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Gold(III) Catalyzed Overman Rearrangements: Controlling Steric Interactions using Pincer-Type Ligands

Silène Engbers,[a] Evgeniya A. Trifonova,[a] Kirsten M. van der Geest,[a] Wietske J. Nauta,[a] Kristopher M. Hess,[a] and Johannes E. M. N. Klein*[a]

Spatial control of reactivity is intrinsically difficult in gold catalysis due to the linear coordination mode of Au(I) and the commonly flat ligands employed for Au(III) complexes. Our recent report of a novel and sterically encumbered $(NNN)_{diiPr}Au–OH$ complex (*Eur. J. Inorg. Chem.* **2021**, 3561–3564.) suggested that the (NNN) ligand framework is capable of sterically interacting with substrates through its conveniently oriented aryl groups. We have now examined these steric properties in more detail by varying the *ortho*-substituent of the aryl group in $(NNN)_xAu–Cl$ complexes. With just small modifications we were able to vary the buried volume around the Cl atom and correlate this to yields obtained in a Au-catalyzed Overman rearrangement. Computationally we further elucidate that the stark difference in yields obtained originates from a shift in binding mode of the substrate to the Au catalyst in the rate limiting step of the reaction. We thus conclude that delicate spatial control can be exercised in gold catalysis and propose the (NNN) ligand framework to be an attractive platform for the efficient design of Au(III) complexes for stereoselective catalysis.

Introduction

Homogeneous gold catalysis is rapidly growing in popularity due to the unique reactivity and high functional group tolerance exhibited by Au catalysts.[1] Most studies use gold(I) chloride complexes, typically L–Au–Cl where L is a monodentate ligand, or alternatively simple gold(III) salts (such as $NaAuCl_4$) as their catalyst. These gold(I) (pre)catalysts are often activated by chloride scavenging agents, such as silver salts, generating a mono-ligated cationic species, $L–Au^+$, which has a coordination site available for interacting with a substrate.[2] The resulting gold-substrate complex, L–Au–S, is linear,[3] resulting in a large distance between the ligand and substrate (Figure 1). This makes stereocontrol in gold-catalyzed reactions particularly challenging, an aspect that has recently been reviewed extensively.[4] Nevertheless, stereocontrol of reactivity and enantioselective Au(I) catalysis have been achieved in certain cases *via* intricate design of very bulky ligands which need to reach around to the substrate binding site.[5]

A more convenient and newly emerging approach to steric control is the use of Au(I)/Au(III) redox catalysis, wherein the Au(I) complex bears a (chiral) hemilabile bidentate ligand.[4l,m,6]

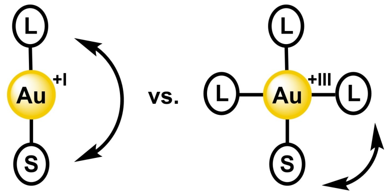

Figure 1. Typical geometries of Au(I) complexes (left) versus Au(III) complexes (right).

In such examples, the ligand is monodentate when Au is in the +I oxidation state and linear in coordination geometry, and is bidentate when Au is in the formal +III oxidation state featuring a square planar coordination geometry. In the square planar geometry, parts of the ligand(s) is(are) in closer proximity to the bound substrate, facilitating steric interactions between the two and hence providing more straightforward avenues for ligand design.[7]

A simpler approach to steric tuning, which does not require changing oxidation states, may be the use of square planar gold(III) complexes, which allow for more straightforward and predictable steric control *via* ligand design.[8] However, gold(III) complexes have received significantly less attention compared to their gold(I) counterparts. This is largely due to the tendency of Au(III) complexes to reduce to Au(I) or Au(0) in the presence of electron-rich substrates, as well as their tendency to undergo protodemetallation.[9] A few examples of gold(III) catalyzed enantioselective reactions have nevertheless been reported.[8] In all cases, the catalyst bears only a mono- or bidentate chiral ligand,[8b,10] with the exception of a chiral CNN pincer complex from the Sánchez group which can perform asymmetric hydrogenations.[11] Tridentate ligands have the advantage that they are more tightly bound due to the chelate effect, and that

