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[Methoxy(*p*-tolylimino)methyl](triphenylphosphine)gold(I), $C_{27}H_{25}AuNOP$

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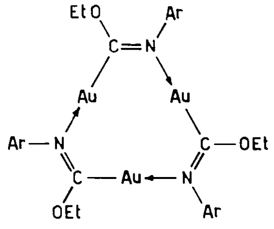
(*Received* 16 *February* 1984; *accepted* 20 *September* 1984)

Abstract. $M_r = 607{\cdot}441$, triclinic, $P\bar{1}$, $a = 21{\cdot}710\ (16)$, $b = 17{\cdot}235\ (12)$, $c = 10{\cdot}316\ (8)$ Å, $\alpha = 77{\cdot}9\ (1)$, $\beta = 104{\cdot}7\ (1)$, $\gamma = 95{\cdot}4\ (1)°$, $V = 3647\ (5)$ Å^3, $Z = 6$, $D_m = 1{\cdot}64$, $D_x = 1{\cdot}659$ Mg m^{-3}, Mo $K\bar{\alpha}$, $\lambda = 0{\cdot}71069$ Å, $\mu = 6{\cdot}12$ mm^{-1}, $F(000) = 1776$, $T = 295$ K, $R = 0{\cdot}0438$ for 7302 unique observed reflections. There are three crystallographically independent, but pratically identical, molecules. In each molecule the gold atom is linearly coordinated by the P atom from PPh_3 and by a C atom from the organic ligand. The intermolecular Au···Au distances are very long so that no metal–metal interaction is observed.

Introduction. By the reaction of an isocyanide, *R*NC, with a metal complex dissolved in an alcohol, *R*′OH, in the presence of an alkali, various species having the general formula $L_nM[-C(OR')=NR]_m$ were obtained, where *M* includes Hg, Ag, Au or Pt, *L* may be a phosphine or an isocyanide, *m* is equal to the oxidation number of the metal *M*, and *n* = 0, 1 or 2 (Minghetti & Bonati, 1972, 1974; Minghetti, Bonati & Massobrio, 1973, 1975; Minghetti, Bonati & Banditelli, 1973, 1976; Bonati, Minghetti & Banditelli, 1976; Banditelli, Bonati & Minghetti, 1977, 1980; Bonati & Clark, 1979; Banditelli, Bandini, Minghetti & Bonati, 1979; Banditelli, Bandini, Bonati, Goel & Minghetti, 1982).

Formally these species can be considered in several ways, *i.e.* either as substituted metal alkyls, or as *C*-metallated derivatives of an ester of formimidic acid, $H-C(OR')=NR$ (Minghetti, Banditelli & Bonati, 1975), or even as carbeniates, which are compounds obtained by deprotonation of a carbene complex of a metal, $M \leftarrow C(OR')(NHR)$ (Schmidbauer, 1980). Accordingly they were indicated as (alkoxy)(*N*-alkylimino)methylmetal, or *C*-metallated alkyl formimidate, or, more recently, metal (alkoxy)(*N*-alkylimino)carbeniate.

Although these complexes are generally stable, they have been characterized simply by analytical and spectroscopic techniques and among them only one X-ray crystal structure has been determined, namely that of $[Au-C(OEt)=N(p\text{-tolyl})]_3$, (1), (Tiripicchio, Tiripicchio Camellini & Minghetti, 1979), a homoleptic gold alkyl, where an ennea-atomic ring is present, to be compared with the recently reported $[Au(mesityl)]_5$ (Gambarotta, Floriani, Chiesi Villa & Guastini, 1983). Since the structure determination of (1) revealed certain peculiar characteristics, such as both *intra*- and *inter*molecular interactions, it was decided to extend our investigations to a related complex, namely $[Ph_3PAu-C(OEt)=N(p\text{-tolyl})]$, (2).



(1)

Here the results of the X-ray crystal structure determination are reported and their significance is discussed.

