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Article

Sesquicarbene Complexes: Bonding at the Interface Between M−C Single Bonds and M═C Double Bonds

Florian F. Mulks,* A. Stephen K. Hashmi, and Shirin Faraji

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ABSTRACT: Allylic dimetalated complexes $[M_2C(vinyl)]^+$ (M = Au(IPr) and $Cr(CO)_5^-$) incorporate a new coordination mode of carbon. Digold complexes of this type have recently been detected experimentally. The intrinsic bond orbitals, partial charges, and structural parameters of the gold complexes and of chromium analogs were studied computationally and compared to those of the respective monometalated species and hydrocarbons. This showed that such digold complexes have a carbene character at both Au−C bonds comparable to typical carbene complexes of gold. Dichromium complexes with their stronger π-backdonation compete for interaction with carbon's π-orbital; each of the chromium atoms partakes in double bonding that is significant but weaker than that in the carbene analogs. Containing two M−C bonds on the interface between single and double bonds, these bridged complexes can be conceived as "sesquicarbene complexes". The π-system acted in a very adaptive manner and employed additional stabilization of the vinyl system only where needed. Significant carbene character is found simultaneously in both M−C bonds at the same carbon center. The discovery of these complexes with relatively strong double bond character between one carbon and two metal atoms could bring unusual single-carbon-centered organometallic cascade reactions to the horizon.
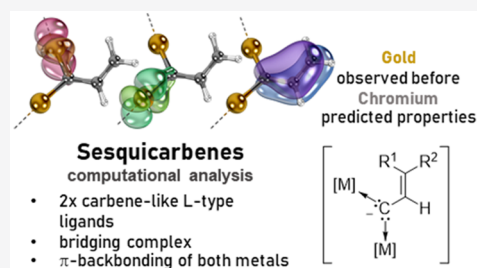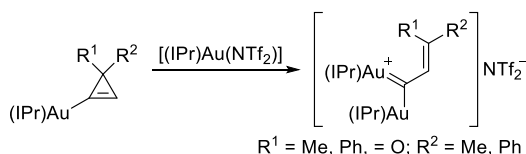
INTRODUCTION

The elucidation of new binding modes or coordination complexes of carbon is one of the keys to uncovering the landscape of organic and organometallic reactions. Gold(I) can coordinate and stabilize extremely reactive carbon species which together give it a central role in the discovery of some of these binding modes.[1−4] Prominent examples are carbon(0) coordination complexes, which were first established in digold complexes of carbodiphosphoranes.[5] Recent efforts focused on carbon(0) coordinated by one or two carbon donors in phosphaallenes and in carbodicarbenes.[6−19] These have been shown to be useful as strong σ-donor ligands in metal catalysis and as potent Lewis bases in frustrated Lewis pair chemistry.[19−21]

In the exploration of a similar new M−C binding mode in $[M_2C(vinyl)]^+$ species, we used the ring-opening reaction of cyclopropenes with cationic gold(I) (Scheme 1).[22−27] By reacting cyclopropen-1-ylgold(I) complexes with gold(I) cations, we synthesized highly reactive 1,1-diaurated allylium

cations.[28,29] They contain a bridging carbon atom with a formal cationic charge which allows for π-backbonding. They showed absorption bands in the near IR spectrum, lower energy excitations than in any gold carbene complex. Analysis of their molecular orbitals indicated stabilization with π-contributions originating from the ligand system and from both metal centers (Figure 1).
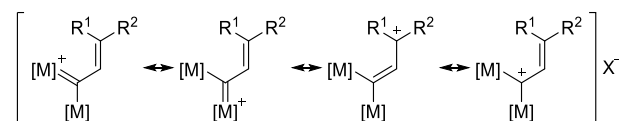
Figure 1. Mesomeric structures contributing to the structure of allylic dimetalated complexes or sesquicarbene complexes.

These results granted access to the interface between M−C single bonds and M═C double bonds. With σ-bonds to two metal centers and the capacity for π-backbonding shared across the two, they can be described as sesquicarbene complexes. We now report our computational investigation of the electronic

Scheme 1. Reported Synthesis of 1,1-Diaurated Allylium Cations

R^1 = Me, Ph, = O; R^2 = Me, Ph

structure of the experimentally investigated digold complexes and of dichromium complexes with stronger π-backdonation to gain an understanding of these complexes and of their potential applications.