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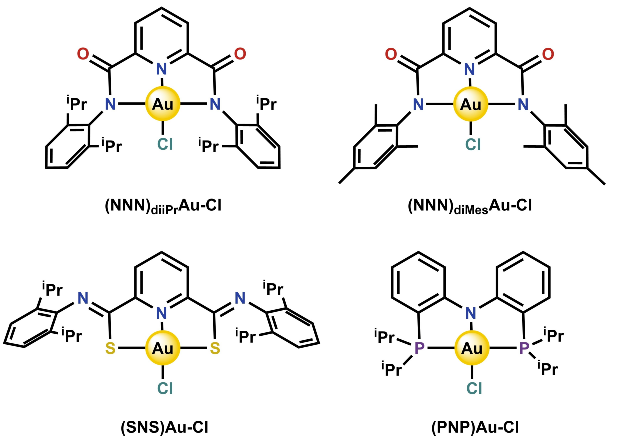
they have more predictable/controllable coordination geometries.[12]

Pincer-type ligands used for Au(III) complexes are generally planar,[13] which is not ideal for the design of complexes that impose spatial control. In the last decade though, a number of Au(III) complexes bearing pincer-type ligands that depart from the commonly flat landscape have emerged in the literature (Figure 2).[9b,14] We recently reported the use of the $(NNN)_{diiPr}H_2$ ligand in the synthesis of a novel Au(III)-OH complex which shows suppressed oxygen atom transfer reactivity.[15] Hence, we envision that this (NNN) ligand framework may provide a good starting point to explore Au(III) catalyzed transformations in which steric interactions are used to control reactivity in a predictable fashion.

To probe this hypothesis, we chose the Overman rearrangement, a [3,3]-sigmatropic rearrangement of allylic trichloroacetimidates to allylic trichloroacetamides, as a model reaction.[16] This reaction is a convenient way to prepare allylic amines from readily available allylic alcohols, as the acetimidate is easily generated by reaction of the alcohol with trichloroacetonitrile and the resulting trichloroacetyl group can easily be removed from the product by hydrolysis (Scheme 1).[16c,17] It is also interesting to note that the Overman rearrangement has been employed in the synthesis of various natural products.[16c] Although the thermal reaction proceeds at elevated temperatures (eg. refluxing xylene),[17] it can also conveniently be performed at room temperature through the use of for example Hg(II),[16a] Pd(II),[18] Pt(II),[18] Pt(IV),[18] Au(I),[18–19] or Au(III)[18] catalysts.[16c] Some examples of enantioselective Pd(II) catalyzed Overman rearrangements have also been reported.[20] Hence, we believe this model reaction to be suitable to probe the steric control exhibited by $(NNN)_x$Au–Cl complexes with varying steric footprints.



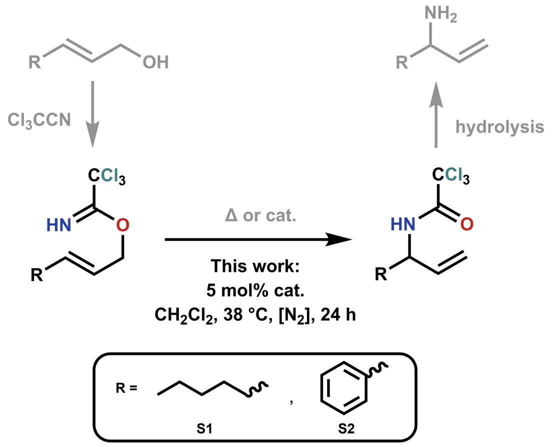
$(NNN)_{diiPr}$Au-Cl

$(NNN)_{diMes}$Au-Cl

(SNS)Au-Cl

(PNP)Au-Cl

Figure 2. Reported Au(III) complexes bearing sterically demanding pincer ligands. (refs. [9b,14])

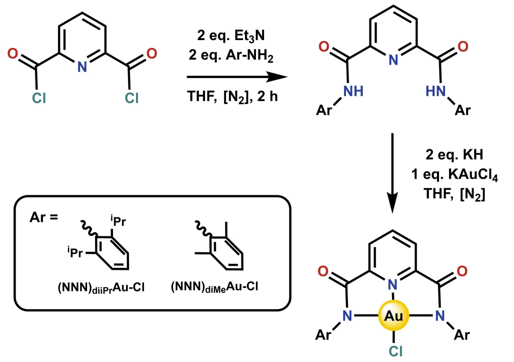


Scheme 1. The Overman rearrangement. Grey: general conditions and its use in converting allylic alcohols into allylic amines. Black: reaction conditions for the Au(III) catalyzed Overman rearrangement explored in this work, $R = C_5H_{11}$ (**S1** to **P1**), or C_6H_5 (**S2** to **P2**).

