Agostic Interactions

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Experimental and Theoretical Evidence for an Agostic Interaction in a Gold(III) Complex

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Dedicated to Professor Hubert Schmidbaur

Abstract: *The first agostic interaction in a gold complex is described. The presence of a bonding C–H···Au interaction in a cationic "tricoordinate" gold(III) complex was suggested by DFT calculations and was subsequently confirmed by NMR spectroscopy at low temperature. The agostic interaction was analyzed computationally using NBO and QTAIM analyses (NBO = natural bond orbital; QTAIM = quantum theory of atoms in molecules).*

About 30 years after the crystallographic characterization of the first σ-complex, agostic interactions, that is, the coordination of σ(C–H) bonds to transition metals,[1] have become a well-documented bonding situation for organometallic species.[2,3] Over the years, the presence of agostic interactions has been documented in numerous complexes. A large body of experimental and theoretical data has been progressively collected providing in-depth understanding of the scope, nature, and characteristics of this weak metal–ligand interaction. Agostic interactions are not only of fundamental interest, but they have also been found to play a major role in the reactivity of many organometallic species. They have been found to be ubiquitous in all C–H activation processes, regardless of the associated mechanism (for example oxidative addition, σ-metathesis, or β–H elimination).

Compared to other transition metals, complexes containing coinage metals tend to behave singularly, that is, the formation of σ bonds within their complexes remains extremely rare. A few σ complexes of Cu have been recently characterized (Figure 1),[4–7] but the question of whether or not σ complexes with gold can exist remains an open question.[8]

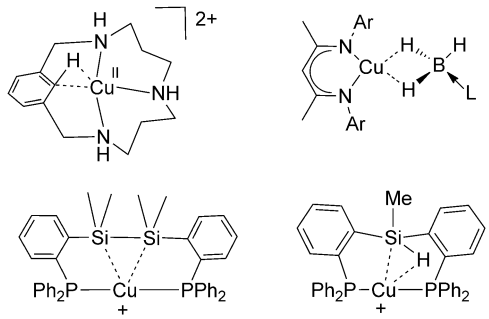

Figure 1. Simplified structures of the few known Cu σ complexes.

The presence of short Au···H(C) contacts has been identified in a few gold(I) and gold(III) complexes, and the possible existence of agostic interactions in gold complexes has been speculated upon.[9,10] However, no evidence has been presented to support the presence of a covalent bonding interaction between the C–H bonds and the gold center, and computational studies suggest that the short Au···H distances result instead from conformational constraints.[11,12] The topic has been recently reviewed by Schmidbaur et al.,[13] who actually came to the conclusion that "*gold(I) and gold(III) centers are generally very poor acceptors for Au···H–C interactions*" and that "*there is currently no evidence for agostic interactions in organogold compounds*".[14] Herein, we report NMR spectroscopic characterization and DFT analysis of a cationic organogold(III) complex and provide thereby conclusive evidence for an agostic interaction in a gold complex.

In the frame of our research program on the reactivity of gold complexes,[15,16] we recently reported the migratory insertion of norbornene into Au–C bonds.[17] Dimethyl gold(III) complex **1** was reacted with $B(C_6F_5)_3$ in the presence of

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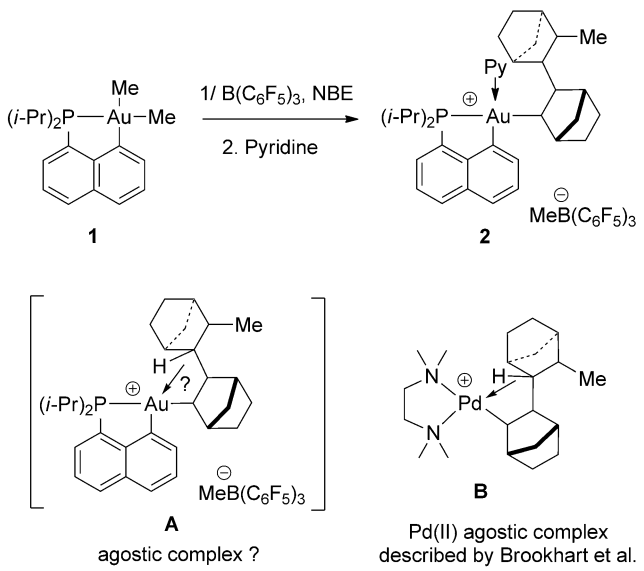

Scheme 1. NBE insertion into Au^{III}–C bonds to form complex **2** and the structure of the putative tricoordinate gold(III) intermediate **A**, showing the possible existence of a C–H···Au interaction. This structure is analogous to the C–H···Pd interaction detected in a related Pd complex **B**.[18]

