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Organometallic Chemistry Hot Paper

σ-Cyclopropyl to π-Allyl Rearrangement at Au^{III}

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Dedicated to Michel Etienne

Abstract: The possibility for Au^{III} σ-cyclopropyl complexes to undergo ring-opening and give π-allyl complexes was interrogated. The transformation was first evidenced within (P,C)-cyclometalated complexes, it occurs within hours at −50 °C. It was then generalized to other ancillary ligands. With (N,C)-cyclometalated complexes, the rearrangement occurs at room temperature while it proceeds already at −80 °C with a dicationic (P,N)-chelated complex. Density Functional Theory (DFT) calculations shed light on the mechanism of the transformation, a disrotatory electrocyclic ring-opening. Intrinsic Bond Orbital (IBO) analysis along the reaction profile shows the cleavage of the distal σ(CC) bond to give a π-bonded allyl moiety. Careful inspection of the structure and bonding of cationic σ-cyclopropyl complexes support the possible existence of C–C agostic interactions at Au^{III}.

Introduction

The recent development of homogeneous gold catalysis largely finds its roots in the ability of gold complexes to activate π-CC bonds. Because ring strain confers partial π-character to σ bonds, strained carbocycles have been shown to display rich reactivity towards gold(I). In particular, alkylidene cyclopropanes turned out to be very powerful substrates in gold catalysis, affording rapid access to complex structures via ring-opening or ring-expansion.[1]

Nonetheless, very little is known about the behavior of strained carbocycles towards gold(III). The spectacular progress achieved over the last 10–15 years in Au^{III} chemistry[2] suggests that there is much potential in the field and probably a lot to discover. Of note, Nevado et al. recently explored the possibility to achieve ring-opening of alkylidene cyclopropanes at gold by pyridine chelation.[3] Upon reaction with gold(I) precursors, pyridine coordination without any further reaction was observed. In stark contrast, upon reaction with gold(III) salts such as $NaAuCl_4$, proximal ring-opening led to original pyridine alkenyl (N,C)-cyclometalated Au^{III} complexes (Figure 1a). Our interest for reactive organo Au^{III} complexes, including π-allyl Au^{III} complexes that remained unknown until recently,[4] prompted us to explore the chemistry of Au^{III} cyclopropyl complexes. Indeed, the rearrangement of σ-cyclopropyl into π-allyl complexes is known,[5] although examples are relatively rare, with no precedent in gold chemistry, to the best of our knowledge.

Here we report that Au^{III} σ-cyclopropyl complexes are indeed prone to rearrange into Au^{III} σ-allyl complexes via

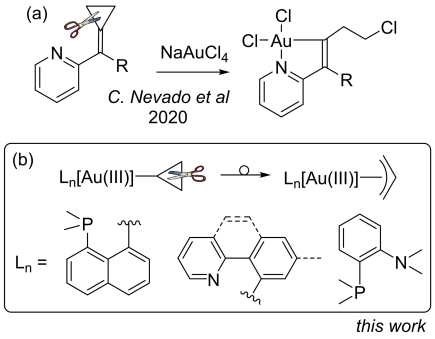

Figure 1. Ring-openings of alkylidene cyclopropane/cyclopropyl moieties at gold.

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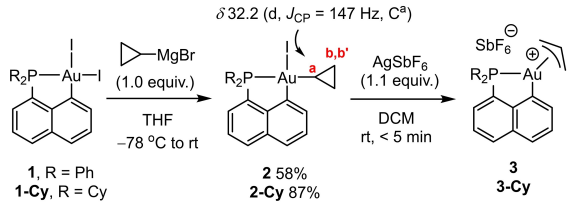
distal ring-opening (Figure 1b). The generality of the process, initially discovered with (P,C)-cyclometalated complexes, was examined. The reaction mechanism was thoroughly investigated computationally, suggesting the possible existence of C–C agostic interactions in Au^{III} complexes.

Results and Discussion

(P,C)-Cyclometalated Au^{III} complexes are readily accessible via P-chelation assisted oxidative addition.[6] The (P,C) ligand enables the stabilization of Au^{III} allowing for the preparation of a wide variety of different Au^{III} complexes.[7] The ligand properties can easily be modified in terms of sterics and electronics by varying the substituents at phosphorus. For this study, the phenyl-substituted (Ph_2P,C) ligand was chosen as a model system to avoid crowding of the aliphatic areas in the ^{1}H and ^{13}C NMR spectra. The Au^{III} σ-cyclopropyl complex **2** was prepared from the previously reported complex **1**[6] upon reaction with cyclopropyl magnesium bromide (Scheme 1). Complex **2** was characterized by mass spectrometry and multinuclear NMR. The characteristic ^{1}H NMR resonances of the cyclopropyl moiety were observed at δ 1.66 ppm (H^a), and 1.33/1.12 ppm ($H^{b,b'}$). In line with the higher *trans* influence of naphthyl-C compared to naphthyl-P, the cyclopropyl group is located *trans* to P, as shown by the large coupling constant between the cyclopropyl carbon C^a (δ 32.2 ppm, d, J_{C^aP} = 147 Hz) and P (Scheme 1).

