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[1,3-Bis(4-nitrophenyl)triazenido](triphenylphosphine)gold(I)

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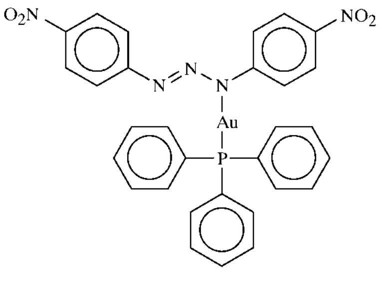
In the title complex, $[Au(C_{12}H_8N_5O_4)(C_{18}H_{15}P)]$, the coordination geometry about the Au^I ion is linear, with one deprotonated 1,3-bis(4-nitrophenyl)triazenide ion, $[O_2NC_6H_4N{=}N{-}NC_6H_4NO_2]^-$, acting as a monodentate ligand (two-electron donor), and one neutral triphenylphosphine molecule completing the metal coordination. The triazenide ligand is almost planar (r.m.s. deviation = 0.0767 Å), with the largest interplanar angle being 11.6 (7)° between the phenyl ring of one of the terminal 4-nitrophenyl substituents and the plane defined by the N=N—N triad. The Au—N and Au—P distances are 2.108 (5) and 2.2524 (13) Å, respectively. Pairs of molecules generated by centrosymmetry are associated into a supramolecular array *via* intermolecular C—H···O interactions, and N···C and N···O π–π interactions.

Comment

Although metal complexes with 1,3-diaryl-substituted triazenide ligands, $[ArNNNAr]^-$, have been extensively investigated in the past, only a few reports of mononuclear gold(I) complexes with monodentate triazenide ligands are found in the literature. More recently, monodentate diaryltriazenide complexes have received attention in connection with the fluxional behaviour of such compounds, in which transition metal fragments ML_n, such as $AuPPh_3$, show N1–N3 σ–σ migration on the nitrogen chain (Peregudov *et al.*, 1998, 2000). Besides the $AuPPh_3$ group, to date only six monodentate diaryltriazenide complexes incorporating ML_n fragments (where L is phosphine) have been characterized by single-crystal X-ray diffraction: *cis*-chlorobis(triphenylphosphine)(1,3-di-*p*-tolyltriazenido)palladium(II) and *cis*-chlorobis(triphenylphosphine)(1,3-di-*p*-tolyltriazenido)platinum(II) chloroform solvate (Bombieri *et al.*, 1976), *trans*-hydridobis(triphenylphosphine)(1,3-di-*p*-tolyltriazenido)platinum(II) (Immirzi *et al.*, 1976), *cis*-bis(triphenylphosphine)bis(1,3-diphenyltriazenido)platinum(II) benzene solvate (Brown *et al.*, 1976), *trans*-carbonyl(1,3-di-*p*-tolyltriazenido)bis(triphenylphosphine)iridium(I) (Immirzi *et al.*, 1980) and *trans*-[1,3-bis(4-fluorophenyl)-1-triazenato-*N*](2-methylphenyl)bis(triethylphosphine)nickel(II) (Peregudov *et al.*, 2000).

Recently, the analogy between the isolobal species $[(Ph_3P)Au]^+$ and H^+ was connected with the formal zwitterionic bond structure of the complex *N*-(triphenylphosphinegold)-*N*-(5-methoxyquinolyl-8)-2,4,6-trinitroaniline, compared with the structure of free *N*-(5-methoxyquinol-8-yl)-2,4,6-trinitroaniline obtained by *ab initio* quantum-chemical calculations (Kuz'mina *et al.*, 2001).

Based on the fact that $[(Ph_3P)Au]^+$ and H^+ are isolobal particles, and on the potential of triazenes for sigmatropic migration of the H atom on the nitrogen triad, our goal was to investigate the title complex, (I), resulting from the substitution of H^+ on the diazoamine group of 1,3-bis-(4-nitrophenyl)triazene by the $[(Ph_3P)Au]^+$ cation, and the results are presented here.



(I)

The crystal structure of (I) reveals discrete asymmetric two-coordinate mononuclear Au^I complexes. The deprotonated 1,3-bis(4-nitrophenyl)triazenide ion acts as an N1-η^1 monodentate (two-electron donor) ligand, while one neutral triphenylphosphine molecule completes the coordination environment of the metal ion to an almost linear arrangement (Fig. 1).

Deviations from normal N—N and N—C_{aryl} bond lengths in (I) (Table 1) provide evidence for the delocalization of the π electrons on the N—N=N group towards the terminal aryl substituents. The N2=N3 bond [1.290 (7) Å] is longer than the typical value for a double bond (1.24 Å), while N1—N2 [1.324 (6) Å] is shorter than the characteristic value for a single bond (1.44 Å; *International Tables for X-ray Crystallography*, 1985, Vol. III, p. 270). Both N1—C1*B* [1.390 (8) Å] and N3—C1*A* [1.402 (7) Å] are shorter than expected for an N—C_{aryl} single bond (1.452 Å for secondary amines, NHR_2, with R = Csp^2; Orpen *et al.*, 1989). These values are in good agreement with the distances found in the related compound *trans*-[1,3-bis(4-fluorophenyl)-1-triazenato-*N*](2-methylphenyl)bis(triethylphosphine)nickel(II) [N1=N2 = 1.298 (7) Å and N2—N3 = 1.326 (7) Å; Peregudov *et al.*, 2000].

