Different positions of the formally isolobal moieties H⁺ and (AuPPh₃)⁺ in N-(5-methoxyquinolyl-8)-2,4,6-trinitroaniline and its auration product

Lyudmila G. Kuz'mina,*ᵃ Alexander A. Bagatur'yants,ᵇ Andrei V. Churakovᵃ and Judith A. K. Howardᶜ

ᵃ *Institute of General and Inorganic Chemistry, Russian Acad. Sci., Leninskii pr. 31, Moscow, 119991 Russia. E-mail: kuzmina@igic.ras.ru*
ᵇ *Center of Photochemistry, Russian Acad. Sci., Novator Str. 7a, Moscow, 117421 Russia. E-mail: sasha@photonics.ru*
ᶜ *Department of Chemistry, University of Durham, South Road, Durham, UK DH1 3LE. E-mail: j.a.k.howard@durham.ac.uk*

It has been shown by an X-ray crystallographic analysis of N-(triphenylphosphinegold)-N-(5-methoxyquinolyl-8)-2,4,6-trinitroaniline 1 and quantum chemical calculations on N-(5-methoxyquinolyl-8)-2,4,6-trinitroaniline 2 that H⁺ and (AuPPh₃)⁺ sub-units in 1 and 2 occupy different positions at the amine and quinoline nitrogen atoms, respectively.

This paper is part of our systematic investigations into the structural chemistry of gold(ɪ) compounds. It is well known that the singly charged heavy-metal complex cation AuL⁺ (L = neutral ligand) is isolobal with the cation HgR⁺ (R = acido ligand). Both these metals commonly form 14-electron linear complexes QAuL or QHgR (Q = organic ligand). In real structures, the strict collinearity of metal bonds can be disturbed because of weak interactions (secondary bonds) of the metal with a heteroatom (X) involved in Q.[1] Commonly, the HgR⁺ moiety behaves like a proton. Structures of chemically related organic and organomercury compounds display high similarity and secondary bonds M···X formed by Hg in QHgR are analogous to hydrogen bonds H···X in the corresponding organic compounds QH.[2] In accordance with isolobal analogy, it could be expected that the AuL⁺ moiety also behaves like a proton; that is, in QAuL compounds, it forms a covalent bond with the same atom as the proton in QH compounds.

To explore the limits of the analogy between the corresponding isolobal particles AuL⁺, HgR⁺ and H⁺, we subjected compound **2** to auration and investigated the structures of compounds **1** and **2** (Scheme 1.)

The X-ray structure of complex **1** and selected geometric parameters are shown in Fig. 1. The gold atom of the AuPPh₃ moiety forms a chemical bond with the quinoline nitrogen N(2) in **1**. The Au(1) atom adopts a T-shaped coordination. Two covalent bonds Au(1)–N(2) and Au(1)–P(1) are of normal length [2.121(8) and 2.231(3) Å, respectively].[3–6] The Au(1)···N(1) distance [2.621(9) Å] corresponds to a secondary bond. A similar distance [2.627(9) Å] was found in (8-Squ)AuPPh₃ (8-Squ = 8-mercaptoquinolinate) for the
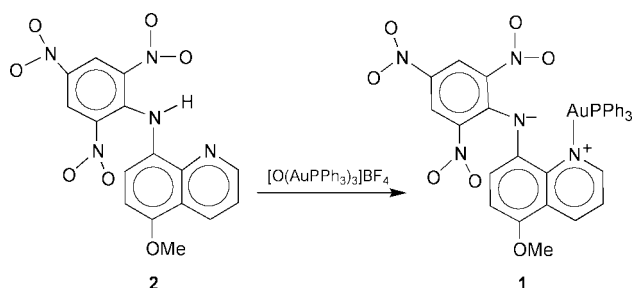
Au···N(quinoline) secondary bond.[6] The N(2)–Au(1)–P(1) bond angle is equal to 168.4(2)° with the Au(1)–P(1) bond bent away from N(1). In contrast to AuPPh₃⁺ in **1**, the proton in N-substituted 2,4,6-trinitroanilines is always located at the amino nitrogen atom. According to the CSD,[2] the N(amino)–C(Ar) bond length varies within 1.33–1.37 Å, the C(ipso)–C(ortho) bond lengths range within 1.41–1.45 Å, and the other C–C bonds in the aniline Ph ring lie within 1.37–1.39 Å. Thus, the bonds C(ipso)–C(ortho) are longer than the others in the ring and no bond length alternation is observed within the C(ortho)···C(para) fragment. The C(ortho)–C(ipso)–C(ortho) angle varies within 112–115°.