Experimental. D_m by flotation, prismatic crystal 0·35 × 0·25 × 0·12 mm, Siemens AED diffractometer, Nb-filtered Mo $K\alpha$, lattice parameters refined by least squares of 18 reflections ($8 < \theta < 14°$), 12 853 independent reflections ($3 \leq \theta \leq 25°$, $\theta/2\theta$ scan), $-25 \leq h \leq 24$, $-19 \leq k \leq 20$, $0 \leq l \leq 12$, 7302 reflections with $I \geq 2\sigma(I)$ considered observed (1 standard

Table 1. *Final fractional atomic coordinates* ($\times 10^4$) *and isotropic thermal parameters* ($\text{Å}^2 \times 10^4$ *for* Au, P; $\text{Å}^2 \times 10^3$ *for* O, N, C) *with e.s.d.'s in parentheses*

$U_{eq} = \frac{1}{3}\,\text{trace}\,\tilde{\mathbf{U}}$.

	x	y	z	U_{eq} or U_{iso}
Au(1)	2882 (1)	5154 (1)	5064 (1)	475 (2)
P(1)	3145 (2)	5543 (2)	7136 (4)	485 (14)
O(1)	2110 (5)	4324 (6)	3045 (11)	70 (3)
N(1)	3005 (6)	4846 (8)	2405 (13)	68 (4)
C(11)	2664 (7)	4761 (9)	3245 (14)	55 (4)
C(21)	1926 (9)	3992 (11)	1813 (19)	87 (5)
C(31)	3563 (7)	5300 (8)	2572 (14)	76 (5)
C(41)	3567 (7)	6128 (8)	2263 (14)	108 (7)
C(51)	4145 (7)	6569 (8)	2392 (14)	103 (6)
C(61)	4719 (7)	6181 (8)	2830 (14)	130 (8)
C(71)	4715 (7)	5354 (8)	3139 (14)	267 (20)
C(81)	4137 (7)	4913 (8)	3010 (14)	195 (13)
C(91)	5369 (16)	6698 (20)	2998 (34)	182 (13)
C(101)	2479 (4)	5839 (6)	7654 (10)	50 (3)
C(111)	2497 (4)	5808 (6)	9026 (10)	62 (4)
C(121)	1967 (4)	6010 (6)	9394 (10)	77 (5)
C(131)	1417 (4)	6242 (6)	8390 (10)	79 (5)
C(141)	1398 (4)	6273 (6)	7019 (10)	88 (5)
C(151)	1929 (4)	6071 (6)	6651 (10)	67 (4)
C(161)	3473 (5)	4726 (5)	8487 (10)	50 (3)
C(171)	3059 (5)	4118 (5)	8932 (10)	67 (4)
C(181)	3302 (5)	3457 (5)	9902 (10)	79 (5)
C(191)	3958 (5)	3403 (5)	10428 (10)	97 (6)
C(201)	4372 (5)	4011 (5)	9983 (10)	183 (12)
C(211)	4129 (5)	4673 (5)	9013 (10)	132 (9)
C(221)	3754 (4)	6347 (6)	7214 (11)	50 (3)
C(231)	4156 (4)	6430 (6)	6326 (11)	67 (4)
C(241)	4639 (4)	7025 (6)	6359 (11)	85 (5)
C(251)	4721 (4)	7536 (6)	7280 (11)	92 (6)
C(261)	4319 (4)	7453 (6)	8168 (11)	104 (6)
C(271)	3836 (4)	6859 (6)	8135 (11)	102 (6)
Au(2)	−243 (1)	7157 (1)	7043 (1)	482 (2)
P(2)	−67 (2)	7525 (2)	9113 (4)	447 (12)
O(2)	−718 (6)	6099 (7)	5189 (12)	83 (3)
N(2)	−193 (6)	7159 (8)	4174 (13)	68 (4)
C(12)	−370 (8)	6813 (10)	5210 (16)	64 (4)
C(22)	−827 (12)	5774 (15)	3905 (26)	126 (8)
C(32)	122 (5)	7900 (6)	4151 (11)	54 (4)
