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Synthesis of a Sterically Encumbered Pincer Au(III)–OH Complex

Silène Engbers,^[a] Evgeniya A. Trifonova,^[a] Kristopher M. Hess,^[a] Folkert de Vries,^[a] and Johannes E. M. N. Klein^{*[a]}

We report the synthesis and crystallographic characterization of a novel Au(III)–OH complex featuring a N[^]N[^]N-pincer ligand. Reactivity studies towards oxygen atom transfer (OAT), a type of reactivity previously reported for a Au(III)–OH complex, indicate that this complex provides both a sterically encumbered Au atom and a sterically poorly accessible OH group leading to no reactivity with a series of phosphines. The steric encumbrance sets this example apart from the known examples of Au(III)–OH (pincer) complexes, which commonly feature planar ligands that provide little control over steric accessibility of the Au and O atoms in these complexes. Implications for the mechanism of OAT from Au–OH complexes are briefly discussed.

Only few examples of structurally defined Au(III) hydroxide complexes have been reported featuring pincer-type ligands,^[1] and for most, little is known regarding their reactivity (Figure 1).^[2] A notable feature of all reported complexes thus far is that the ligands are planar and therefore provide comparable steric environments. Au–OH complexes in general, both Au(I) and Au(III), can be used as synthons to introduce for example anionic ligands, such as a hydride, aryls, and N-heterocycles by ligand exchange.^[2c,3]

Among the Au(III)–OH complexes an exceptionally well-studied example is the (C[^]N[^]^C)Au–OH complex from the Bochmann group, which not only serves as a synthon, but also undergoes oxygen atom transfer (OAT) with various phosphines to form the corresponding phosphine oxides and Au(III)–H (Figure 2).^[4] Based on a series of experiments, the Bochmann group proposed a concerted mechanism for OAT in which there is planar attack of the phosphine directly onto the oxygen leading to both P=O bond formation and proton reduction giving a Au–H (Figure 2). The possibility of an initial Au–P interaction was judged unlikely based on DFT calculations^[4] and further corroborated by a computational study on the corre-

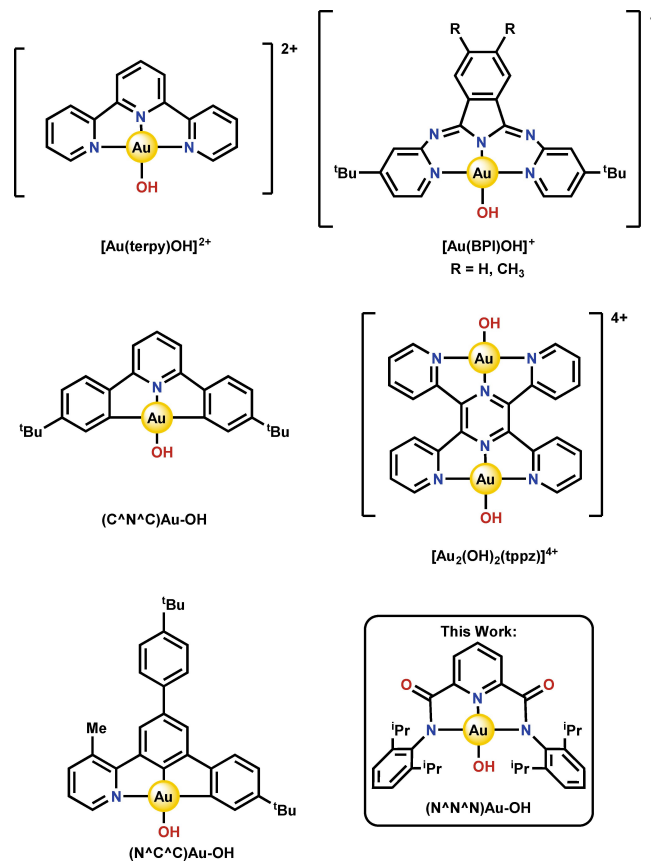


Figure 1. Examples of known structurally defined Au(III)–OH complexes.^[2]