Having in hands the Au^{III} σ-cyclopropyl complex **2**, we were interested to see if a rearrangement would occur upon liberating a coordination site at gold. Gratifyingly, iodide abstraction with $AgSbF_6$ led to the clean rearrangement of the Au^{III} σ-cyclopropyl complex **2** into the corresponding Au^{III} π-allyl complex **3** (Scheme 1). Complex **3** was unambiguously authenticated by the characteristic ^{1}H NMR signature of the π-allyl moiety, matching that of the previously reported (iPr_2P,C) and (Cy_2P,C) analogues.[4a,b] Variable temperature ^{1}H and ^{31}P NMR monitoring of the reaction of complex **2** with $AgSbF_6$ showed that the rearrangement occurs already at −50 °C. To generalize the transformation, the corresponding (Cy_2P,C) Au^{III} σ-cyclopropyl complex **2-Cy** was also prepared and its rearrangement was investigated. Changing from the (Ph_2P,C) ligand to the more electron donating (Cy_2P,C) ligand did not affect the reaction in any noticeable manner. Upon treatment of **2-Cy** with $AgSbF_6$, the reaction evolved similarly under the same conditions, and complex **3-Cy**[4b] was unambiguously authenticated as the product of the reaction (Scheme 1).

To gain more insight into this σ-cyclopropyl to π-allyl rearrangement at Au^{III}, Density Functional Theory (DFT) was used. Calculations were performed on the Ph-substituted naked cations $\mathbf{2}^+/\mathbf{3}^+$ at the B3PW91/SDD + f(Au), 6-31G**(other atoms) level of theory in the gas phase (Figure 2). Of note, calculations taking into account solvent and dispersion effects [SMD(CH_2Cl_2)-B3PW91, B3PW91-D3(BJ) and SMD(CH_2Cl_2)-B3PW91-D3(BJ)] showed very little changes (Figures S36–S38, Tables S1 and S2).[8] The structures of the energy *minima* and transition states (TS) were not altered significantly. The thermodynamic balance and activation barrier of the transformation also varied only marginally. Both the *trans* and *cis* isomers of the starting complex $\mathbf{2}^+$ were considered. In line with our experimental observations and the larger *trans* influence of C over P, the *trans* isomer $\mathbf{2}^+$**-trans** is the most stable. The *cis* isomer $\mathbf{2}^+$**-cis** sits only 6.1 kcal mol^{-1} higher in energy and the activation barrier for *trans*/*cis* isomerization can be readily crossed at 11.4 kcal mol^{-1}. The *trans* and *cis* forms of $\mathbf{2}^+$ connect with transition states **TS-ro** and **TS-ro′** associated with the ring-opening of the distal σ(CC) bond of the cyclopropyl moiety, leading to the π-allyl complex $\mathbf{3}^+$. The transformation is strongly exergonic ($\Delta G = -24.6$ kcal mol^{-1} from $\mathbf{2}^+$**-trans**). Inspection of the rotation of the two CH_2 moieties along the Intrinsic Reaction Coordinate (IRC) shows that the ring-opening proceeds via an outward disrotatory process.[8] The transition states **TS-ro** and **TS-ro′** are very close in energy and readily accessible at ≈19.5 kcal mol^{-1}. Their geometric features indicate that the



Scheme 1. Synthesis of the (P,C)-cyclometalated σ-cyclopropyl Au^{III} complexes **2**/**2-Cy**, and their rearrangement into the corresponding Au^{III} π-allyl complexes **3**/**3-Cy** upon treatment with $AgSbF_6$. The NMR data given are for the (Ph_2P,C) complex **2**. For the (Cy_2P,C) complex **2-Cy**, see Supporting Information.[8]

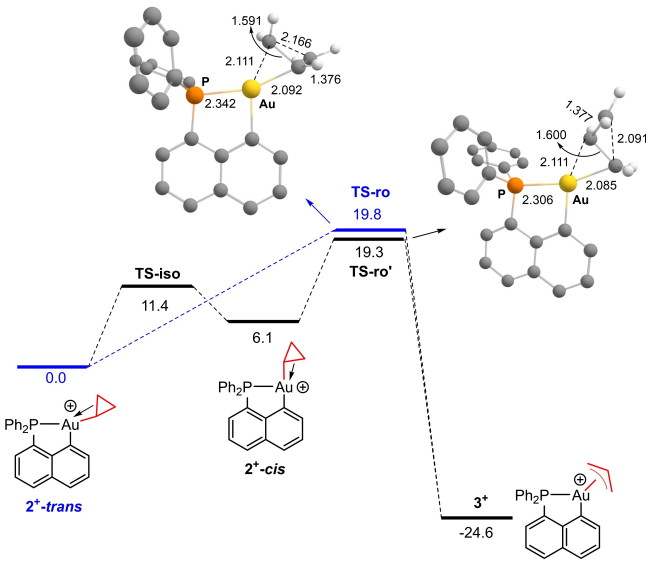


Figure 2. Energy profile computed for the ring-opening (C–C distal bond) of the (Ph_2P,C) Au^{III} σ-cyclopropyl complex $\mathbf{2}^+$ to give the corresponding π-allyl complex $\mathbf{3}^+$. Δ*G* values in kcal mol^{-1}, main distances in Å. Profile computed in the gas phase at the B3PW91/SDD + f(Au), 6–31G** (other atoms) level of theory.

ring-opening is very advanced. The distal σ(CC) bond is elongated by as much as ≈40 % (2.17/2.09 Å in **TS-ro**/**TS-ro**′ compared to 1.54/1.52 Å in the σ-cyclopropyl complexes $\mathbf{2}^{+}$-***trans***/$\mathbf{2}^{+}$-***cis***) while one Au–CH_2 bonds is essentially formed (2.11/2.09 Å).

