

The elusive Au(I)⋯H-O hydrogen bond: Experimental verification

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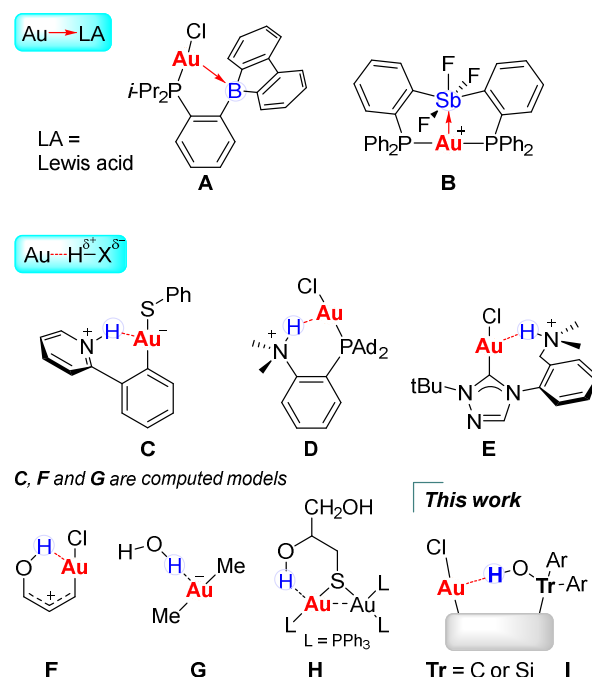
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ABSTRACT: Our longstanding interest in atypical bonding situations has recently led us to target complexes in which a metallobasic gold(I) center is hydrogen-bonded to a nearby OH functionality. Here, we report on the synthesis and characterization of two neutral gold(I) indazol-3-ylidene complexes bearing a carbinol or silanol group at the 4-position. As indicated by X-ray diffraction, ¹H NMR spectroscopy, IR spectroscopy, and extensive computational modeling, the OH group of these derivatives is engaged in a *bona fide* Au⋯H-O interaction. In addition to shedding light on an elusive bonding situation, these results also indicate that increasing the acidity of the OH functionality is not necessarily beneficial to the stability of the Au(I)⋯H-O interaction.

Advances in the chemistry of gold have shed light on the unique metallobasic character that this metal displays, especially when coordinated to ambiphilic ligands with accessible Lewis acidic sites¹ as in the case of **A** and **B** (Chart 1).² The Lewis basic behavior that gold displays in such complexes is further illustrated by the recent demonstration that adequately substituted gold(I) centers are prone to protonation³ or amenable to the formation of Au⋯H-X HBs (HB = hydrogen bond, X = electronegative element).⁴ The formation of Au⋯H-X interactions was originally supported by calculations as in the case of **C**,^{4e} and later experimentally verified for cationic derivatives such as **D** and **E**.^{4f-h} The stability of such HBs benefits from the metallobasic character of gold as well as its electronegativity which strengthens the charge transfer and Coulombic term of the Au⋯H-X interaction, respectively. Dispersion forces, enhanced by relativistic effects at gold, are also invoked as substantial contributors.^{4f}

Contending that the HB in **D** and **E** may benefit from the protic character of the R₃NH⁺ group, we have now questioned whether related Au⋯H-X HBs could be observed between gold(I) and a neutral OH group. While such motifs have been predicted as in **F**⁵ and **G**,⁶ their existence in the condensed state is limited to the case of **H**.⁷ This complex features an Au⋯H distance of 2.393 Å, hinting at the presence of an Au⋯H-O HB.^{4c, 7} However, **H** is fluxional, suggesting that the HB may not stand unperturbed in solution. Herein, we report two examples of complexes of type **I** which possess *bona fide* Au⋯H-O HBs.

