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Gold-Catalyzed Reactions

Gold(III) Complexes Catalyze Deoximations/Transoximations at Neutral pH**

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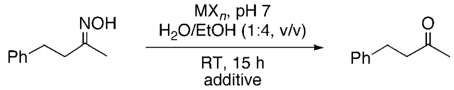
Dedicated to Professor José Barluenga on the occasion of his 70th birthday

The reaction of gold trihalides with reducing agents such as thiols, sodium borohydride, and hydroxylamine results in gold nanoparticles (AuNPs).[1] In particular, NH_2OH is used to facilitate the growth of smaller particles or the formation of thin films of gold.[2] Our interest in developing a mild catalytic method for the conversion of nitro, oxime, and nitrone groups into carbonyl groups led us to examine the interaction of gold(III)[3] with simple oximes as a potential approach for deoximation.[4] The hydrolysis of the coordination complexes of oximes and glyoximes with gold(III)[5] has not been investigated. If a partial hydrolysis of oximes into RR′C=O and NH_2OH took place, NH_2OH would be oxidized in situ by gold(III), and the equilibrium would be shifted to the right.

Our first challenge was to find a water soluble and stable gold complex that could catalyze the hydrolysis of the robust oxime group[6] at neutral pH, and when possible at room temperature. A polyfunctional molecule containing groups that are prone to hydrolysis should survive under these reaction conditions. Lewis acids that are soluble and stable in aqueous media, that is $Sc(OTf)_3$, $LaCl_3{\cdot}7H_2O$, FeX_n, $RuCl_3$, $RhCl_3$, $PtCl_4$, CuX_2, AuX_3, $InBr_3$, and related compounds were screened as catalysts for the hydrolysis of 4-phenyl-2-butanone oxime (Table 1). Only $AuBr_3$ (99.9%) and $AuCl_3$ (99.99%) promoted the hydrolysis of 4-phenyl-2-butanone oxime when the pH was adjusted to pH 7 with a standard solution of NaOH (1.000 M, 99.99%;[7] entries 19–27). Except for AuX_3, none of these salts was a suitable initiator or catalyst at pH 4–8;[8] in fact, in most cases when the solutions were neutralized, the corresponding hydroxides or oxide hydrates precipitated out of solution, as expected. Despite their lack of solubility in water, we also examined a platinum(II) salt (entry 8), copper(I) salts (entries 10–14),[9] and a gold(I) salt (entry 17), because of their success as catalysts in other contexts, but no effect was observed. Among all these common transition-metal cations, only the gold(III) species worked at neutral pH. However, 50 mol% of gold(III) was required to complete the hydrolysis of 4-phenyl-2-butanone oxime (entry 21), because the active Au^{III} species was reduced to $Au^{0/I}$ NPs by NH_2OH, as expected.

Thus, the next challenge was to develop a catalytic version of this hydrolysis. We explored the possibility of trapping

Table 1: Screening of MX_n and additives.[a]



Entry	MX_n, (mol%)	Additive[b]	Conv. [%]
1	$Sc(OTf)_3$ (20)	none	0
2	$LaCl_3$ (20)	none	0
3	$FeCl_2$ (20)	none	0
4	$FeBr_3$ (20)	none	≤ 3
5	$RuCl_3$ (20)	none	≤ 7
6	$RhCl_3$ (20)	none	≤ 6
7	$PdCl_2$ (20)	none	≤ 7
8	$PtCl_2$ (20)	none	0
9	$PtCl_4$ (20)	none	0
10	CuI (20)	none	≤ 4
11	Cu_2Cl_2 (10)	none	0
12	$Cu_2(OTf)_2$[c] (10)	none	0
13	$CuBr_2$ (20)	none	0
14	$Cu(OTf)_2$ (20)	none	10
15	Ag_2SO_4 (20)	none	≤ 4
16	$InBr_3$ (20)	none	0
17	AuCl (20)	none	≤ 2
19	$AuCl_3$ (20)	none	27
20	$AuBr_3$ (20)	none	37[d]
21	$AuBr_3$ (50)	none	100[d]
22	$AuBr_3$ (5)	acetone	60
23	$AuBr_3$ (5)	CH_3COCH_2COOEt	61
24	$AuBr_3$ (5)	$CH_3COCH_2COCH_3$	70
25	$AuBr_3$ (5)	formaldehyde hydrate	88
26	$AuBr_3$ (5)	$CH_3COCOOCH_3$	100
27	$AuBr_3$ (5)	$CH_3COCOCH_3$	100[d]
28	–	$CH_3COCOCH_3$	0
29	$AlBr_3$ (5)	$CH_3COCOCH_3$	0[e]
30	$FeBr_3$ (5)	$CH_3COCOCH_3$	5[f]