To analyse the electron flow associated with this rearrangement, the Intrinsic Bond Orbitals (IBOs) were inspected all along the transformation of $\mathbf{2}^{+}$ into $\mathbf{3}^{+}$. Most noteworthy is the progressive conversion of the distal σ(CC) bond into a 3-center π-orbital, in line with the electrocyclic ring-opening of the cyclopropyl σ-bonded to Au into an allyl moiety π-bonded to Au (Figure 3). In the meantime, the $\sigma(AuCH_{cyclopropyl})$ bond relocalizes into an orbital accounting for the two $\sigma(AuCH_2)$ bonds of the π-allyl complex while the two proximal σ(CC) bonds do not evolve much and the four occupied 5d orbitals at Au also remain essentially unchanged during the whole process (Figure S39).

Cationic 3-coordinate Au^{III} complexes are coordinatively and electronically unsaturated. They have been shown to eventually engage in weak interactions with the surrounding ligands or substrates (complexes **I**–**III**, Figure 4) such as C–H agostic interactions.[7a,c,e,9] Ring strain imparts unusual bonding properties to the cyclopropyl moiety. In particular, the bent *banana* CC bonds are more prone than other σ(CC) bonds to engage in coordination and C–C agostic interactions.[10]

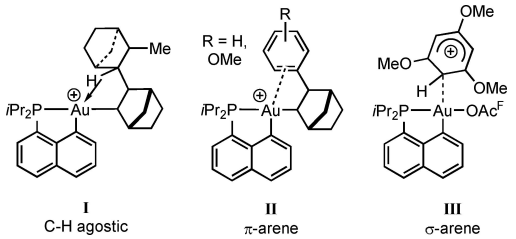


Figure 4. Weak σ/π-interactions arising from 3-coordinate cationic (P,C)-cyclometalated Au^{III} complexes.

In the case of the cationic (P,C)-cyclometalated Au^{III} σ-cyclopropyl complex **2**, both C–H (such as in **I**) and C–C agostic interactions may be envisioned. The structure and bonding of the naked cation $\mathbf{2}^{+}$ was thus thoroughly analysed computationally. In the ground-state structure $\mathbf{2}^{+}$

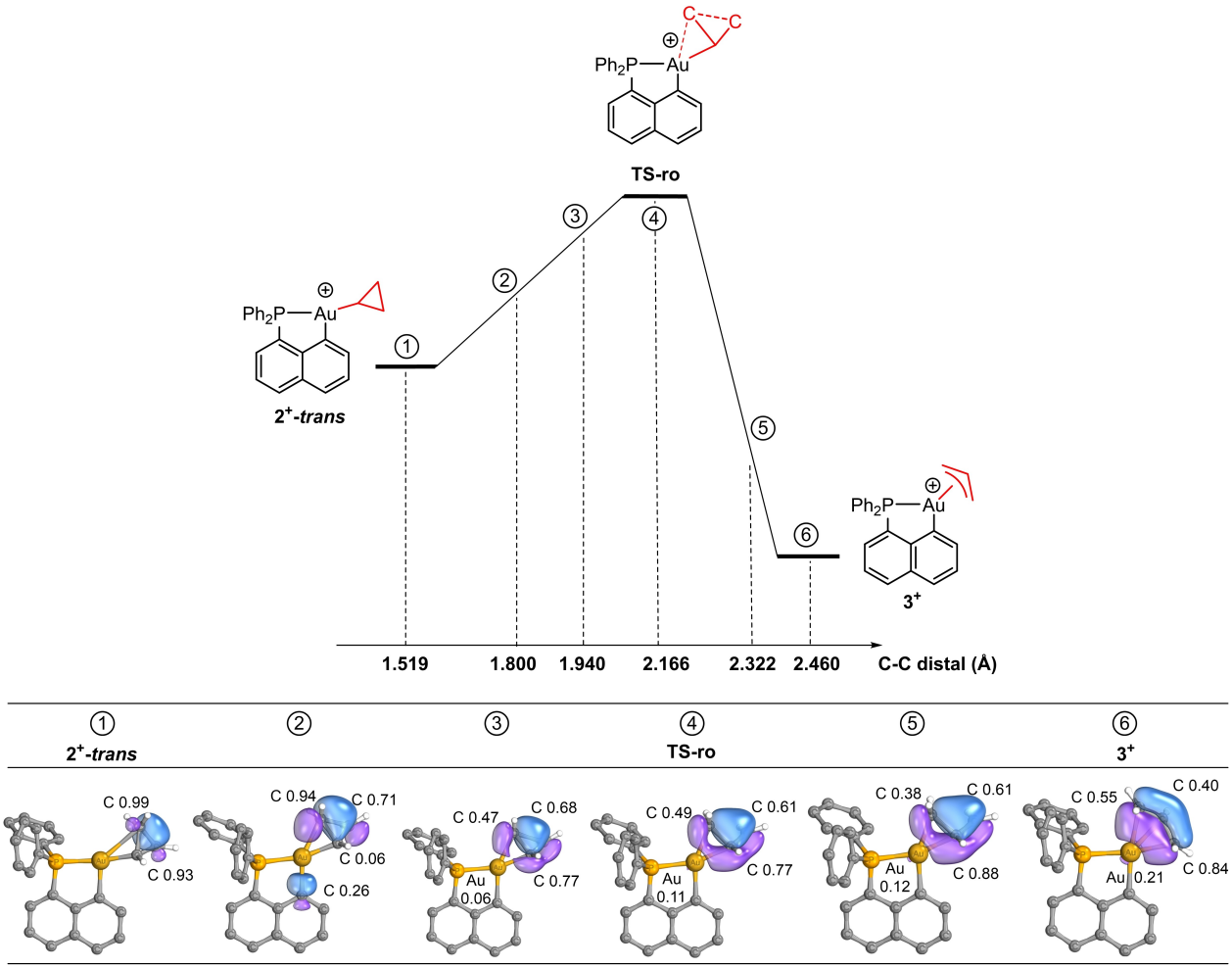


Figure 3. Main IBOs accounting for the ring-opening of the distal σ(CC) bond along the reaction path from the σ-cyclopropyl complex $\mathbf{2}^{+}$ to the π-allyl complex $\mathbf{3}^{+}$. Numbers relate to the fraction of electrons of the doubly occupied orbital assigned to each atom.