■ RESULTS AND DISCUSSION

Methods. With the experimental results in hand, we chose to compare them to nonmetalated and to monometalated analogs as well as to the stronger π-donor metal chromium. It is now beyond controversy that the double-bond character of gold carbene complexes is low.[30−33] For this reason, for possible further applications[34−38] and for their synthetic connection to late transition metal complexes by transmetalation of the carbenes, we chose chromium(−I) in our study. It forms carbene complexes with stronger π-backbonds and thus broadens the perspective on the electronic structures of $[\text{M}_2\text{C(vinyl)}]^+$ species beyond what we have experimentally detected before.[39−43]

This study covers 30 allylium derivatives (Table 1). Starting from the allylium cation **1a**, protons in C^1-position were

Table 1. Overview of the Library of Investigated Compounds and Carbon Atom Numbers

	1	2	3	4	5
$[\text{M}^{cis}]$	H	H	Au(IPr)	H	Cr(CO)$_5^-$
$[\text{M}^{trans}]$	H	Au(IPr)	Au(IPr)	Cr(CO)$_5^-$	Cr(CO)$_5^-$
	a	b	c	d	e	f
R^1	H	Me	Me	Ph	Ph	=O
R^2	H	Me	Ph	Me	Ph	

substituted with one (**2a**) or two (**3a**) (IPr)Au moieties (IPr: 1,3-bis(2,6-diisopropylphenyl)-1,3-dihydro-2H-imidazol-2-ylidene) and with one (**4a**) or two (**5a**) (CO)$_5$Cr$^-$ moieties to give the respective mono- or dimetalated allylium complexes. Different C^3-substitution patterns were introduced for all of these: HH **1a−5a**, MeMe **1b−5b**, (E)-MePh **1c−5c**, (Z)-MePh **1d−5d**, Ph$_2$ **1e−5e**, and =O (3-oxo) **1f−5f**. As a reference, simple non-heteroatom-stabilized carbene complexes, diphenylcarbene complexes $[(\text{IPr})\text{AuCPh}_2]^+$ **6** and $[(\text{CO})_5\text{CrCPh}_2]$ **7**, were employed.

See the Supporting Information for a graphic overview of the optimized structures. Carbon atom numbers are given in blue as reference for the following discussion.

We chose to employ intrinsic bond orbitals (IBOs) to generate localized bond orbitals.[44−46] They are physically equivalent to the canonical molecular orbitals but give an intuitively understandable picture of bonding situations that has been shown to describe both the Lewis contributions and the relevant delocalization contributions well.[46−48]

IBO Examples. Representative 3,3-dimethyl-substituted compounds/complexes **1b−5b** are discussed in detail and compared to the reference gold and chromium diphenylcarbenes. Charge allocations of <0.1 e were disregarded for clarity, unless they concern C^1. The same applies to C−C σ-bonds. Full details of all IBOs with contributions to C^1 can be found in the Supporting Information.

3-Methylbut-2-ene-1-ylium **1b** shows the expected IBO contributions to C^1 (Figure 2). Three σ-bonds and an allylic π-
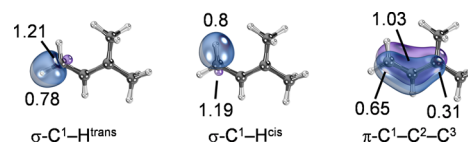

Figure 2. IBOs with contribution to C^1 and their electron distribution in compound **1b** (in e).

system contribute to the stabilization and distribution of the cationic charge. The allylic 3-center π-system is strongly polarized toward C^1. It contributes 33% of its 2 electrons to C^1 and only 15% to C^3; thus, the cationic charge is found to reside primarily in the tertiary position (charge C^1: −0.09 e; C^3: 0.33 e).

Carbene complex **2b** has very little π-contribution from gold to C^1 (Figure 3). From the allylic π-IBO, 0.47 e are donated,
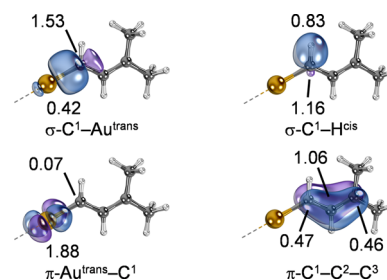

Figure 3. IBOs with contribution to C^1 and their electron distribution in compound **2b** (in e).

and only 0.07 e are donated from binding π-interaction with gold (very similar to $[(\text{Cy}_3\text{P})\text{AuCPh}_2]^+$).[47] With 1.53 e of the gold-coordinating σ-IBO of C^1 located at the carbon center, C^1 is found to be strongly negatively charged (charge C^1: −0.29 e). The C−H bond is found less polarized than in **1b**, with 1.16 e residing at C^1 compared to 1.19 e in the nonmetalated allylium cation **1b**.