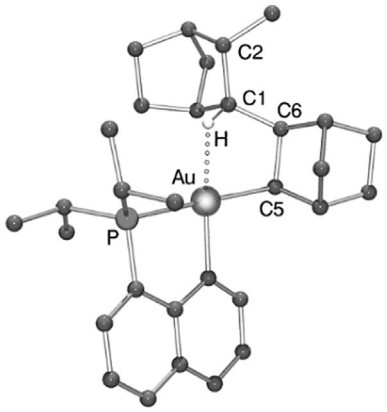

Figure 2. Optimized structure of complex **A** at the B3PW91/SDD + f-(Au),6–31G**(P,C,H) level of theory. Selected bond distances (Å) and angles (°): Au–H = 2.042, Au–C1 = 2.726, C1–H = 1.147, Au–C5 = 2.112, C_{napht}–Au = 2.041, P–Au = 2.454; Au-H-C1 = 114.52, P-Au-H = 98.97, P-Au-C_{napht} = 84.43, C5-Au-C_{napht} = 95.79, C5-Au-H = 80.59. All hydrogen atoms, except the one in close contact with the gold center, have been omitted for clarity.

norbornene (NBE) and then trapped with pyridine to afford the stable tetracoordinate norbornyl gold(III) complex **2** (Scheme 1). The reaction is presumed to proceed by methide abstraction from gold to boron, double insertion of NBE, followed by coordination of the pyridine. Accordingly, formation of **2** should involve the cationic tricoordinate gold(III) species **A** as key intermediate. Complex **A** is similar to the Pd complex **B** reported by Brookhart et al. for which a γ-agostic interaction was evidenced experimentally.[18] This result prompted us to consider and investigate the possible existence of a C–H···Au interaction in **A**.

Tricoordinate gold(III) alkyl species are highly unstable and, to date, have never been characterized.[19,20] Thus, the possible existence and structure of the putative cationic gold(III) intermediate **A** was first assessed by theoretical method. DFT calculations were performed at the B3PW91/SDD + f(Au)/6-31G**(P,C,H) level of theory.[21] The optimized geometry of complex **A** (Figure 2) revealed a tricoordinate T-shape geometry around the gold center (P-Au-C5 = 172.94°, $C_{naphthyl}$-Au-C5 = 95.79°). The two norbornane (NB) units are arranged in a zig-zag fashion (C2-C1-C6-C5 = 168.66°). In addition, a short contact is found between the gold(III) center and a C–H bond of the norbornane not directly linked to Au (Au···HC_γ = 2.042 Å, where C_γ is labelled C1 in Figure 2). The H atom of this C_γ–H bond occupies the "free" coordination site of the gold center, specifically *trans* to the Au-coordinated carbon atom of the naphthyl group ($C_{naphthyl}$), resulting in the formation of a five-membered (Au-C5-C6-C1-H) ring. The Au···H-C_γ bond angle is significantly bent (114.52°), and the C_γ–H bond interacting with gold is noticeably elongated compared to the other C–H bonds of the NB units (1.147 versus 1.08–1.10 Å).

The geometric features of complex **A** are strongly reminiscent of those of the reported Pd complex **B**[18a] and suggest the possible existence of an agostic interaction. In the search for experimental evidence for such a C–H···Au interaction, we attempted to spectroscopically characterize the putative cationic gold(III) intermediate **A**. For that purpose, the reaction of complex **1** with $B(C_6F_5)_3$/NBE was carried out in an NMR tube at very low temperature and the reaction was monitored in situ by NMR spectroscopy. Gratifyingly, analysis of the reaction mixture by ^{31}P NMR spectroscopy at −80 °C indicated the formation of a new compound with a resonance signal at δ = 80.9 ppm (≥ 91 % yield according to ^{31}P NMR analysis). This species is unstable and decomposes above −30 °C, but its structure was completely assessed by multinuclear NMR spectroscopy at low temperature (Figure 3).

The ^1H and ^{13}C NMR spectra display characteristic resonance signals for the P,C-coordinated gold(III) fragment and the $[MeB(C_6F_5)_3]^-$ counterion. In addition, the ^1H NMR spectrum revealed the presence of new signals in the aliphatic region, corresponding to the NB units. The relative integration of the aliphatic and naphthyl ^1H NMR resonance signals confirms the insertion of two NBE molecules into the Au–Me bond. Notably, the ^{13}C NMR resonance signal of the NB C–H group directly linked to the gold center features a large coupling constant to phosphorus (δ = 64.7 ppm, $^2J_{CP}$ = 66.7 Hz), indicating that the norbornyl fragment sits *trans* to the phosphorus atom. All of the ^1H and ^{13}C NMR signals for the NB units could be unambiguously assigned by using 2D HSQC and HMBC experiments.[21] The ^1H NMR resonance signal for the hydrogen atom in the γ position to the Au center is not significantly shifted compared to the other signals of the NB units (δ = 1.50 ppm). This contrasts with the strong "hydridic" shift detected for the corresponding hydrogen atom of the Pd complex **B** (δ = −4.15 ppm). It is not possible to ascertain the presence of an agostic interaction based on ^1H NMR chemical shifts.[22,23]