C(42)	−216 (5)	8589 (6)	3884 (11)	105 (7)
C(52)	109 (5)	9328 (6)	3856 (11)	117 (7)
C(62)	772 (5)	9378 (6)	4095 (11)	82 (5)
C(72)	1110 (5)	8690 (6)	4362 (11)	114 (7)
C(82)	785 (5)	7951 (6)	4391 (11)	108 (7)
C(92)	1122 (11)	10207 (14)	4121 (24)	118 (7)
C(102)	−797 (4)	7706 (5)	9522 (9)	47 (3)
C(112)	−863 (4)	7581 (5)	10861 (9)	57 (4)
C(122)	−1432 (4)	7751 (5)	11116 (9)	73 (4)
C(132)	−1934 (4)	8047 (5)	10033 (9)	75 (5)
C(142)	−1868 (4)	8172 (5)	8694 (9)	75 (5)
C(152)	−1299 (4)	8001 (5)	8438 (9)	59 (4)
C(162)	322 (4)	6760 (5)	10504 (9)	50 (3)
C(172)	−5 (4)	6024 (5)	10682 (9)	76 (5)
C(182)	276 (4)	5395 (5)	11681 (9)	80 (5)
C(192)	884 (4)	5502 (5)	12503 (9)	76 (5)
C(202)	1211 (4)	6238 (5)	12325 (9)	76 (5)
C(212)	930 (4)	6867 (5)	11325 (9)	67 (4)
C(222)	436 (4)	8431 (5)	9211 (10)	48 (3)
C(232)	814 (4)	8662 (5)	8275 (10)	66 (4)
C(242)	1203 (4)	9353 (5)	8308 (10)	83 (5)
C(252)	1214 (4)	9812 (5)	9278 (10)	87 (5)
C(262)	836 (4)	9581 (5)	10215 (10)	83 (5)
C(272)	447 (4)	8891 (5)	10181 (10)	70 (4)
Au(3)	3478 (1)	994 (1)	10886 (1)	473 (2)
P(3)	3431 (2)	768 (2)	8760 (3)	431 (13)
O(3)	3596 (5)	2025 (6)	12782 (10)	66 (3)
N(3)	3396 (6)	763 (7)	13801 (12)	57 (3)
C(13)	3476 (7)	1224 (9)	12718 (14)	54 (4)
C(23)	3541 (8)	2301 (10)	13999 (18)	78 (5)
C(33)	3225 (5)	−48 (4)	13710 (10)	54 (3)
C(43)	3631 (5)	−643 (4)	14497 (10)	69 (4)
C(53)	3456 (5)	−1438 (4)	14446 (10)	79 (5)
C(63)	2875 (5)	−1638 (4)	13609 (10)	81 (5)
C(73)	2469 (5)	−1042 (4)	12822 (10)	83 (5)
C(83)	2644 (5)	−248 (4)	12872 (10)	68 (4)
C(93)	2670 (10)	−2515 (13)	13542 (22)	109 (7)
C(103)	4201 (3)	877 (6)	8374 (9)	44 (3)
C(113)	4269 (3)	835 (6)	7082 (9)	68 (4)
C(123)	4874 (3)	908 (6)	6822 (9)	77 (5)
C(133)	5411 (3)	1023 (6)	7853 (9)	80 (5)
C(143)	5343 (3)	1065 (6)	9145 (9)	74 (5)
C(153)	4738 (3)	992 (6)	9406 (9)	62 (4)
C(163)	2938 (4)	1481 (5)	7436 (8)	40 (3)
C(173)	3170 (4)	2270 (5)	7281 (8)	65 (4)
C(183)	2800 (4)	2862 (5)	6365 (8)	72 (4)
C(193)	2198 (4)	2666 (5)	5603 (8)	66 (4)
C(203)	1966 (4)	1878 (5)	5757 (8)	73 (5)
C(213)	2336 (4)	1285 (5)	6674 (8)	55 (4)
C(223)	3094 (5)	−222 (5)	8501 (10)	53 (3)
C(233)	2959 (5)	−748 (5)	9629 (10)	70 (4)
C(243)	2717 (5)	−1516 (5)	9506 (10)	85 (5)
C(253)	2611 (5)	−1756 (5)	8255 (10)	92 (6)
C(263)	2746 (5)	−1229 (5)	7127 (10)	94 (6)
C(273)	2988 (5)	−462 (5)	7250 (10)	80 (5)