Results and Discussion

Considering that the Overman rearrangement of a variety of substrates can be efficiently catalyzed by AuCl in water[19] and by $AuCl_3$ in organic solvents,[18] we opted to test the reaction using the Au(III) salt $KAuCl_4$. Gratifyingly, we were able to obtain almost quantitative yields of 2,2,2-trichloro-N-(oct-1-en-3-yl)acetamide (**P1**) from the rearrangement of oct-2-en-1-yl 2,2,2-trichloroacetimidate (**S1**). From the rearrangement of cinnamyl 2,2,2-trichloroacetimidate (**S2**), 67 % yield of 2,2,2-trichloro-N-(1-phenylallyl)acetamide (**P2**) was obtained. We attribute the slightly lower yield for **S2** to a side reaction when using $KAuCl_4$ as a catalyst, as the starting material was essentially fully consumed (Figure S20). These reactions were performed under inert atmosphere, with 5 mol% catalyst loading, in CH_2Cl_2, at 38 °C, over 24 hours (Scheme 1). Hence, we conclude that Au(III) is a suitable catalyst for this reaction under these conditions and we proceeded to modifying $(NNN)_x$Au–Cl complexes.

The aryl group of the $(NNN)_{diiPr}H_2$ ligand framework can be altered to $(NNN)_{diMe}H_2$ such as to reduce the steric footprint of the resulting Au complex. These are efficiently synthesized in a two-step procedure (Scheme 2).[9b,15,21] Both complexes are formed through similar pathways. The ligands are generated from the reaction of 2,6-pyridinedicarbonyl dichloride with the



Scheme 2. Synthesis route for the $(NNN)_x$Au(III)-Cl complexes used in this study. For detailed procedures see sections 2 and 3 of the supporting information.

desired aryl-amine. After deprotonation, these are reacted with $KAuCl_4$ to form the desired complexes. In order to quantify the extent to which the steric properties were altered, buried volumes centered at the Cl atom were calculated for both complexes (Table 1, for steric plots see Figure S23). As anticipated, the bulky $(NNN)_{diiPr}$Au–Cl complex proved to have a larger buried volume than $(NNN)_{diMe}$Au–Cl. It should also be noted that these complexes are electronically equivalent. In both cases, the intrinsic bond orbital (IBO)[22] Au/Cl partial charges of the Au–Cl bond (Figure S24) are 0.39/1.58.

Both complexes were capable of catalyzing the rearrangement of **S1** and **S2** under the same conditions as used with $KAuCl_4$ (Table 2). It is evident though that, for the less sterically pronounced substrate **S1**, yields are not substantially affected by the choice of complex. Although they are lower than for the simple Au salt. In the case of **S2**, which is electronically very similar to **S1** but much more rigid and thus sterically more prominent, yields are significantly lower than for **S1**. Moreover, we do see a significant difference in yields in the rearrangement of **S2** depending on the complex used. Changing the catalyst from $(NNN)_{diiPr}$Au–Cl to $(NNN)_{diMe}$Au–Cl causes an increase of 29%. Thus, we can correlate the buried volumes of the complexes to their yield of **S2**, implying that we can indeed modulate reactivity by varying the aryl group of our $(NNN)_x$Au–Cl complexes.

To verify that the lower yield for **S2** truly originates from the increased sterics of the $(NNN)_{diiPr}$Au–Cl complexes compared to $(NNN)_{diMe}$Au–Cl, we performed a computational study. The mechanism of metal catalyzed Overman rearrangements has been studied for Hg[16a] and Pd.[24] In addition, the mechanism of a Au(I) catalyzed Cope rearrangement was studied extensively.[5c] The proposed mechanism for all of these is similar, proceeding via a cyclic intermediate, where the metal has a key role in stabilizing said intermediate, rather than a cyclic transition state as would be the case for the thermal reaction. Hence, it was envisioned that a similar mechanism would be operative for the Au(III) catalyzed Overman rearrangement (Scheme 3). The complex would first be activated by loss of chloride, yielding a free coordination site for substrate binding. This would activate the double bond for attack by the imidate, yielding a cyclic intermediate. Cleavage of the C–O bond results in the formation of an Au-bound acetamide, which can be exchanged for another acetimidate.