-trans, weak donations from the proximal and distal σ(CC) bonds to Au were found as donor-acceptor interactions in Natural Bond Orbital (NBO) analysis with delocalization energies $\Delta E(2)$ of 2.9 and 4.6 kcal mol^{-1}, respectively. The respective σ(CC) bonds are slightly elongated compared to the non-interacting one (1.54 Å for the interacting proximal σ(CC) bond and 1.52 Å for the distal σ(CC) bond, versus 1.48 Å for the other proximal σ(CC) bond) and the distal carbon atom C3 approaches Au (2.78 Å) (Figure 5). Rotating the Au–$C_{cyclopropyl}$ bond to move the cyclopropyl group away from Au results in another energy *minimum* **2$^+$-*trans′*** located 6.3 kcal mol^{-1} higher in energy than **2$^+$-*trans***. In this reference form free of agostic interactions, the three σ(CC) bond lengths are similar (≈1.50 Å). In line with the vacant coordination site at gold being *trans* to P, a weaker donor than C, the *cis* isomer **2$^+$-*cis*** involves stronger C–C agostic interactions than **2$^+$-*trans*** ($\Delta E(2)$ of 12.6 and 3.0 kcal mol^{-1} for the proximal and distal bonds, respectively). As a result, the interacting proximal and distal σ(CC) bonds are even longer in **2$^+$-*cis*** than in **2$^+$-*trans*** (1.58 and 1.54 Å versus 1.54 and 1.52 Å). No significant C–H agostic interaction was observed in **2$^+$-*trans*** and **2$^+$-*cis***. Note also that calculations performed with functionals including dispersion effects (B3PW91-D3(BJ) and M06) gave very similar results, confirming the presence of weak stabilizing C–C agostic interactions in **2$^+$** (Figure S40, Tables S3 and S4).[8] Unfortunately, all our attempts to identify such weak interactions experimentally via 1D selective INADEQUATE NMR experiments (to measure the J_{CC} coupling constant) have remained unsuccessful so far.[11]

Besides ring-opening forming the π-allyl complex by cleavage of the distal σ(CC) bond, other paths are *a priori* conceivable and potentially competitive from the cationic (P,C)-cyclometalated Au^{III} σ-cyclopropyl complex **2$^+$**, namely β-hydride elimination to give a Au^{III} hydride cyclopropene complex **4$^+$** as well as Au insertion into the proximal σ(CC) bond to give a 4-membered ring Au^{III} carbene complex **5$^+$** (Figure 6). We also considered these processes computationally but found them not to compete with the formation of the π-allyl complex **3$^+$** (Figures S41 and S42).[8] The transformations of **2$^+$** into **4$^+$** and **5$^+$** involve substantially larger activation barriers (29.6 and 27.6 kcal mol^{-1}, respectively) and they are not thermodynamically favored ($\Delta G = 28.5$ and 18.6 kcal mol^{-1}, respectively), making the ring-opening of the distal σ(CC) bond to give **3$^+$** strongly preferred.

We then questioned the generality of the ring-opening process at Au^{III} and varied the ancillary ligand. Besides the (P,C)-cyclometalated Au^{III} π-allyl complexes reported by our group, Tilset et al. described simultaneously a related (N,C)-cyclometalated derivative based on the *p*-tolyl pyridine ligand.[4d] In contrast to the highly symmetric π-allyl coordination found with (P,C) ligands, the (N,C) Au^{III} π-allyl complex was shown to adopt an asymmetric σ+π-type coordination mode. We were thus intrigued to see whether the rearrangement would also occur in (N,C) Au^{III} σ-cyclopropyl complexes.

The (N,C)-cyclometalated Au^{III} σ-cyclopropyl complex **7** was prepared in 52 % yield by reacting (N,C)Au(OAc^F)$_2$ **6** (OAc^F = OCOCF$_3$)[12] with cyclopropyl magnesium bromide (Scheme 2).[13] In complex **7**, the cyclopropyl group sits *trans* to the nitrogen, as ascertained by the Nuclear Overhauser Effect (NOE) correlations between the protons of the cyclopropyl moiety and the proton of the *p*-tolyl ring in α position to Au in the ^{1}H-^{1}H NOESY spectrum.[8] Similarly to the (P,C) complexes **2** and **2-Cy**, the (N,C) complex **7** undergoes ring-opening upon halide abstraction with $AgSbF_6$. However, room temperature was required for the σ-cyclopropyl to π-allyl rearrangement to occur, in contrast to the (P,C) system where it occurred already at −50 °C. The π-allyl (N,C) complex **8** is not stable at room temperature