reflection, checked after every 20, no decomposition of specimen), Lp correction, absorption correction following Walker & Stuart (1983) using *ASSORB* (Ugozzoli, 1983) (max. 1·193004, min. 0·642625); atomic scattering factors and anomalous-scattering corrections from *International Tables for X-ray Crystallography* (1974); heavy-atom technique, first isotropic blocked full-matrix least squares (*SHELX*76; Sheldrick, 1976), then full-matrix least squares (anisotropic for Au and P and isotropic for all other non-hydrogen atoms, phenyl rings as rigid groups), ΔF synthesis not valuable in locating all H atoms; $\sum w|\Delta F|^2$ minimized, unit weights in all stages of refinement (after analysing the variation of $|\Delta F|$ with respect to $|F_o|$), hydrogen atoms (except those of methyl groups) placed at calculated positions and introduced in final structure factor calculation, final $R = 0{\cdot}0438$, $R_w = 0{\cdot}0500$, $S = 0{\cdot}8882$,* $(\Delta/\sigma)_{max} = 0{\cdot}22$, max. height in final difference Fourier synthesis $= 0{\cdot}91$ e Å^{-3}; Cyber 76 computer of the 'Consorzio per la gestione del Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale', Casalecchio, Bologna, with financial support of the University of Parma. Table 1 gives coordinates for non-hydrogen atoms.

Discussion. The crystal structure of (2) consists of three crystallographically independent, but nearly identical, molecules separated by normal van der Waals distances. The gold atom is linearly coordinated by a phosphorus atom from PPh_3 and by a carbon atom from the carbeniate ligand. The C—Au—P angles range from 177·0 (6) to 178·1 (7)°. In Fig. 1 one of the three independent complexes is represented together with the atomic numbering scheme. Selected bond distances and angles in the three complexes are given in Table 2. They present very similar structural parameters, which differ only slightly in the conformation of the PPh_3 ligand, probably for steric-hindrance reasons owing to the packing.

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* Lists of structure factors, anisotropic thermal parameters and calculated H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39757 (33 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

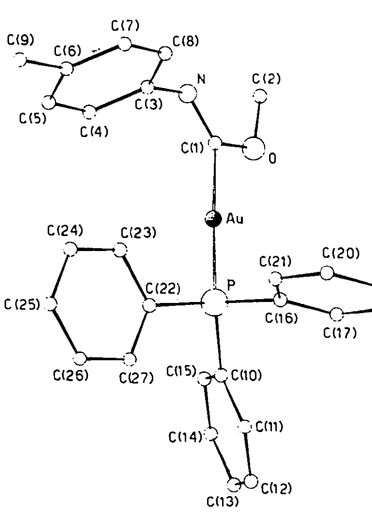

Fig. 1. View of one of the three independent, but very similar, complexes [$Ph_3PAu–C(OMe)=N(p\text{-}C_6H_4–Me)$] with the atomic numbering scheme.

Table 2. *Selected bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

	Molecule 1	Molecule 2	Molecule 3
Au–P	2·292 (5)	2·284 (5)	2·282 (4)
Au–C(1)	2·056 (16)	2·044 (18)	2·012 (16)
C(1)–N	1·254 (22)	1·242 (22)	1·269 (18)
N–C(3)	1·372 (19)	1·389 (17)	1·428 (14)
C(1)–O	1·351 (18)	1·383 (20)	1·393 (19)
O–C(2)	1·451 (23)	1·500 (32)	1·468 (24)
P–C(10)	1·812 (12)	1·810 (11)	1·799 (9)
P–C(16)	1·815 (9)	1·820 (9)	1·823 (8)
P–C(22)	1·823 (10)	1·825 (9)	1·837 (10)
P–Au–C(1)	177·6 (5)	178·1 (7)	177·0 (6)
Au–C(1)–N	126·8 (1·3)	129·2 (1·4)	130·7 (1·3)
Au–C(1)–O	113·0 (1·0)	111·4 (1·1)	112·9 (1·0)
N–C(1)–O	120·0 (1·5)	119·4 (1·6)	116·4 (1·4)
C(1)–N–C(3)	121·1 (1·4)	120·0 (1·4)	116·5 (1·2)
C(1)–O–C(2)	117·2 (1·4)	116·3 (1·6)	119·3 (1·2)
Au–P–C(10)	114·7 (5)	112·6 (5)	112·3 (5)
Au–P–C(16)	110·4 (4)	111·9 (5)	111·3 (4)
Au–P–C(22)	112·5 (5)	112·8 (4)	113·5 (4)
C(10)–P–C(16)	104·5 (6)	105·9 (6)	105·5 (6)
C(10)–P–C(22)	108·0 (7)	106·4 (7)	107·3 (7)
C(16)–P–C(22)	106·1 (6)	106·8 (6)	106·4 (5)