[a] An aqueous solution of NaOH (1.000 M) solution was added to the solution of MX_n in H_2O/EtOH (1:4) until a pH of 7 was achieved, and then the oxime was added. [b] Used 100 mol% except in the case of acetone, which was used in excess (entry 22). [c] Copper(I) trifluoromethanesulfonate·toluene, 99.99%. [d] The same result was achieved when using THF, CH_3CN, 1,4-dioxane, 2-propanol, and MeOH instead of EtOH (always with 20% H_2O, v/v). [e] Under these reaction conditions, Ba^{2+}, Ca^{2+}, Cr^{3+}, Mg^{2+}, Mn^{2+}, Mn^{3+}, Ni^{2+}, Sb^{3+}, Sn^{2+}, Sn^{4+}, Ti^{4+}, and Zn^{2+} also gave 0% yield. [f] $RuCl_3$, $RhCl_3$, $PdCl_2$, CuI, $Cu(OTf)_2$, and Ag_2SO_4 gave <2% yield. Tf = trifluoromethanesulfonyl. THF = tetrahydrofuran.

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NH_2OH with carbonyl compounds that are capable of forming oximes that are more stable than the starting oxime (Table 1, entries 22–27). The best results for this transoximation process were obtained with methyl pyruvate ($CH_3COCOOCH_3$, entry 26) and with diacetyl ($CH_3COCOCH_3$, entry 27).[10] At the same time in silico screening, at the MP2 level of theory,[11] indicated that the diacetyl monoxime ($CH_3COC(=NOH)CH_3$) is especially stable compared with many other oximes. The Au^{III} species is crucial because without $AuBr_3$ the exchange between 4-phenyl-2-butanone oxime and diacetyl did not occur (entry 28), even at 100 °C (microwave reactor).

To rule out the participation of the commonly reported impurities contained in 99.9 % $AuBr_3$ (at the ppm level; Aldrich trace analysis), the effect of 5 mol % or more of the following salts at pH 7 was studied in the presence of diacetyl: $AlBr_3$, $BaCl_2$, $CaCl_2$, $CrCl_3$, $MgBr_2$, $MnCl_2$, MnF_3, NaBr (200 mol %), $NiBr_2$, $SbCl_3$, $SnCl_2/SnCl_4$ (1:1), $TiCl_4/Ti(O\textit{i}Pr)_4$ (1:1), and $ZnBr_2$. All were inactive (entry 29).

The Au^{III} species involved as either the initiator(s) or catalyst(s) were examined by electrospray ionization mass spectroscopy (ESIMS, negative mode). Aqueous solutions of $AuBr_3$ were adjusted to different pH values by the addition of an NaOH solution and investigated by ESIMS methods to afford the spectra shown in Figure 1; these spectra were registered with a potential of 20 V because no signals were observed below this value, whereas above 20 V fragmentations of the main species occurred. At pH 5.4 (Figure 1 a) the major anionic species $[AuBr_3(OH)]^-$ appeared as a quartet as a result of the almost 1:1 $^{79}Br/^{81}Br$ isotopic distribution, but an equilibrium was noted between this complex and $[AuBr_4]^-$ (quintet) and $[AuBr_2(OH)_2]^-$ (triplet), as a result of a quick exchange of bromide and hydroxide ions (Scheme 1). At pH 7.0, $[AuBr_2(OH)_2]^-$ predominated (Figure 1 b). Finally, at pH 7.9, the less intensely colored species $[AuBr_2(OH)_2]^-$ and $[AuBr(OH)_3]^-$ (doublet) were predominant (Figure 1 c). All this data agrees with the spectrophotometric data previously reported for these species.[12]

