Crystal Structure of 1,3-Bis(4-nitrophenyl)triazenido- $\kappa^2N^1N^3$]-bis(triphenylphosphine)copper(I), $[\text{Cu}(\text{O}_2\text{NC}_6\text{H}_4\text{NNNC}_6\text{H}_4\text{NO}_2)(\text{C}_{18}\text{H}_{15}\text{P})_2]$

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The reaction between $[\text{CuCl}(\text{PPh}_3)_3]$ and 1,3-bis(4-nitrophenyl)triazene deprotonated with metallic sodium in methanol yields crystalline $[\text{Cu}(\text{O}_2\text{NC}_6\text{H}_4\text{NNNC}_6\text{H}_4\text{NO}_2)(\text{C}_{18}\text{H}_{15}\text{P})_2]$, the first mononuclear triazenide complex of Cu(I) including a $[\text{Cu}(\text{PPh}_3)_2]^+$ fragment. The crystals belong to the monoclinic system, space group $P2_1/c$ with the cell dimensions $a = 15.8852(3)$, $b = 11.9539(3)$, $c = 23.2094(6)$ Å, $\beta = 94.646(1)^\circ$, $V = 4392.75(18)$ Å³, $Z = 4$. The crystal structure reveals a bidimensional assembling of complex molecules linked through intermolecular non-classical C-H...O hydrogen bonds.

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Triazenide ligands have attracted considerable attention because of the versatility of their coordination forms, yielding a variety of coordination compounds with large structural diversity. Although metal complexes with 1,3-diaryl-substituted triazenide ligands, $[\text{ArNNNAr}]^-$, have been extensively investigated in the

past, to date only five monocatenated diaryltriazenide complexes with copper(I) have been characterized by single-crystal X-ray diffraction: bis(μ_2 -(diazoaminobenzene)-dicopper(I),^{1,2} bis(μ_2 -1,3-bis(2-methoxycarbonylphenyl)-triazenide- N,N',O)dicopper(I),³ tetrakis(μ_2 -1,3-bis(4-trifluoromethylphenyl)triazenido)- N,N' -tetracopper(I), and tetrakis(μ_2 -1,3-bis(4-fluorophenyl)triazenido)tetracopper(I).⁴ A

Fig. 1 Chemical diagram.

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

Cu–N(13)	2.092(3)
Cu–N(11)	2.237(3)
Cu–P(2)	2.2494(10)
Cu–P(1)	2.2525(10)
N(11)–N(12)	1.306(4)
N(12)–N(13)	1.308(4)
N(13)–Cu–N(11)	58.06(11)
N(13)–Cu–P(2)	116.58(9)
N(11)–Cu–P(2)	119.09(8)
N(13)–Cu–P(1)	119.07(9)
N(11)–Cu–P(1)	104.67(8)
P(2)–Cu–P(1)	121.47(4)
N(11)–N(12)–N(13)	107.3(3)

review of the literature showed that no X-ray crystal data have been reported on a mononuclear triazenide complex with copper(I). In this work, we report on the crystal structure of the title complex, (I), (Fig. 1) based on a single-crystal X-ray structural analysis.

The synthesis of the title complex included reagents and solvents of reagent grade, which were used without further purification. 1,3-Bis(4-nitrophenyl)triazene and $[\text{CuCl}(\text{PPh}_3)_3]$ were prepared according to reported methods.⁵ 1,3-Bis(4-nitrophenyl)triazene (28.7 mg, 0.1 mmol) was dissolved in methanol (20 mL) and treated with small portions of metallic sodium powder, resulting in an intense-red mixture. Excess sodium metal was filtered off and small portions of powdered $[\text{CuCl}(\text{PPh}_3)_3]$ (88.6 mg, 0.1 mmol) were added under continuous stirring while the color of the reaction mixture changed to orange-red. Stirring was continued for 2 h. An orange-red microcrystalline solid, insoluble in the common organic solvents, was filtered off. Orange-red block-shaped crystals of $[\text{Cu}(\text{O}_2\text{NC}_6\text{H}_4\text{NNNC}_6\text{H}_4\text{NO}_2)(\text{C}_{18}\text{H}_{15}\text{P}_2)]$ (I) suitable for X-ray diffraction were obtained by slow evaporation of the filtrate at room temperature. Yield 45% (39.3 mg), m. p. 190°C. IR (CsI pellet, cm^{-1}) 1224.6 (ν_{as} NNN) vs; 1508.1 (ν_{as} NO_2) vs; 1330.7 (ν_s NO_2) vs. (IR data: vs, very strong).