Chart 1. Selected examples illustrating the metallobasicity of Au(I) (top) or featuring Au⋯H-N and Au⋯H-O HBs (bottom)



Since such interactions should benefit from the strong σ donor properties of an *N*-heterocyclic carbene ligand,^{6a} we selected the indazol-3-ylidene unit as a backbone⁸ on

Figure 1. The Au...H distance of **5** (2.27(5) Å) is comparable to that measured in **D** (2.24(3) Å). It is also worth noting that the OH group approaches the gold atom along a direction of maximum metallobasicity, perpendicular to the C-Au-Cl sequence. Additional evidence for the presence of an Au...H-O HB was obtained by IR measurements which afforded $\nu_{\text{OH}} = 3309 \text{ cm}^{-1}$ and 3417 cm^{-1} for **5** and **6**, respectively (Figure S23 and S28). These frequencies are lower than the $3600\text{--}3645 \text{ cm}^{-1}$ range characteristic of free OH groups,¹² corroborating the presence of an Au...H-O bond in both **5** and **6**. The assignment of the IR band was confirmed by deuteration of the OH groups, which led to OD stretches at $\nu_{\text{OD}} = 2457 \text{ cm}^{-1}$ ($\nu(\text{OH})/\nu(\text{OD}) = 1.35$) for **5** and 2543 cm^{-1} ($\nu(\text{OH})/\nu(\text{OD}) = 1.37$) for **6** (Figure S23 and S28).

To support these results, we have also computed the structures of these derivatives using DFT methods (functional: B3PW91; basis sets: SDD+f for gold and 6-31G** for all other atoms). The most stable structures identified for these compounds match those determined experimentally, with the O-H group pointing at the gold atom. As shown in Figure 1, the metrical parameters calculated for conformers **5a** and **6a** are in good agreement with those determined experimentally. Exploration of the potential energy surface of **5** and **6** indicates the presence of other local minima, referred to as **5b** and **6b**, in which the O-H functionality is oriented away from the gold center, thus preventing any Au...H-O bonding. These local minima lay 6.5 kcal/mol and 3.8 kcal/mol above the calculated structures of **5a** and **6a**, respectively. In the case of **5**, a third minimum (**5c**) was identified. It resembles **5a**, except that the oxygen-bound hydrogen atom points upward, away from the gold atom. Conformer **5c** is 3.2 kcal/mol above **5a**, which may provide a measure of the strength of the Au...H-O HB present in the latter. The computed O-H bond length of **5a** and **6a** are longer than those of **5b**, **5c**, and **6b** (see metrical parameters listed in Figure 1), which we propose is caused by the transfer of electron density from gold into the $\sigma^*(\text{H-O})$ orbital. A congruent picture emerges from Atom in Molecules (AIM) analyses which indicates that the electron density ($\rho(r)$) at the O-H bond critical point (BCP) is lower in **5a** (0.353 e-bohr⁻³) and **6a** (0.350 e-bohr⁻³) than in conformers **5b** (0.366 e-bohr⁻³), **5c** (0.366 e-bohr⁻³) and **6b** (0.362 e-bohr⁻³) that lack the Au...H-O interaction. Finally, $\rho(r)$ at the Au...H BCP of **5a** and **6a** fall in the range of values expected for moderately strong HBs.¹³

The above results suggest that the gold atom of **5** and **6** act as a HB acceptor. To solidify this view and bearing in mind that classical hydrogen bonding is under the concomitant control of Coulombic and charge transfer effects, we decided to inspect the electrostatic potential (ESP) map of the computed structures. In the case of **5a** and **6a**, the proton is associated to a positive potential value that is paired with the more negative surface over the gold atom (Figure 1), confirming the $\text{H}^{\delta+}\text{-Au}^{\delta-}$ nature of the interaction. Accordingly, the non-covalent interaction (NCI) plot, which shows a reduced density gradient isosurface ($\text{sign}(\lambda_2) \times \rho$) of negative sign around the Au...H-O BCP of **5a**, indicates a stabilizing hydrogen bonding interaction (Figure 3). The NCI plot of **6a** shows similar features even if the NCI indexes

at the HB BCP are less negative, as expected from the weaker Au...H-O interaction of **6a** (Figure S38). There is also evidence of significant charge transfer as suggested by Natural Bond Orbital (NBO) analyses which shows multiple $\text{lp}(\text{Au}) \rightarrow \sigma^*(\text{H-O})$ donor-acceptor bonding interactions (Figure 3, Figure S32 and S34). Deletion calculations indicate that these interactions contribute $E_{\text{del}} = 10.6 \text{ kcal/mol}$ and $E_{\text{del}} = 5.0 \text{ kcal/mol}$ to the stability of **5a** and **6a**, respectively. The AIM/NCI plot of **5a** also reveals an Au...H-C interaction ($\lambda_2 @ \text{BCP} < 0$) which, as expected, is comparatively less stabilizing than the Au...H-O interactions as indicated by the lowest $\rho(r)$ value of $0.016 \text{ e-bohr}^{-3}$.¹⁴