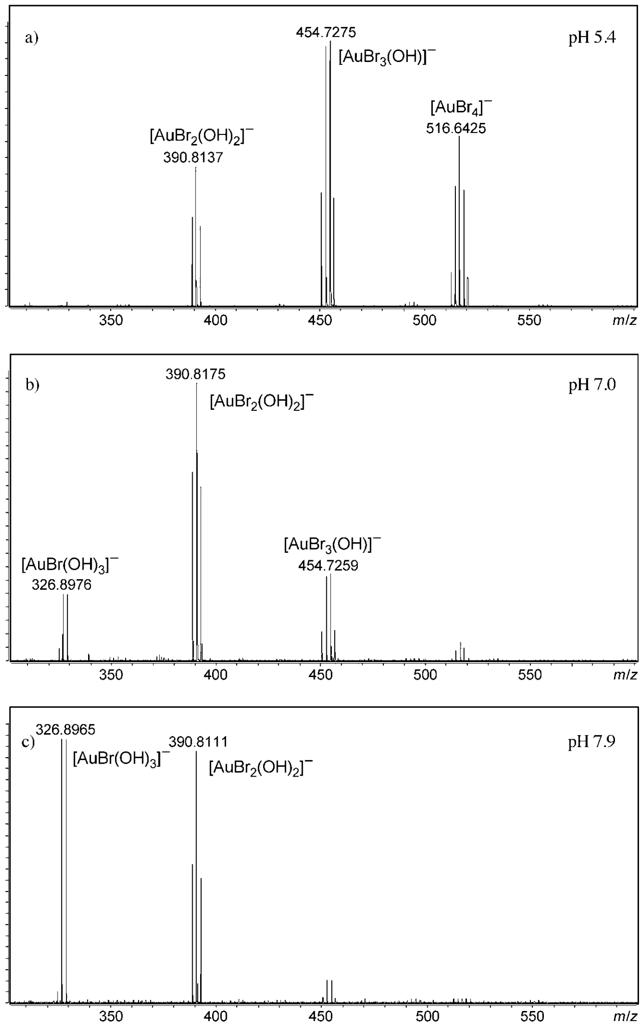
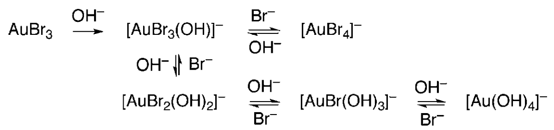


Figure 1. ESIMS (negative mode, 20 V) results for 0.1 M $AuBr_3$ 99.9% + NaOH. a) Added ca. 100 mol% of NaOH, pH 5.40. The major species is $[AuBr_3(OH)]^-$ (*m/z* 450.73/452.73/454.73/456.73) in equilibrium with $AuBr_4^-$ (quintet, centered at 516.64) and $[AuBr_2(OH)_2]^-$ (triplet, centered at 390.81). b) Added ca. 170 mol% of NaOH, pH 7.00. c) With ca. 240 mol% of NaOH, pH 7.89.

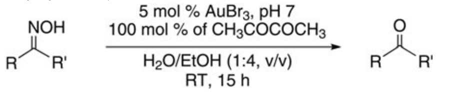


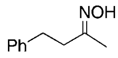
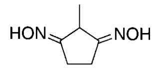
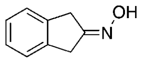
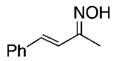
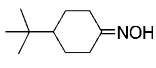
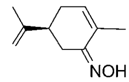
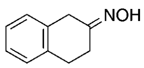
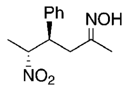
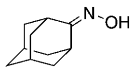
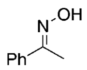
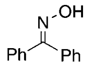
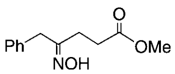
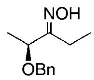
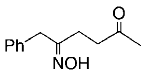
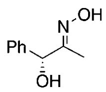
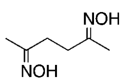
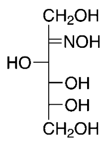
Scheme 1. Gold(III) species in equilibria.