X-ray data were collected by graphite-monochromated Mo K_α radiation ($\lambda = 0.71073$ Å). The crystal and experimental data are listed in Table 1. The structure was solved by direct methods using SHELXS97.⁶ The non-hydrogen atoms were refined anisotropically by the full-matrix least-squares method using SHELXL97.⁶ The positional parameters of the H atoms were obtained geometrically, with the C–H distances fixed (0.93 Å for Csp^2), and refined as riding on their respective C atoms, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{Csp}^2)$. The nitro O atoms have elongated displacement ellipsoids (Fig. 2). Split peaks for these atoms were not observed, and consequently a disorder model was not used in the refinement. Selected bond distances and angles are given in Table 2. Figure 2 represents the molecular structure of the title complex.

The crystal structure of (I) consists of discrete mononuclear complexes in which the Cu(I) ion has a distorted tetrahedral coordination environment. One deprotonated 1,3-bis(4-nitrophenyl)triazene ion acts as a (N11)- η^1 , (N13)- η^1 bidentate (four-electron donor) ligand. Two neutral triphenylphosphine molecules complete the coordination sphere of the metal ion to a distorted tetrahedron. The Cu–N11 and Cu–N13 distances are significantly different at 2.237(3) and 2.092(3) Å, and can be compared to those Cu–N distances in bis(μ_2 -1,3-bis(2-methoxycarbonylphenyl)triazene- N,N',O)-di-copper(I) of 1.909(4) and 1.905(4) Å.³ Due to the fact that the 1,3-bis(4-nitrophenyl)triazene ion acts as a bidentate ligand in complex(I), the copper–nitrogen distances are longer than as

those observed in bis(μ_2 -1,3-bis(2-methoxycarbonylphenyl)triazene- N,N',O)-dicopper(I), in which two triazenide ions bridges two copper centers as monodentate ligands. On the other hand, the Cu–P distances in complex(I) are very similar at 2.2494(10) and 2.2525(10) Å, and can be compared to those Cu–P distances in $[\text{Cu}(\text{N}_3)(\text{dmpymtH})(\text{PH}_3)_2]$ [dmpymtH = 4,6(dimethylpyrimidine-2(1H)-thione)] of 2.2658(11) and 2.2799(11) Å.⁷ The P1–Cu–P2 angle of 121.47° observed in complex(I) is smaller than the correspondent angle of 124.96(4)° observed in $[\text{Cu}(\text{N}_3)(\text{dmpymtH})(\text{PH}_3)_2]$. The smaller P–Cu–P angle observed in complex(I) can be attributed to steric effects of the 1,3-bis(4-nitrophenyl)triazene ligand on both the triphenylphosphine ligands in the copper coordination sphere.

Complexes in the structure of (I) are linked by hydrogen bridges in two dimensions. The O atoms of NO_2 groups of one complex form non-classical C–H...O hydrogen bonds to the H atoms of the PPh_3 groups of each four neighbored complexes. The linked complexes are spread out parallel to the b - c -plane: $[\text{C63}\cdots\text{O12}' = 3.089(6)$ Å and $\text{C63-H63}\cdots\text{O12}' = 122^\circ$; symmetry code: (') $1-x, 1-y, -z$], $[\text{C53}\cdots\text{O22}'' = 3.171(6)$ Å and $\text{C53-H53}\cdots\text{O22}'' = 137^\circ$; symmetry code: (") $x, 3/2-y, 1/2+z$], $[\text{C54}\cdots\text{O11}''' = 3.279(6)$ Å and $\text{C54-H54}\cdots\text{O11}''' = 150^\circ$; symmetry code: (") $1-x, 1/2+y, 1/2-z$]. This expanded system of intermolecular hydrogen bonds probably causes the unexpected insolubility of the compound.

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