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Two Amphoteric Silver Carbene Clusters

Alexander G. Tskhovrebov, Richard Goddard, and Alois Fürstner*

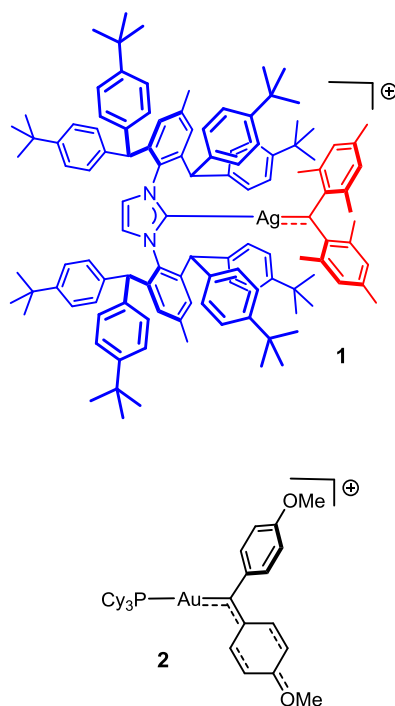
Abstract: *Two highly labile silver carbene cluster complexes are described which are unique in that they mark the transition point at which the carbene center transmutes from a fairly common NHC-like nucleophilic behavior to an electrophilic character befitting reactive silver carbene intermediates of relevance in various catalytic transformations. This amphoteric character is the distinguishing attribute of a μ -bridged donor/donor carbene entity that connects two silver atoms of the triangular or tetrahedral metallic core unit of complexes **4** and **5**, respectively.*

Silver salts are amongst the best promoters of the Wolff rearrangement that allows diazoketones to be transformed into ketenes and their downstream products.^{1,2} The intervention of electrophilic silver carbene intermediates in this reaction is highly likely, even though a rigorous proof is still missing, not least because of the presumably very low stability of such intermediates.¹⁻³ Actually it cannot be firmly excluded that silver carbenes decompose in statu nascendi, especially when carrying electron withdrawing carbonyl substituents; in doing so, the carbene ligand might get released into solution where the actual rearrangement could take place in the unbound state.⁴ A similar ambiguity surrounds even more recent reports on silver carbene chemistry,^{5,6} including applications to the C–H activation of alkanes^{7,8,9} as well as activation of the C–X bond of certain alkyl halides:¹⁰ once again, the intervention of electrophilic silver carbenes is plausible and probable;¹¹ yet, it has been prudently mentioned in the literature that free carbenes afford similar products or product distributions.^{7a,10} The fact that silver catalysts allow otherwise poorly reactive olefins to be cyclopropanated is also strong but again only indirect evidence for participation of silver carbene intermediates.^{12,13} Similar arguments pertain to silver-catalyzed Doyle-Kirmse reactions¹⁴ and ring expansions of

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cyclopropyldiazomethane derivatives.¹⁵ Even attempted asymmetric silver catalysis was not fully conclusive: the very modest ee's and/or low yields achieved in intramolecular C–H insertion as well as aziridination reactions upon silver catalyzed diazo decomposition have indeed been rationalized by assuming that the chosen chiral silver complexes merely act as Lewis-acid catalysts rather than as sources of true silver carbenes.^{16,17} Only recently has a highly enantioselective intramolecular dearomatization reaction been reported which makes a strong case for the intervention of discrete silver carbenes.¹⁸ Along the same lines, silver catalyzed (vinylogous) –OH or –NH insertion reactions of diazo derivatives were originally proposed to be Lewis-acid catalyzed transformations,^{16a,19} whereas recent DFT calculations speak for true silver carbene intermediates.^{20,21,22} Collectively, these examples illustrate that this entire research area remains somewhat opaque.



