

Crystal Structure of [1-Phenyl-3-(4-nitrophenyl)triazenido 1-oxide- κ^2N^3,O]-bis(triphenylphosphine)silver(I), [Ag(O₂-NC₆H₄NNOC₆H₅)(C₁₈H₁₅P)₂]

Manfredo HÖRNER,[†] Bernardo Almeida IGLESIAS, Paulo Roberto MARTINS, and Paulo Cesar Mendes VILLIS

Departamento de Química, Universidade Federal de Santa Maria, Cx. Postal 5031, 97110-900 Santa Maria, RS, Brazil

The reaction between [Ag(PPh₃)₃(NO₃)] and 1-phenyl-3-(4-nitrophenyl) triazene 1-oxide desprotonated with potassium hydroxide in methanol yields crystalline [Ag(O₂NC₆H₄NNOC₆H₅)(C₁₈H₁₅P)₂], the first mononuclear triazenido 1-oxide complex of Ag(I) including a [Ag(PPh₃)₂]⁺ fragment. In the asymmetric title complex, the coordination geometry about the Ag⁺ ion is tetrahedral, with one triazenido 1-oxide anion acting as a bidentate ligand (four-electron donor). The crystal belongs to the monoclinic system, space group *P*₂₁/*c* with the cell dimensions *a* = 19.551(7), *b* = 19.342(9), *c* = 11.124(6) Å, β = 95.453(15)°, *V* = 4187(3) Å³, *Z* = 4.

(Received December 11, 2007; Accepted May 1, 2008; Published on web July 1, 2008)

Monocatenated triazenes 1-oxide molecules have been structurally well investigated, and have attracted attention as potential bidentate ligands by the deprotonation of the triazene 1-oxide moiety, [N(H)=N-N→O]. The aim of this work was the investigation of the steric effect of triphenylphosphine in the presence of a triazenido 1-oxide ligand stabilizing a [Ag(PPh₃)₂]⁺ fragment. A review of the literature showed that no X-ray crystal data have been reported including a triazenido 1-oxide ligand coordinated to Ag(I) and, in particular, stabilizing a [Ag(PPh₃)₂]⁺ ion. In this work, we report on the crystal structure of the title complex, (1), (Fig. 1) based on a single-crystal X-ray structural analysis.

Our synthesis of the title complex included reagents and solvents of reagent grade, which were used without further purification. 1-Phenyl-3-(4-nitrophenyl) triazene 1-oxide (50 mg, 0.19 mmol) was dissolved in methanol (15 mL) and treated with an excess of KOH (50 mg, 1 mmol), resulting in an intense-purple mixture. Small portions of powdered [Ag(PPh₃)₃(NO₃)] (0.185 mg, 0.19 mmol) were added under continuous stirring, while the color of the reaction mixture changed to purple-red. Stirring was continued for 1 h. A deep-red precipitate was isolated and washed with small portions of cool methanol. The crude product was dried over P₂O₅ under a vacuum, and

recrystallized in 20 mL of an acetonitrile/pyridine (1:1) mixture. Deep-red bar-shaped crystals of (1), suitable for X-ray analysis, were obtained by slow evaporation of the solvent mixture at room temperature. Yield, 55% (0.09 g, 0.11 mmol), based on [Ag(PPh₃)₃(NO₃)]; m.p., 235 – 236°C. IR (KBr pellet, cm⁻¹), 1483.2 (ν_{as} NO₂) s; 1332.1 (ν_s NO₂) vs.; 1230.7 (ν N-O) vs; 1205.3 (ν_s N-N) vs; 1161.4 (ν_{as} N-O) m; 517.8 (ν Ag-N) m. (IR data: vs, very strong; s, strong; m, medium).