μ-Allylium digold complexes **3** have more pronounced covalent σ-bonds compared to monogold references **2** (Figure 4); 0.46 and 0.47 e of the 2-electron σ-bonds are located at the gold centers in **3b**, respectively. Only 0.42 e were found for the single gold atom in **2b**. The IBO localization method confirms that two distinct σ-bonds from an sp^2-hybridized C^1 to the gold centers give a viable description of the σ-system (earlier data suggested that a 3-center 4-electron interaction with an
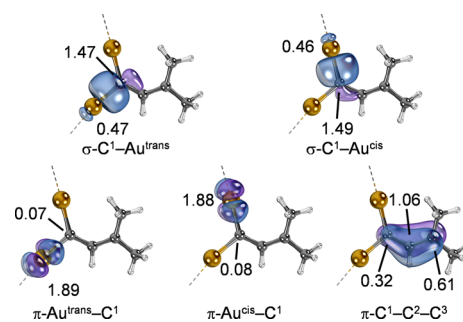

Figure 4. IBOs with contribution to C^1 and their electron distribution in compound **3b** (in e).

sp-hybridized C^1 would best describe the bonding in complexes **3**).[28] Interestingly, these complexes also show a slightly stronger π-backdonation of 0.07 and 0.08 e. One carbon center bridges the gold centers by simultaneously forming two carbene-complex-like dative bonds while accepting π-backdonation through a single orbital. Although sharing one carbon p-atom orbital for π-backbonding, no decreased carbene character is found in the digold sesquicarbene complexes.

The bonding situation of C^1 in reference carbene complex **6** seems similar to the one observed in the monogold allylium **2b**, even though the latter only has one π-stabilizing group conjugated (Figure 5). The two phenyl systems donate 0.23 e
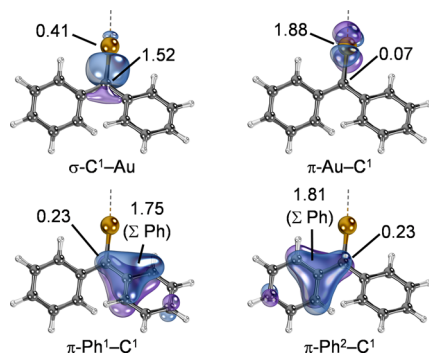

Figure 5. IBOs with contribution to C^1 and their electron distribution in compound **6** (in e).

each, introducing substantial stabilization. This is similar to the donation that the vinyl group alone gives in **2b** (0.47 e). In comparison, the observed shift of the cationic charge from C^1 to C^3 in **1b** is accompanied by a donation of 0.65 e, with 0.31 e remaining at C^3. Of the σ-bond, 0.41 e is located at the gold center; π-backdonation contributes 0.07 e to C^1. Interestingly, this is less than each of the gold centers of **3b** donates back indicating that both gold centers have a higher carbene character than the reference.

As expected, chromium donates electrons to C^1 much more strongly via π-interactions (Figure 6). While resulting complex
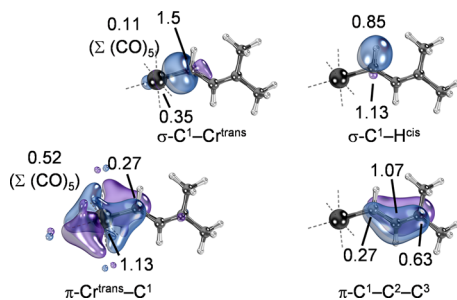

Figure 6. IBOs with contribution to C^1 and their electron distribution in compound **4b** (in e).

4b is formally neutral, an allyl IBO is still found; 0.27 e of it is located at C^1. This is the same amount of donation found for the π-donation of chromium. Only 0.35 e of the σ-bond between C^1 and Cr is located at chromium, indicating a lower grade of covalent character of this bond compared to the respective gold complexes.

Anionic dichromium complex **5b** shows an interesting structural discrepancy to all other complex groups discussed

before (Figure 7); with the strong σ- and π-donation from two chromium centers the allyl system is pushed back and acts as
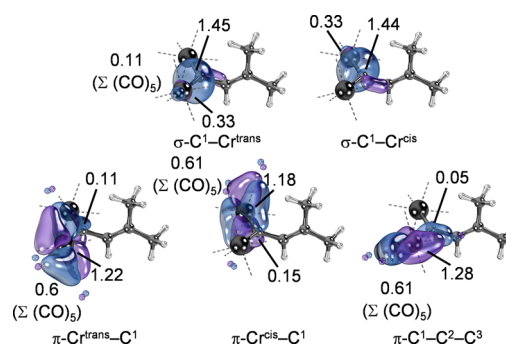

Figure 7. IBOs with contribution to C^1 and their electron distribution in compound **5b** (in e).