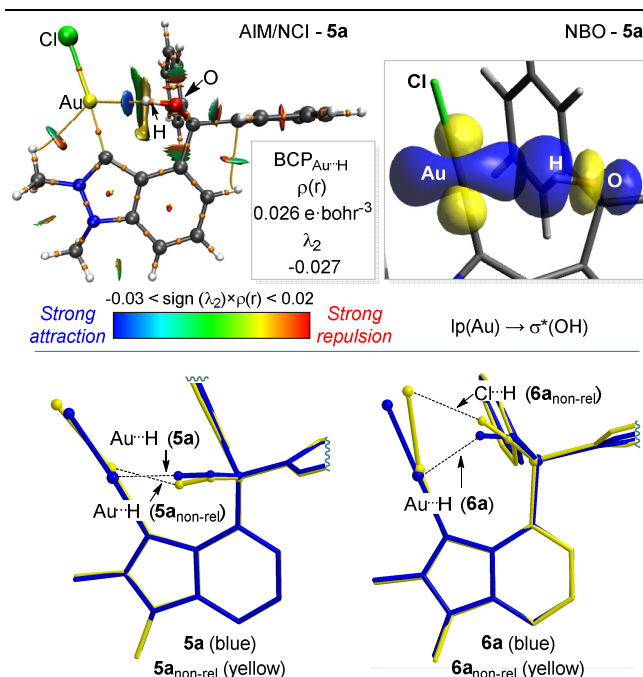


Figure 3. Top: NCI/AIM analysis plot and representative NBOs involved in the Au → H-O interactions for **5a**. For the NCI plot, the gradient isosurfaces (0.43 a.u.) are colored according to a blue-green-red scale. All values are in a.u. Bottom: structure overlay for **5a/5a_{non-rel}** (left) and **6a/6a_{non-rel}** (right).

Relativistic effects enhance the electronegativity of gold, the metallobasicity of its d-orbitals, and its ability to engage in dispersion interactions,¹⁵ three effects that contribute to the ability of this metal to engage in hydrogen bonding interactions.^{4f} Accordingly, turning off these effects computationally should diminish the HB. Inspired by a recent investigation,¹⁶ **5** was re-optimized using the non-relativistic ECP60MHF basis set for gold. The resulting structure, referred to as **5a_{non-rel}**, shows substantially weakened Au...H-O bonding as indicated by the longer Au...H distance (2.468 Å), the lower E_{del} value and the lower $\rho(r)$ at the Au...H BCP as shown in Table 1. This effect is more acute in the case of the silicon analog since **6a_{non-rel}** features a Cl...H rather than an Au...H interaction (Table 1 and Figure S36). These findings underscore the prevalent influence of relativistic effects over the Au...H bonding interaction present in these compounds.