In practice, Au^{III} solutions at pH 5.4 were slightly more catalytically active (50 % conversion after 6 h, under the reaction conditions stated in Table 1, entry 27, with 4-phenyl-2-butanone oxime) than those at pH 7.0 (50 % conversion after 8 h), whereas those at pH 7.9 were less catalytically active (50 % conversion after ca. 12 h) and those at pH $\geq$ 8.5, where $[Au(OH)_4]^-$ predominated (Scheme 1), were completely inactive. The addition of NaBr (from 10 equiv to 100 equiv) stopped the progress of these reactions.[13]

We then examined the scope of the reaction at pH 7. Our protocol could be applied to many ketoximes (Table 2), without any formation of the corresponding amides through the Beckmann rearrangement. In general, 5 mol % of $AuBr_3$ was enough for the full conversion of each ketoxime and diacetyl into the ketone and $CH_3COC(=NOH)CH_3$. In some cases only 2 mol % of $AuBr_3$ was required either at room temperature or at 60 °C. Under these reaction conditions: 1) an ester group (entry 7) was not hydrolyzed, 2) mono- and dioximes of diketones (entries 8 and 9) did not cyclize and the diketones generated did not undergo self-aldol reactions, 3) conjugate additions to α,β unsaturated ketoximes (entries 11 and 12) or to the resulting ketones were not observed, and 4) the $CHNO_2$ stereocenter shown in entry 13 did not epimerize. Hydroxy protecting groups such as tBuMe_2Si (TBS) and 1,2-diol protecting groups such as isopropylidene were not affected,[14] which was expected because the medium was not acidic. The enantiopure compounds of entries 16 and 17[15] did not racemize and no epimerization was noted in the case of D-fructose oxime (entry 18). Free hydroxy groups did not interfere with the hydrolysis (entries 17 and 18).

Table 2: Gold(III)-Catalyzed transoximation of ketoximes.



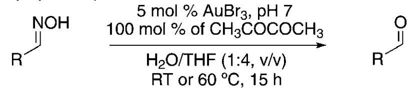
Entry	Oxime	Ketone yield [%]	Entry	Oxime	Ketone yield [%]
1		98	10		100[d]
2		100	11		91[a]
3		100[c]	12		92[b]
4		96	13		93[a,c]
5		100	14		100[a]
6	$(CH_2)_{14}C{=}NOH$	100	15		97[a,c]
7		100[a]	16		92[a]
8		94	17		91
9		100[d]	18		100[c,e]

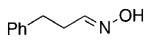
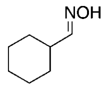
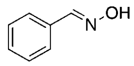
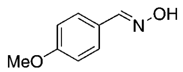
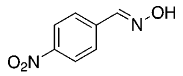
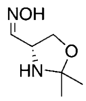
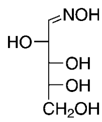
[a] Reaction carried out at 60 °C. [b] At 100 °C for 6 h. [c] With 2 mol% of $AuBr_3$ at pH 7. [d] 200 mol% of diacetyl was added. [e] In D_2O/THF (1:4)the expected mixture[16] of β-D-fructopyranose (major), β-D-fructofuranose, and α-D-fructofuranose was obtained.

The application of our protocol to aliphatic and aromatic aldoximes (Table 3, entries 1–5) gave aldehydes without dehydration to nitriles. THF was a preferable solvent to EtOH or MeOH, because contamination of the products with hemiacetals and acetals is avoided. The oxime of Garner's aldehyde (entry 6) and D-arabinose oxime (entry 7) were hydrolyzed with full retention of the configuration of their α stereogenic centers.