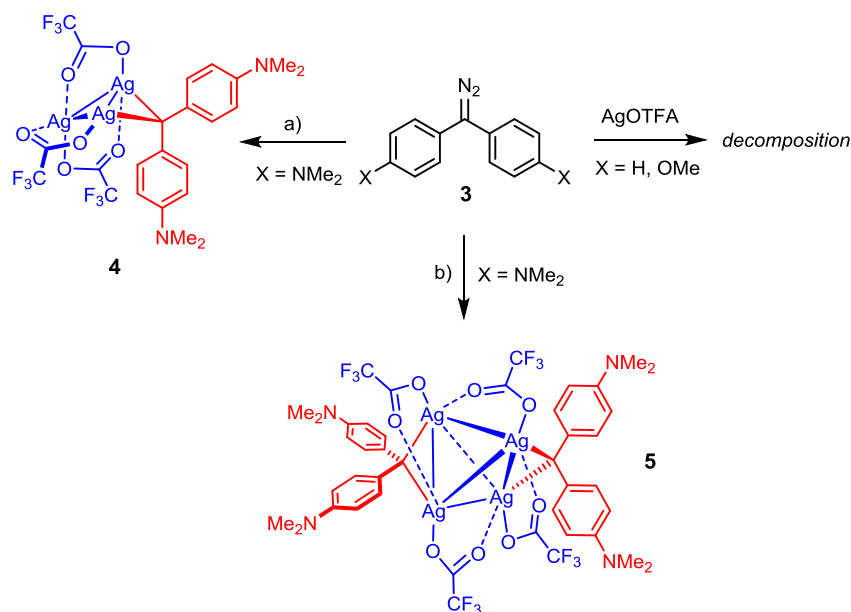
The problem is amplified by the paucity of secured experimental information about structure and bonding of reactive silver carbenes. To the best of our knowledge only a single example of an electrophilic silver carbene complex has been characterized by spectroscopic and crystallographic means.^{23,24} Specifically, complex **1** features a dimesityl carbene unit (red) that, in itself, is highly shielded by virtue of the twisting of the aryl rings enforced by the *ortho*-substituents; on top, the strongly electron donating and massively overcrowded ancillary ligand (blue) safeguards the reactive

carbene site to the maximum extent. This special design notwithstanding, **1** proved highly fragile; it was the least stable carbene complex amongst the Group 11 triad (Ag < Cu < Au), a trend that had already been noticed before for Fischer-type carbenes.²⁵ The homolysis-prone Ag–C bond in combination with marginal back-donation of electron density from the Ag atom into the carbene center and missing stabilization of the carbene LUMO of largely p-character by the flanking arene rings accounts for the sensitivity of **1**.²³ Unfortunately, no reactivity data whatsoever were reported for this unique complex.

A much larger experimental data set is available for silver complexes carrying N-heterocyclic carbene (NHC) or diamino-substituted cyclopropenylidene ligands, many of which are air- and moisture-stable and thermally fairly robust.^{26,27,28,29} NHC's (and relatives) are nucleophilic rather than electrophilic at carbon; for their strong donor properties, steric bulk and inertia, they find widespread use as ancillary ligands in organometallic chemistry;³⁰ the NHC contained in **1** (blue) used to stabilize the fragile complex illustrates this aspect. Silver-NHC complexes can also be used as versatile carbene transfer agents.^{28,29,31} It is therefore not clear if the available structural information about silver-NHC complexes has any particular relevance for a better understanding of the catalytic transformations outlined above which likely involve highly electrophilic silver carbene intermediates. It is of note, however, that silver-NHC complexes show quite diverse bonding motifs, encompassing monomeric, bridging and staircase-like species as well as a few cluster architectures.^{27,32}

As evident from this brief summary, the structural space populated by *reactive* silver carbenes is largely uncharted. Apprehensive of the experimental challenges to be met when working with such sensitive compounds, our initial foray was built on the lessons learnt in the related gold carbene arena.³³ With complex **2** comprising a substituted diphenyl carbene backbone, our group had isolated and characterized the first reactive gold carbene:^{34,35} as this species cyclopropanates styrene derivatives even at low temperature, its structure is relevant for a better understanding of gold catalysis.^{36,37} Since **2** obviously reacts as an ordinary electrophilic carbene despite the remote heteroelement substituents, it must not be mistaken for a vinylogous NHC-Au complex. Therefore, we hoped that analogous silver carbenes derived from diphenyldiazo derivatives **3** might also be sufficiently stable for full characterization yet reactive enough to be significant in the realm of catalysis. For the same reason, ordinary silver salts as commonly used for preparative purposes were

chosen for this study rather than silver sources endowed with specially designed ancillary ligand frameworks. Moreover, different substituents X in substrates of type **3** should provide a handle for tuning the character of the resulting silver carbene, at least to some extent.