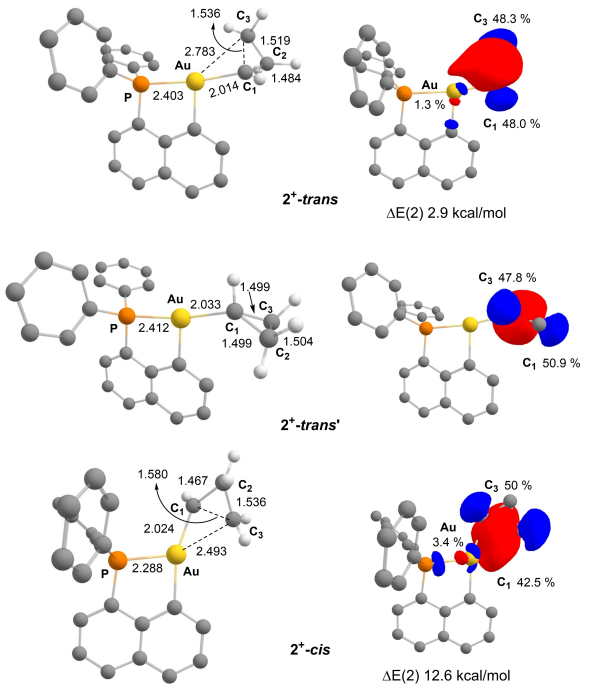


Figure 5. Optimized geometries of **2$^+$-*trans***, **2$^+$-*trans′*** and **2$^+$-*cis*** (main C–C and Au–C distances in Å). NLMOs (cutoff: 0.03) accounting for the proximal σ(C_1C_3) bond involved in agostic interactions in **2$^+$-*trans*** and **2$^+$-*cis***, but not in **2$^+$-*trans′***. C and Au contributions in % and stabilizing $\sigma_{C1C3} \rightarrow \sigma^*_{AuCnaphthyl}/\sigma^*_{AuP}$ interactions, $\Delta E(2)$, in kcal mol^{-1}.

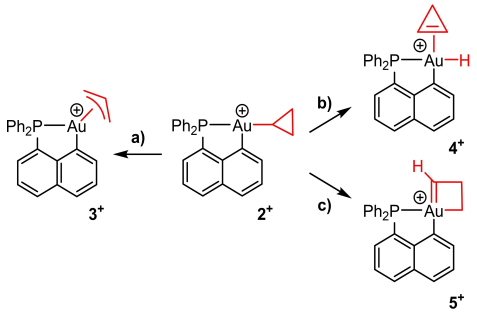
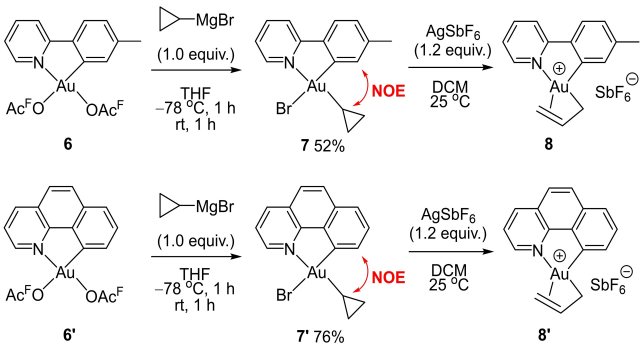
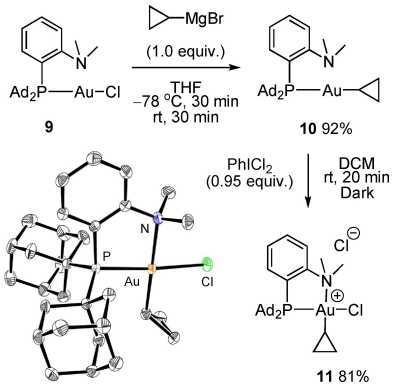


Figure 6. Schematic representation of the pathways envisioned from complex **2$^+$**: a) insertion of Au into the distal σ_{CC} bond, b) β-H elimination, c) insertion of Au into the proximal σ_{CC} bond.



Scheme 2. Synthesis of the (N,C)-cyclometalated σ-cyclopropyl Au^{III} complexes **7** and **7′**, and their rearrangement into the corresponding Au^{III} π-allyl complexes **8** and **8′**.



Scheme 3. Synthesis and molecular structure of the (P,N)-ligated σ-cyclopropyl Au^{III} complex **11**. For sake of clarity, the hydrogen atoms and chloride counteranion are omitted. Ellipsoids at 50% probability. Selected bond lengths (in Å) and angles (in °): P–Au 2.305(1), N–Au 2.203(2), Au–C 2.058(3), P–Au–Cl 175.47(2), N–Au–C 179.43(10).

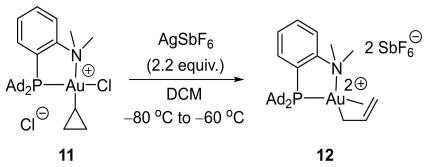
and slowly decomposes during its formation. Nonetheless, it could be unambiguously authenticated by its ^{1}H NMR spectrum which showed a diagnostic pattern of an asymmetric π-allyl matching that previously reported.[4d]

To assess the influence of the rigidity of the ancillary ligand on the σ-cyclopropyl to π-allyl rearrangement, the *p*-tolyl pyridine ligand was replaced for the more rigid benzoquinoline.[14] The (N,C) Au^{III} σ-cyclopropyl complex **7′** was prepared using the same methodology as for **7** (Scheme 2). As for complex **7**, the position of the cyclopropyl moiety in **7′**, *trans* to nitrogen, was substantiated by a ^{1}H-^{1}H NOESY experiment.[8] The rearrangement of the σ-cyclopropyl to the π-allyl occurs under the same conditions as for the more flexible *p*-tolyl pyridine complex **7**, indicating that the increased rigidity of the ancillary ligand has no noticeable influence. The ensuing π-allyl complex **8′** slowly decomposes during its formation, but its ^{1}H NMR spectrum shows a π-allyl pattern very similar to that of **8**.[8]

