Table 2. *Selected geometric parameters (Å, °)*

Zr—O2	2.1126 (11)	C1—C7	1.485 (2)
Zr—O1	2.1436 (11)	C7—C8	1.386 (2)
Zr—Cl	2.5484 (9)	C8—C9	1.386 (3)
O1—C7	1.277 (2)	C9—C10	1.484 (2)
O2—C9	1.287 (2)		
O2—Zr—O2^i	115.81 (2)	O2—Zr—Cl	78.02 (3)
O2—Zr—O1^i	149.67 (5)	O1—Zr—Cl	132.30 (3)
O2—Zr—O1	76.55 (4)	C7—O1—Zr	134.57 (10)
O2^i—Zr—O1	77.80 (4)	C9—O2—Zr	136.28 (10)
O1^i—Zr—O1	79.66 (5)		

Symmetry code: (i) $1 - y, x - y, z$.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *SDP-Plus* (Frenz, 1988). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*3 for *Windows* (Farrugia, 1997).

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(9,10-Dioxo-9,10-dihydro-1-anthrylaminato-*N*)(triphenylphosphine-*P*)gold

ANDREI V. CHURAKOV,[a]† LYUDMILA G. KUZ'MINA[a] AND JUDITH A. K. HOWARD[b]

[a]*N. S. Kurnakov Institute of General and Inorganic Chemistry of Russian Academy of Science, 31 Leninskii prospect, Moscow 117907, Russia, and* [b]*Department of Chemistry, University of Durham, Science Laboratories, South Road, Durham DH1 3LE, England. E-mail: andrei.churakov@durham.ac.uk*

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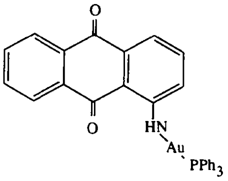
Abstract

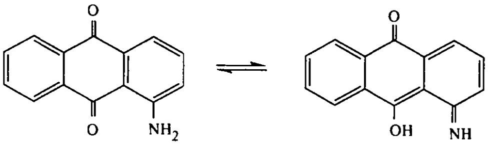
In the title compound, $[Au(C_{14}H_8NO_2)(C_{18}H_{15}P)]$, the $AuPPh_3$ group is located at the amino group. The Au—N and Au—P distances are 2.019 (3) and 2.2420 (8) Å, respectively. The amino group H atom is involved in an intramolecular hydrogen bond with a carbonyl O atom. The bond-length distribution in the aminoanthraquinone ligand is slightly different from that in the free ligand, manifesting itself as a more pronounced contribution from the quinoid structure.

Comment

The title compound, (1), is a (triphenylphosphine)gold derivative of 1-aminoanthracene-9,10-dione, (2). The initial photochromic organic compound (2) can exist in two tautomeric forms, amino and imino (see scheme below).



(1)



(2)

In the imino form, two types of imino group configuration, resulting in different kinds of hydrogen bonds, may be proposed. Based on X-ray structural investiga-

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† Current address: Department of Chemistry, University of Durham, Science Laboratories, South Road, Durham DH1 3LE, England.

tions, only the amino form has been found to occur in the crystalline state of (2) (Almond *et al.*, 1983; Foitzik & Paulus, 1986), although examples of organic molecules existing in both tautomeric forms in the crystal are known, for example, 2-pyridone-6-chloro-2-hydroxypyridine (Almlöf *et al.*, 1971).

The title compound is the first representative of a series of mono- and poly-aurated amino derivatives of anthraquinone, which we regard as models for structures with chains of intermolecular Au···Au interactions.

The structure determination of the title compound shows that the amino tautomeric form exists in the crystal, revealing a change in the geometrical parameters of the aminoanthracene chromophore due to the introduction of the $AuPPh_3$ substituent at the amino group. In the amino form, either a hydrogen bond or an Au···O secondary bond stabilizes the structure of (1). The latter has been observed in three crystalline modifications of (8-hydroxyquinolinato)(triphenylphosphine)gold (Kuz'mina, Dvortsova *et al.*, 1989) and in (8-quinolinato-*O*,*N*)bis(triphenylphosphine)digold(I) tetrafluoroborate (Kolb *et al.*, 1993).