Scheme 1. a) AgOTFA (excess), THF, -78°C , > 95% (NMR, **4**+**5**, see Text); b) AgOTFA (2 equiv.), DME, $-55^{\circ}\text{C} \rightarrow 0^{\circ}\text{C}$, 57%; DME = 1,2-dimethoxyethane; TFA = trifluoroacetyl

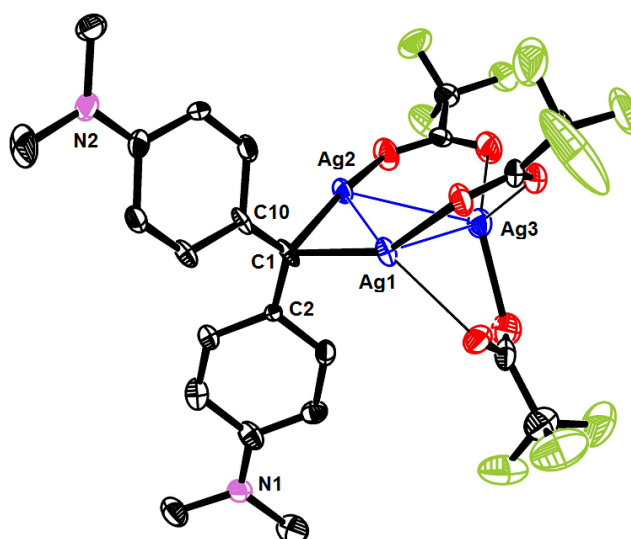


Figure 1. Structure of the silver carbene cluster **4** in the solid state; only one of the two independent molecules in the unit cell is shown; likewise, the loosely associated THF molecules in the unit cell are omitted for clarity (for details, see the Supporting Information)

Unfortunately though, silver carbenes generated from **3a** (X = H) or **3b** (X = OMe) defied attempted isolation even at very low temperatures. Only complexes derived from **3c** carrying the supposedly more stabilizing $-NMe_2$ substituents were sufficiently stable for full characterization as long as kept cold ($\leq -20^\circ\text{C}$) under Ar in the dark (Scheme 1). The outcome of the reaction strongly depended on the chosen conditions in that two distinct carbene clusters with different global architectures could be isolated even though they comprise the very same μ -carbene entity.

Specifically, reaction of **3c** with AgOTFA in THF at -78°C was fairly clean as judged by NMR. Yet, two distinctly different complexes co-crystallized from the intense green solution, which could be easily distinguished as one of them is dichroic yellow/green, whereas the other one is dichroic purple/green. It is not clear at this point whether these distinct species equilibrate on the NMR timescale in solution or whether their spectra are indistinguishable on a 500 MHz spectrometer; in this context, it is of note that complex **4** basically represents one face of complex **5**. The sensitive yellow/green fraction (**4**) consists of a triangular silver core carrying a μ -bridging carbene entity (Figure 1); the other coordination sites are occupied by three trifluoroacetate groups. The bridging carbene center C1 is equidistant to Ag1 and Ag2 [av. 2.17(1) Å] but does not make any contact to the distal Ag3 atom. The resulting four-membered framework is puckered; the trifluoroacetyl groups at Ag1 and Ag3 are pseudo-axially oriented, whereas the third trifluoroacetate is di-equatorially disposed. As a single resonance is observed by ^{19}F NMR, this particular pose in the solid state can only be a snapshot of a dynamic ligand environment in **4** that averages out on the NMR time scale.

The purple/green fraction, which had to be hand-picked from the conglomerate that crystallized from THF, consists of a tetrahedral Ag-cluster. Gratifyingly, this particular complex can be prepared much more selectively when the reaction of **3c** with AgOTFA (2 equiv.) is carried out in DME rather than THF at low temperature. The signal at $\delta_c = 221.1$ ppm most likely indicates the presence of a *bridging* carbene unit;³⁸ in any case, it is very different from the resonance of the *terminal* carbene in **1** ($\delta_c = 359.3$ ppm).²³ Careful recrystallization at low temperature afforded single crystals suitable for X-ray diffraction (Figure 2). In contrast to **4**, complex **5** was found to consist of a tetrahedral Ag-core unit with *two* bridging carbenes entities in the periphery and decorated with four (weakly) bridging trifluoroacetyl ligands,³⁹ variously bound. As in the case of **4**, the pose of the trifluoroacetates in the

solid state is only one of several interconverting conformers which render these anionic ligands equivalent on the NMR time scale.

