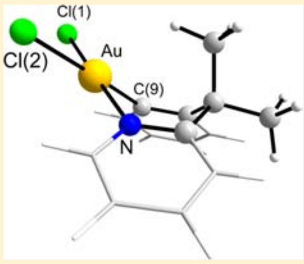
Inorganic Chemistry
Article
pubs.acs.org/IC

Tracing Hydrogen Bonding Au···H−C at Gold Atoms: A Case Study

Florian Kraus,*[†] Hubert Schmidbaur,*[†,‡] and Salih S. Al-juaid[‡]

[†]Department Chemie, Technische Universität München, Lichtenbergstrasse 4, Garching 85747, Germany
[‡]Chemistry Department, King Abdulaziz University, Jeddah, Saudi Arabia

ABSTRACT: It has been shown in preceding experimental work that cyclometalated 6-benzylpyridines with gold(III) centers in the metallacycle (**1**) adopt a boat conformation reminiscent of the structure of 9,10-dihydroanthracene. There is a conspicuously short Au···H−C contact with a pseudoaxial methyl group suggesting a significant interaction which may be the prototype for $Au^{III}\cdots H-C$ hydrogen bonding. Quantum chemical calculations on the B3LYP/def2-TZVP level have now shown that the ground state structures and conformations adopted by the homologues with two hydrogen atoms, two methyl groups, and a hydrogen atom and a methyl group at the carbon atom bridging the two (hetero)arene rings can be explained on the basis of simple conformation rules. There is no evidence that the $Au^{III}\cdots H-C$ contact leads to an attractive interaction. The results are discussed in the context of literature data for Pt(II) analogues. Examples for potential $Au^{III}\cdots H-X$ interactions presented in other references appear to be of a similar character.



INTRODUCTION

Weak interatomic forces determining the conformation of molecules and the molecular packing in crystals are currently the focus of extended studies. Hydrogen bonding is one of the most important components of the manifold of weak interactions between structural units,[1,2] and even their weakest variants may contribute significantly to the bonding in and between molecules.[3] In classical terms, and according to newly conceived IUPAC recommendations,[4,5] the bonding between typical hydrogen bond donors **X**−H and acceptors **Y**(Z) to form a bridge **X**−H···**Y**−Z is well-defined for the most electronegative elements **X** and **Y** (the latter carrying a set of substituents or ligands Z) which deprive the hydrogen atom of electrons and give the bonding a pronounced polar character $X^{\delta-}-H^{\delta+}\cdots Y^{\delta-}$. The bridges **X**−H···**Y** are expected to have large angles close to linearity, and the bonds **X**−H are expected to be significantly affected by the interaction with **Y**(Z) leading to marked changes, e.g., in vibrational (IR, Raman) or NMR spectroscopic characteristics (chemical shifts, coupling constants).

The energy associated with these interactions is in the range 5−15 kcal/mol in standard cases of this type, addressed as "classical" or "conventional" hydrogen bonding. There is little controversy about the fundamentals of this phenomenon which is encountered in extreme cases like $F-H\cdots F^-$, in ubiquitous interactions like O−H···O or O−H···N, or in contacts like C−H···O yielding only marginal energy contributions.

By contrast, interactions between units with less electronegative elements **X** and **Y** are still a matter of debate, and this is particularly true for the combination of typical hydrogen bond donors **X**−H with *metal* centers **M** as hydrogen bond acceptors, **Y**(Z) = **M**(Z).[6−13] Seen in full scope, it is obvious that contacts of the type **X**−H···**M**(Z) include such diverse interactions as the "agostic bonding" **C**−H···**M**(Z) with **M** taken from the group of electron-deficient early transition metals at the one hand,[14,15] and "anagostic" bonding with **M** selected from the later transition metals.[16] For a long time, the representative units therein have been described as 3-center−2-electron or 3-center−4-electron systems, respectively, but there is not a well-defined border region in between. Finally, the literature has the category of "unconventional (or non-conventional) hydrogen bonding" used mainly when **M** is a particularly electron-rich center such as Au^-.[17] The terms set in quotation marks above are just the more common examples which reflect the uncertainty and confusion about the phenomenon. Others are "not agostic",[18] "pre-agostic" and "pseudo-agostic",[6,18] or "electron-rich agostic"[20] and "multi-center hetero-acceptor hydrogen bonding".[6] There is much less information about the preferred structural characteristics of **X**−H···**M** contacts as far as, e.g., the optimum **X**−H···**M** angle or specific H···**M** distances are concerned, and only for very few cases the associated energies could be estimated. While for "agostic interactions" small angles **X**−H···**M** are assumed to be advantageous, for "anagostic interactions" the preference is less clear.