To conclude this study, we have also simulated some of the spectroscopic features related to the HB in **5** and **6** (Table 1). Although the computed ν_{OH} for **5a** and **6a** deviate from those observed experimentally by $\sim 150\text{ cm}^{-1}$, we will note that the difference in the ν_{OH} of these two models ($\nu_{\text{OH}}(\mathbf{6a}) - \nu_{\text{OH}}(\mathbf{5a}) = 94\text{ cm}^{-1}$) is very close to that determined experimentally ($\nu_{\text{OH}}(\mathbf{6}) - \nu_{\text{OH}}(\mathbf{5}) = 108\text{ cm}^{-1}$). The higher ν_{OH} of **6a** is also consistent with a weaker $\text{Au}\cdots\text{H}$ HB. Even higher ν_{OH} values are obtained for **5b** (3663 cm^{-1}), **5c** (3653 cm^{-1}) and **6b** (3726 cm^{-1}) in line with the absence of hydrogen bonding in these model structures. The ν_{OH} of **5a_{non-rel}** is higher than that of **5a**, because of weaker $\text{Au}\cdots\text{H}$ hydrogen bonding in the former (Table 1). However, **6a_{non-rel}** displays a greatly reduced ν_{OH} because of the presence of a $\text{Cl}\cdots\text{H-O}$ interaction. GIAO calculations show corroborating results. The chemical shift of the proton involved in the HB is clearly deshielded in the experimental spectra of **5** and **6**, as noted above. Downfield chemical shifts are also obtained computationally for **5a** and **6a** and these values are in excellent agreement with the experimental ones (Figure 2). The calculated resonances of **5b** (1.89 ppm), **5c** (3.05 ppm) and **6b** (2.03 ppm) are upfield, again matching the absence of a HB. As shown in Table 1, the weakened $\text{Au}\cdots\text{H-O}$ bond of **5a_{non-rel}** also shifts the resonance upfield. However, **6a_{non-rel}** is again a special case, given that the $\text{Cl}\cdots\text{H-O}$ interaction leads to further deshielding of the resonance.

Table 1. The outputs of AIM and NBO analyses and spectroscopic data of **5a**, **5a_{non-rel}**, **6a** and **6a_{non-rel}**.

	5a	5a_{non-rel}	6a	6a_{non-rel}
$\rho(r)_{\text{Au}\cdots\text{H}}$ ($\text{e}\cdot\text{bohr}^{-3}$)	0.026	0.017	0.017	-
$\rho(r)_{\text{O-H}}$ ($\text{e}\cdot\text{bohr}^{-3}$)	0.353	0.360	0.350	0.341
E_{del} ($\text{Au}\rightarrow\text{H-O}$, kcal/mol)	10.6	4.41	5.0	-
$\nu_{\text{O-H}}$ (cm^{-1})	3456	3544	3550	3466
$\nu_{\text{O-D}}$ (cm^{-1})	2517	2581	2614	2528
$\delta_{\text{O-H}}$ (ppm)	5.33	4.16	4.05	4.86

In conclusion, we have characterized two complexes featuring an $\text{Au}\cdots\text{H-O}$ HB both in solution and in the solid state. Such interactions had been proposed but only succinctly explored experimentally. Our results also show that this interaction is sensitive to the nature of the interacting moieties, as illustrated by the weaker $\text{Au}\cdots\text{H-O}$ HB found in **6**. We speculate that this weaker interaction has structural origins, with the larger size of the silicon atom inducing a misalignment of the OH functionality with the gold atom. It is also possible that the greater acidity of the silanol proton reduces dispersion interactions with the neighboring gold atom.

ASSOCIATED CONTENT

Supporting Information

Experimental and computational details. Crystallographic data in cif format. Optimized structures in xyz format. These materials are available free of charge via the Internet at <http://pubs.acs.org>.

Accession Codes

CCDC 2094095-2094100 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (a) Amgoune, A.; Bourissou, D., σ -Acceptor, Z-type ligands for transition metals. *Chem. Commun.* **2011**, 47, 859-871; (b) Kameo, H.; Nakazawa, H., Recent Developments in the Coordination Chemistry of Multidentate Ligands Featuring a Boron Moiety. *Chem. Asian J.* **2013**, 8, 1720-1734; (c) Inagaki, F.; Matsumoto, C.; Okada, Y.; Maruyama, N.; Mukai, C., Air-Stable Cationic Gold(I) Catalyst Featuring a Z-Type Ligand: Promoting Enyne Cyclizations. *Angew. Chem. Int. Ed.* **2015**, 54, 818-822; (d) Bouhadir, G.; Bourissou, D., Complexes of ambiphilic ligands: reactivity and catalytic applications. *Chem. Soc. Rev.* **2016**, 45, 1065-1079; (e) Jones, J. S.; Gabbaï, F. P., Coordination- and Redox-Noninnocent Behavior of Ambiphilic Ligands Containing Antimony. *Acc. Chem. Res.* **2016**, 49, 857-867.
- (a) Bontemps, S.; Bouhadir, G.; Miqueu, K.; Bourissou, D., On the versatile and unusual coordination behavior of ambiphilic ligands *o*-P₂P(Ph)BR'₂. *J. Am. Chem. Soc.* **2006**, 128, 12056-12057; (b) Yang, H.; Gabbaï, F. P., Activation of a Hydroamination Gold