All stationary points in the reaction mechanism indicated in Scheme 3 were optimized using PBEh-3c[25]/cPCM[26](CH_2Cl_2) and electronic energies were obtained using DLPNO–CCSD(T)[27]/def2-TZVPP[28]/cPCM[26](CH_2Cl_2) (Figure 3). The $\Delta G^{\ddagger}$ of the rate determining **TS1** is 6.5 kcal mol^{-1} higher in the case of $(NNN)_{diiPr}$Au–Cl. Considering the identical electronic properties of both complexes, *vide supra*, this increase in barrier can be anticipated to originate from the increased steric footprint of the $(NNN)_{diiPr}$Au–Cl complex. We note that the $\Delta G^{\ddagger}$ values for **TS1**, 38.8 and 45.3 kcal mol^{-1}, for $(NNN)_{diMe}$Au–Cl and $(NNN)_{diiPr}$Au–Cl, respectively, are rather high. We attribute this to be artificially high due to the crude description of solvation effects of the charged intermediates when referencing to the charge-neutral complexes **RS**.[29] The formation of a contact-ion pair (CIP) was therefore considered, which lowers $\Delta G^{\ddagger}$ to a more reasonable 28.1 kcal mol^{-1} in the case of $(NNN)_{diMe}$Au–Cl, further indicating that the solvation model leads to an overestimation of barriers (see Table S3 and Figure S25). We expect the actual barriers to be even lower due to further charge separation artifacts introduced by the solvation model.

To further inspect the role that sterics play in influencing reaction yields, we performed activation strain energy decomposition for **TS1** (Table 3).[30] As expected, the distortion energy of $(NNN)_x$Au, referenced to the Au–Cl complexes, is larger for the complex bearing the diiPr substituents ($\mathbf{TS1_{diiPr}}$) compared to diMe ($\mathbf{TS1_{diMe}}$). The diiPr complex leads to an increase in distortion energy of the $(NNN)_x$Au moiety of 4.3 kcal mol^{-1} compared to diMe. Interestingly though, the distortion energy for **S2** is actually smaller in $\mathbf{TS1_{diiPr}}$, resulting in a larger total distortion energy for $\mathbf{TS1_{diMe}}$ by 1.2 kcal mol^{-1}. This is compensated for by the Au-substrate interaction energy, which is more

Table 1. Buried volumes centered at the Cl atoms of the $(NNN)_x$Au–Cl complexes.

$(NNN)_x$Au–Cl	Buried volume [%][a]
diMe	41.4
diiPr	49.7

[a] Calculated from the PBEh-3c/cPCM(CH_2Cl_2) optimized structures with Cavallo's SambVca tool v 2.1.[23]

Table 2. Yields (in %) obtained from catalytic runs using the $(NNN)_x$Au–Cl complexes.[a]

Catalyst/Substrate	S1	S2
diMe	88	34
diiPr	85	5

[a] 83 mM in dry CH_2Cl_2, 5 mol% catalyst, under N_2 atmosphere, 38 °C, 24 h. Yields determined by ^{1}H-NMR with 1,3,5-trimethoxybenzene as internal standard. Performed in triplicate. No product is formed in the absence of catalyst under these conditions.

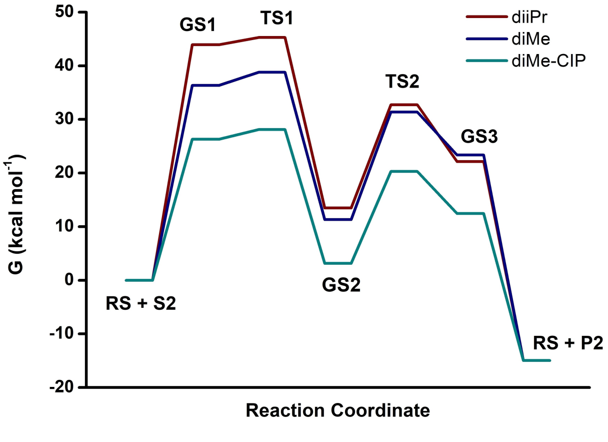


Figure 3. DLPNO–CCSD(T)/def2-TZVPP/cPCM(CH_2Cl_2)//PBEh-3c/cPCM(CH_2Cl_2) Gibbs free energy profiles for the Overman rearrangement of S2 catalyzed by both of the $(NNN)_x$Au–Cl complexes as well as the lowest energy contact-ion pair (CIP) containing pathway for $(NNN)_{diMe}$Au–Cl. For exact values see Table S3.