With the rapid growth of structural data in *gold chemistry* an increasing number of reports appeared where short intra- and intermolecular contacts **X**−H···**Au** have been described and discussed. As summarized in a review to be published shortly,[21] there are numerous cases where potential hydrogen bond donors like O−H, N−H, and C−H approach gold centers in various oxidation states, including Au^-, Au^+, Au^{2+}, and Au^{3+}. In theoretical work, this scope also includes gold clusters $[Au_n]^{m\pm}$ with the metal atoms in mixed oxidation states.[17,22−25] The gold ions Au^- and Au^+ are interesting borderline cases owing to their closed shell configurations $5d^{10}6s^2$ and $5d^{10}$, respectively. Moreover, these electron configurations are subject to extreme relativistic effects making gold atoms the most electronegative of the metal atoms.[26] The question therefore arises if gold

Received: June 11, 2013
Published: July 26, 2013

dx.doi.org/10.1021/ic4014762 | *Inorg. Chem.* 2013, 52, 9669−9674

atoms in these two oxidation states can function as hydrogen bond acceptors.

The few experimental studies of crystalline aurides $[E]^+[Au]^-$, with $[E]^+$ representing quaternary ammonium cations or crown ether-coordinated alkali metal cations, have provided evidence[27−29] that there is indeed a clear analogy between the performance of Au^- and that of the heavy halide anions Br^- or I^-, and theoretical investigations of model systems like $[Au(H_2O)_n]^-$ have confirmed significant attractive interactions $Au^- \cdots H{-}C/N/O$.[17,22−25] However, a critical evaluation of pertinent observations reported in the literature has shown that the evidence for hydrogen bonding at Au^+ in a variety of its complexes is generally very poor.[21,30] It therefore appears that this cation in spite of its closed-shell character ($5d^{10}$ for ligand-free Au^+) is not a good hydrogen bond acceptor, and this is true even for species $[X{-}Au{-}X]^-$, $[X{-}Au{-}L]$, or $[L{-}Au{-}L]^+$ with strong donor ligands L and X^- which might provide additional electron density for the metal atom and partially compensate its positive charge. This result is perhaps not really surprising because there is also very little information on hydrogen bonding to the congeners Cu^+ and Ag^+ and to isoelectronic Hg^{2+}.[6−15] Complexes of Au^+ have also not been considered as plausible candidates for agostic bonding in pertinent reviews,[14,15,20] and a recent experimental study supported this attitude.[31]

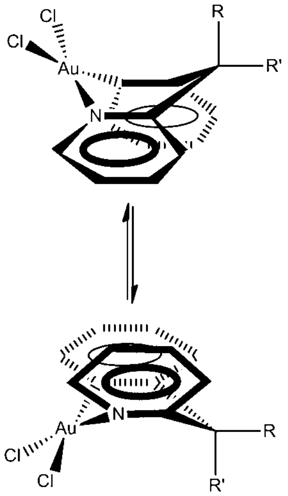
The literature on compounds for which hydrogen bonding to Au^{3+} with its $5d^8$ electron configuration has been considered is much more limited.[32−41] In less than a dozen cases the authors of these reports have tried to explain certain structural anomalies or restricted molecular dynamics by assuming attractive $Au^{3+} \cdots H{-}X$ interactions. The arguments appeared to be supported by analogous findings for complexes of isoelectronic Pt^{2+} which had been discussed very extensively in the 1990s.[42,43]

A prominent case has been reported from the work of the group of Cinellu and Minghetti, who prepared gold(III) complexes **1a**−**c** by cyclometalation of the corresponding 2-substituted pyridines (Scheme 1).[37]

The compounds **1a** and **1c** were found to have NMR-inequivalent groups R in dichloromethane solution at ambient temperature, and for **1b** two diastereomers were observed. This result was explained by assuming a rigid boat conformation of the central metallacycle which does not undergo rapid inversion in solution on the NMR time scale. The assumption was confirmed for **1c** by a single crystal X-ray diffraction analysis which showed the methyl groups to occupy pseudoaxial (*pa*) and pseudoequatorial positions (*pe*). In a consideration of the structural details it was further noted that the position of one of the hydrogen atoms of the *pa* methyl group is very close to the gold atom [Au···H 2.56(5) Å] and thus "well below the value reported as upper limit for long-range metal−hydrogen interactions in platinum chemistry",[37] referring to ref 42.

Because this observation may be the key reference case, we have tried to investigate by quantum chemical calculations if the conformation of the molecules **1a**−**c** in all its details is indeed determined, or at least significantly influenced, by what may be described as $Au^{3+} \cdots H{-}C$ hydrogen bonding.