- Catalyst by Oxidation of a Redox-Noninnocent Chlorostibine Z-Ligand. *J. Am. Chem. Soc.* **2015**, *137*, 13425-13432.
3. (a) Kleinhans, G.; Hansmann, M. M.; Guisado-Barrios, G.; Liles, D. C.; Bertrand, G.; Bezuidenhout, D. I., Nucleophilic T-Shaped (LXL)Au(I)-Pincer Complexes: Protonation and Alkylation. *J. Am. Chem. Soc.* **2016**, *138*, 15873-15876; (b) Jerabek, P.; Vondung, L.; Schwerdtfeger, P., Tipping the Balance between Ligand and Metal Protonation due to Relativistic Effects: Unusually High Proton Affinity in Gold(I) Pincer Complexes. *Chem. Eur. J.* **2018**, *24*, 6047-6051.
 4. (a) Brammer, L., Metals and hydrogen bonds. *Dalton Trans.* **2003**, 3145-3157; (b) Kryachko, E. S., Where gold meets a hydrogen bond? *J. Mol. Struct.* **2008**, *880*, 23-30; (c) Schmidbaur, H.; Raubenheimer, H. G.; Dobrzańska, L., The gold-hydrogen bond, Au-H, and the hydrogen bond to gold, Au...H-X. *Chem. Soc. Rev.* **2014**, *43*, 345-380; (d) Schmidbaur, H., Proof of Concept for Hydrogen Bonding to Gold, Au...H-X. *Angew. Chem. Int. Ed.* **2019**, *58*, 5806-5809; (e) Berger, R. J.; Schoiber, J.; Monkowius, U., A Relativity Enhanced, Medium-Strong Au(I)...H-N Hydrogen Bond in a Protonated Phenylpyridine-Gold(I) Thiolate. *Inorg. Chem.* **2017**, *56*, 956-961; (f) Straka, M.; Andris, E.; Vícha, J.; Růžička, A.; Roithová, J.; Rulíšek, L., Spectroscopic and Computational Evidence of Intramolecular AuI...H+-N Hydrogen Bonding. *Angew. Chem. Int. Ed.* **2019**, *58*, 2011-2016; (g) Rigoulet, M.; Massou, S.; Sosa Carrizo, E. D.; Mallet-Ladeira, S.; Amgoune, A.; Miqueu, K.; Bourissou, D., Evidence for genuine hydrogen bonding in gold(I) complexes. *Proc. Natl. Acad. Sci. U.S.A.* **2019**, *116*, 46; (h) Rocchigiani, L.; Klooster, W. T.; Coles, S. J.; Hughes, D. L.; Hrobárik, P.; Bochmann, M., Hydride Transfer to Gold: Yes or No? Exploring the Unexpected Versatility of Au...H-M Bonding in Heterobimetallic Dihydrides. *Chem. Eur. J.* **2020**, *26*, 8267-8280.
 5. Lin, X.; Mo, Y., Resonance-Assisted but Antielectrostatic Intramolecular Au...H-O Hydrogen Bonding in Gold(I) Complexes: A Computational Verification. *Inorg. Chem.* **2021**, *60*, 460-467.
 6. (a) Groenewald, F.; Dillen, J.; Raubenheimer, H. G.; Esterhuysen, C., Preparing Gold(I) for Interactions with Proton Donors: The Elusive [Au]...HO Hydrogen Bond. *Angew. Chem. Int. Ed.* **2016**, *55*, 1694-1698; (b) Kumar, M.; Francisco, J. S., Evidence of the Elusive Gold-Induced Non-classical Hydrogen Bonding in Aqueous Environments. *J. Am. Chem. Soc.* **2020**, *142*, 6001-6006.
 7. López-de-Luzuriaga, J. M.; Sladek, A.; Schmidbaur, H., Mixed co-ordination numbers and geometries of gold(I) in a dinuclear complex of thioglycerol. *J. Chem. Soc., Dalton Trans.* **1996**, 4511-4512.