Having studied (P,C) and (N,C)-cyclometalated ligands, we then turned to the (P,N)-chelating ligand MeDalphos as ancillary ligand. We recently characterized the corresponding dicationic Au^{III} π-allyl complex by NMR spectroscopy at low temperature.[4c] It is a key intermediate in the catalytic allylation of indoles via ligand-enabled Au^I/Au^{III} catalysis. Here also, the electronic dissymmetry of the ligand (P is significantly more donating than N) results in asymmetric σ+π-type coordination of the allyl moiety. The (P,N)-ligated Au^{III} σ-cyclopropyl complex **11** (Scheme 3) was prepared by a different synthetic route than the related (P,C)/(N,C)-cyclometalated complexes. We have recently shown that gold(I) complexes containing the hemilabile MeDalphos ligand undergo ligand-assisted oxidation when treated with $PhICl_2$ and *o*-quinones to afford the corresponding (P,N)-chelated cationic Au^{III} complexes.[15] Using this approach, the Au^I cyclopropyl complex **10** was synthesized by reacting the commercially available gold chloride **9** with cyclopropyl magnesium bromide, and it was then oxidized with $PhICl_2$ to give the (P,N)-chelated cationic Au^{III} σ-cyclopropyl complex **11**. A small excess of gold complex **10** was required to avoid over-chlorination and formation of the (MeDalphos)$AuCl_3$ complex. The cyclopropyl moiety sits *cis* to phosphorus, as apparent from single-crystal X-ray diffraction and NMR analyses (Scheme 3).[8,16] Complex **11** adopts the expected square-planar geometry and the short Au–N distance (2.203 Å) witnesses the coordination of N to Au.

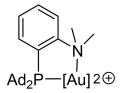
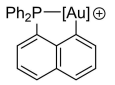
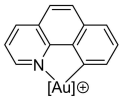
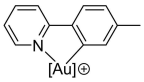
From complex **11**, the σ-cyclopropyl to π-allyl rearrangement required two equivalents of $AgSbF_6$ due to the chloride counterion (Scheme 4). Low-temperature NMR monitoring showed that the ring-opening occurs in this case already at −80 °C and reaches completion when the reaction mixture is warmed to −60 °C. The ensuing π-allyl complex **12** was unambiguously authenticated by the presence of the characteristic ^{1}H NMR signature of the asymmetric π-allyl moiety, matching that of the previously prepared (P,N) Au^{III} π-allyl.[4c] The σ-cyclopropyl to π-allyl rearrangement thus appears significantly easier for the (P,N)-chelated complex than for the (P,C)- and (N,C)-cyclometaled complexes.

Calculations were also performed on the σ-cyclopropyl to π-allyl rearrangement at Au^{III} with the (N,C) and (P,N) ancillary ligands (Table 1).[8] In all cases, energy profiles similar to that of the (P,C)-cyclometalated complex were obtained. The reaction is exergonic (by 19–20 kcal mol^{-1}) and the ring-opening of the distal σ(CC) bond occurs in one step (Figures S43–S45). The corresponding activation barriers follow the experimental observations. The lowest barrier was found for the (P,N)-chelated dicationic complex (15.7 kcal mol^{-1}), while the rearrangements of the cationic (C,N)-cyclometalated complexes require significantly larger barriers (26.4–27.1 kcal mol^{-1}).



Scheme 4. Rearrangement of the (P,N)-ligated σ-cyclopropyl Au^{III} complex **11** into the corresponding Au^{III} π-allyl complex **12**.

Table 1: Activation barriers $\Delta G^{\ddagger}$ and Gibbs free energies ΔG (in kcal mol^{-1}) computed in the gas phase at the B3PW91/SDD+f(Au), 6-31G** (other atoms) level of theory for the Au^{III} σ-cyclopropyl to π-allyl rearrangement with the four different ancillary ligands.

	$\Delta G^{\neq}$	ΔG
	15.7	−20.1
	19.8	−24.6
	26.4	−19.1
	27.1	−18.7

IBO analysis of the reaction profile for the ring-opening of the [(PN)Au(σ-cyclopropyl)]$^{2+}$ complex parallels that of the [(Ph$_2$P,C)Au(σ-cyclopropyl)]$^{+}$ complex and is consistent with an electrocyclic rearrangement at Au^{III} with cleavage of the distal σ(CC) bond and formation of a π-bonded allyl moiety (Figures S46 and S47).[8] The structure of the dicationic [(PN)Au(σ-cyclopropyl)]$^{2+}$ complex was also examined in-depth to probe further the possible existence of C–C agostic interactions in such Au^{III} complexes (Figure 7, Tables S5 and S6). Only one structure was located as energy *minimum* in this case. The cyclopropyl group sits *cis* to P and the Au^{III} center is stabilized by interactions with one proximal σ(CC) bond and the distal σ(CC) bond. The involved σ(CC) bonds are noticeably elongated (at 1.55 and 1.54 Å, versus 1.47 Å for the other proximal σ(CC) bond) and the NBO delocalization energies for the σ(CC)→Au donor-acceptor interactions amount to 6.9 and 6.4 kcal mol^{-1}, respectively.[8]