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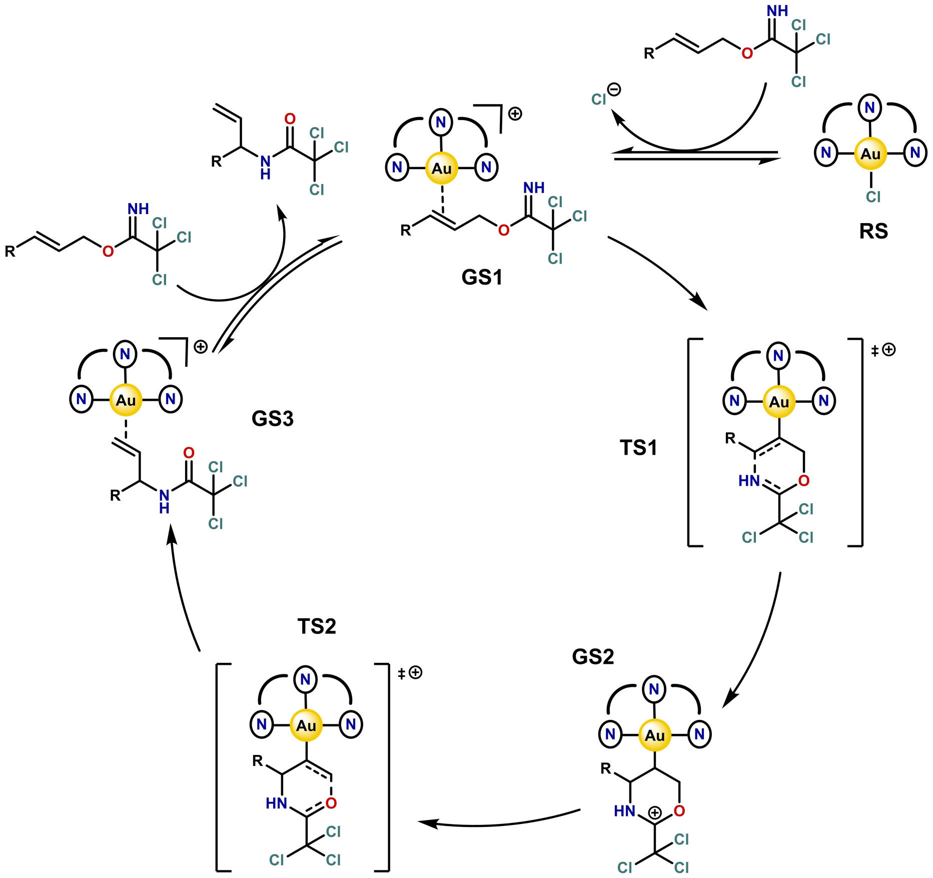

Scheme 3. Proposed catalytic cycle for the $(NNN)_x$Au–Cl catalyzed Overman rearrangement. $R = C_5H_{11}$ or C_6H_5.

Table 3. Activation strain energy decomposition for TS1, referenced to the $(NNN)_x$Au–Cl complexes, as well as relevant bond lengths, angles, and IBO partial charges of TS1. Energies in kcal mol^{-1} and bond lengths in Å.

	diiPr	diMe
$(NNN)_x$Au distortion E.	8.2	3.9
S2 distortion E.	9.3	14.8
Total distortion E.	17.5	18.7
Interaction E.	16.2	10.0
Total electronic E.	33.7	28.7
Au–C bond lengths[a]	Au–C_1: 2.25 Au–C_2 :2.42	Au–C_1: 2.18 Au–C_2 : 2.73
IBO partial charges[a]	Au: 0.49 C_1: 0.93 C_2: 0.53	Au: 0.60 C_1: 1.05 C_2: 0.28
Angle between the Ph and N–Au–C planes	24.3	65.5

[a] Here C_1 refers to the carbon which forms the Au–C σ-bond in GS2 whereas C_2 refers to the benzylic carbon.

favorable in **TS1$_{\text{diMe}}$** by 6.2 kcal mol^{-1}. As a result, the total interaction energy is still larger for **TS1$_{\text{diiPr}}$**, consistent with the lower yields obtained experimentally.