 8. Carreras, J.; Pereira, A.; Zanini, M.; Echavarren, A. M., Variations on the Theme of JohnPhos Gold(I) Catalysts: Arsine and Carbene Complexes with Similar Architectures. *Organometallics* **2018**, *37*, 3588-3597.
 9. (a) Schafer, A. G.; Wieting, J. M.; Fisher, T. J.; Mattson, A. E., Chiral Silanediols in Anion-Binding Catalysis. *Angew. Chem. Int. Ed.* **2013**, *52*, 11321-11324; (b) Yamamura, M.; Kondo, S.-i.; Unno, M., Ion pair recognition of ditopic receptor bearing silanol groups as anion recognition sites and a 2,2'-bipyridine moiety as a metal-coordination site. *Tetrahedron Lett.* **2014**, *55*, 646-649; (c) Diemoz, K. M.; Wilson, S. O.; Franz, A. K., Synthesis of Structurally Varied 1,3-Disiloxanediols and Their Activity as Anion-Binding Catalysts. *Chem. Eur. J.* **2016**, *22*, 18349-18353.
 10. (a) Takemura, H.; Kaneko, M.; Sako, K.; Iwanaga, T., The intramolecular C-F...HO hydrogen bond of 2-fluorophenyldiphenylmethanol. *New J. Chem.* **2009**, *33*, 2004-2006; (b) Okada, Y.; Oba, M.; Arai, A.; Tanaka, K.; Nishiyama, K.; Ando, W., Diorganotelluride-Catalyzed Oxidation of Silanes to Silanols under Atmospheric Oxygen. *Inorg. Chem.* **2010**, *49*, 383-385.
 11. Vícha, J.; Foroutan-Nejad, C.; Straka, M., ¹H NMR is not a proof of hydrogen bonds in transition metal complexes. *Nat. Commun.* **2019**, *10*, 1643.
 12. Coates, J., Interpretation of Infrared Spectra, A Practical Approach. In *Encyclopedia of Analytical Chemistry*, 2000; Vol. 12, pp 10815-10837.
 13. Kolandaivel, P.; Nirmala, V., Study of proper and improper hydrogen bonding using Bader's atoms in molecules (AIM) theory and NBO analysis. *J. Mol. Struct.* **2004**, *694*, 33-38.
 14. (a) Bakar, M. A.; Sugiuchi, M.; Iwasaki, M.; Shichibu, Y.; Konishi, K., Hydrogen bonds to Au atoms in coordinated gold clusters. *Nat. Commun.* **2017**, *8*, 576; (b) Pandey, M. K.; Kunchur, H. S.; Mondal, D.; Radhakrishna, L.; Kote, B. S.; Balakrishna, M. S., Rare Au...H Interactions in Gold(I) Complexes of Bulky Phosphines Derived from 2,6-Dibenzhydryl-4-methylphenyl Core. *Inorg. Chem.* **2020**, *59*, 3642-3658; (c) dos Passos Gomes, G.; Xu, G.; Zhu, X.; Chamoreau, L.-M.; Zhang, Y.; Bistri-Aslanoff, O.; Roland, S.; Alabugin, I. V.; Sollogoub, M., Mapping C-H...M Interactions in Confined Spaces: (α-ICyDMe)Au, Ag, Cu Complexes Reveal "Contra-electrostatic H Bonds" Masquerading as Anagostic Interactions**. *Chem. Eur. J.* **2021**, *27*, 8127-8142.
 15. Schwerdtfeger, P., Relativistic effects in properties of gold. *Heteroat. Chem.* **2002**, *13*, 578-584.
 16. Groenewald, F.; Raubenheimer, H. G.; Dillen, J.; Esterhuysen, C., Gold setting the "gold standard" among transition metals as a hydrogen bond acceptor – a theoretical investigation. *Dalton Trans.* **2017**, *46*, 4960-4967.

