum(IV) with a Tripod Ligand

BY RICHARD E. MARSH, WILLIAM P. SCHAEFER, DAVID K. LYON, JAY A. LABINGER AND JOHN E. BERCAW

Division of Chemistry and Chemical Engineering* and The Beckman Institute, Mail Code 139–74, California Institute of Technology, Pasadena, California 91125, USA

Abstract. $[1(\eta^5)$-Cyclopentadienyl]-tris-μ-(dimethyl-phosphito-$1\kappa P{:}2\kappa O$)(trimethyl-$2\kappa^3 C$)cobaltplatinum, $[CoPt(C_2H_6O_3P)_3(C_5H_5)(CH_3)_3]$, $M_r = 691.35$, triclinic, $P\bar{1}$, $a = 9.106\,(3)$, $b = 14.803\,(3)$, $c = 15.147\,(3)$ Å, $\alpha = 112.95\,(2)$, $\beta = 103.68\,(2)$, $\gamma = 95.10\,(2)°$, $V = 1788.9\,(9)$ Å^3, $Z = 3$, $D_x = 1.93$ g cm^{-3}, $\lambda(\text{Mo }K\alpha) = 0.71073$ Å, $\mu = 68.69$ cm^{-1}, $F(000) = 1014$, room temperature, $R = 0.038$ for 4620 reflections with $F_o^2 > 3\sigma(F_o^2)$. The trimethylplatinum(IV) completes octahedral coordination by bonding to three O atoms of the tripod-shaped methoxy Kläui ligand. There are two independent molecules in the cell, one disordered about a center of symmetry. The ordered molecule has normal bond distances and angles; Pt—C = 2.001 (11) and Pt—O = 2.173 (5) Å. Many distances in the disordered molecule are uncertain, particularly in the areas of the Cp C atoms and the CH$_3$ groups, which overlap in the two orientations.

Introduction. Interest in the activation and functionalization of saturated hydrocarbons by aqueous platinum chloride solutions (Shilov, 1984, 1989;

Labinger, Herring & Bercaw, 1990*a,b*) has led to our synthesizing model Pt complexes containing 'hard' ligands (Herring, Henling, Labinger & Bercaw, 1991). Model complexes analogous to the putative Pt(R)Cl$_4$(H$_2$O)$^-$ species that have been proposed as intermediates in the activation/functionalization of alkanes by Pt (Shul'pin, Shilov, Kitaigorodskii & Zeile Krevor, 1980; Shibaera, Rozenberg, Lobkovskaya, Shilov & Shul'pin, 1981; Shul'pin, Nizova & Nikitaev, 1984; Khrushch, Laurushki, Misharin, Moravsky & Shilov, 1983) are thus attractive targets, but few examples of structurally well characterized complexes are available. The tripod ligand $(\eta^5\text{-}C_5H_5)\text{Co[P(O)(}OR)_2]_3^-$ (henceforth abbreviated to L_{OR}) behaves as a hard ligand, with field strengths approximately equal to that of three F$^-$ ligands (Kläui, 1990). Recently the synthesis of Pt(CH$_3$)$_3L_{OR}$, where $R =$ Me and Et, as well as the crystal and molecular structure of the latter, have been reported (Nettle, Valderrama, Contreras, Scotti, Peters, von Schnering & Werner, 1988). In the course of preparing these complexes for study of their chemical behavior, we obtained crystals of Pt(CH$_3$)$_3L_{OMe}$, and decided to determine its structure for purposes of comparison. Formation of methanol