Scheme 1



1a R = R' = H;

1b R = Me, R' = H;

1c R = R' = Me

■ EXPERIMENTAL SECTION

The structures of the studied species were investigated with the ab initio hybrid density functional B3LYP method in Gaussian09.[44,45] The def2-TZVP basis sets and an additional ECP for Au were applied in the calculations.[46] All structures were fully optimized, and the optimized structures were confirmed as true local minima by performing harmonic frequency calculations. It should be noted that although DFT methods typically fail for van der Waals interactions, they have been shown to yield reliable results for hydrogen bonding.[47]

■ RESULTS

Ground State Conformation of 1a. A first hint regarding the influence of a **Au···H−C**(methyl) interaction on the molecular conformation in **1c** was expected from the calculated structure of **1a** where the methyl groups are absent. The results have shown that **1a** also has a boat conformation as the ground state in an innocent environment (Figure 1).

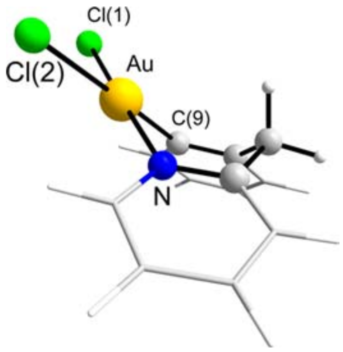


Figure 1. Calculated ground state structure of the molecule **1a**.

The central metallacycle is folded with the methylene carbon atom and the gold atom displaced from the reference plane of the remaining four atoms of the central six-membered ring (N, C, C, C) by 0.631 and 0.884 Å, respectively. The corresponding folding angles are 48.09° and 36.09°. The dihedral angle between the benzene and the pyridine ring amounts to 120.92°, and the gold atom is in its common square planar coordination. All these data are in good agreement with the values found in the crystal structure analysis of **1c** (Table 1).[37] The boat conformation is also present in CH_2Cl_2 solution (and rigid on the NMR time scale at room temperature), since the methylene protons were found to be diastereotopic exhibiting an AB pattern (δ 4.56, 4.08 ppm; $^2J(H,H)$ 15 Hz).[37]

Ground State Conformation of 1c. In order to rule out a major influence of the molecular packing in the crystal on the conformation of **1c**, its structure was also calculated. The results

Table 1. Comparison of Atom Distances (Å) and Angles (deg) for Molecules **1a**−**c**

	1c(exp)	**1a**	**1b**(*pa*)	**1c**
Au−Cl(1)	2.282(1)	2.288	2.291	2.293
Au−Cl(2)	2.390(1)	2.401	2.404	2.405
Au−N	2.041(3)	2.105	2.103	2.098
Au−C(9)	2.021(3)	2.059	2.057	2.053
Cl(1)−Au−Cl(2)	91.6(4)	92.50	91.94	91.87
Cl(1)−Au−N	176.2(8)	178.06	178.23	177.78
Cl(2)−Au−N	91.9(9)	89.18	89.51	90.26
Cl(1)−Au−C(9)	90.8(1)	90.52	90.84	91.58
Cl(2)−Au−C(9)	177.4(1)	176.92	177.20	176.50
N−Au−C(9)	85.7(1)	87.81	87.71	86.30
methylene-C folding angle	44.69(22)	48.09	43.88	46.11
Au folding angle	38.08(15)	36.09	34.73	34.84
benzene−pyridine dihedral angle	116.97(14)	120.92	124	119.56

are in very good agreement with the experimental data[37] (Figure 2a, Table 1).

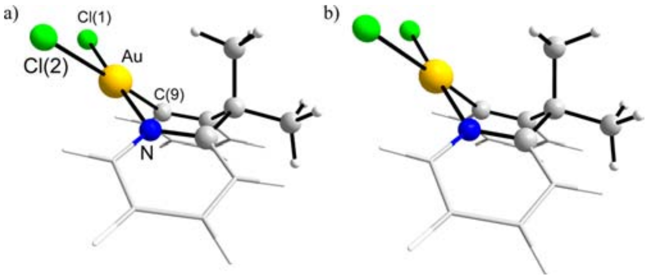


Figure 2. (a) Calculated global ground state structure of the molecule **1c**. (b) Calculated local ground state structure of molecule **1c** with the *pa* methyl group rotated by 60°.

Most structural details of **1c**(exp) and **1c**(calc) as well as of **1a**(calc) are very similar, including in particular the folding angles (see Table 1). This conformation is also present exclusively in CD_2Cl_2 solution at room temperature, where two proton resonances are observed for the two methyl groups (δ 2.35, 2.06 ppm). In addition, it is noteworthy that the calculated ground state structure of **1c** in an innocent environment has the *pa* methyl groups rotated into a conformation with one hydrogen pointing in the direction of the gold atom as also suggested on the basis of the X-ray data. However, the hydrogen atoms of the *pa* methyl group are not resolved in a 1:2 ratio in the NMR spectrum at room temperature.[37] This aspect will be considered further below.