localized double bond in 2-position. **5a**−**e** lack allylic stabilization and even adopt geometries with the C^2−C^3 bond roughly orthogonal to the Cr−C^1 bonds. Similar to **4b**, only 0.33 e of the σ-bonds to C^1 are located at each of the chromium centers in **5b**. The *cis* chromium center only donates 0.15 e via π-bonding; the *trans* center distributed only 0.16 e among two π-IBOs. In striking contrast to digold complexes **3**, we found the chromium centers to share a similar amount of π-donation as found in the chromium carbene (**5b** total: 0.31 e, **4b**: 0.27 e). The individual Cr−C^1 bond is of roughly half the double-bond character of the monochromium analog, yet both of them still have a significant carbene character. Dichromium complexes **5** are sesquicarbene complexes with a much stronger carbene character than that of digold complexes **3**. They push the capabilities of this ligand class and show that stronger π-donor metals face limitations due to the finite π-acceptor capacity of the organic system.

Dichromium complex **5f** is the only example of the dichromium complexes **5** that adopted a planar structure (Figure 8); 66% of the total π-stabilization of C^1 is from the
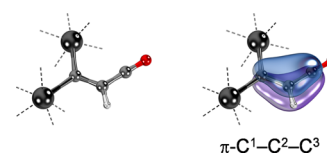
Figure 8. Structure and allyl IBO of compound **5f**.

allyl IBO (0.28 e). Only very little π-donation originates from the chromium centers (*trans*: 0.08 e, *cis*: 0.06 e); the latter is even less than from any of the gold centers in this study. C^1 (and the chromium atoms) still ends up far stronger negatively charged than the analogs in **5a**−**e**, with strong overall donation from the positively charged C=C=O unit (see also Figure 10b).

The comparison with reference diphenylcarbene chromium complex **7** reveals that the Cr−C^1 bond alone has a double bond character comparable to both chromium atoms in **5a**−**e** combined (Figure 9); 0.31 e are donated to C^1 via π-interaction. Interestingly, chromium's strong π-donation leads to one of the phenyl groups rotating out of plane just like it was computed for sesquicarbene systems **5**. The remaining phenyl in **7** donates 0.19 e via π-interactions with C^1 which is slightly less than the allylic donation found in **5b** (0.27 e). The
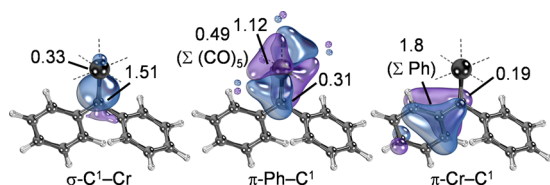
Figure 9. IBOs with contribution to C^1 and their electron distribution in compound **7** (in e).

σ-coordination is very polarized toward C^1 (0.33 e at Cr, 1.51 e at C^1); this is less donation to chromium than in **4b** and very similar to that in **5b**.

We generally found contributions to the stabilization of C^1 from the expected σ-bonds and from carbene π-backbonds. A 3-center, 2-electron allyl IBO constitutes the main π-electron donor of C^1. For this reason, the electronic structure of cations **3** and monoaurated and -chromated examples **2** and **4** are still best described as allyl compounds stabilized by one or two carbene-like coordinated metals.

The allyl IBO surprisingly is not necessary for stabilizing the sesquicarbene in dichromium complexes **5a−5e**. C^3 is rotated nearly orthogonally out of the plane with the chromium atoms in these complexes. The π-backbonds of the metal moieties outweigh the influence of the $C^2−C^3$ π-system strongly, so no conjugation with the π-orbitals at C^1 is detected. The former allyl system is found to be a localized double bond at the $C^2−C^3$ position, so steric pressure leads to rotation of this moiety out of the plane. Dichromium complex **5f** with the strongly electron-withdrawing carbonyl function is the only example of the six complexes, **5**, that adopted a planar structure to allow an allyl interaction. The π-system is sufficiently saturated to almost diminish π-acidity of C^1.

Partial Charges. Apart from the HH-substituted compounds, mainly C^3 carries the positive charge that is observed in the organic groups. This is dissipated to the metal moieties with increasing metal substitution (Figure 10).

C^1 is slightly negatively charged in **1b** (charge C^1: −0.09 e, charge C^3: 0.33 e). In **2b**, it is strongly negatively charged (C^1: −0.29 e), while a decreasing positive charge is found for C^3 (C^3: 0.26 e). This tendency continues for **3b**, giving rise to a −0.53 e C^1 charge and only a 0.14 e C^3 charge. Reference gold carbene complex **6** has a much lower negative charge on C^1 (−0.13 e). With the long Au−C bonds and well-known lack of Au−C π-bonding capability, the system mainly compensates the cationic charge through the σ-system reducing the necessity for π-stabilization. Relative to other gold carbene

complexes and to **2**, digold complexes **3** still show a significant double-bond character.