The most simple and reliable spectroscopic evidence for an agostic interaction is certainly the value of the

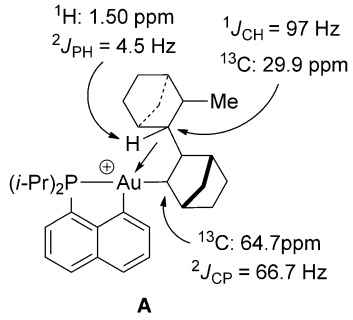

Figure 3. Selected NMR data for the "tricoordinate" gold(III) agostic complex **A** at −80 °C.

$^1J_{CH}$ coupling constant, which is unusually low (ranging from 50 to 100 Hz) compared to classical C–H bonds (about 135 Hz).[1,2c] To determine the $^1J_{CH}$ coupling constants within the norbornene units of complex **A**, a 2D *J*-resolved ^{13}C NMR analysis was performed at −80 °C (Figure 4). Accordingly,

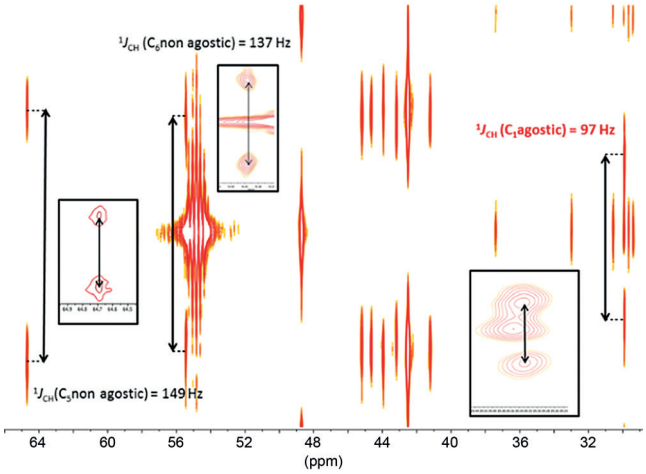

Figure 4. 2D *J*-resolved ^{13}C NMR spectroscopy of complex **A** showing the $^1J_{CH}$ coupling constants for the agostic C–H bond and non-agostic C–H bonds (see Figure 2 for atom labelling).

a significantly lower $^1J_{CH}$ coupling constant was detected for the C–H bond in the γ-position to the gold center (97 Hz) compared to the other C–H bonds (> 130 Hz). Another indication of the coordination of the H_γ atom of the C–H_γ bond to the gold center is provided by the 2D HMQC ^{1}H–^{31}P spectrum, which displays a correlation between the H_γ proton and the phosphorus atom, with an associated $^2J_{PH}$ coupling constant of 4.5 Hz (Figures S9–10).[21]

To confirm the diagnostic, low $^1J_{CH}$ coupling constant detected for **A** and thus, the presence of the agostic interaction, the $^1J_{CH}$ coupling constants were also computed for the DFT-optimized geometry (using the GIAO method implemented in Gaussian, IGLOO II basis set (P, C, H)). From these calculations, the same trend was found: the $^1J_{C\gamma H}$ coupling constant was computed to have a value of 88 Hz while the other C–H bonds of the NB units display $^1J_{CH}$ values greater than 125 Hz. Additionally, similar measurements performed on the tetracoordinate pyridine adduct **2** revealed an increase of the $^1J_{C\gamma H}$ coupling constant value to 130 Hz, corresponding to the loss of the agostic interaction (the "free" coordination site at gold is blocked by N coordination).

The bonding situation in complex **A** was further examined computationally by means of natural bond orbital (NBO) and quantum theory of atoms in molecules (QTAIM) analyses.[24] NBO calculations identified, at the second-order perturbation level, a donor–acceptor interaction between the C_γ–H bond (σ_{CH} orbital) and the gold center ($\sigma^*_{AuC(naphthyl)}$ orbital *trans* to the vacant site at the Au center) with a stabilizing energy $\Delta E^{(2)}$ of 18.6 kcal mol^{-1} (Figure 5a). The QTAIM molecular graph (Figure 5b) shows a bond path (BP) and a bond critical point (BCP) between the γ-H atom and the gold center. The values of the electron density ρ ($\rho = 0.048$ e bohr^{-3}) and of the