Finally, to gain insight into the role of the Au^{III} complexes, several experiments were followed by ESIMS methods.[11] One representative example is shown in Figure 2. In this experiment we chose a solution of $AuBr_3$ at pH 6. A saturated solution of 4-phenyl-2-butanone oxime in water was added to the stirred Au^{III} solution and after analysis the spectrum in Figure 2 a was obtained. The intensities of the triplet, quartet, and quintet had decreased and new peaks had appeared (Figure 2 a, see arrows) that corresponded to new complexes: $[AuBr(OH)_2(oximate)]^-$ (**1**, doublet; see Scheme 2 for structures), $[AuBr_2(OH)(oximate)]^-$ (**3**, triplet), and $[AuBr_3(oximate)]^-$ (**5**, quartet). These new complexes are most likely explained by the replacement of one bromide ion by the

Table 3: Gold(III)-catalyzed conversion of aldoximes into aldehydes.



Entry	Oxime	Aldehyde yield [%]
1		100[a] 92[a,c]
2		100[b]
3		100[b]
4		100[b]
5		60[b] 91[b,d]
6		90[a]
7		100[a,e]

[a] Reaction carried out at RT. [b] Reaction carried out at 60 °C. [c] With 2 mol% of $AuBr_3$ at pH 7. [d] 10 mol% of $AuBr_3$ at pH 7 and 120 mol% of diacetyl. [e] In 1:4 D_2O/THF the anomeric mixture[16] of β- and α-D-arabinopyranose (major) was isolated.

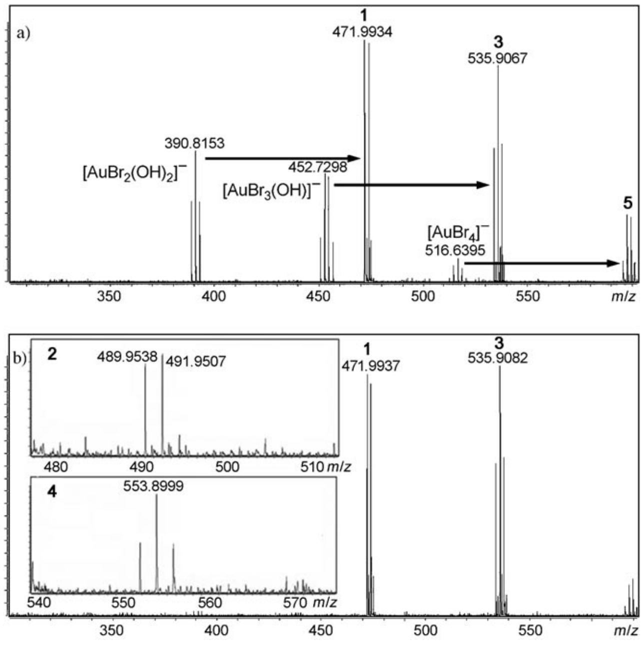
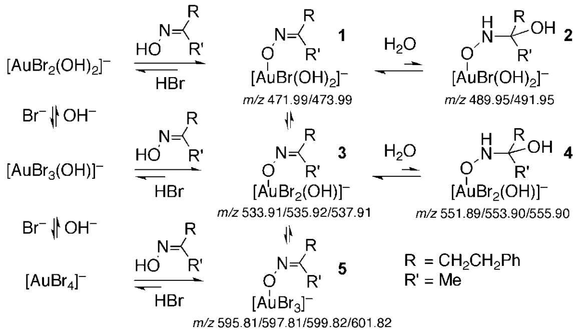


Figure 2. ESIMS spectra of the reaction of gold(III) complexes with 4-phenyl-2-butanone oxime in H_2O. a) Approximately at pH 6.0, after adding the oxime. b) After 2 h, when the wine-red color of the solution had faded; regions where the main hydrated intermediates could appear are expanded. See the main text and Scheme 2 for discussion.

oxime with concomitant loss of a proton. The many spectra obtained at different times over the course of the reaction seem to indicate that the Br^-/OH^- and HBr/H_2O exchanges occur quickly at standard concentrations to give equilibrium mixtures including oximate-containing complexes (Scheme 2). After 2 hours (Figure 2b) the signals of