The same tendencies are true for the chromium complexes. **4b** (−0.26 e) has a less negatively charged C^1 than that of **5b** (−0.35 e). The charge of C^3 even shifts from 0.17 e to a negative charge (−0.05 e). The C^1 charge in reference complex **7** is only −0.11 e. With the introduction of a second chromium atom, the overall charge of the organic substituent $C{=}CR_2$ shifts to negative values. The total charge of these complexes being monoanionic leads to the former positive charge being mainly stabilized by the two chromium atoms. They even adopted a nonplanar geometry, and the net charge of −1 is almost evenly distributed between C^1 and the two chromium atoms.

C^1 is negatively charged in all examples, and metal substitutions have a strong impact on this tendency giving higher negative charges at C^1 due to the polarity of the dative σ-bonds and the additional backbond to the carbon center (Figure S1 and Table S3). Additionally, the (formal) cationic charge in sesquicarbene complexes is well-stabilized by resonance with the neighboring metal centers and the allylic system. The second gold atom in complexes **3** almost doubles this effect compared to that of complexes **2**, while a second chromium atom in **5** leads to only marginally increased negative C^1 charge with much of the negative charge residing at the metal atoms in these monoanionic complexes.

Absolute π-Electron Donation. We then took a perspective that isolates charge donation via π-bonds from the partial charge and compared the weight of the different mesomeric influences for the stabilization of the formal cationic charge on C^1. Therefore, we analyzed the electron donation to C^1 over the different π-IBOs that contribute to its valence (Figure 11, Table S2). The absolute stabilization, i.e., π-electron donation, must be kept in mind, as σ-donation of the metal centers dissipates parts of the polarization.

Throughout all complex classes, the largest relative π-stabilization originating from the metal centers is found for HH-substituted compounds **2a−5a**, and the smallest ones are found for 3-oxo compounds **2f−5f**.

The data for reference complexes **6** and **7** is in accordance with the strong difference of the tendency for π-donation of the metal units (IPr)Au and $(CO)_5Cr^-$. Only 17% of the total stabilization at C^1 originates from gold in **6**, while chromium in **7** even surpasses the contribution of the two phenyl substituents and contributes 62% of the π-donated electron density.
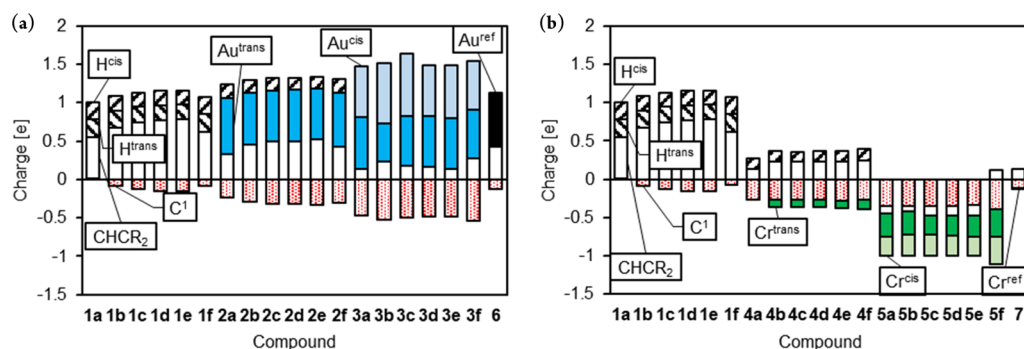