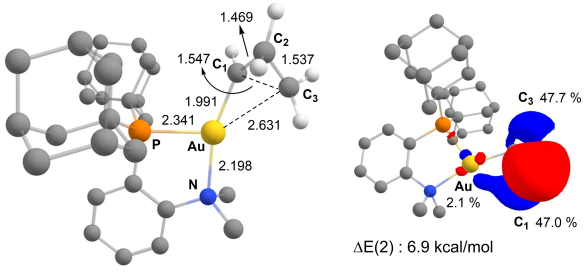


Figure 7. Optimized geometry of the dicationic [(PN)Au(σ-cyclopropyl)]$^{2+}$ (main C–C and Au–C distances in Å). NLMO (cutoff: 0.03) accounting for the proximal σ(C$_1$C$_3$) bond involved in agostic interaction. C and Au contributions in % and stabilizing $\sigma_{C1C3}\rightarrow\sigma^{*}_{AuP}$ interaction, $\Delta E(2)$, in kcal mol^{-1}.

Conclusion

Au^{III} σ-cyclopropyl complexes have been shown to readily rearrange into the corresponding Au^{III} π-allyl complexes upon liberating a coordination site at Au^{III}. The transformation is general, it proceeds with (P,C)/(N,C)-cyclometalated as well as (P,N)-chelating ligands. The ancillary ligand strongly affects the temperature at which the reaction occurs, with a span of *ca* 100 °C. For the (P,N) complex, it proceeds already at −80 °C, whereas the (N,C) complexes rearrange only at 25 °C. The (P,C) complexes are found in-between (−50 °C).

The transformation was analyzed in-depth by computational means. Accordingly, the ring-opening proceeds via an outward disrotatory process. IBO analysis along the reaction profile distinctly shows the cleavage of the distal σ(CC) bond and the formation of a π-bonded allyl moiety at Au^{III}. Depending on the ancillary ligand, the activation barrier for this rearrangement ranges from 15.7 to 27.1 kcal mol^{-1}, in good agreement with the experimental trend. Alternative paths, β-hydride elimination and Au insertion into the proximal σ(CC) bond, were also considered but found not to compete.

The possible existence of C–C agostic interactions in Au^{III} cyclopropyl complexes was thoroughly examined. Although no experimental evidence could be obtained so far, the structure and bonding of the (P,C)Au(σ-cyclopropyl)$^{+}$ and (P,N)Au(σ-cyclopropyl)$^{2+}$ complexes unambiguously support the presence of weak coordinations of the proximal σ(CC) bond. Donor-acceptor interaction energies up to 12.6 kcal mol^{-1} were found by NBO analysis. Besides their fundamental interest in terms of chemical bonding, such σ-complexes are synthetically important, as they likely represent initial stages of σ(CC) bond activation at transition metals.[17]

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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 Supporting Information of this article.

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[1] D. Li, W. Zang, M. J. Bird, C. J. Hyland, M. Shi, *Chem. Rev.* **2021**, *121*, 8685–8755.

[2] a) R. Kumar, C. Nevado, *Angew. Chem. Int. Ed.* **2017**, *56*, 1994–2015; b) L. Rocchigiani, M. Bochmann, *Chem. Rev.* **2021**, *121*, 14, 8364–8451.

[3] J. A. González, F. Verdugo, J. L. Mascareñas, F. López, C. Nevado, *Angew. Chem. Int. Ed.* **2020**, *59*, 20049–20054.

[4] a) J. Rodriguez, G. Szalóki, E. D. Sosa Carrizo, N. Saffon-Merceron, K. Miqueu, D. Bourissou, *Angew. Chem. Int. Ed.* **2020**, *59*, 1511–1515; b) J. Rodriguez, M. S. M. Holmsen, Y. García-Rodeja, E. D. S. Carrizo, P. Lavedan, S. Mallet-Ladeira, K. Miqueu, D. Bourissou, *J. Am. Chem. Soc.* **2021**, *143*, 11568–11581; c) J. Rodriguez, D. Vesseur, A. Tabey, S. Mallet-Ladeira, K. Miqueu, D. Bourissou, *ACS Catal.* **2022**, *12*, 993–1003; d) For a (N,C)-cyclometalated Au^{III} π-allyl complex, see: M. S. M. Holmsen, A. Nova, S. Øien-Ødegaard, R. H. Heyn, M. Tilset, *Angew. Chem. Int. Ed.* **2020**, *59*, 1516–1520; e) Au^{I} π-allyl complexes have recently been proposed as transition states for the isomerization of Au^{I} σ-allyl complexes, see: L. O'Brien, S. P. Argent, K. Ermanis, H. W. Lam, *Angew. Chem. Int. Ed.* **2022**, *61*, e202202305.

[5] For examples with Pt, Rh, Fe and W, see: a) R. L. Phillips, R. J. Puddephatt, *J. Organomet. Chem.* **1977**, *136*, C52–C54; b) R. L. Phillips, R. J. Puddephatt, *J. Chem. Soc. Dalton Trans.* **1978**, 1732–1735; c) R. A. Periana, R. G. Bergman, *J. Am. Chem. Soc.* **1986**, *108*, 7332–7346; d) N. J. Conti, D. J. Crowther, S. Tivakornpannarai, W. M. Jones, *Organometallics* **1990**, *9*, 175–184; e) O. Tatjana, N. J. Conti, W. M. Jones, *Organometallics* **1991**, *10*, 913–917; f) K. D. J. Parker, L. Vendier, M. Etienne, *Organometallics* **2018**, *37*, 1221–1224; g) K. D. J. Parker, S. Labat, J.-M. Sotiropoulos, K. Miqueu, V. Pimienta, L. Vendier, M. Etienne, *Eur. J. Inorg. Chem.* **2019**, 4555–4563.