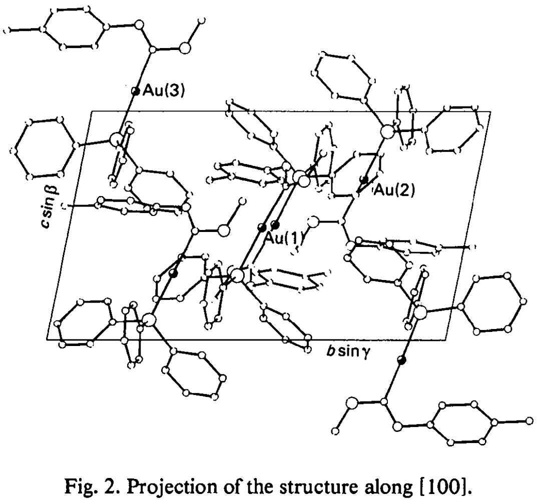

Fig. 2. Projection of the structure along [100].

The Au–P bonds [2·292 (5), 2·284 (5) and 2·282 (4) Å] are comparable to those reported for other bicoordinated gold(I) compounds where the P atom lies opposite a variety of σ-bonded organic groups, *e.g.* 2·279 (8) Å in $MeAuPPh_3$ (Gavens, Guy, Mays & Sheldrick, 1977), 2·28 (1) Å in $Ph_3PAuC(CF_3)=C(CF_3)AuPPh_3$ (Gilmore & Woodward, 1971) or 2·29 Å in $Me_3PAuC(CF_3)=C(CF_3)AuMe_2PMe_3$ (Jarvis, Johnson & Puddephatt, 1973).

Similarly, the Au–C bonds [2·056 (16), 2·044 (18) and 2·012 (16) Å] are comparable to those found in several $Ph_3PAu–R$ complexes, where R is bonded to the gold atom through an sp^2-hybridized carbon, *e.g.* 2·07 (2) Å in $Ph_3PAuC_6F_5$ (Baker & Pauling, 1972) or 2·05 (6) Å in $Ph_3PAuC(CF_3)=C(CF_3)AuPPh_3$ (Gilmore & Woodward, 1971). The Au–C bonds in (2) are appreciably longer than in (1) (in the range 1·935–1·975 Å, Tiripicchio *et al.*, 1979), where the carbon is *trans* to a nitrogen atom; indeed the Au–C length is very sensitive to the nature of the ligand *trans* to it, as can be seen in the series LAu(CN), where L is CN (2·12 Å, Rosenzweig & Cromer, 1959) or MeNC [2·01 (4) Å, Esperas, 1976] or Ph_3P [1·85 (4) Å, Bellon, Manassero & Sansoni, 1969].

Inside the carbeniate ligands the C=N bonds [1·254 (22), 1·242 (22) and 1·269 (18) Å] are comparable to that found in another heavy-metal derivative containing a similar moiety, namely *trans*-$PtI(CMe=NC_6H_4\text{-}p\text{-}Cl)(PEt_3)_2$ [1·287 (13) Å, Wagner, Treichel & Calabrese, 1974] and can be assumed as normal values for bond distances within a metal-bonded $\overset{|}{C}=N–$ moiety of an organic ligand. The values for these bonds found in (1) [1·375 (35), 1·369 (38) and 1·223 (31) Å] must be considered exceptional and a satisfactory explanation of these differences is not easy to supply. The remarkable differences in the C–N distances and the lack of planarity in the ennea-atomic ring could be attributed to the intra- and intermolecular metal interactions.

