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Alvaro Rodríguez, MM.; Aprile ., C.; Corma Canós, A.; Ferrer Ribera, RB.; García Gómez, H. (2006). Influence of radical initiators in gold catalysis: Evidence supporting trapping of radicals derived from azobis(isobutyronitrile) by gold halides. *Journal of Catalysis*. 245(1):249-252. doi:10.1016/j.jcat.2006.10.003



The final publication is available at

<https://doi.org/10.1016/j.jcat.2006.10.003>

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Additional Information

Influence of radical initiators in gold catalysis: Evidence supporting trapping of radicals from AIBN by gold halides.

Mercedes Álvaro^a, Carmela Aprile^a, Avelino Corma^{*a}, Belén Ferrer^a and Hermenegildo García^{*a}

5 Gold halides (AuCl₃, HAuCl₄ and AuCl) efficiently trap the carbon centred radical generated in the room-temperature photochemical reaction of AIBN to give an organogold H[(CH₃)₂CCN]₂AuCl₂ compound that has been characterized by ¹H- ¹³C- NMR and by HR-mass spectrometry. This organogold compound in the absence of any other gold source is able to catalyze the aerobic oxidation of cyclohexane to a mixture of epoxide and cyclic hydroxyl compounds, that is similar to that observed in the aerobic oxidation of cyclohexene using conventional gold supported catalysts.

15 Catalysis by gold has emerged as one of the currently most active research fronts¹⁻⁴. In contrast to platinum, palladium and other noble metals, gold is catalytically inert until particles of sufficiently small size in the nanometer range are obtained. The aim for increasing the catalytic activity of gold has led heterogeneous and homogeneous catalysis to converge in the quest for small particles or soluble monoatomic compounds. Gold halides have also been found to promote an array of reactions including cycloisomerizations, benzoannulations and oxidations⁵⁻¹¹.

Recently, it has been reported that the activity of gold nanoparticles in aerobic oxidation reactions can be largely promoted by adding small amounts of azobis(isobutyronitrile) (AIBN)¹². The influence of the presence of AIBN in gold catalysis is intriguing and mechanistic proposals to rationalize this effect were not given. Herein, using gold halides as model gold compounds, we have performed a product and mechanistic study of the reaction of gold with AIBN that eventually leads to an enhancement of the catalytic activity of the noble metal.

AIBN is a well known radical initiator¹³. Upon thermal or photochemical activation, AIBN decomposes to form 1-cyano-1-methylethyl radicals that can evolve in an array of different pathways such as coupling, hydrogen abstraction, electrophilic addition, disproportionation and so on, depending on the nature of the medium and the presence of radical traps. In our hands, working in perdeuterated acetonitrile, AIBN decomposes photochemically at room temperature to give 2,3-dicyano-2,3-dimethylbutane arising from the radical coupling as the only detectable product by ¹H NMR characterized by a singlet at 1.52 ppm corresponding to the methyl groups. Scheme 1 indicates the most reasonable route to explain the formation of the dicyanobutane compound.

Scheme 1.

Photochemical decomposition was also performed under the same conditions in the presence of an equimolar amount of AuCl₃. The progress of the photochemical reaction could be conveniently followed by ¹H NMR spectroscopy, in where the disappearance of the singlet at 1.70 ppm corresponding to the iso methyl groups of AIBN was accompanied by a concomitant

increase of the singlet corresponding to the radical coupling product at 1.52 ppm and, more importantly, the appearance of a new peak at 1.98 ppm. The latter chemical shift appears at an unusually low field, indicating that the methyl groups are bonded to a strongly electron withdrawing group. We tentatively attributed this new peak to an organogold product arising from the radical trapping by the gold atom as indicated in Scheme 2.

Scheme 2

Figure 1 shows a selected region of the ¹H NMR spectra to illustrate the differences observed when AIBN irradiation is carried out in the absence or in the presence of AuCl₃. Similar ¹H NMR spectra, with minor ratio variations between the radical coupling product and the organogold compound, were recorded when AIBN was photolyzed in the presence of HAuCl₄ or AuCl, indicating that most probably the same kind of compound is formed.