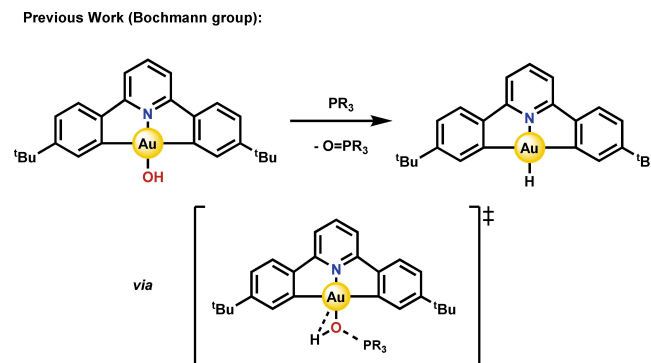


Figure 2. Reported OAT reactivity for (C[^]N[^]^C)Au(III)–OH by the Bochmann group.^[4] R = C₆H₅, *p*-Me-C₆H₄, *p*-MeO-C₆H₄, *p*-F-C₆H₄.

[a] S. Engbers, Dr. E. A. Trifonova, K. M. Hess, F. de Vries, Dr. J. E. M. N. Klein
Molecular Inorganic Chemistry, Stratingh Institute for Chemistry,
Faculty of Science and Engineering, University of Groningen
Nijenborgh 4, 9747 AG Groningen, The Netherlands
E-mail: j.e.m.n.klein@rug.nl

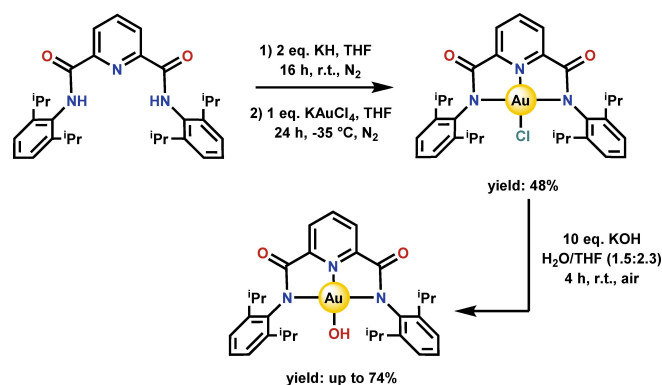
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sponding Au(III) methoxide complex, (C[^]N[^]C)Au–OMe, which also readily performs OAT.^[5] A notable feature of these computations is that a relatively large activation barrier for this process was computed.^[5] In contrast to the known Au(III)–OH case, OAT has been reported unsuccessful for IPr–Au(I)–OH, suggesting that Au(III)–OH may be more suited for the reaction.^[6] This is noteworthy as in the reaction no change in formal oxidation state takes place and both the Au(I)^[7] and Au(III)^[8] hydride complexes are known.

In this article we report the synthesis of a novel Au(III) hydroxide complex, (N[^]N[^]N)Au–OH. The N[^]N[^]N pincer ligand framework is notably different as the two anionic nitrogen donor atoms carry iPr substituents on the ortho position of the aryl groups which lead to steric bulk in the vicinity of the Au–OH unit. We will report studies towards OAT reactivity for this complex and rationalize the lack of such reactivity through the analysis of the steric properties.

We began the preparation of the target complex by preparing the known Au–Cl complex (Scheme 1).^[9] Using a slightly modified procedure the ligand was deprotonated using



Scheme 1. Preparation of (N[^]N[^]N)Au–OH.

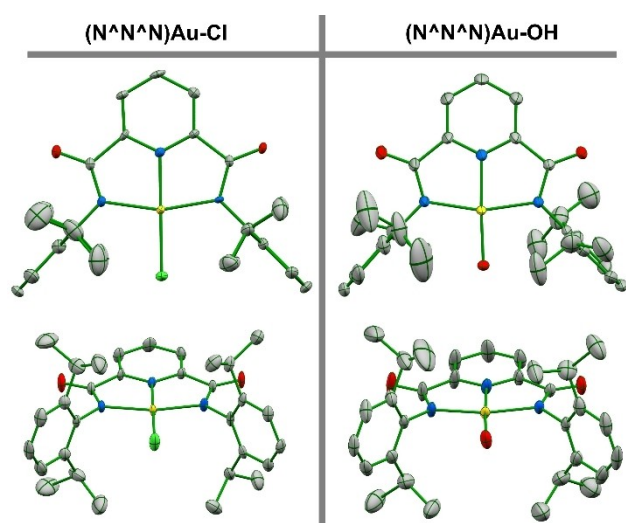


Figure 3. Crystal structures of (N[^]N[^]N)Au–Cl and (N[^]N[^]N)Au–OH. Hydrogen atoms are not shown for clarity.