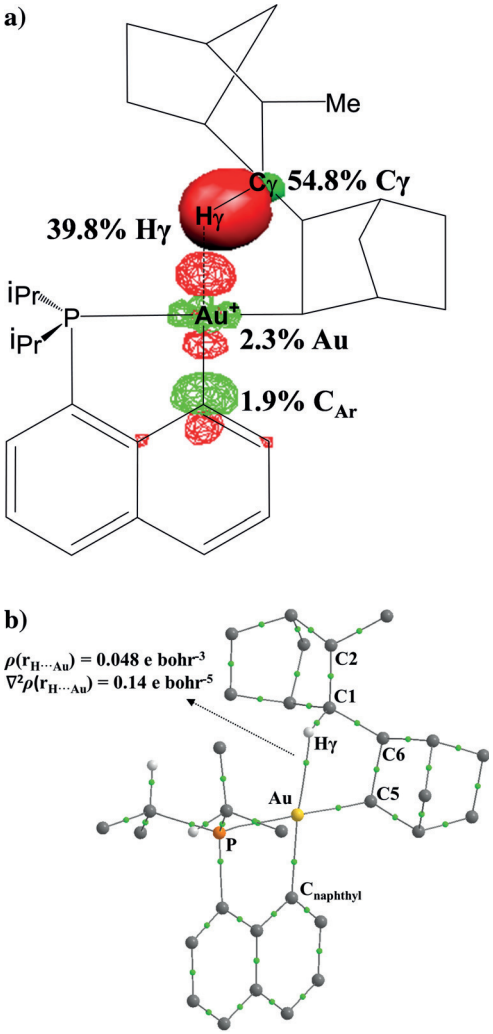

Figure 5. a) Superposition of the donor σ_{CH} and acceptor σ^*_{CAu} NBOs (plot cutoff: 0.08 au) associated with the γ-agostic interaction in complex **A** ($\Delta E^{(2)} = 18.6$ kcal mol^{-1}). The σ^*_{CAu} NBO is shown in "chicken-wire" format, the σ_{CH} NBO in solid colors. Atomic contributions in the corresponding σ_{CH} natural localized molecular orbital (NLMO) are given. b) Atoms-in-molecules (AIM) molecular graph showing the C–H···Au BP and the main electron density properties computed at the C–H···Au bond critical points (BCPs). Green circles indicate BCPs.

Laplacian ($\nabla^2\rho = 0.14$ e bohr^{-5}) at the H···Au BCP fall in the range of those typically detected for agostic interactions.[24,25] In addition, the electron density is lower at the BCP of the C_γ–H bond ($\rho = 0.24$ e bohr^{-3}) than at the BCP of other NB C–H bonds ($\rho \approx 0.27$ e bohr^{-3}), in line with some stretching and weakening of the agostic C–H bond upon coordination to the gold center. For comparison, computational studies were also carried out on Pd complex **B** reported by Brookhart et al.[18,21] NBO and QTAIM analyses corroborate the presence of an agostic interaction in gold complex **A**, the nature and magnitude of which are similar to those of the agostic interaction in Pd complex **B**.

In conclusion, experimental and computational evidence for a C–H···Au agostic interaction is provided for the first time. A "tricoordinate" cationic alkyl gold(III) complex has been characterized by NMR spectroscopy and its bonding situation has been thoroughly analyzed. The existence of agostic interactions within gold complexes is not only of fundamental interest (complex **A** is the first σ complex of gold to be verified) but it also has important implications for studying the reactivity of organogold complexes. Indeed, agostic interactions are likely to play a significant role in C–H activation processes and now it is clear that β–H elimination reactions, although hitherto unknown, can be envisioned with gold complexes.[14]

The characterization of complex **A** also extends the variety of reported, highly reactive organogold(III) species. For some time very little was known about the structures, stability, and reactivity of organogold(III) compounds because of the intrinsic instability of gold species in high oxidation states and the challenges associated with their syntheses. However, the field has significantly progressed over the last few years.[26] A variety of new organometallic gold(III) compounds have been isolated and important insights have been gained into their intrinsic properties.[27] The new class of organogold(III) compounds described in this study, a type of "tricoordinate" cationic organogold(III) species, is also very interesting. Complexes of this type are highly electrophilic and coordinatively unsaturated, opening up promising perspectives in terms of their reactivity.[28] Future work in our group will seek to explore further C–H···Au agostic interactions and their implications on the stability and reactivity of organogold(III) complexes.

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[28] Toste and co-workers recently reported that tricoordinate cationic [(IPr)Au^{III}(biphenyl)] species generated in situ are catalytically active for Michael additions as well as for [4+2] and [2+2] cycloadditions to α,β-unsaturated carbonyl compounds. The active species was trapped by Lewis bases (H_2O, DMF, chloride) and the trapped compounds were characterized as stable four-coordinate gold(III) adducts. See: C. Y. Wu, T. Horibe, C. B. Jacobsen, F. D. Toste, *Nature* **2015**, *517*, 449 – 454.

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