Figure 1

¹³C NMR spectra of the reaction mixture after complete disappearance of AIBN in the absence and presence of gold halides also show the same features as those commented for ¹H NMR spectroscopy. Thus, the radical coupling product exhibits in CD₃CN a peak corresponding to the methyl groups at 22 ppm. The quaternary carbon of the radical coupling product was not observed at all and the nitrile carbon of this product must appear together with the CN carbon of the solvent. When AIBN is photolyzed in the presence of gold halides, in addition to the peak of the coupling product a new down-field peak at 32 ppm was also recorded. DEPT confirmed that this new peak corresponds to a methyl group that we assigned to the geminal methyl groups of the organogold compound previously observed in ¹H NMR. No evidence for a quaternary carbon connected to gold was obtained. This could be due to an inefficient relaxation of this quaternary carbon. To test this hypothesis, the ¹³C NMR was re-recorded increasing the pulse delay time to 2 s and in this way a new signal at 100 ppm attributable to a quaternary carbon bonded to a positive gold atom was observed. DEPT confirmed that this peak at 100 ppm corresponds to a quaternary carbon. Figure 2 shows a representative ¹³C NMR spectrum of the AIBN photolyzated in the presence of AuCl₃, together with the corresponding DEPT spectra.

Figure 2

Given the very different nature between the radical coupling product and the presumed organogold compound, they could be separated in a simply way by partitioning the reaction mixture after photolysis and acetonitrile removal between D₂O and CDCl₃, whereby the organogold compound becomes dissolved in the aqueous phase. Room temperature decomposition of this organogold compound in water over the time was observed, thus precluding recording a ¹³C NMR in this phase. However, the stability was sufficient to record a ¹H NMR spectrum in which

the characteristic peak corresponding to the radical coupling product was absent. Figure 1 shows this ^1H NMR spectrum of the D_2O phase.

High resolution mass spectrometry of the organogold compound gives a peak at 369.### daltons corresponding to a molecular formula of $\text{C}_6\text{H}_{13}\text{N}_2\text{AuCl}$ (exact mass 369.####) that is compatible with an ion such as $[(\text{CH}_3)_2\text{CCN}]_2\text{AuClH}^+$ arising from chloride loss of an organogold compound such as that indicated in Scheme 2. This ionic $[(\text{CH}_3)_2\text{CCN}]_2\text{AuCl}_2^-$ organogold(III) compound is compatible with all the available NMR spectroscopic data (including unusual down-field chemical shifts due to the strong electron withdrawing influence of positive gold atom) and also with the mass spectrum (after loss of a chloride in the molecular ion). This cationic organogold compound would arise from the trapping of the 1-cyano-1-methylethyl radical by the gold atom. Also presumably, this positive compound is likely to be soluble in water and would undergo chloride substitution by hydroxyl groups in water that would explain its instability in aqueous phase. Radical trapping by transition metal atoms and ions, such as Cu(I) and palladium are not unprecedented, and our finding would correspond to an analogous behaviour for gold.

In contrast to water, $[(\text{CH}_3)_2\text{CCN}]_2\text{AuCl}_2^-$ is stable in CD_3CN , even after prolonged heating at 70 oC. When cyclohexene is added to this organogold compound in the presence of air but in the absence of AIBN or other gold species, formation of a mixture of oxidized products including cyclohexenol and cyclohexene epoxide was observed.

We performed a continuous flow catalytic reaction in which ceria supported gold nanoparticles (Au/CeO_2) was used to promote the aerobic oxidation of cyclohexene at 60 oC. As expected in view of earlier precedents, only traces of oxidation products were observed under these conditions. However, when AIBN was added in small quantities (1 %) to the catalyst, a remarkable increase in cyclohexene conversion was observed. The product distribution included the corresponding cyclohexene epoxide (20 %) together with 2-cyclohexenol (15%) and some other minor products. This product distribution is analogous to that observed with the $\text{H}[(\text{CH}_3)_2\text{CCN}]_2\text{AuCl}_2$ without addition of AIBN.

