

Gold complexes as catalysts: Chemoselective hydrogenation of nitroarenes

Avelino Corma^{a,1}, Camino González-Arellano^{b,c,2}, Marta Iglesias^{c,*}, Félix Sánchez^{b,2,*}

^a Instituto de Tecnología Química, CSIC-UPV, Avda de los Naranjos, s/n, 46022 Valencia, Spain

^b Instituto de Química Orgánica General, CSIC, C/Juan de la Cierva 3, 28006 Madrid, Spain

^c Instituto de Ciencia de Materiales de Madrid, CSIC, C/Sor Juana Inés de la Cruz 3, Cantoblanco, 28049 Madrid, Spain

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ABSTRACT

Nitro groups on different compounds – containing double bonds, carbonyl, nitrile or halide groups – have been successfully hydrogenated with well-defined homogeneous gold and palladium complexes as catalysts using a batch reactor under low H₂ pressure. Gold complexes show high chemoselectivity towards reduction of the nitro group at near-complete conversion of the substrate. The corresponding amino derivatives are isolated in high yields.

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1. Introduction

Aminoaromatics are produced by the selective catalytic hydrogenation of corresponding nitro precursors. The reduction of simple nitro compounds is readily carried out with various commercial catalysts [1] (supported copper, cobalt, palladium and nickel), but the selective reduction of a nitro group with H₂, when other reducible groups are present in the same molecule, is more challenging. Functionalized anilines are important intermediates for agrochemicals, pharmaceuticals, dyestuffs, urethanes and other industrially important products and fine chemicals [2,3], there is a strong incentive to develop chemoselective catalysts for the reduction of nitro groups. These reductions have mainly been performed using stoichiometric reagents as SnCl₂, Zn, etc. [4]. Raney nickel is widely used as catalyst but suffers the twin disadvantages of being moisture sensitive and pyrophoric [5,6]. Palladium on carbon is also known to catalyze this reaction but it is more expensive and also quite sensitive to trace impurities [7,8]. Nanoparticles of Co and NiPd, derived from colloidal precursors and supported on commercially available no ordered mesoporous silica, are also highly effective, cheap, recyclable and industrially viable catalysts for the hydrogenation of nitro-cresols under mild

conditions. [9] A number of homogeneous catalysts encompassing macromolecule–metal complexes as well as mono- and bi-metallic platinum- or palladium-based heterogeneous catalysts and polymer-anchored palladium anthranilic acid complexes have also been reported as viable catalysts for this hydrogenation [10–13]. However, low turnover numbers and the concomitant use of external sources of hydrogen (such as trimethyl ammonium or methyl formate), hydrogen-transfer media (e.g. cyclohexane in ethanol), involvement of a suitable base (tri-*n*-butylamine or pyridine) in the catalytic cycle, reflux temperatures and high pressures (6150 kPa) coupled with longer reaction times, and diffusion limitations (where microporous solids are used) preclude the wider commercial applicability of these catalysts.

Catalysis by gold continues to show a fascinating future in the field of catalysis [14,15]. Nanosized Au particles in interaction with a variety of support materials showed special selectivity as an active redox catalyst for oxygen-containing hydrocarbons, such as alcohols and carbonyl compounds, but do not interact with alkenes [16,17]. For reduction, gold can catalyze hydrogenation, although at different rates, alkenes, alkynes, imines and carbonyls [18–20] in the presence of H₂. For the reduction of nitro compounds with H₂, Au/TiO₂, Au/Fe₂O₃ and Au/SiO₂ catalysts were recently found to be very specific in reducing the nitro group in various compounds containing other functional groups [21–25]. Because Pt and Pd are not chemoselective catalysts for the reduction of nitro groups and because alkenes and NO₂ adsorb differently on Pt and Pd than on Au [26], we explored a series of well-defined gold complexes (Fig. 1) as potential chemoselective catalysts for the reduction of

* Corresponding author. Tel.: +34 91 3349000; fax: +34 91 3720623.

E-mail addresses: acorma@itq.upv.es (A. Corma), marta.iglesias@icmm.csic.es (M. Iglesias), felix-igo@icmm.csic.es (F. Sánchez).

¹ Tel.: +34 96 3877800; fax: +34 96 3877809.

² Tel.: +34 91 5622900; fax: +34 91 5644853.