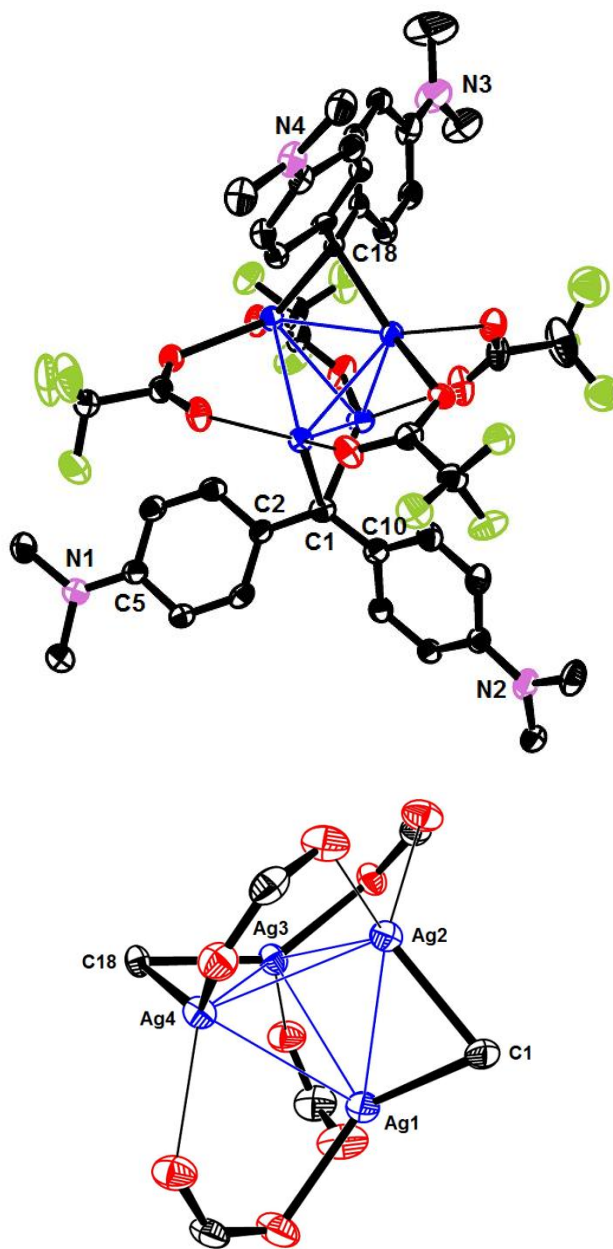
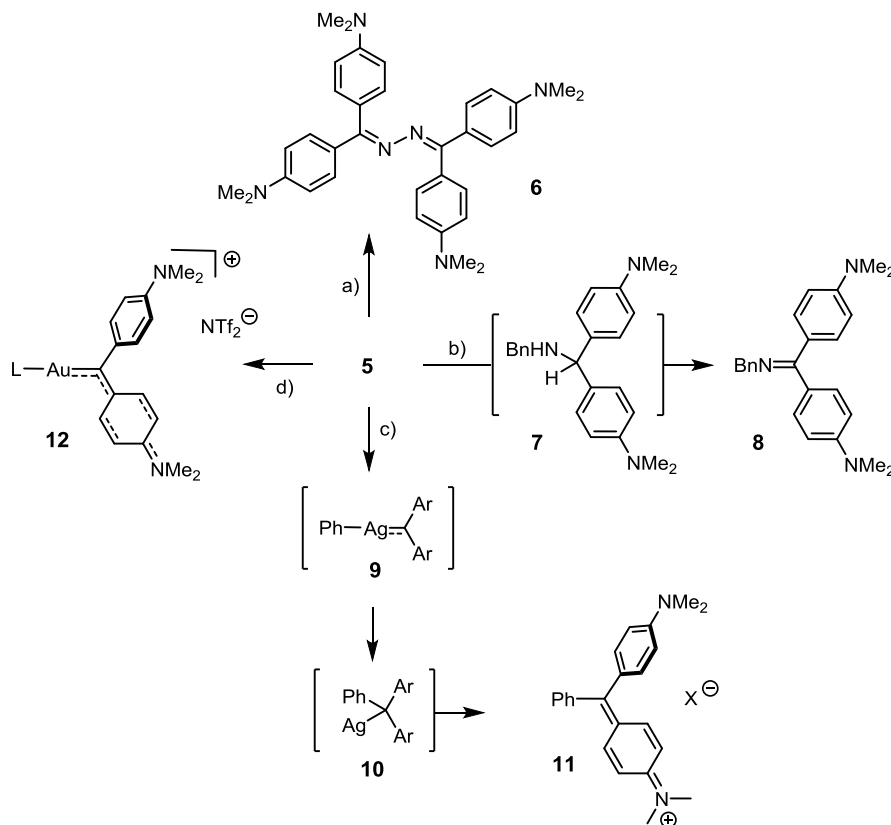