Figure 10. Partial charges of C^1, the metal centers (including ligand), and organic substituents in the gold complexes **2** and **3** (a) and chromium complexes **4** and **5** (b) in reference to **1** and **6** or **7**.
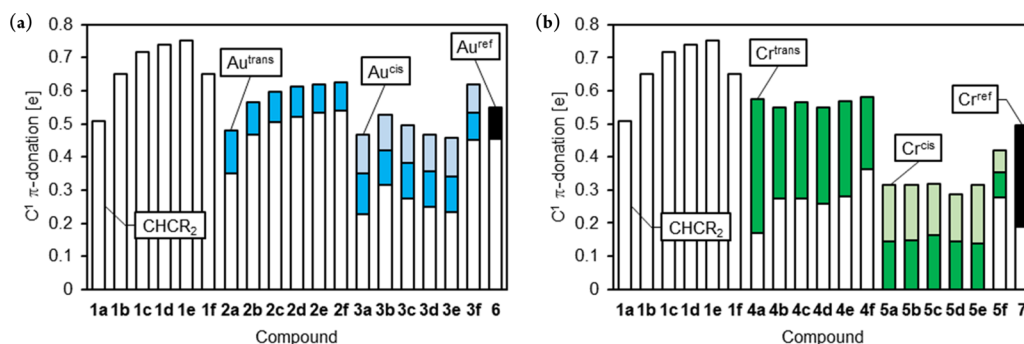
Figure 11. Absolute electron donation to C^1 via π-IBOs of gold complexes **2** and **3** (a) and chromium complexes **4** and **5** (b) in reference to **1**, **6**, and **7**.
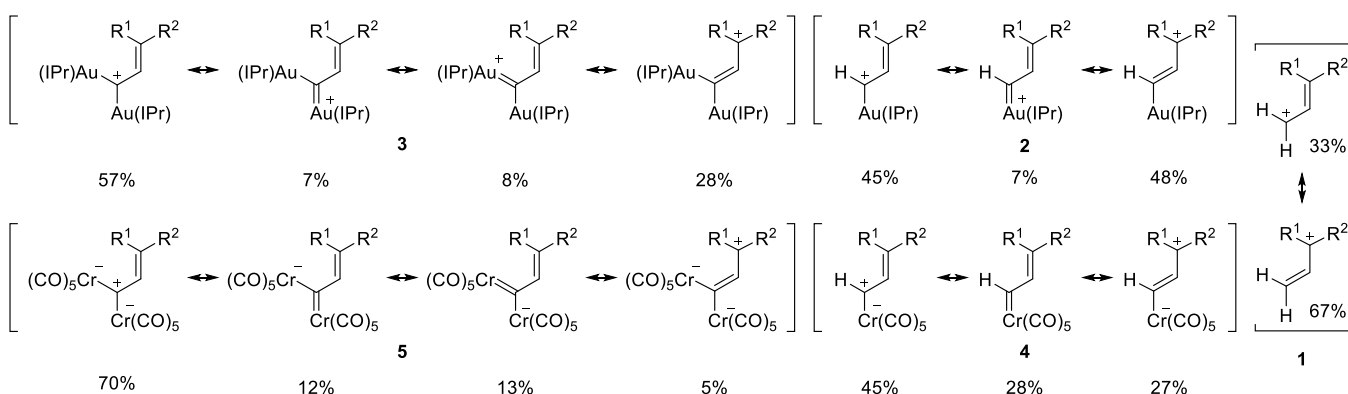

Figure 12. Absolute weight of the resonance structures stabilizing sesquicarbene complexes **3** and **5** in comparison to carbene complexes **2** and **4** and allylium cation **1**. The weights are derived from the absolute electron donation of π-IBOs to C^1. Minor π-contributions from the substituents R were omitted for clarity.

2a shows an exceptionally high relative contribution of gold (27%). The gold atoms of **2b**–**f** only contribute 17−13%, but the total π-stabilization is higher due to strong donation from the organic substituent. In most cases, the individual gold atoms of digold complexes **3** contribute more electron density via π-interactions than the respective gold atom of **2**. Roughly half of the stabilizing density at C^1 (51−41%) is donated from the combined gold π-orbitals (with the exception of **3f** with only 27%).

HH-Substituted chromium complex **4a** has a high carbene character with 70% of the π-electrons at C^1 originating from chromium. Complexes **4b**–**e** give roughly equal relative contributions from the chromium atom (50−53%) and the C═C unit. The 3-oxo species, **4f**, has a decreased donation from the metal center (37%). Complexes **5a**–**e** are structurally unusual with the organic substituent twisted out of the plane. No π-contribution from the C═C system is found for them. They have roughly a 1:1 contribution from the two chromium atoms (52−44% of the total π-donation). The combined contribution is only slightly higher than the contribution of the single chromium atom of respective complexes **4**. These complexes are monoanionic, and the chromium atoms with their low electronegativity donate strongly through the σ-system. This leads to a decreased backdonation through the π-system. **5f** is the only complex in which planar conformation of the organic moiety was found to be the most stable structure. Only 34% of the stabilizing electrons are from the chromium atoms, but it has by far the largest amount of overall π-contribution of complexes **5**.

We found that both gold centers in previously experimentally detected digold sesquicarbenes **3** have a double-bond character comparable to gold carbene complexes, averaging to 7% (*trans*) and 8% (*cis*) for the two bonds versus 7% in monogold complexes **2** (Figure 12). Hypothetical dichromium sesquicarbenes **5** have a reduced carbene character (*trans*: 12% and *cis*: 13%) compared to that of monochromated complexes **4** (28%), but exceeding gold by far in this respect. They participate in substantial π-backbonds for a significant carbene character at both centers.