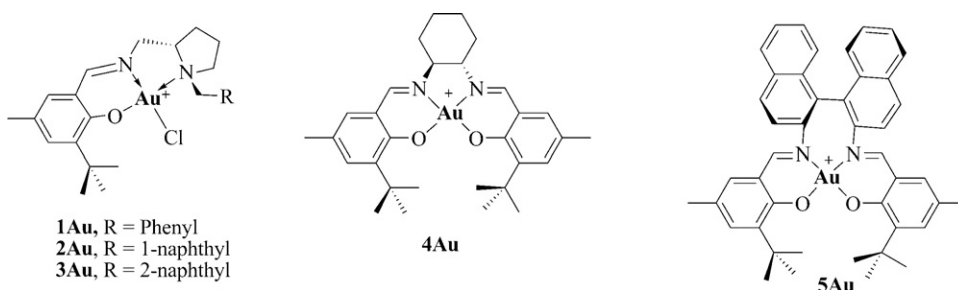


Fig. 1. Gold complexes.

nitroarenes in the presence of other reducible functional groups. Au catalysts were compared with AuCl(PPh₃), supported Au/TiO₂, the corresponding Pd(II) complex, and supported Pd/C.

2. Experimental

All ligands and their respective gold(I) and gold(III) complexes relevant for this work have been obtained in high yields as we have described previously [27–30]. For comparison purposes, the respective palladium(II) complex [31], AuCl(PPh₃) [32] and supported Au/TiO₂ (1.5% Au on TiO₂ was synthesised by the World Gold Council, gold reference catalysts) and Pd/C (Commercial samples of 5% Pd on active charcoal was provided by Sigma–Aldrich Co.) catalysts have been tested under the same reaction conditions.

2.1. Catalytic experiments

2.1.1. Hydrogenation of nitro aromatics

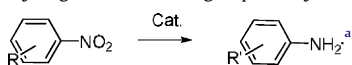
The catalytic properties, in hydrogenation of nitro aromatics reactions, of the Pd and Au complexes were examined under

conventional conditions for batch reactions in a reactor (Autoclave Engineers) of 100 ml capacity in ethanol and 1/500 metal/substrate molar ratio pressure and temperature were optimized in each case to obtain the higher activity and selectivity. The nitro compound was dissolved in ethanol and the catalyst (0.2 mol%) was added. The mixture was charged to an autoclave. After purging with H₂, the reaction mixture was heated to desired temperature and stirred (1500 rpm). The product composition was determined by means of gas chromatography (GC) and the reaction mixture was filtered through a short pad of celite for removing the catalyst and washed thoroughly with ethanol. The solvent was evaporated in vacuum. The products were identified by GC–mass spectrometry (GC–MS) and also by spectroscopy (IR and NMR) comparing with commercially pure products (Sigma–Aldrich Co.). Only experiments with mass balances >95% were considered.

3. Results and discussion

The catalytic activity of the gold compounds for the hydrogenation of nitroarenes was evaluated. Reactions were carried out with Au(I), Au(III), and Pd(II) in ethanol. Tables 1 and 2 summarize

Table 1
Hydrogenation of nitro groups of aryl compounds in the presence of several functional groups.



Catalyst ^b	R	$P \times 10^{-5}$ (Pa)	T (°C)	t (h)	Conv. (%)	R'	TOF ^c
Au(III)	2-CH ₃	5	40	5	100	CH ₃	390
	4-CH ₃			4	100	CH ₃	500
	4-Cl			6	100	Cl	280
	3-NH ₂			5	100	NH ₂	400
	4-OCH ₃			4	100	OCH ₃	350
Au(III)	4-CHO ^d	5	22	6	100	CH ₂ OH	130
		1	22	4	89	CHO	91
AuCl(PPh ₃)	4-CHO ^d	5	80	1	100	CHO	600
Au(I)	4-CHO ^d	5	80	2.5	100	CHO	235
Au/TiO ₂	4-CHO ^{d,e}	9	120	6	99	CHO	140
Pd(II)	4-CHO ^d	5	80	1	100	CH ₂ OH	150
		1	22	2.5	100	CHO	209
Pd/C	4-CHO ^d	10	100	0.03	92	CH ₂ OH/CHO	160
Au(III)	Br	6	80	2	100	Br	310
Au(I)	Br	6	80	24	55	Br	95
Au/TiO ₂	Br ^e	25	140	10	0.5	Br	
Pd(II)	Br	6	80	1	97	Br	580
Pd/C	Br ^e	10	140	8	25	Br	50
Au(III)	CN	6	80	1	98	CN	437
Au(I)	CN	6	80	1	90	CN	394
Au/TiO ₂	CN ^e	25	140	1.25	99	CN	
Pd(II)	CN	6	80	2	83	CN	258
Pd/C	CN ^e	25	140	2	99	CN	

^a Reactions were carried in a reactor (Autoclave Engineers) of 100 mL capacity in ethanol and 1/500 metal/substrate molar ratio. Yields were determined by GC.

^b 1.5 wt% Au/TiO₂, 5% Pd on active charcoal.

^c TOF (mmol subs./mmol cat. h.)

^d Mass balances were between 80 and 90% because of an unavoidable polymerization of 4-aminobenzaldehyde.

^e Solvent, THF.

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