[6] J. Guenther, S. Mallet-Ladeira, L. Estevez, K. Miqueu, A. Amgoune, D. Bourissou, *J. Am. Chem. Soc.* **2014**, *136*, 1778–1781.

[7] a) F. Rekhroukh, L. Estévez, C. Bijani, K. Miqueu, A. Amgoune, D. Bourissou, *Angew. Chem. Int. Ed.* **2016**, *55*, 3414–3418; b) F. Rekhroukh, L. Estevez, S. Mallet-Ladeira, K. Miqueu, A. Amgoune, D. Bourissou, *J. Am. Chem. Soc.* **2016**, *138*, 11920–11929; c) F. Rekhroukh, C. Blons, L. Estévez, S. Mallet-Ladeira, K. Miqueu, A. Amgoune, D. Bourissou, *Chem. Sci.* **2017**, *8*, 4539–4545; d) A. Pujol, M. Lafage, F. Rekhroukh, N. Saffon-Merceron, A. Amgoune, D. Bourissou, N. Nebra, M. Fustier-Boutignon, N. Mézailles, *Angew. Chem. Int. Ed.* **2017**, *56*, 12264–12267; e) M. S. M. Holmsen, C. Blons, A. Amgoune, M. Regnacq, D. Lesage, E. D. S. Carrizo, P. Lavedan, Y. Gimbert, K. Miqueu, D. Bourissou, *J. Am. Chem. Soc.* **2022**, *144*, 22722–22733.

[8] See Supporting Information for details.

[9] L. Rocchigiani, J. Fernandez-Cestau, P. H. M. Budzelaar, M. Bochmann, *Chem. Commun.* **2017**, *53*, 4358–4361.

[10] M. Etienne, A. S. Weller, *Chem. Soc. Rev.* **2014**, *43*, 242–259.

[11] For experimentally authenticated C–C agostic cyclopropyl complexes (M = Nb, Y, Sc and Rh), see: a) J. Jaffart, M. Etienne, M. Reinhold, J. E. McGrady, F. Maseras, *Chem. Commun.* **2003**, *7*, 876–877; b) J. Jaffart, M. L. Cole, M. Etienne, M. Reinhold, J. E. McGrady, F. Masera, *Dalton Trans.* **2003**, *21*, 4057–4064; c) C. Boulho, T. Keys, Y. Coppel, L. Vendier, M. Etienne, A. Locati, F. Bessac, F. Maseras, D. A. Pantazis, J. E. McGrady, *Organometallics* **2009**, *28*, 940–943; d) Y. Escudié, C. Dinoi, O. Allen, L. Vendier, M. Etienne, *Angew. Chem. Int. Ed.* **2012**, *51*, 2461–2464; e) C. Xu, G. Li, M. Etienne, X. Lenga, Y. Chen, *Inorg. Chem. Front.* **2020**, *7*, 4822–4831; f) S. K. Brayshaw, J. C. Green, G. Kociok-Köhn, E. L. Sceats, A. S. Weller, *Angew. Chem. Int. Ed.* **2006**, *45*, 452–456; g) S. K. Brayshaw, E. L. Sceats, J. C. Green, A. S. Weller, *Proc. Natl. Acad. Sci. USA* **2007**, *104*, 6921–6929.

[12] E. Langseth, C. H. Görbitz, R. H. Heyn, M. Tilset, *Organometallics* **2012**, *31*, 6567–6571.

[13] Trifluoroacetate instead of halide ligands were used to increase solubility.

[14] a) J. Serra, T. Parella, X. Ribas, *Chem. Sci.* **2017**, *8*, 946–952; b) J. Serra, P. Font, E. D. S. Carrizo, S. Mallet-Ladeira, S. Massou, T. Parella, K. Miqueu, A. Amgoune, X. Ribas, D. Bourissou, *Chem. Sci.* **2018**, *9*, 3932–3940.

[15] a) G. Szalóki, J. Babinot, V. Martin-Diaconescu, S. Mallet-Ladeira, Y. García-Rodeja, K. Miqueu, D. Bourissou, *Chem. Sci.* **2022**, *13*, 10499–10505; b) M. Navarro, A. Tabey, G. Szalóki, S. Mallet-Ladeira, D. Bourissou, *Organometallics* **2021**, *40*, 1571–1576.

[16] Deposition Number 2256185 contains 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.

[17] For rare examples of σ(CC) bond activation at gold, see reference 3 and: a) C. Y. Wu, T. Horibe, C. B. Jacobsen, D. Toste, *Nature* **2015**, *517*, 449–454; b) M. Joost, L. Estévez, K. Miqueu, A. Amgoune, D. Bourissou, *Angew. Chem. Int. Ed.* **2015**, *54*, 5236–5240; c) J. Chu, D. Munz, R. Jazzar, M. Melaimi, G. Bertrand, *J. Am. Chem. Soc.* **2016**, *138*, 7884–7887; d) P. Font, H. Valdés, G. Guisado-Barrios, X. Ribas, *Chem. Sci.* **2022**, *13*, 9351–9360; e) J. A. Cadge, P. J. Gates, J. F. Bower, C. A. Russell, *J. Am. Chem. Soc.* **2022**, *144*, 19719–19725; f) P. Gao, J. Xu, T. Zhou, Y. Liu, E. Bisz, B. Dziuk, R. Lalancette, R. Szostak, D. Zhang, M. Szostak, *Angew. Chem. Int. Ed.* **2023**, *62*, e202218427.

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