The packing of the three independent complexes is represented in Fig. 2. Noteworthy is the absence of the rather common Au···Au interaction, the shortest Au···Au intermolecular distances are: Au(1)···Au(2) $(-x, 1-y, 1-z)$ = 6·814 (8), Au(1)···Au(3) = 8·301 (10), Au(3)···Au(3) $(1-x, -y, 2-z)$ = 8·472 (7), Au(2)···Au(2) $(-x, 1-y, 2-z)$ = 8·533 (10) Å so that no metal–metal interaction is possible, probably because of the steric hindrance of the bulky triphenylphosphine ligand. In fact, all the molecules are disposed with the P–Au–C fragments nearly parallel to one another and this arrangement is the least favourable for determining short distances between gold atoms of different complexes (Fig. 2).

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Structure of the Ionic Polynuclear Tantalum(V) Derivative Bis{tri-μ-chloro-bis[dichloro-(η-pentamethylcyclopentadienyl)tantalum(V)]} 2,3;2,3-Di-μ-chloro-1,1,1,1,1,2,2,2,3,3,3,4,4,4,4,4-hexadecachloro-1,2;3,4-di-μ-oxo-tetratantalate(V),* $2[\{Ta(\eta\text{-}C_5Me_5)Cl_2\}_2(\mu\text{-}Cl)_3]^+.[\{TaCl_5(\mu\text{-}O)TaCl_3\}_2(\mu\text{-}Cl)_2]^{2-}$

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(*Received* 10 *April* 1984; *accepted* 26 *September* 1984)

Abstract. $M_r = 3155{\cdot}0$, monoclinic, $P2_1/c$, $a = 16{\cdot}839\,(3)$, $b = 15{\cdot}225\,(4)$, $c = 17{\cdot}065\,(7)$ Å, $\beta = 111{\cdot}18\,(3)°$, $U = 4079{\cdot}5$ Å^3, $Z = 2$, $D_x = 2{\cdot}57$ Mg m^{-3}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å, $\mu = 12{\cdot}33$ mm^{-1}, $F(000) = 2888$, room temperature, $R = 0{\cdot}050$ for 2087 independent observed reflections. The compound consists of dinuclear monovalent cations and tetranuclear divalent anions. The former have one η^5-C_5Me_5 group, two terminal Cl atoms and three bridging Cl atoms bonded to each Ta^V. The anions can be described in terms of a central dinuclear $[O{=}TaCl_3(\mu\text{-}Cl)_2Cl_3Ta{=}O]^{2-}$ unit bonded through the O atoms to two tantalum pentachloride, $[TaCl_5]$, molecules. Both in the cations and in the anions the geometry round each Ta atom is that of a distorted octahedron (the C_5 rings considered as point ligands); the distortion is greater in the cations, as expected from their greater bridge multiplicity.

Introduction. Cyclopentadienyl Nb and Ta tetrahalides, $[(\eta\text{-}C_5R_5)MX_4]$, can be conveniently prepared by means of the reaction between the corresponding metal pentahalide, $[MX_5]$, and tin reagents of the type $[(C_5R_5)SnR'_3]$ (Labinger, 1982):

$$[MX_5] + [(C_5R_5)SnR'_3] \rightarrow [(\eta\text{-}C_5R_5)MX_4] + [SnXR'_3]$$

$R = \text{H or alkyl group} \qquad M = \text{Nb or Ta}$

$R' = \text{alkyl group} \qquad X = \text{halogen.}$

Reaction of $[TaCl_5]$ with $[Sn(Bu^n)_3(C_5Me_5)]$ in refluxing dichloromethane and subsequent recrystallization of

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* Part of this work has been briefly communicated: Green, Overton, Prout & Marín (1983).

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