KH as a base at room temperature. Subsequent addition of KAuCl₄ at –35 °C yielded the desired complex in 48% yield upon purification, a comparable yield to the previously reported procedure. Simple treatment of the Au–Cl complex with KOH in a mixture of H₂O and THF (1.5:2.3) produced the target complex in up to 74% yield.

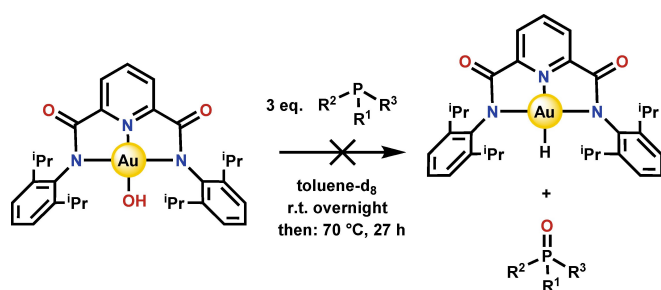
Both complexes were obtained as solids and crystals suitable for X-ray diffraction were readily obtained (Figure 3). (N[^]N[^]N)Au–Cl (CCDC 2053431) was obtained as an orange solid and (N[^]N[^]N)Au–OH (CCDC 2053430) as a yellow solid. These two complexes feature very similar Au–N distances. For the Au–N_{py} distances of 1.960 Å and 1.949 Å are found for the Au–Cl and Au–OH complexes, respectively. In addition, the Au–N_{iPr} distances are also comparable with 2.029/2.018 Å for the Au–Cl complex and 2.025/2.018 Å for the Au–OH complex. The Au–Cl and Au–OH distances are 2.262 Å and 1.945 Å.

The key bond distance that we are interested in is the Au–OH bond distance. A comparison to previously reported Au(III)–OH complexes with pincer-type ligands is provided in Table 1. From the data it can be seen that the Au(III)–OH bond distances range from 1.984–2.010 Å, whereas a shorter bond distance is found for the (N[^]N[^]N)Au(OH) complex. This is the shortest reported Au–OH bond length for Au(III)–OH complexes featuring pincer-type ligands. Notably, the listed examples carry charges between 0 and +2, which has no obvious effect on this bond distance. A brief look at some recently reported Au(III)–OH₂ complexes indicates that in these cases the Au–O bonds are, as expected, ~0.1 Å longer. In addition, longer Au–O distances are also observed for the related Au(I)–OH complexes (IPr)Au(I)(OH) and (SiPr)Au(I)(OH), which are 2.078 and 2.019 Å, respectively.

With the desired (N[^]N[^]N)Au–OH complex in hand we briefly examined if this complex would undergo OAT, as reported for the (C[^]N[^]C)Au(OH) example.^[4] Adding PPh₃ in toluene-d₈ resulted in no reaction at room temperature and prolonged heating to 70 °C also did not produce Ph₃P=O (Scheme 2). We hypothesized that the phosphine was sterically not able to access the Au–OH unit for OAT and decided to test this reaction with the sterically less demanding phosphines Ph₂MeP and PhMe₂P. Again, no oxidation of the phosphines was observed at room temperature. A notable feature of the

Table 1. Comparison of Au–O bond distances for crystallographically characterized Au(III)–OH pincer complexes and examples of representative recently reported Au(III)–OH₂ and Au(I)–OH complexes.

Complex	Au–OH [Å]	Ref.
(IPr)Au(I)(OH)	2.078	[3]
(SiPr)Au(I)(OH)	2.019	[10]
(terpy)Au(III)(OH) ²⁺	2.000	[2a]
(BPI)Au(III)(OH) ⁺ , R=H	1.984	[2d]
(BPI)Au(III)(OH) ⁺ , R=CH ₃	1.992	[2d]
(C [^] N [^] C)Au(III)(OH)	2.010	[2c]
(N [^] N [^] N)Au(III)(OH)	1.945	<i>this work</i>
	Au–OH ₂ [Å]	Ref.
(IPr)(CC) Au(III)(OH ₂) ⁺	2.156	[11]
(IPr)(Ar)(Succ) Au(III)(OH ₂) ⁺	2.088	[12]
(IPr)(Ar)(CF ₃) Au(III)(OH ₂) ⁺	2.100	[12]



Scheme 2. Exploration of OAT reactivity for (N^{^N^N})Au–OH with various phosphines.