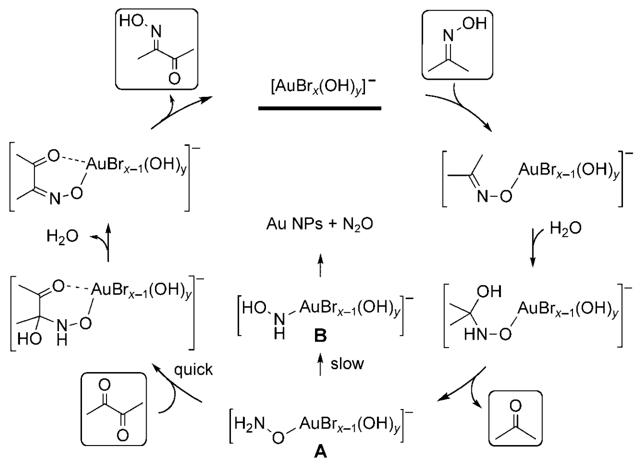
Scheme 2. Gold(III) species involved in Figure 2.[17]

$[AuBr_x(OH)_y]^-$ had almost disappeared and the main peaks now corresponded to the oximato-containing complexes (**1**, **3**, **5**). Their hydrated forms (**2**, **4**; Scheme 2), which are the obvious transient intermediates in any oximation or hydrolytic deoximation procedure, were obscured by noise. Nevertheless, by enhancing the sensitivity by 100-fold, even these relatively unstable intermediates could be observed (Figure 2b, left expansions). In contrast, we could not detect the hydrated form $[AuBr_3(O\text{-}NH\text{-}CRR'OH)]^-$ (signals too low).

With the acetone oxime we observed the *O*-oximato species[11] $[AuBr_2(OH)(O\text{-}N{=}CMe_2)]^-$ (*m*/*z* 443.86/445.86/447.86) and its hydrated form (*m*/*z* 461.82/463.82/465.82), in spite of its relatively short half life. Experiments with the ^{15}N-labeled acetone oxime[11] validated the structures of the intermediates. In the presence of diacetyl, complexes of diacetyl monoxime with Au^{III} were also detected (*m*/*z* 471.86/473.85/475.85).

In Scheme 3, we suggest a plausible general mechanism at a pH value between 5.4 and 7.9 for the transoximation between acetone oxime and diacetyl. In the absence of diacetyl the complexes of type **A** (Scheme 3, bottom) may isomerize to the complexes of type **B** (by hydrolysis and/or by an O to N exchange). It is likely that these **B** species are involved in the known redox process that affords AuNPs and "HNO" ($2\,HNO \rightarrow N_2O + H_2O$).[18]

In summary, neutral $AuBr_3$ solutions catalyze the deoximation of 25 oximes, many of which are really robust,[6,19] by transoximation with diacetyl at room temperature (in most cases). No other metallic salts catalyzed this reaction between pH 4 and 8. The reaction conditions are extremely mild: α stereocenters do not epimerize, other functional groups and standard protecting groups are inert, ketoximes do not undergo Beckmann rearrangements, and aldoximes are not converted into nitriles. It is a paradox that the secret of success is to avoid the formation of AuNPs, which are so important in other contexts, because their formation results in the disappearance of the Au^{III} species. Thus, a new episode in the gold catalysis story is uncovered here. Studies of the performance of the $[AuBr_x(OH)_y]^-$ species in other reactions at neutral pH, where the central atom is still surprisingly active as a Lewis acid, are in progress.



Scheme 3. Plausible mechanism for the hydrolysis of acetone oxime in the presence of gold(III) and diacetyl at neutral pH.

Experimental Section

Representative deoximation procedure: Diacetyl (27 μL, 26 mg, 0.3 mmol) and the Au^{III} stock solution[7] (175 μL, 0.015 mmol) were added to a solution of the ketoxime (0.3 mmol) in ethanol/water (4:1 v/v, 2 mL). The mixture was stirred at ca. 20 °C for 15 h in a closed vial. An N_2 atmosphere was unnecessary. Afterwards, the solution was diluted with dichloromethane (10 mL), and water was then added and the layers were separated. The aqueous layer was re-extracted with dichloromethane. The organic extracts were dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude reaction mixture was analyzed by ^1H NMR spectroscopy. Several reactions were performed later at 1.0 or 2.0 mmol scale. When purification was required it was carried out by flash column chromatography on silica gel with hexanes/EtOAc (1:1).