The Au—N1 bond distance of 2.108 (5) Å in (I) is close to the sum of the covalent radii (2.144 Å; Allen *et al.*, 1987; Teatum *et al.*, 1960) and corresponds to a covalent single bond.

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This value is longer than that observed in the related compound [Au(RN1═N2—N3—N4═N5R)(PPh$_3$)], hereinafter (II) [where R is p-tolyl; Au—N3 = 2.082 (5) Å; Beck, 1988], suggesting that the 1,3-bis(4-nitrophenyl)triazenide ion possesses minor basicity compared with the 1,5-ditolyl-1,4-pentazadienide ion, [(tolN$_5$tol)]$^-$, as a consequence of the π acidity of both terminal 4-nitrophenyl substituents. On the other hand, the Au—P bond distance of 2.2524 (13) Å in (I) is significantly shorter than the sum of the covalent radii (2.530 Å; Allen *et al.*, 1987; Teatum *et al.*, 1960) and is in good agreement with that found in (II) [Au1—P1 = 2.234 (3) Å].

The coordination angle of the Au^I ion in (I) [N1—Au—P = 178.70 (13)°] deviates only slightly from the ideal value of 180° and is very close to that found in (II) [N3—Au1—P1 = 178.35°]. Due to the delocalization of the π electrons over the nitro groups and the C1*A*–C6*A* and C1*B*–C6*B* phenyl rings towards the N1—N2═N3 chain, the triazenide ligand is nearly planar, with interplanar angles as follows: 5 (1)° between the O1*A*/N6/O2*A* plane and the C1*A*–C6*A* ring, 3.5 (7)° between the C1*A*–C6*A* ring and N1—N2═N3, 11.6 (7)° between the C1*B*–C6*B* ring and N1—N2═N3, 3 (1)° between the O1*B*/N5/O2*B* plane and the C1*B*–C6*B* ring, and 8.9 (4)° between the C1*A*–C6*A* and C1*B*–C6*B* rings.

The crystal structure of (I) reveals pairs of molecules generated by centrosymmetry, which are associated into a supramolecular array *via* intermolecular C—H···O interactions (Table 2), and N···C and N···O π–π interactions (Fig. 2), with N6···C6B^i = 3.282 (8), N3···C6B^{ii} = 3.357 (8), N6···O1B^{iii} = 3.136 (9) and O1A···N5^{iii} = 3.234 (9) Å [symmetry codes: (i) $x, 1 + y, z$; (ii) $-x, 1 - y, -z$; (iii) $-x - 1, 1 - y, -z$]. These values are similar to those for π–π contacts found in free 1,3-bis(3-nitrophenyl)triazene [N···C = 3.387 (3) Å, and N···O = 2.992 (2), 3.304 (3) and 3.023 (2) Å; Zhang *et al.*, 1999]. On the other hand, simultaneous weak intermolecular N6···C6B^i and N3···C6B^{ii} contacts hinder the coplanarity of the C1*B*–C6*B* phenyl ring with the plane defined by the N1—N2═N3 group [interplanar angle = 11.6 (7)°]. All phenyl rings in (I) are planar within experimental error (average r.m.s. deviation = 0.0062 Å).

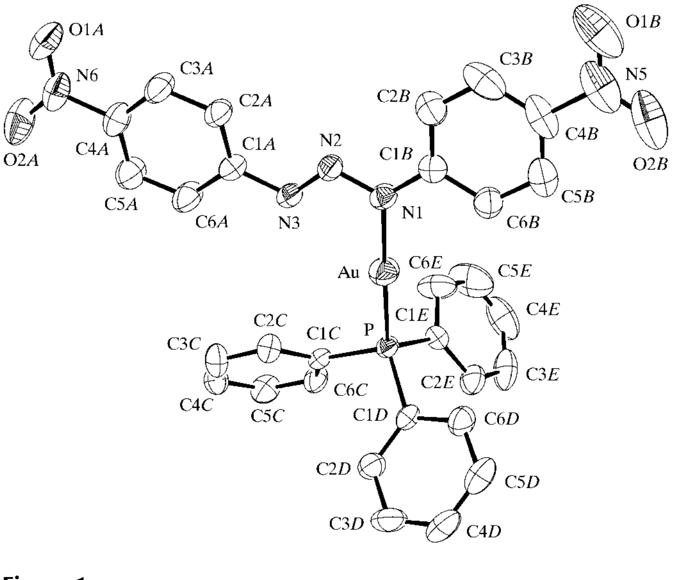

Figure 1
The molecular structure of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability and H atoms have been omitted for clarity.