Figure 2. Top: Structure of the silver carbene cluster **5** (prepared in DME and crystallized from hexane) in the solid state; bottom: core region showing the symmetry-related μ -carbene centers (C1, C18) as well as the bridging trifluoroacetyl ligands, which interconvert in solution on the NMR time scale (all ligands are truncated for the sake of clarity). Except for conformational details, the structure of the complex crystallized from THF is akin (see the Supporting Information)

As expected for a μ -bridging carbene, the C–Ag bonds in **5** are short [2.19(1)–2.22(1) Å], yet distinctly longer than those in the terminal silver carbene **1** [2.05(2) Å].²³ By virtue of simultaneous ligation to two Ag^I fragments, the carbene acceptor orbital in **5** (as well as **4**) benefits from enhanced net back donation of electron density compared to a terminal carbene contained in complex **1**. A similar situation had previously been encountered in the copper series, where μ -bridging dicopper carbene complexes proved more stable than their terminal cousins.^{40,41,42,43} The fact that the carbene units in **4** and **5** entertain three-center four-electron bonding modes is vaguely reminiscent of the situation in electrophilic dirhodium carbenes, despite the linearity of the Rh–Rh–C core.^{44,45} Moreover, Figures 1 and 2 suggest that the electron rich arene rings in **4** and **5** help stabilize these carbene species.^{34,35} Specifically, the C1–C2/C1–C10 bonds (1.41/1.43 Å) in **5** are slightly contracted relative to the corresponding C–C_{ipso} bonds in the terminal carbene **1** (1.45 Å), and the –NMe₂ groups are coplanar with the arenes so as to maximize orbital overlap.

The presence of a three-center four-electron interaction in **4** and **5** is thought to indicate an electron-deficient carbene unit, which in turn implies electrophilic behavior; yet, it is not intuitive to which extent the mesomeric effect of the distal –NMe₂ substituents compensates this electronic attribute. Neither **4** nor **5** would cyclopropanate styrene to any appreciable extent, perhaps because the olefin substrate is incapable of disassembling the cluster to a potentially more reactive terminal carbene. Since μ -bridged dicopper carbene complexes described in the literature had previously also failed in cyclopropanation,^{40,41} they had been profiled by reaction with a diazo derivative, the nucleophilic N-terminus of which will attack an electrophilic carbene center very efficiently.⁴⁶ Even though azine formation constitutes a highly sensitive probe, the reaction had not been overly effective in the copper series.⁴⁰ In stark contrast, treatment of the silver complexes **4** or **5** with **3c** afforded azine **6** in almost quantitative yield, indicating electrophilic behavior (Scheme 2).⁴⁷ The same is manifest in the formation of imine **8**, which is thought to derive from N–H insertion followed by oxidation of amine **7** by the concomitantly released Ag^I cation. Furthermore, complex **5** proved amenable to formal cross coupling on treatment with PhMgBr at low temperature; this nucleophile was chosen because the transmetalation of Grignard reagents with Ag^I salts is known to be facile.⁴⁸ In contrast to the rapidly growing number of cross coupling reactions involving transition metal carbene intermediates,⁴⁹ the putative primary adduct **10** cannot stabilize itself by β -hydride elimination or protonation;^{50,51} the

redox capability of silver, however, opened an alternative outlet which ultimately furnished the stable cation **11** in good yield together with precipitated Ag^0 .