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[4] Most deoximation procedures involve strong oxidants, reducing agents, acidic reaction conditions, or stoichiometric amounts of other reagents. For a recent review, see: A. Corsaro, M. A. Chiacchio, V. Pistarà, *Curr. Org. Chem.* **2009**, *13*, 482 – 501.
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[6] The stability of oximes to hydrolysis is paradigmatic; see: J. Kalia, R. T. Raines, *Angew. Chem.* **2008**, *120*, 7633 – 7636; *Angew. Chem. Int. Ed.* **2008**, *47*, 7523 – 7526, and references therein.
[7] An aqueous solution of NaOH (1.000 M) was added to a solution of $AuBr_3$ in water (0.100 M) until pH 7.0 was obtained (monitored with a pH meter). The resulting wine-red solution that was 0.086 M Au^{III} (stock solution) was stable for months when stored in a closed vial. $AuCl_3$ was almost as active as $AuBr_3$ but solutions of $AuCl_3$ at pH 7.0 were unstable (a precipitate was formed).
[8] Under the reaction conditions stated in Table 1 (entries 1–20) but without neutralization, $EtOH/H_2O$ (4:1) solutions of $CuBr_2$ (pH 2.17), $Cu(OTf)_2$ (pH 1.90), and $RuCl_3$ (pH 1.37) turned out to be more efficient than those of $AuBr_3$ (pH 1.45, 30 % yield of ketone), and $PtCl_4$ solutions gave an outcome similar to $AuBr_3$, whereas all the remaining salts were very inefficient (< 15 % of ketone). However, the addition of only 100 mol % of NaOH (pH value ≥ 4) deactivated Cu^{II}, Ru^{III}, and Pt^{IV} salts completely. In other words, only Au^{III} complexes are still active at neutral pH values.
[9] For a recent review on copper(I)-catalyzed azide–acetylene cycloadditions (click reactions), see: a) J. E. Hein, V. V. Fokin, *Chem. Soc. Rev.* **2010**, *39*, 1302 – 1315; for the $Cu_2(OTf)_2$-catalyzed formation of tetrazoles from azides and cyanides, see: b) L. Bosch, J. Vilarrasa, *Angew. Chem.* **2007**, *119*, 4000 – 4004; *Angew. Chem. Int. Ed.* **2007**, *46*, 3926 – 3930.
[10] We prefer the food additive diacetyl to methyl pyruvate because: 1) it is cheaper, 2) it has a lower boiling point and therefore any excess of additive may be readily removed, 3) its monoxime is more soluble in water thus making the workup easier, and 4) it has two equivalent CO groups per molecule. In aqueous media it is only partially hydrated; for example, see: K. Miyata, K. Nakashima, M. Koyanagi, *Bull. Chem. Soc. Jpn.* **1989**, *62*, 367 – 371.
[11] See the Supporting Information.
[12] A. Usher, D. C. McPhail, J. Brugger, *Geochim. Cosmochim. Acta* **2009**, *73*, 3359 – 3380.
[13] This is understandable if the substitution of the oxime for a bromide ion, in the gold complex, is one of the key reaction steps, which seems likely.
[14] TBSO- and isopropylidene-containing fragments, which were synthesized in our lab during the total syntheses of macrolides, were used as models.
[15] As checked by measuring the optical rotation (entry 16, Table 2; entry 6, Table 3) and HPLC analysis using a chiral stationary phase of the TBS derivative of the ketone of entry 17 in Table 2.
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[17] Elucidating the possible reactivity differences between *E* and *Z* oximes and between *cis*- and *trans*-aurates is outside the scope of this work.
[18] V. Soni, R. N. Mehrotra, *Transition Met. Chem.* **2003**, *28*, 893 – 898.
[19] Provided that they are less robust than the very stable diacetyl monoxime. The mono- and dioxime of 2,4-pentanedione can be hydrolyzed, with 5 mol % of $AuBr_3$ at pH 7, overnight, by adding 110 mol % and 220 mol % of diacetyl, respectively, whilst the oxime of the methyl pyruvate requires heating and a much larger excess of diacetyl.