Ground State Conformation of 1b. The structure of **1b** was calculated in order to detect any preference for the position of the methyl group in the *pa* or *pe* positions. It was found that the isomer with a boat conformation and with the methyl group in the *pa* position is lowest in energy. However, the isomer with the methyl group in the *pe* position is less stable by only 6.6 kJ mol^{-1} (Figure 3).

The structure is again very similar to that of **1a**(calc), **1c**(calc), and **1c**(exp), which suggests a very minor, if any, influence of the methyl group in the *pa* position where it could interact with the gold atom. As expected, the folding angles (see Table 1) are again close to those of the two symmetrically substituted analogues (**1a**, **c**). In agreement with the small energy difference between the two isomers calculated in the present work, both species are present in solution ($CDCl_3$) according to the published NMR data.[37] They can be distinguished by their two sets of proton resonances (δ 2.16, d; 1.94, d; 4.43, q; 4.68, q, ppm; ^3J (H,H) 7.2 Hz). The A_3B pattern is very similar for $CD_3S(O)CD_3$ solutions, but the molar ratio of the isomers changes from 2:1 to 3:1 indicating an equilibrium of the conformers. Since molecules **1b** are chiral, the NMR spectra do not allow the assignment of a certain conformation (chair, boat), but the calculations have shown a clear preference again for the boat conformation.

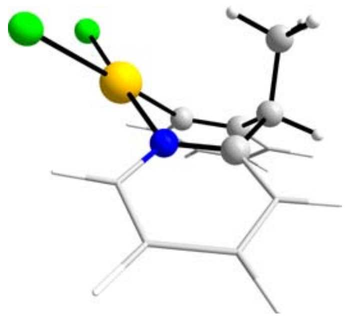


Figure 3. Calculated global ground state structure of the molecule **1b**.

Rotation of the *pa* Methyl Group in 1c. In order to follow the energy profile of the methyl rotation in the *pseudoaxial* position of **1c**, the structures have been calculated for 5° intervals of a turn from 0° to 120° (Figure 4).

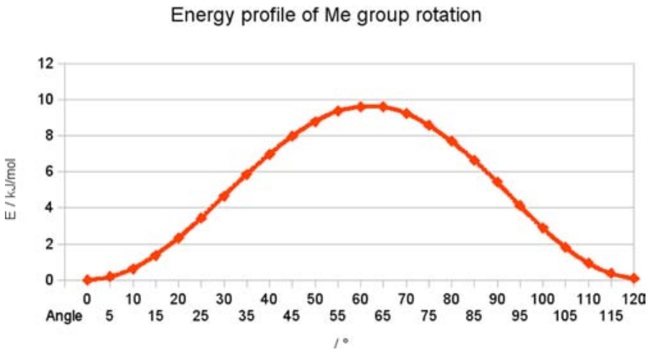
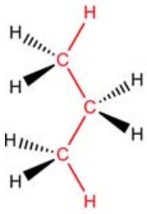


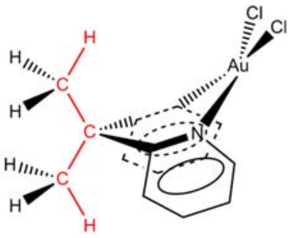
Figure 4. Calculated energy profile for the rotation of the pseudoaxial methyl group in molecule **1c**.

Starting from the ground state rotamer with one C−H bond directed toward the gold atom (Figure 2a), the energy increases continuously to a maximum at 60° in which the gold atom resides on the plane bisecting the extrovert H−C−H angle of the methyl group concerned. This rotamer (Figure 2b) is 9.6 kJ mol^{-1} higher in energy. The energy bottom is reached again after a 120° rotation.

An investigation of the consequences of the *pa* methyl rotation for the remainder of the structure of **1c** has shown that a significant breathing motion of the gold atom in its coordination environment is associated with this rotation: The gold atom moves closer to the *pa* methyl carbon atom (from 3.2739 Å for the eclipsed to 3.1652 Å for the staggered conformation) and then retreats to its original position. Surprisingly, the *pe* methyl group does not follow the rotation of the *pa* methyl group and remains in its ground state orientation, as do all other atoms of the molecule. An inspection of details of formula **1b** and Figure 2a shows that the two methyl groups, *pa* and *pe*, adopt the conformation also found for the two methyl groups in propane (**3**). Obviously, the central carbon atom requires staggered arrangements for both methyl groups (**4**), and this dictates the orientation of one C—H bond of the *pa* methyl group toward the gold atom and places the extrovert C—H bond of the *pe* methyl group on the pseudomirror plane of the molecule (ignoring the N atom which breaks this symmetry).