The amino tautomeric form of a molecule of (1) is shown in Fig. 1. Competition between an intramolecular hydrogen bond and an intramolecular Au···O secondary bond is resolved in favour of the hydrogen bond. The H···O1 and N···O1 distances [1.95 (5) and 2.686 (4) Å, respectively] are comparable with those in the free molecule of (2). The Au—N distance of 2.019 (3) Å is somewhat shorter than those in other $AuPPh_3$ derivatives of arylamines, *e.g.* 2.038 (6) (Kuz'mina, Burtseva *et al.*, 1989), 2.050 (6) (Perevalova *et al.*, 1988) and 2.046 Å (Kuz'mina *et al.*, 1990). We have shown previously that the Au—P bond length is sensitive to a *trans* ligand in Au^I compounds (Kuz'mina, 1992). The Au—P bond length of 2.2420 (8) Å is typical of Au^I compounds containing a P—Au—N linear fragment.

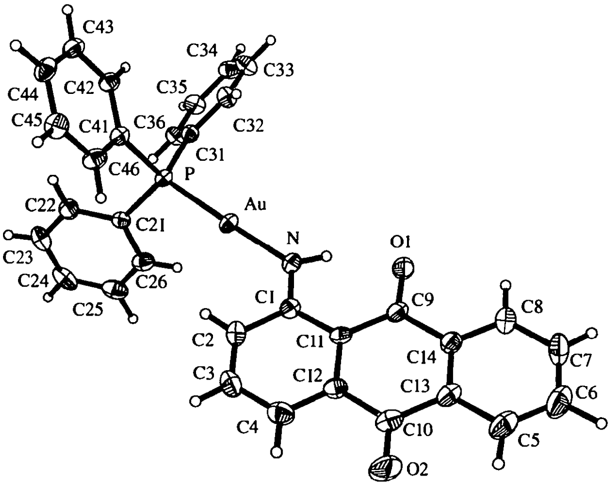

Fig. 1. The molecular structure of (1) showing 50% probability displacement ellipsoids.

In the aminoanthraquinone fragment of (1), the bond-length distribution is slightly but significantly different from that observed in (2). In (1), the N—C1 bond [1.336 (4) Å] is shorter than in (2) [1.357 (4) Å found by Almond *et al.* (1983) and 1.358 Å reported by Foitzik & Paulus (1986)]. In addition, the amino-substituted ring shows some localization of double-bond character at C2—C3 [1.365 (5) Å] and C4—C12 [1.375 (5) Å]. Such a bond-length distribution, typical of the imino tautomeric form, is less pronounced in (2) [comparable bond lengths are 1.377 (4) and 1.384 (4) Å reported by Almond *et al.* (1983), and 1.371 and 1.385 Å reported by Foitzik & Paulus (1986)]. The observed reduction of the C—C—C angle at atom C1 [116.7 (3)°] in (1) compared with those in (2) (118.4 and 118.5°) may be considered as an indication of the greater positive inductive effect of the $AuPPh_3$ substituent compared with hydrogen. A similar effect of some quinoid-like contribution to the general benzenoid structure is also observed in the above-mentioned tautomeric hydroxypyridine derivative. The remaining geometrical parameters of the ligand closely resemble those of (2).

The two C—O bonds, 1.247 (4) and 1.229 (5) Å, differ by 0.018 (6) Å. The elongation of the O1—C9 bond is due to the involvement of O1 in the hydrogen bond.

In the crystal, the molecules are packed in stacks running along the *a* axis. In such a stack, any two adjacent molecules are related by a symmetry centre. None of the interatomic distances is less than the sum of the corresponding van der Waals radii. The mean interplanar distances between molecules related by two different symmetry centres (0,0,0 and $\frac{1}{2}$,0,0) are 3.42 and 3.59 Å, respectively.

Experimental

The title compound was prepared by reaction of 1-amino-anthracene-9,10-dione with tris(triphenylphosphinegold)oxonium tetrafluoroborate in the presence of aqueous potassium carbonate. Single crystals were grown from a chloroform–ether (1:7) solution.