The formation of the Au–N covalent bond with the quinoline rather than amine nitrogen atom is the most interesting property of molecule **1**. This fact means that the formal zwitterionic bond structure is characteristic of this molecule. As a result, a
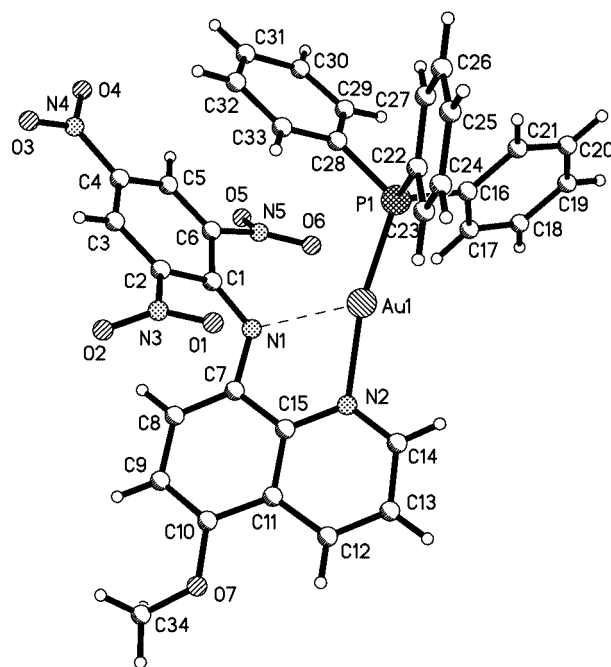

Fig. 1 Molecular structure of **1**. Bond lengths (Å) and bond angles (°) are: Au(1)–P(1) 2.231(3), Au(1)–N(2) 2.121(8), N(2)–Au(1)–P(1) 168.4(2), Au(1)···N(1) 2.621(9), N(1)–Au(1)–N(2) 71.6(3), N(1)–Au(1)–P(1) 120.0(2), N(1)–C(1) 1.30(1), C(1)–C(2) 1.47(1), C(1)–C(6) 1.47(1), C(2)–C(3) 1.36(1), C(6)–C(5) 1.35(1), C(3)–C(4) 1.38(1), C(4)–C(5) 1.39(1), N(1)–C(7) 1.44(1), C(1)–N(1)–C(7) 120.5(8), N(2)–C(15) 1.36(1), N(2)–C(14) 1.33(1), C(14)–N(2)–C(15) 121.4(8).

Scheme 1

DOI: 10.1039/b102938j

significant redistribution of bond lengths in the trinitroaniline moiety should be observed for molecule **1**. Actually, in **1**, the N(1)–C(1) bond 1.30(1) Å is shorter, both the C(1)–C(2) and C(1)–C(6) bonds 1.47(1) Å are longer, and the C(2)–C(1)–C(6) angle is more strongly reduced [109.5(8)°] than the analogous parameters in *N*-substituted 2,4,6-trinitroanilines. A pronounced alternation of bond lengths corresponding to the *para*-quinoid structure of the aniline sub-unit is observed; the C(2)–C(3) and C(5)–C(6) bonds [1.36(1) and 1.35(1) Å] are systematically shorter than the C(3)–C(4) and C(4)–C(5) bonds [1.38(1) and 1.39(1) Å]. Apparently, because of the contribution of the *para*-quinoid structure to the total molecular structure of **1**, the colour of this compound is deeper (black) than those of *N*-aryl-2,4,6-trinitroanilines (tones of red).†

The structure of **1** also contrasts with that of *N*-(5-methoxyquinolyl-8)-2,4,6-trinitroaniline **2**. To provide an insight into subtle geometric changes in the molecular skeleton caused by substituting the proton for the AuPPh$_3$ moiety, *ab initio* quantum chemical calculations were performed for **2**.

Geometry optimisation[7] resulted in the structure shown in Fig. 2. Molecule **2** exists in the same neutral form as all substituted trinitroanilines.