3

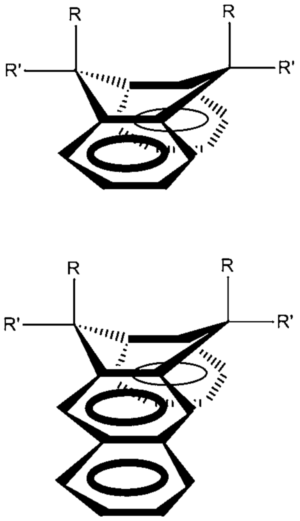


4 (1c)

■ DISCUSSION

Implications of the Structure of 1a. The calculated structure of the methylene-bridged molecule **1a** shows that it also has the boat conformation known for the twice methyl-substituted homologue **1c**. The deviation of the methylene carbon atom from the N,C,C,C basal plane of the boat amounts to 0.631 Å, while that of the folded 9,10-dihydroanthracene molecule is 0.444 Å (Scheme 2, **2a**).[48]

Scheme 2



2a R = R' = H
2b R = Me, R = H
2c R = R' = Me

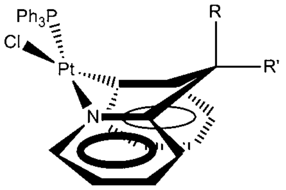
2d

The dihedral angles between the two (hetero)arene rings are also different (120.92° vs. 144.5°), but better agreement is not to be expected, because the presence of a square-planar coordinated gold atom instead of another methylene group must lead to some marked gradual differences.

There is extensive literature on the folding of 9,10-dihydroanthracenes **2** (Scheme 2) with different substitution patterns, and it has been shown that where structures have been determined all of them have the boat conformation. This was demonstrated predominantly by variable temperature NMR studies which allowed distinguishing *pseudoaxial* and *pseudo-equatorial* substituents in the 9- and 10-positions.[49−52] The energy profile for the inversion of the parent 9,10-dihydroanthracene **2a** from one boat conformer to the other has been calculated and found to have two rather shallow troughs,[52] which explains the observation that the inversion is rapid on the NMR time scale in solution even at −60 °C. The folding angles were found in the range 135−160°. A recent crystal structure determination of 5,12-dihydrotetracene (2,3-benzannelated 9,10-dihydroanthracene, **2d**) has given a folding angle of 136°.[53]

These results show that the folding of the metallacycle in **1a** must not to be associated with, or taken as caused by any Au···H—C hydrogen bonding, for which the distances Au···H and Au···C with 3.0187 and 3.1445 Å, respectively, are much too long. At this point it is worthwhile to remember the observations made by the Minghetti-Cinellu group on the related Pt(II) complex **5a** (Scheme 3).[54]

Scheme 3



5a R = R' = H
5b R = H, R' = Me
5c R = R' = Me

The NMR spectra of this complex (in $CDCl_3$ at ambient temperature) show diastereotopic methylene protons as an AX pattern with a geminal coupling ^2J(H,H) = 13.7 Hz. The low-field doublet of the two resonances exhibits side bands of a long-range ^{195}Pt−^{1}H coupling (16 Hz) which was absent for the upfield doublet. This result suggested to the authors a "possible", but "at most a very weak metal−hydrogen interaction". It is known from the extensive work by the Pregosin-Albinati group that these long-range spin−spin couplings need not indicate bonding, i.e., attractive interactions, and simply indicate that the corresponding nuclei are held close enough in the molecule to "know of each other" through spin−spin communication. Similar arguments hold for the observations made in nuclear Overhauser effect (NOE, NOESY) studies. Both techniques are reliable indicators of these weak through space interactions, whereas for the evaluation of chemical shift values δ there may be pitfalls which can lead to erroneous conclusions.[42]

It is noteworthy that the Pd-analogue of **5a** has also been found to have the boat conformation, but the inversion barrier is much lower such that separate signals of the two methylene protons and the geminal coupling can only be observed at −35 °C (in $CHCl_3$; ^2J(H,H) 14 Hz).[55] The reason for this reduced rigidity as compared to **5a** is not known.

Implications of the Structure of 1b. The calculations have shown that the two chiral diastereomers of **1b** have very similar energies with a difference of only 6.6 kJ mol^{-1}. This result explains the findings in previous NMR studies,[37,38] which indicated the presence of an equilibrium between the two species depending on solvent and temperature. The isomer with the methyl group in the *pa* position was found to be slightly more stable which can be ascribed to a reduced steric hindrance for the methyl group in this orientation, but notwithstanding, the possibility of an interaction with the gold atom must not be ignored. This point is addressed below again in the comments on **1c**.