Scheme 2. a) **3c** (X = NMe₂), CH₂Cl₂, -78°C → RT, 96%; b) BnNH₂, CH₂Cl₂, -78°C → RT, 65%; c) PhMgBr, THF, -78°C → RT, then HCl, 75%; d) LAuNTf₂, CH₂Cl₂, -50°C → 0°C, **12a** (63%, L = IPr), **12b** (84%, L = XPhos); Bn = benzyl; IPr = 1,3-bis(2,6-di-isopropylphenyl)-imidazol-2-ylidene; Tf = trifluoromethanesulfonyl; XPhos = 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl

An additional set of experiments showed that complex **5** is actually amphoteric in nature in that it does not only exhibit modest electrophilic reactivity but can evidently act as a nucleophilic entity too (Scheme 2). In analogy to silver-NHC complexes, which serve coordination chemistry well as carbene transfer agents,³¹ **5** reacted with LAuNTf₂ at low temperatures to give the corresponding terminal gold carbene complexes **12a** (L = IPr) and **12b** (L = XPhos). The structures of **12a** (Figure 3) and **12b** (Figure S6) in the solid state resemble those of the other known – but still exceedingly rare – donor/donor gold carbenes.^{33,34,35} The characteristic quinoid distortion in **12a** with short C1–C2 (1.433 Å) and C5–N1 (1.359 Å) bonds shows that the electron rich carbene backbone rather than the

metal center largely accounts for the metastability of this complex. In contrast, the actual C1–Au1 carbene unit itself seems to lack significant π -back donation:⁵² in this particular case it has the exact same length [2.023(6) Å] as the bond between the gold atom and the IPr ligand, which is appreciated by the organometallic community for its poor π -acceptor qualities.^{28,30}

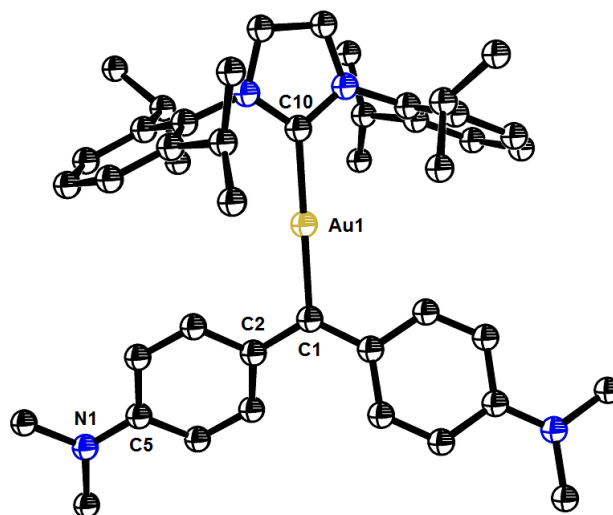


Figure 3. Structure of the cationic gold carbene complex **12a** (L = IPr) in the solid state; the disordered [NTf₂][−] counterion is not shown for clarity

Although a systematic investigation into how *para*-substituents X with different electronic properties impact on structure and reactivity of silver carbene species has not worked out as originally planned for stability reasons, the example with X = NMe₂, which was obtained in two different cluster formats, led to several important insights. The carbene unit bridges two silver centers and shows electrophilic as well as nucleophilic behavior; this peculiar amphoteric nature marks the transition point at which silver carbenes transmute from an NHC-like behavior to the electrophilic reactivity mode characteristic for intermediates invoked in a variety of catalytic transformations. In this context reference is made to a very recent study on a gold carbene solely characterized by spectroscopic means, which also seems to exhibit amphoteric character due to interaction of the carbene ligand with a cluster surface.^{53,54} In any case, the newly isolated cluster species speak for an extraordinary propensity of (electrophilic) silver carbenes to assemble to larger aggregates unless they carry massively overcrowded and/or strongly donating ancillary ligands; this tendency is likely relevant for mechanistic discussions and attempted optimizations of silver-catalyzed reactions of diazo

derivatives (or other relevant carbene sources), which are usually carried out with bare unligated silver salts. We suspect that the two specimens presented herein provide nothing but a glimpse of a potentially large structural diversity, which future investigations into this challenging field promise to uncover.

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