Depending on the substitution pattern sesquicarbene complexes can range from 2- to 3-fold shared coordination of the carbon atom's π-orbital. The vinyl function offers an adaptive stabilization mechanism for the sesquicarbene unit which participates in a π-bond as long as only weak metal π-backdonation is present. When two $(CO)_5Cr$ units are present in the C^1 position without oxo-substitution in the C^3 position, the mesomeric stabilization of the vinyl domain is overweighed. It rotates out of plane to generate the sterically more stable rotamer.

Similar to *N*-heterocyclic carbene (NHC) ligands, sesquicarbenes act mainly as strong σ-donors. They are weak π-acceptors. As such, the most important resonance structure is the one lacking any resonance stabilization. The direct comparison to the IPr ligand that was employed in digold sesquicarbenes **3** reveals that they are far stronger σ-donors. On average, each of the gold centers receives 0.34 e from the NHC carbon σ-bonds and 0.45 e from the σ-bond to the sesquicarbene carbon.
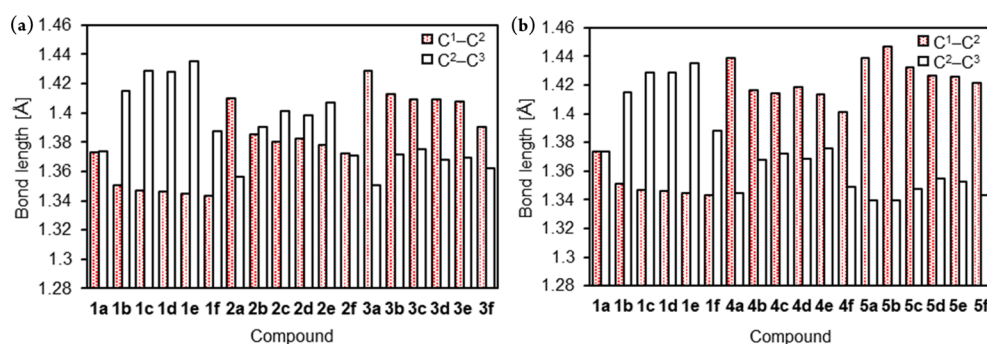
Figure 13. Bond lengths within the allyl system of **1** and gold complexes **2** and **3** (a) and of **1** and chromium complexes **4** and **5** (b).
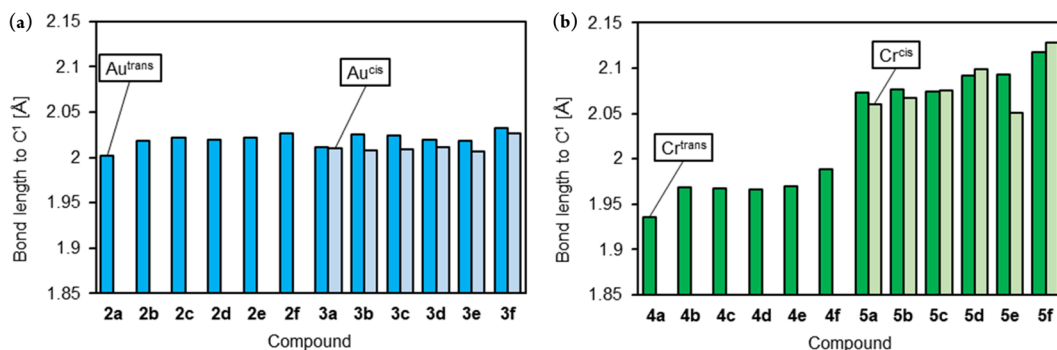

Figure 14. Bond lengths of the M−C bonds in gold complexes **2** and **3** (a) and in chromium complexes **4** and **5** (b).

Only 55% of the formal cationic C^1 charge is dissipated via π-interactions in the carbene complexes of both gold **2** and chromium **4**. For digold sesquicarbene complexes **3**, this is just 43% and for dichromium complexes **5** with their lack of allylic stabilization even only 30%.

Employing different metal centers in sesquicarbene systems strongly impacts the polarity of the π-system. Digold complexes **3** have a trilaterally mesomery-stabilized cationic π-system with only minor contributions from the gold centers (28% donation from the allyl system, 7 and 8% from the gold centers). The bridging carbon atom is electrophilic allowing for the addition of nucleophiles (also proven earlier by the addition reaction of DMSO to the C^1 of one of the complexes).[28] The bonding of anionic dichromium sesquicarbene complexes **5** is best described as shared π-backbond with a shared negative charge between the chromium centers. Stabilization by 1,3-bond shift of the allylic domain is almost negligible (5%). With their net negative charge, dichromium complexes **5** should act less electrophilic while the π-system remains polarized for nucleophilic attacks at C^1.