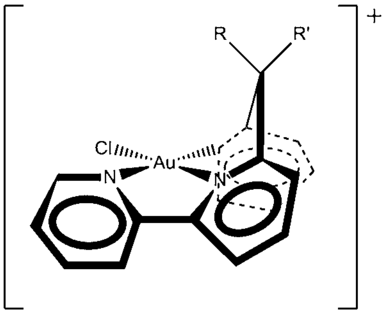
A glance at the Pt(II) complex **5b** sheds some light on the two alternative structures. An X-ray diffraction study of the crystals obtained from $CHCl_3/Et_2O$ has demonstrated that the form with the methyl group in the *pe* position is present in this crop. However, NMR studies of solutions in CHCl$_3$ at ambient temperature have shown that *both* isomers are present (in a molar ratio 3:2). Both exhibit the d−q pattern for the ethylidene CH_3CH unit with a vicinal coupling ^3J(H,H) of 7.2 Hz, but the resonance for the *pa* methyl group is accompanied by side bands for the long-range coupling J(Pt,H) = 5.7 Hz. Obviously, there is an excellent agreement in the structural performance of **1b** and **5b** on one hand, and of **1b** and **5a** on the other (above): The transannular distance Pt···H(Me) in the crystal is 2.95(4) Å, justly addressed by the authors as "at the upper end" suggested for weak long-range interactions.[43,54] The fact that, upon crystallization from the equilibrated solution of the compound (containing both isomers), only the isomer with the *pe* methyl group is obtained may simply be due to the lower solubility of this isomer (owing to a more efficient packing of the molecules in the crystal) and does not necessarily indicate that this isomer is the more stable one.

Implications of the Structure of 1c. The calculated and the experimentally determined structure of **1c** are in excellent agreement. The structure can be rationalized on the basis of conventional rules of molecular conformation: The folding into a boat conformation is also a common phenomenon for 9,10-dihydroanthracene analogues driven by a minimization of steric interactions, and the rotation of both methyl groups into staggered conformations with regard to the other substituents at the bridgehead carbon atom agrees with the standard conformation of propane-type molecules. Therefore, there is no reason to assume that this conformation results from a significant attractive Au···H interaction (at a distance of 2.56 Å) found in the crystal and in the calculations. The NMR data for the solution state also show no anomalies as compared to reference systems.

Again, the Pt(II) analogue **5c** provides complementary data. Its NMR spectrum shows separate singlet signals for the two methyl groups, but in this case the *pa* methyl resonance does not exhibit a long-range ^{195}Pt−^{1}H coupling as observed in **5a** and **5b** (above). The contact Pt···H−C will therefore be even less intimate than in **5b**. The triads **1** and **5** are rather rigid in solution and undergo only slow inversion on the NMR time scale, showing a close analogy which they do not share, e.g., with the Pd analogues.[55] The crystal structure of **5c** has not been determined.

If the skeleton of **1c** is extended by another pyridyl unit into a cyclometalated 2,2-bipyridine cation (**6**, Scheme 4), the structure found for **6c** in the crystal (of the AuCl$_4^-$ salt) remains largely the same as in **5c**. The principle of the conformation is the same, and the distance Au···H(methyl) is 2.62 Å. Surprisingly, the barrier to inversion appears to be smaller since in solution (acetone-d_6) at ambient temperature the hydrogen atoms in **6a** and the methyl groups in **6c** give only a single singlet, and for **6b** only one d−q pattern is observed.[38]

Scheme 4



6a R = R' = H
6b R = Me, R' = H
6c R = R' = Me

■ SUMMARY

This complementary study has shown by quantum chemical calculations that for gold(III) compounds of the types **1** and **6** there is no compelling evidence for significant Au···H−C hydrogen *bonding*. As already correctly pointed out by the authors in the discussion of the preceding experimental work,[37,38,43,54] relatively short *contacts* across the metallacycle between the gold atom in its square planar environment and a methyl group in a pseudoaxial position are indeed established, but all details of this arrangement can be explained applying simple conformational rules. The relation to parent compounds like the 9,10-dihydroanthracenes on one hand or analogous Pt(II) complexes on the other is obvious and follows the same pattern.

Therefore, the unique hydrogen atoms of the *pa* methyl groups in **1b**,**c** are not drawn to the gold atom. The NMR characteristics of these methyl groups are "normal" and there is no report of any shifts of ν(C−H) bands in the vibrational spectra. Hence, these organometallic compounds should not be considered as reference cases for Au^{III}···H−C hydrogen bonding. This result agrees with the findings regarding most tentative assignments of Au^{I}···H−C hydrogen bonds.[21]

There are only very few other cases where Au^{III}···H−X interactions were explicitly considered (X = N, C).[32−41] Two of these are intermolecular contacts in crystals with no obvious directionality,[39,40] two other ones concern intramolecular Au···H−N contacts in a protonated 1,4,7-triazacyclononane cage chelating a gold(III) center[36] and between 2-aminothiazoline and 2-aminopyridine ligands at Au(C$_6$F$_5$)$_3$, and (C$_6$F$_5$)$_2$AuCl, respectively,[34,35] both with Au···H−N distances of ca. 2.62 Å. The two remainder examples actually are proof of the contrary in that they show that −CH$_2$−NMe$_2$H$^+$ groups dangling at a ligand of a gold(III) center are *not* drawn toward this metal atom.[32,33]

This small number of not really representative cases with gold(III) as a potential hydrogen bonding acceptor is in contrast with the long list of platinum(II) analogues. However, it remains to be demonstrated that this series really contains compounds characterized not only by Pt···H−C *contacts* as shown by Pt···H distances in crystals and NMR phenomena in solution or in solids, but by true Pt···H−C hydrogen *bonding*. To the best of our knowledge, no thermochemical data are available.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: Florian.Kraus@tum.de (F.K.); H.Schmidbaur@lrz.tum.de (H.S.).