Table 1 Crystal and experimental data

Formula:	C ₄₈ H ₃₉ AgN ₄ O ₃ P ₂
Formula weight:	889.64
Temperature:	295(2)K
Crystal system:	monoclinic
Space group:	<i>P</i> ₂ ₁ / <i>c</i> <i>Z</i> = 4
<i>a</i> =	19.551(7) Å
<i>b</i> =	19.342(9) Å
<i>c</i> =	11.124(6) Å
β =	95.453(15)°
<i>V</i> =	4187(3) Å ³
<i>D</i> _x =	1.411 g/cm ³
Absorption coefficient =	0.605 mm ⁻¹ , λ = 0.71073 Å (Mo <i>K</i> α)
<i>F</i> (0 0 0) =	1824
Crystal dimensions (mm) =	0.20 × 0.06 × 0.03
<i>R</i> =	0.0493
<i>R</i> _w =	0.0897
θ range for data collection:	2.28 to 25.50°
Completeness to θ = 25.50°	85.2 %
Goodness-of-fit =	0.932
($\Delta\rho$) _{max} =	0.427 e. Å ⁻³
($\Delta\rho$) _{min} =	-0.357 e. Å ⁻³
No. of reflections used =	6640
No. of parameters =	524
Data collection:	COSMO/APEX2; Bruker, 2004
Cell refinement and data reduction:	SAINT; Bruker, 2004
Absorption correction:	multi-scan (SADABS; Bruker, 2004)
Molecular graphics:	DIAMOND
CCDC	669662

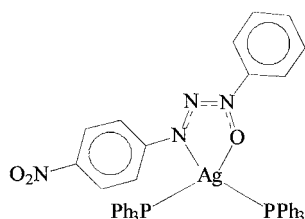


Fig. 1 Structural chemical diagram of (1).

[†] To whom correspondence should be addressed.
E-mail: hoerner@smail.ufsm.br

Table 2 Selected bond distances (Å) and angles (°)

N13–Ag	2.290(4)	N1–N11–O1	125.2(4)
O1–Ag	2.423(3)	N11–N12–N13	114.5(4)
P1–Ag	2.4463(15)	N12–N13–C21	110.9(4)
P2–Ag	2.4641(17)	N12–N13–Ag	121.0(3)
N1–O11	1.225(6)	C21–N13–Ag	128.1(3)
N1–O12	1.213(6)	N12–N11–O1	125.2(4)
N11–N12	1.284(5)	N12–N11–C11	116.1(4)
N11–O1	1.304(5)	O1–N11–C11	118.7(4)
N12–N13	1.331(5)	N11–O1–Ag	111.8(3)
C11–N11	1.434(6)	N13–Ag–O1	66.70(13)
C21–N13	1.402(6)	N13–Ag–P1	125.94(10)
C24–N1	1.439(7)	O1–Ag–P1	114.55(9)
		N13–Ag–P2	109.97(10)
		O1–Ag–P2	112.98(10)
		P1–Ag–P2	116.65(5)

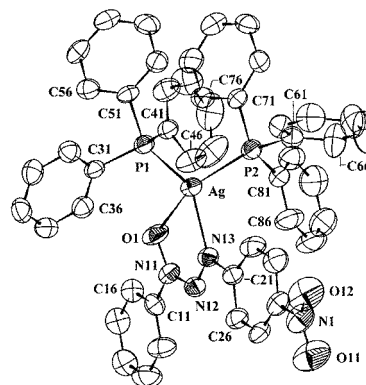


Fig. 2 Molecular structure of the Ag(I) complex along with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

The crystal and experimental data are listed in Table 1. Selected bond distances and angles are given in Table 2. The molecular structure is shown in Fig. 2.