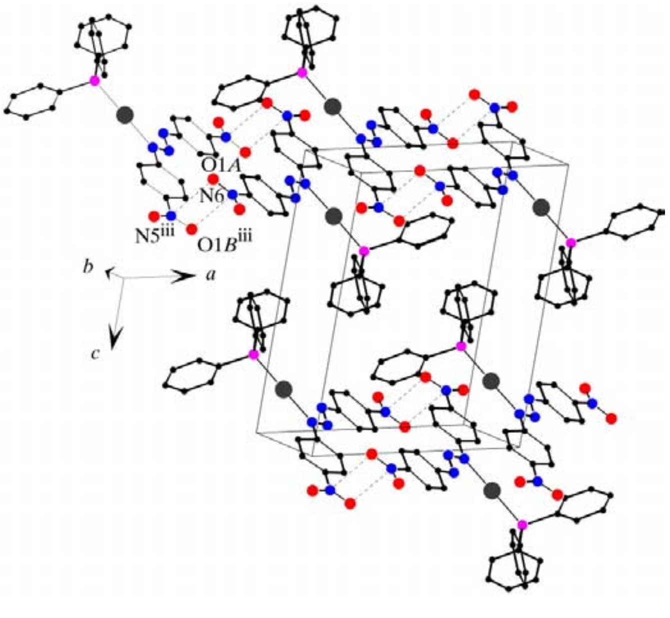

Figure 2
The unit cell of (I) in a view inclined slightly towards [010]. The intermolecular N···O π–π interactions are shown as dashed lines [symmetry code: (iii) $-x - 1, 1 - y, -z$].

Experimental

1,3-Bis(4-nitrophenyl)triazene (28.7 mg, 0.1 mmol) was dissolved in absolute tetrahydrofuran (20 ml) and treated with small portions of metallic sodium powder until H$_2$ evolution stopped. The resulting intense-red mixture was filtered over a sintered-glass frit to remove excess metallic sodium. A solution of Ph$_3$PAuCl (49.5 mg, 0.1 mmol) in absolute tetrahydrofuran was added slowly with continuous stirring. After stirring at room temperature for 1 h, the yellow precipitate of the title complex was filtered off and dried *in vacuo*. Red prism-shaped crystals of (I) suitable for X-ray diffraction were obtained by slow evaporation at room temperature of a solution of the complex in pyridine (yield: 41 mg, 55%; m.p. 506–507 K).

Crystal data

[Au(C$_{12}$H$_8$N$_5$O$_4$)(C$_{18}$H$_{15}$P)]
M_r = 745.47
Triclinic, $P\overline{1}$
a = 10.2034 (4) Å
b = 10.7550 (2) Å
c = 14.0941 (5) Å
α = 93.987 (2)°
β = 102.148 (2)°
γ = 103.930 (2)°
V = 1455.73 (8) Å^3
Z = 2
D_x = 1.701 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 11 145 reflections
θ = 1.0–27.5°
μ = 5.15 mm^{-1}
T = 296 (2) K
Prism, red
0.30 × 0.20 × 0.10 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: analytical (Alcock, 1970)
$T_{\min} = 0.438$, $T_{\max} = 0.648$
15 644 measured reflections
6639 independent reflections
5647 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.034$
$\theta_{\max} = 27.5°$
$h = -13 \rightarrow 13$
$k = -13 \rightarrow 11$
$l = -18 \rightarrow 17$

Refinement

Refinement on F^2
$R(F) = 0.047$
$wR(F^2) = 0.133$
$S = 1.09$
6639 reflections
370 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0698P)^2 + 3.1565P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0$
$\Delta\rho_{\max} = 1.27$ e Å^{-3}
$\Delta\rho_{\min} = -1.20$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Au—N1	2.108 (5)	N6—O2*A*	1.227 (9)
Au—P	2.2524 (13)	C4*B*—N5	1.467 (9)
N1—N2	1.324 (6)	N5—O1*B*	1.198 (12)
N1—C1*B*	1.390 (8)	N5—O2*B*	1.209 (12)
N2—N3	1.290 (7)	P—C1*C*	1.809 (5)
N3—C1*A*	1.402 (7)	P—C1*E*	1.812 (6)
C4*A*—N6	1.466 (8)	P—C1*D*	1.816 (5)
N6—O1*A*	1.211 (9)		
N1—Au—P	178.70 (13)	N3—N2—N1	110.4 (5)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
C4*C*—H4*C*⋯O1*B*$^{\rm i}$	0.93	2.55	3.304 (9)	139
C5*D*—H5*D*⋯O1*A*$^{\rm ii}$	0.93	2.53	3.330 (8)	144

Symmetry codes: (i) $1+x, 1+y, 1+z$; (ii) $1+x, y-1, z$.

The positional parameters of the H atoms were obtained geometrically, with the C—H distances fixed (0.93 Å for Csp^2), and these atoms were refined as riding on their respective C atoms, with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C}sp^2)$. The nitro O atoms show a large thermal motion, indicated by their elongated displacement ellipsoids (Fig. 1). Splitpeaks for these atoms were not observed and consequently a disorder model was not used in the refinement.

Data collection: *COLLECT* (Nonius, 1997–2000); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 1996); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ1026). Services for accessing these data are described at the back of the journal.

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