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors acknowledge support by the Deutsche Forschungsgemeinschaft (Heisenberg fellowship for F.K.), by Fonds der Chemischen Industrie (H.S.), and by the Deanship of Scientific Research (DSR), King Abdulaziz University, Jeddah, under Grant 22-3-1432/HiCi (H.S., S.S.A.-j.). We thank Dr. A. J. Karttunen, University of Jyväskylä, Finland, for helpful discussions regarding the calculations.

■ REFERENCES

(1) Jeffrey, G. A. *An Introduction to Hydrogen Bonding*; Oxford University Press: New York, 1997.

(2) Gilli, G.; Gilli, P. *The Nature of the Hydrogen Bond*; Oxford Univesity Press: Oxford, 2009; p 49 ff.

(3) Desiraju, G. R.; Steiner, T. *The Weak Hydrogen Bond in Structural Chemistry and Biology*; Oxford University Press: Oxford, 1999; p 246.

(4) Defining the Hydrogen Bond: An Account (IUPAC Technical Report): Arunan, E.; Desiraju, G. R.; Klein, R. A.; Sadlej, J.; Scheiner, S.; Alkorta, I.; Clary, D. C.; Crabtree, R. H.; Dannenberg, J. J.; Hobza, P.; Kjaergaard, H. K.; Legon, A. C.; Menucci, B.; Nesbitt, D. J. *Pure Appl. Chem.* **2011**, *83*, 1619.

(5) Definition of the Hydrogen Bond (IUPAC Recommendations 2011): Arunan, E.; Desiraju, G. R.; Klein, R. A.; Sadlej, J.; Scheiner, S.; Alkorta, I.; Clary, D. C.; Crabtree, R. H.; Dannenberg, J. J.; Hobza, P.; Kjaergaard, H. K.; Legon, A. C.; Menucci, B.; Nesbitt, D.; et al. *Pure Appl. Chem.* **2011**, *83*, 1637.

(6) Braga, D.; Grepioni, F.; Tedesco, E.; Birasha, K.; Desiraju, G. M. *Organometallics* **1997**, *16*, 1846.

(7) Braga, D.; Grepioni, F.; Desiraju, G. T. *Chem. Rev.* **1998**, *98*, 1375.

(8) Alkorta, I.; Rozas, I.; Elguero, J. *Chem. Soc. Rev.* **1998**, *27*, 163.

(9) Yao, W.; Eisenstein, O.; Crabtree, R. H. *Inorg. Chim. Acta* **1997**, *254*, 105.

(10) Desiraju, G. R. *J. Chem. Soc., Dalton Trans.* **2000**, 3745.

(11) Desiraju, G. R. *Angew. Chem., Int. Ed.* **2011**, *50*, 52.

(12) Calhorda, M. J. *Chem. Commun.* **2000**, 801.

(13) Martin, A. *J. Chem. Educ.* **1999**, *76*, 578.

(14) Brookhart, M.; Green, M. L. H.; Parkin, G. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 6908.

(15) Brammer, L. *Dalton Trans.* **2003**, 3145.

(16) Sundquist, W. I.; Bancroft, D. P.; Lippard, S. J. *J. Am. Chem. Soc.* **1990**, *112*, 1590.

(17) Kryachko, E. S. *J. Mol. Struct.* **2008**, *880*, 23.

(18) Bortolin, M.; Bucher, U. E.; Rüegger, H.; Venanzi, L. M.; Albinati, A.; Lianza, F.; Trofimenko, S. *Organometallics* **1992**, *11*, 2514.

(19) Cotton, F. A.; Luck, R. L. *Inorg. Chem.* **1989**, *28*, 3210.

(20) Scherer, W.; McGrady, G. S. *Angew. Chem., Int. Ed.* **2004**, *43*, 1782.

(21) Schmidbaur, H.; Raubenheimer, H. G.; Dobrzanska, L. Manuscript in preparation.

(22) Martínez, A. *J. Phys. Chem. A* **2009**, *113*, 1134.

(23) Schneider, H.; Boese, A. D.; Weber, J. *J. Chem. Phys.* **2005**, *123*, 084307.