The crystal structure of (**1**) consists of discrete asymmetric mononuclear complex molecules, $C_{48}H_{39}AgN_4O_3P_2$, in which the Ag(I) ion shows a distorted tetrahedral coordination geometry. One 1-phenyl-3-(4-nitrophenyl) triazenido 1-oxide ion acts as a (N13)- η^1 , (O1)- η^1 bidentate (four-electron donor) ligand. Two neutral triphenylphosphine ligands complete the coordination sphere of Ag(I) to a distorted tetrahedron with an interplanar angle P1–Ag–P2/Ag–O1–N11–N12–N13 of 84.12(9)°. The Ag–N13 and Ag–O1 distances differs significantly at 2.290(4) and 2.423(3) Å. On the other hand, the Ag–P distances are similar at 2.4463(15) and 2.4641(17) Å, and can be compared to those Ag–P bond distances observed in the single stranded polymer...Ag(PPh₃)₂(CN)Ag(CN)(PPh₃)₂...(**2**) [Ag–P = 2.466(2) and 2.471(2) Å].¹ The P1–Ag–P2 angle of 116.65(5)° observed in complex (**1**) is smaller than the correspondent angle of 123.45(6)° observed in (**2**).¹ The smaller P–Ag–P angle observed in complex (**1**), may be attributed to steric effects of the triazenido 1-oxide ligand on both the triphenylphosphine ligands in the Ag(I) coordination sphere.

As expected, the molecular structure of (**1**) shows the commonly observed *trans* stereochemistry about the N11–N12 fragment with a double-bond character of the triazenido 1-oxide ligand. The N11–O1 bond [1.304(5) Å] in (**1**) is longer than the N–O bond length, comparatively observed in neutral non-coordinated neutral triazene 1-oxides, such as 3-(*o*-carboxyphenyl)-1-ethyltriazeno 1-oxide [N–O = 1.288(3) Å].² Complex (**1**) shows a lengthening of the N11=N12 bond [1.284(5) Å] compared with the characteristic value for a double bond (1.236 Å), whereas the N12–N13 bond [1.331(5) Å] is shorter than the characteristic value for a single bond (1.404 Å).³ On the other hand, the C11–N11 [1.434(6) Å] and C21–N13 [1.402(6) Å] bonds are shorter than the characteristic N–C_{aryl} single bonds (secondary amines, R₂NH, R = Csp²; 1.452 Å).⁴ These values are in good agreement with those observed in a similar compound, *trans*-Bis [1-methyl-3-(*p*-nitrophenyl) triazenido 1-oxide- κ^2N^3,O] dipyrindine-nickel(II), hereafter(III) [N11=N12 = 1.273(2) Å and N12–N13 = 1.332(2) Å].⁵ The bond angles similar to 120° including atoms N11 and N13

characterize the *sp*² character of this atoms attached to the respective terminal phenyl rings of the triazenido 1-oxide moiety (Table 3), and demonstrate delocalization of the π electrons over the whole ligand anion. The whole triazenido 1-oxide anion deviates slightly from planarity (r.m.s. deviation = 0.1377 Å from the least-squares plane through the non-H atoms).

Even with the presence of a nitro group in the ligand, which commonly makes favourable intermolecular interactions *via* hydrogen bonding, the crystal structure of (**1**) reveals the absence of this kind of secondary non-covalent interactions.

Acknowledgements

This work received partial support from CNPq (proc. 477569/2006-4). M. H. thanks CNPq (proc. 309008/2006-9), B. A. I. thanks CNPq, and P. C. M. V. thanks Capes for grants. The diffractometer was supported by the Financiadora de Estudos e Projetos (FINEP, CT-Infra 03/2001).

References

1. G. A. Bowmaker, Effendy, J. C. Reid, C. E. F. Rickard, B. W. Skelton, and A. H. White, *J. Chem. Soc., Dalton Trans.*, **1998**, 2139.
2. C. Samanta, A. K. Mukherjee, and M. Mukherjee, *Acta Crystallogr.*, **1998**, C54, 1544.
3. F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, and R. Taylor, *J. Chem. Soc. Perkin Trans.*, **1987**, 2, S1; E. Teatum, K. Gschneider, and J. Waber, Report LA-2345. Los Alamos Scientific Laboratory, New Mexico, USA, **1960**.
4. A. G. Orpen, L. Brammer, F. H. Allen, O. Kennard, D. G. Watson, and R. Taylor, *J. Chem. Soc. Dalton Trans.*, **1989**, S1.
5. M. Hörner, J. S. de Oliveira, J. Bordinhao, and J. Beck, *Acta Crystallogr.*, **2002**, C58, m586.