(C^{^N^C})Au(OH) example is that the OAT reaction readily occurred at low temperatures.^[4]

We decided to probe the steric properties by evaluation of the accessibility of the Au center and the O atom using Cavallo's SambVca tool v 2.1.^[13] We selected the (C^{^N^C})Au(OH) and (N^{^N^N})Au(OH) complexes for this purpose. To avoid bias from crystal packing we first optimized both geometries at the B97-3c level of theory^[14] in the gas phase, which also provided us with appropriate positioning of the H atoms. We subsequently computed the buried volumes^[15] for the positions of the Au and O atoms in the complex retaining all other atoms (Table 2). We do find that the buried volumes for the Au and O atom is indeed more pronounced for the (N^{^N^N})Au(OH) complex and one might simply attribute the lack of reactivity to the lower accessibility of the O atom. However, for the known Cu-containing equivalent complex (N^{^N^N})Cu(OH) a variety of X–H bond oxidation reactions have been reported.^[16] For these reactions it has been well established that bond activation occurs *via* direct access to the oxygen atom of the Cu–OH unit. We therefore also computed the buried volumes for the positions of the Cu and O atoms (Table 2). The obtained values are found to be in close agreement with those for the Au congener.

From this data we can see that, although the accessibility is reduced in case of the (N^{^N^N})Au(OH) complex, it should in principle not prevent reactivity that relies on the direct accessibility of the oxygen atom. Therefore, we entertain the idea that a Au–P interaction preceding OAT might be relevant for this reaction to proceed. This becomes more evident when inspecting the crystal structure of (N^{^N^N})Au(OH) (Figure 3, bottom right). The positioning of the ⁱPr groups is such that they would prevent approach to the O atom of a P atom bound to/interacting with Au. This steric shield is not present in the (C^{^N^C})Au(OH) complex. A similar steric interaction is present

Complex	[%] V Buried	
	M	O
(C ^{^N^C})Au(OH)	62.9	36.9
(N ^{^N^N})Au(OH)	79.3	60.7
(N ^{^N^N})Cu(OH)	81.0	64.7

for the (N^{^N^N})Cu(OH) complex. Notably, a related Cu complex, which also features the same type of N^{^N^N} pincer type ligand carrying Me rather than ⁱPr groups, reacts with MeCN to form a cyanomethide complex in the +II oxidation state.^[17] Among the various mechanistic proposals put forward for this transformation, it was indeed also considered that MeCN binding to Cu could play a role. We notice that the steric footprint of MeCN compared to a phosphine is smaller and thus attribute the lack of OAT reactivity to the steric separation of Au and O in the present case.

We also note here that the complexes (C^{^N^C})Au(OH) and (N^{^N^N})Au(OH) both are charge neutral leading to no bias regarding overall charge. Furthermore, we computed IAO partial charges^[18] for the Au and O atoms in these complexes to evaluate if the difference in reactivity could arise from different levels of electrophilicity and ultimately reactivity for the Au(OH) complexes. Partial charges of Au/O are 1.067/–0.825 and 1.077/–0.814 for (C^{^N^C})Au(OH) and (N^{^N^N})Au(OH), respectively. This indicates that the (C^{^N^C})Au(OH) complex does not exhibit a bias towards reacting with a phosphine due to partial charge at these sites. In addition, we computed the partial charge distribution for the Au–OH bond based on intrinsic bond orbitals (IBOs)^[18] indicating again very similar features (see ESI for depiction). For the Au–O σ -bonds partial charge distributions of Au/O 0.510/1.447 and 0.484/1.469 are found supporting the notion that the Au–O bonds are similar in nature.

In summary, we have reported the synthesis of a novel Au(III)–OH complex that features sterically more encumbered Au and O atoms. The absence of OAT reactivity is rationalized on the basis of structural analysis and leads us to suggest that an interaction between Au and P is part of OAT for related complexes reported by the group of Bochmann^[4] that display this type of reactivity. Further studies addressing the interplay of sterics and reactivity are currently underway in our laboratory.

Deposition Numbers 2053431 (for (N^{^N^N})Au–Cl) and 2053430 (for (N^{^N^N})Au–OH) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Gold Hydroxides · Oxidation · Oxygen Atom Transfer · Steric Interactions

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