The distribution of bond lengths in **2** agrees well with that observed for *N*-(naphthyl)-2,4,6-trinitroaniline **3**.[8] However, the general conformation of **2** differs significantly from that found for **3**. For instance, dihedral angles between the C(1)–N(1)–C(7) fragment and C(1)⋯C(6) and C(7)⋯C(15) rings are 27.3 and 12.3° in **2**, whereas these angles are of 17.4 and 49.8°, respectively, in **3**. The N–H group in **2** forms a bifurcated hydrogen bond with the quinoline nitrogen (H⋯N 2.104 Å) and one of the oxygen atoms of one *ortho*-nitro group (H⋯O 1.862 Å). Therefore, the geometry of **2** is somewhat flattened compared to that of **3**, where the N–H group forms only one hydrogen bond with the oxygen of the *ortho*-nitro group. This
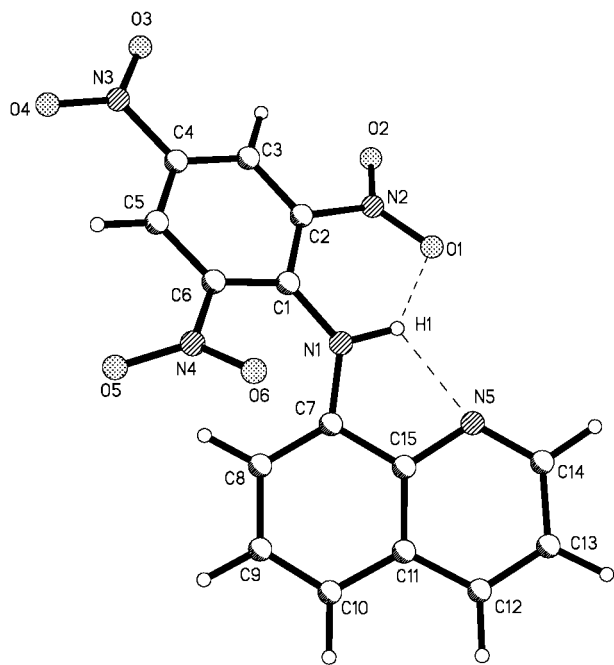
particular *ortho*-nitro group is twisted from the C(1)⋯C(6) plane by only 16.8°, whereas another *ortho*-nitro group is twisted by 52.0°. In **2**, these values are equal to 5.3 and 38.0°.

In **1**, the C(1)–N(1)–C(7)/C(1)⋯C(6) dihedral angle is also rather small (27.0°). The flattened conformation at the formally double N(1)–C(1) bond is a result of a compromise between two effects. One of these is conjugation between the formally double N(1)–C(1) bond and the C(1)⋯C(6) benzene ring while the other is steric interaction between two ring systems. There is no weak interaction between Au(1) and the nearest *ortho*-nitro group N(5)–O(5)–O(6). Because of steric interactions both *ortho*-NO$_2$ groups are strongly twisted from the C(1)⋯C(6) plane by 43.4 and 38.1°.

On the other hand, the C(1)–N(1)–C(7)–C(8) torsion angle in **1** is 41.7° (*cf.* 49.8° in **3**), indicating that there is no significant conjugation between the amine nitrogen lone pair and the quinoline moiety. The coordination of Au(1) with the aminoquinoline moiety causes only minor changes in the geometry of the quinoline fragment. Only the endocyclic angle at N(2) increases to 121.4(8)° *vs.* 117.0° in aminoquinolines and 117.7° in **2**. Such an increase in this angle is typical for *N*-protonated pyridines (CSD).

Notes and references

1 L. G. Kuz'mina, *Russ. J. Coord. Chem.*, 1999, **25**, 599.
2 F. H. Allen and O. Kennard, *Chem. Des. Autom. News*, 1993, **8**, 1.
3 A. V. Churakov, L. G. Kuz'mina and J. A. K. Howard, *Acta Crystallogr., Sect. C*, 1998, **54**, 212.
4 A. V. Churakov, L. G. Kuz'mina, J. A. K. Howard and K. I. Grandberg, *Acta Crystallogr., Sect. C*, 1998, **54**, 54.
5 L. G. Kuz'mina, A. A. Bagatur'yants, J. A. K. Howard, K. I. Grandberg, A. V. Karchava, E. S. Shubina, L. N. Saitkulova and E. V. Bakhmutova, *J. Organomet. Chem.*, 1998, **575**, 39.
6 L. G. Kuz'mina, N. V. Dvortsova, O. Yu. Burtseva, M. A. Porai-Koshits, E. I. Smyslova and K. I. Grandberg, *Metalloorg. Khim.*, 1990, **3**, 364.
7 The calculations were carried out using the MP2 method with the 3-21G* basis sets. Full geometry optimisation was performed starting from two initial geometries. In the first the quinoline fragment was considered as coplanar to the amino group and the N(2)–O(1)–O(2) nitro group was twisted by 60° from this plane. In the second this nitro group was considered as coplanar to the amino group, whereas the quinoline fragment was twisted by 60° from this plane. Both calculations converged to the same flattened geometry.
8 G. V. Gridunova, V. N. Petrov, Yu. T. Struchkov, I. G. Il'ina and O. V. Mikhalev, *Kristallografiya*, 1990, **35**, 59.

Fig. 2 Structure of **2** on the basis of *ab initio* quantum chemical calculation (MP2). Bond lengths (Å) and bond angles (°): N(1)–C(1) 1.374, C(1)–C(2) 1.426, C(1)–C(6) 1.436, C(2)–C(3) 1.390, C(6)–C(5) 1.388, C(3)–C(4), 1.388, C(4)–C(5) 1.388, N(1)–C(7) 1.405, C(1)–N(1)–C(7) 131.0, N(2)–C(15) 1.386, N(2)–C(14) 1.347, C(14)–N(2)–C(15) 117.7.