(24) Zheng, W.; Li, X.; Eustis, S.; Grubisic, A.; Thomas, O.; de Clercq, H.; Bowen, K. *Chem. Phys. Lett.* **2007**, *444*, 232.

(25) Wu, C.-Y.; Duan, S.; Liu, X.-M.; Xu, Y.-C.; Jiang, Y.-X.; Ren, B.; Xu, X.; Lin, S. H.; Tian, Z.-Q. *J. Phys. Chem. A* **2008**, *112*, 1313.

(26) Pyykkö, P. *Chem. Soc. Rev.* **2008**, *37*, 1967.

(27) Nuss, H.; Jansen, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 4369.

(28) Nuss, H.; Jansen, M. *Z. Naturforsch.* **2006**, *61b*, 1205.

(29) Dietzel, P. D. C.; Jansen, M. *Chem. Commun.* **2001**, 2208.

(30) Scherf, L. M.; Baer, S. A.; Kraus, F.; Bawaked, S. M.; Schmidbaur, H. *Inorg. Chem.* **2013**, *52*, 2157.

(31) Klatt, G.; Xu, R.; Pernpointner, M.; Molinari, L.; Hung, T. Q.; Rominger, F.; Hashmi, A. S. K.; Köppel, H. *Chem.—Eur. J.* **2013**, *19*, 3954.

(32) Abram, U.; Mack, J.; Ortner, K.; Müller, M. *J. Chem. Soc., Dalton Trans.* **1998**, 1011.

(33) Ortner, K.; Abram, U. *Polyhedron* **1999**, *18*, 749.

(34) Bardaji, M.; Laguna, A.; Reyez Perez, M. *Organometallics* **2002**, *21*, 1877.

(35) Barranco, E. M.; Crespo, O.; Conception Gimeno, M.; Jones, P. G.; Laguna, A. *Eur. J. Inorg. Chem.* **2004**, 4820.

(36) Shi, P.; Jiang, Q.; Lin, J.; Zhao, Y.; Lin, L.; Guo, Z. *J. Inorg. Biochem.* **2006**, *100*, 939.

(37) Cinellu, M. A; Zucca, A.; Stoccoro, S.; Minghetti, G.; Manassero, M.; Sansoni, M. *J. Chem. Soc., Dalton Trans.* **1995**, 2865.

(38) Cinellu, M. A.; Zucca, A.; Stoccoro, S.; Minghetti, G.; Manassero, M.; Sansoni, M. *J. Chem. Soc., Dalton Trans.* **1996**, 4217.

(39) Bulak, E.; Sarper, O.; Dogan, A.; Lissner, F.; Schleid, T.; Kaim, W. *Polyhedron* **2006**, *25*, 2582.

(40) Lo Schiavo, S.; Nicoló, F.; Scopelliti, R.; Tresoldi, G.; Piraino, P. *Inorg. Chim. Acta* **2000**, *304*, 108.

(41) Afanas'eva, V. A.; Glinskaya, L. A.; Klevtsova, R. F.; Mironov, I. V. *Russ. J. Coord. Chem.* **2011**, *37*, 325.

(42) Pregosin, P. S.; Wombacher, F. *Magn. Reson. Chem.* **1991**, *29*, S106.

(43) Minghetti, G.; Cinellu, M. A; Stoccoro, S.; Zucca, A. *Gazz. Chim. Ital.* **1992**, *122*, 455.

(44) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(45) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Menucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; and Fox, D. J. *Gaussian 09, Rev. B.01*; Gaussian, Inc.: Wallingford CT, 2010.

(46) Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297.

(47) Sousa, S. F.; Fernandes, P. A.; Ramos, M. J. *J. Phys. Chem. A* **2007**, *111*, 10439.

(48) Ferrier, W. G.; Iball, J. *Chem. Ind. (London)* **1954**, 1296.

(49) Rabideau, P. W. *Acc. Chem. Res.* **1978**, *11*, 141.

(50) Rabideau, P. W.; Mooney, J. L.; Lipkowitz, K. B. *J. Am. Chem. Soc.* **1986**, *108*, 8130.

(51) Dalling, D. K.; Zilm, K. W.; Grant, D. M.; Heeschen, W. A.; Horton, W. J.; Pugmire, R. J. *J. Am. Chem. Soc.* **1981**, *103*, 4817.

(52) Sygula, A.; Holak, T. A. *Tetrahedron Lett.* **1983**, *24*, 2893.

(53) Segawa, Y.; Stephan, D. W. *Chem. Commun.* **2012**, *48*, 11965.

(54) Minghetti, G.; Zucca, A.; Stoccoro, S.; Cinellu, M. A.; Manassero, M.; Sansoni, M. *J. Organomet. Chem.* **1994**, *481*, 195.

(55) Hiraki, K.; Fuchita, Y.; Takechi, K. *Inorg. Chem.* **1981**, *20*, 4316.