Upon further inspection of the geometries of the two **TS1** structures (Table 3 and Figure 4), it becomes evident that the larger **S2** distortion energy and more favorable Au-substrate interaction energy in **TS1$_{\text{diMe}}$** is caused by a perturbation of the Au-substrate binding mode between the two complexes. The Au–C bond lengths and IBO partial charges on the carbons indicate that binding is much more asymmetric in the case of **TS1$_{\text{diMe}}$**. Furthermore, the angle between the Ph and N–Au–C planes is significantly larger in **TS1$_{\text{diMe}}$**, as the phenyl has twisted such as to be planar with the Au-bound C=C bond, allowing for conjugation and hence delocalization of charge onto the ring. This distortion of **S2** to allow a more favorable binding mode appears to be inhibited by the additional steric bulk introduced by the isopropyl groups.

It is interesting to note that the geometries and activation strain energy decompositions for **GS1** (Table S4) are very similar to that of **TS1**, which is in line with the early transition state observed in the energetics (Figure 3). In contrast, the activation strain energy decomposition for **GS2** is rather different from that of **TS1** (Table S5). Although the distortion energy of $(NNN)_x$Au is larger for **GS2$_{\text{diiPr}}$** by 2.5 kcal mol^{-1}, there is no difference in the distortion energies of **S2** between the two complexes. Similarly, the difference in binding energies is negligible. Hence, the destabilization of **GS2$_{\text{diiPr}}$** compared to **GS2$_{\text{diMe}}$** originates exclusively from the strain induced into the $(NNN)_x$Au moiety as a result of the added steric bulk in the ligand.

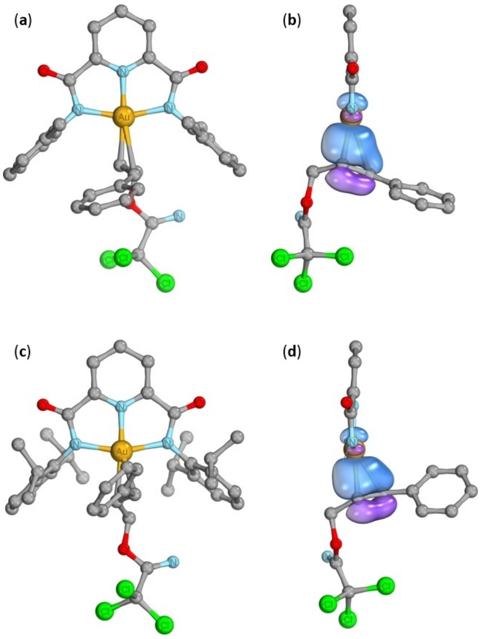

Figure 4. (a) and (c) PBEh-3c/cPCM(CH_2Cl_2) optimized structures of $TS1_{diMe}$ and $TS1_{diiPr}$, respectively; (b) and (d) IBOs for the Au–S2 interaction in $TS1_{diMe}$ and $TS1_{diiPr}$, respectively. Hydrogen atoms, and aryl groups in (b) and (d), omitted for clarity.

Conclusion

In conclusion, a small variation in the (NNN) ligand framework can lead to a significant difference in steric control of a Au(III) catalyzed Overman rearrangement. Not only do we see an inverse correlation between the buried volume of the complex and the yield it provides for the rearrangement of **S2**, but computational studies elucidate that the additional bulk of the $(NNN)_{diiPr}$ ligand prohibits the formation of an energetically favorable binding mode between **S2** and the complex in the rate determining transition state. Thus, we envision that this ligand framework could provide a valuable starting point for further efficient design of chiral complexes for asymmetric Au catalysis,[4] where subtle steric modifications may allow for spatial control.

Experimental Section

Procedures for the synthesis of the Au complexes and substrates were adapted from the literature.[15,21,31]

General procedure for the Au(III) catalyzed Overman rearrangement: Under an atmosphere of N_2, the desired Au complex (8.3 µmol, 5 mol%) was dissolved in 2 mL anhydrous CH_2Cl_2. The desired substrate (166 µmol, 1 eq.) was then added and the reaction mixture stirred at 38 °C for 24 h. The solvent was subsequently removed under reduced pressure and the resulting oil re-dissolved in 0.5 mL $CDCl_3$ containing 1,3,5-trimethoxybenzene as internal standard. Product analysis was performed *via* quantitative ^1H-NMR. All reactions were performed in triplicate.

The general considerations, detailed procedures, product characterization, as well as the computational details and Cartesian coordinates of optimized geometries can be found in the supporting information.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Gold Catalysis · Ligand Design · Steric Control · Rearrangements · Computational Chemistry

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