Crystal data

$[Au(C_{14}H_8NO_2)(C_{18}H_{15}P)]$
M_r = 681.45
Triclinic
$P\bar{1}$
a = 8.8328 (2) Å
b = 9.4173 (2) Å
c = 16.1617 (3) Å
α = 96.941 (1)°
β = 98.159 (1)°
γ = 101.396 (1)°
V = 1289.06 (5) Å^3
Z = 2
D_x = 1.756 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 9492 reflections
θ = 1.29–27.51°
μ = 5.799 mm^{-1}
T = 153 (2) K
Block
0.24 × 0.18 × 0.10 mm
Red

Data collection

Siemens SMART diffractometer
ω scans
Absorption correction: multi-scan (*SHELXTL*; Sheldrick, 1994)
$T_{\min} = 0.287$, $T_{\max} = 0.560$
9492 measured reflections
5842 independent reflections
5407 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.028$
$\theta_{\max} = 27.51°$
$h = -11 \rightarrow 11$
$k = -8 \rightarrow 12$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.064$
$S = 1.120$
5660 reflections
427 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.011P)^2 + 2.5925P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 1.13$ e Å^{-3}
$\Delta\rho_{\min} = -0.67$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0000 (2)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Au—N	2.019 (3)	C3—C4	1.403 (6)
Au—P	2.2420 (8)	C4—C12	1.375 (5)
N—C1	1.336 (4)	C9—C11	1.453 (5)
N—H1	0.89 (5)	C9—C14	1.496 (5)
O1—C9	1.247 (4)	C10—C13	1.485 (6)
O2—C10	1.229 (5)	C10—C12	1.489 (5)
C1—C2	1.433 (5)	C11—C12	1.426 (5)
C1—C11	1.442 (5)	C13—C14	1.404 (5)
C2—C3	1.365 (6)		
N—Au—P	178.21 (9)	C11—C9—C14	119.0 (3)
C1—N—Au	128.0 (3)	O2—C10—C13	120.8 (4)
C1—N—H1	111 (3)	O2—C10—C12	121.3 (4)
Au—N—H1	122 (3)	C13—C10—C12	117.9 (3)
N—C1—C2	119.7 (3)	C12—C11—C1	119.2 (3)
N—C1—C11	123.6 (3)	C12—C11—C9	120.0 (3)
C2—C1—C11	116.7 (3)	C1—C11—C9	120.8 (3)
C3—C2—C1	122.1 (4)	C4—C12—C11	121.6 (3)
C2—C3—C4	121.0 (4)	C4—C12—C10	117.0 (3)
C12—C4—C3	119.4 (4)	C11—C12—C10	121.4 (3)
O1—C9—C11	123.1 (3)	C14—C13—C10	120.3 (3)
O1—C9—C14	117.9 (3)	C13—C14—C9	121.3 (3)

Crystal decay was checked during the data reduction and no decay was observed. The structure was solved by direct methods. H atoms were found from the difference Fourier synthesis and refined in the isotropic approximation. The largest peak in the difference electron-density map was found at a distance of 0.94 Å from the Au atom.

Data collection: *SMART* (Siemens, 1995*a*). Cell refinement: *SAINT* (Siemens, 1995*b*). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL* (Sheldrick, 1994). Software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1166). Services for accessing these data are described at the back of the journal.

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3-(η^3-Allyl)-3,3-dicarbonyl-4-(dimethyl sulfido)-3,1,2-molybdadicarba-*closo*-dodecaborane(12)

KJELD JOHANSEN, GEORGINA M. ROSAIR, ANDREW S. WELLER AND ALAN J. WELCH

Department of Chemistry, Heriot-Watt University, Riccarton, Edinburgh EH14 4AS, Scotland. E-mail: chegmr@bonaly.hw.ac.uk

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Abstract

The title charge-compensated allyl carbamolybdaborane 3-(η^3-C_3H_5)-3,3-$(CO)_2$-4-SMe_2-3,1,2-*closo*-$MoC_2B_9H_{10}$, or [$Mo(C_3H_5)(C_4H_{16}B_9S)(CO)_2$], has been synthesized and its solid-state structure determined. In the solid state, the conformation of the {$Mo(\eta^3$-$C_3H_5)(CO)_2$} fragment is such that the carbonyl ligands are approximately *trans* to the cage C atoms and the conformation of the allyl group is *exo*.