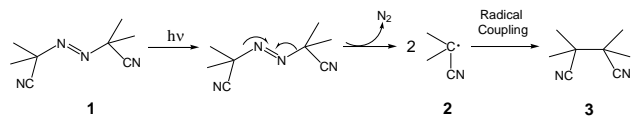
Thus, based on the study of the reactivity of gold chlorides with AIBN and the catalytic tests, we conclude that the most likely operating mechanism for the promotion of the catalytic activity of gold by AIBN in hydrocarbon aerobic oxidation involves the intermediacy of organogold species arising from radical trapping of AIBN derived radicals by gold nanoparticles. The presence of positive gold atoms in gold nanoparticles has been firmly established and these positive gold atoms will act similarly to Au(III) or Au(I) chlorides forming R-Au organogold species on the surface of the gold catalyst. As we have shown before these organogold compounds can promote aerobic oxidation without the need of additional amounts of radical initiator. Scheme 3 illustrates our mechanistic proposal that is different from an obvious alternative arising from hydrogen atom abstraction from an allylic position of cyclohexene to generate allylic radicals. Our study can serve to develop more efficient gold catalysts based on the use of organogold species rather than in purely inorganic gold catalysts.

Scheme 3

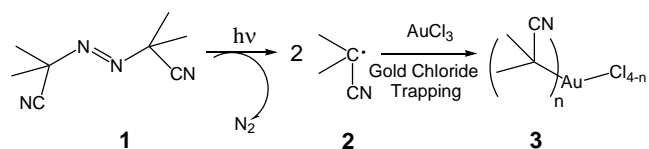
Financial support by the Spanish Ministry of Science and Education is gratefully acknowledged. CA and BF also thank the Spanish Ministry for two Juan de la Cierva contracts as research associates.

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Scheme 1 Photochemical decomposition of AIBN (1) to form 1-cyano-1-methylethyl radicals (2) which evolve to give the radical coupling product 2,3-dicyano-2,3-dimethylbutane (3).



Scheme 2 Radical trapping by the gold atom and formation of the organogold compound 3.

DEPT



^{13}C NMR

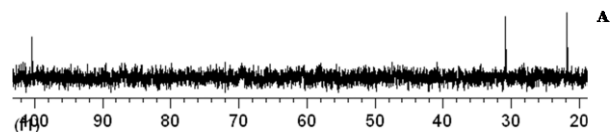
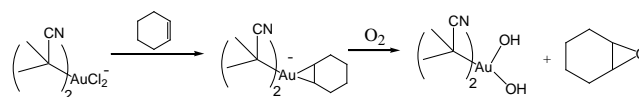


Fig. 2 A. ^{13}C -NMR and B. DEPT spectra of a solution of AIBN and $AuCl_3$ in CD_3CN recorded 20 hours after irradiation



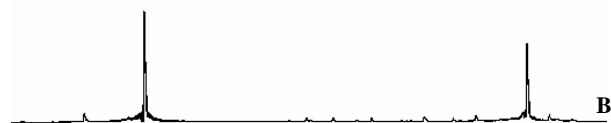
Scheme 3 Mechanistic proposal for the oxidation of cyclohexene by the organogold compound.

After extraction



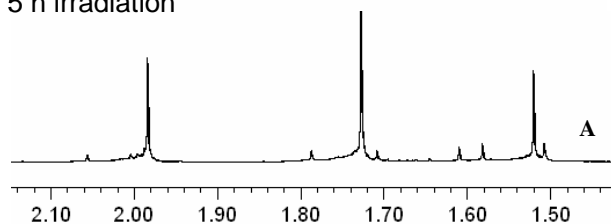
C

20 h irradiation



B

5 h irradiation



A

Fig. 1 1H NMR spectra of a solution of AIBN and $AuCl_3$ in CD_3CN recorded A. 5 hours and B. 20 hours after irradiation. C. 1H NMR spectrum of the purified organogold compound in D_2O .