C−C Bond Length. The bond lengths in the allyl system support the notion of the localization of the π-bond in this system (Figure 13). The different organic substitution patterns **a**−**f** show a very similar impact on the different compound groups. **1a** is obviously symmetric, and any kind of C^3 substitution **b**−**f** leads to stabilization of the charge in C^3 position, indicated by shortened C^1−C^2 bonds. Ketene analogs **f**, however, show rather short C^2−C^3 bonds as well. This suggests mesomeric stabilization of a formal C^1−C^2 double bond, and thus partial double bonds in both bonds.

Introducing metal atoms (**2**, **3**, **4**, and **5**) generally shifts bond length from C^1−C^2 to C^2−C^3, which is consistent with the notion that increasing the carbene character of the M−C bonds pushes π-electron density to the resonance-favored C^2−

C^3 by donating density to the C^1 π-orbital. Double metalation increases this effect. In digold complexes **3**, and both in chromium **4** and dichromium complexes **5**, this leads to C^1−C^2 bonds that are longer than C^2−C^3 bonds. Compared to nonmetalated allylium ions **1**, this shows an inversion of the bond orders in the allyl system, pushing the double bond to the C^2−C^3 position with increasing carbene participation at C^1.

M−C Bond Length. Apart from electronic parameters, the bond lengths of the metal atoms to C^1 were analyzed to give an insight into the strength of the π-backbonding in complexes **2**−**5** (Figure 14). A limited variance is found for the different gold complexes with only 0.03 Å difference between the shortest bond in **2a** and the longest one to the gold atom in *trans* position of **3f**. Again, the carbonyl function stabilizes a C^1−C^2-located double bond, lengthening the bonds to the metal centers in all cases. For the chromium complexes, this range is 0.19 Å between **4a** and the *cis* center in **5f**.

The average bond length of gold complexes **2** is 2.02 Å, and for diaurated complexes **3** no difference is found (2.02 Å). No overall loss of carbene character is indicated here with the *trans* gold centers in **3** showing only insignificantly elongated bonds (mean 2.02 Å), while the *cis* centers compensate this with slightly shorter bonds (mean 2.01 Å).

Similar impacts of different C^3 substitution patterns are visible for the chromium complexes, but the average bond length in the chromium complexes increases strongly when comparing monochromium complexes **4** (mean 1.97 Å) with dichromium complexes **5** (mean 2.08 Å). Being much stronger π-donors, the allyl system cannot adapt sufficiently to accommodate full carbene bonding for both chromium centers.

M−C Bond Length/π-Backbonding Correlation. We found a correlation of the M−C bond lengths with the π-backbonding of the metal centers to C^1. Gold complexes **2**, **3**, and **6** cover only a limited bandwidth of bond strengths and

bond lengths over the different computed substitution patterns (Figures 15a and S2). In the observed region, both digold
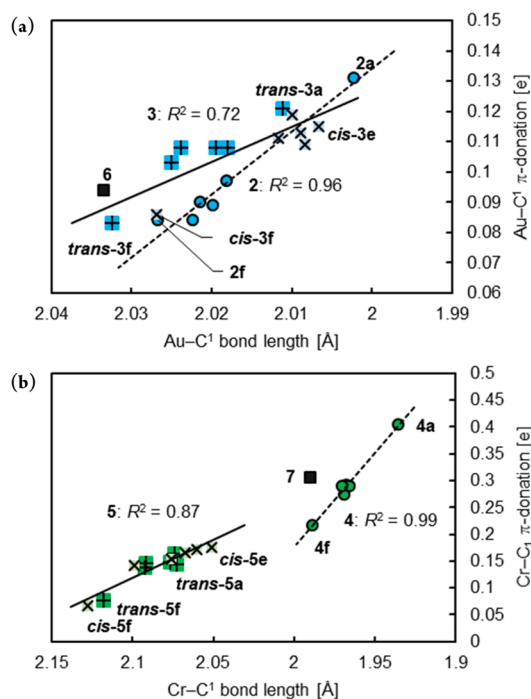

Figure 15. Correlation of M−C^1 bond length to the electron donation to C^1 via M−C^1 binding π-orbital in gold complexes **2**, **3**, and **6** (a) and chromium complexes **4**, **5**, and **7** (b). Solid lines: linear fit over **3**/**5**; dashes lines: linear fit over **2**/**4**.

complexes **3** and monogold complexes **2** show a linear correlation of the π-donation to the C^1−Au bond lengths (coefficients of determination R^2 = 0.72 and 0.96). With a slope of m = −1.15, digold complexes **3** show longer bonds which are shortened less with increasing π-donation. The fit for monogold complexes **2** has a slope of m = −2.08. Steric repulsion of the large gold atoms and their bulky ligands and electronic repulsion of the positively polarized gold centers dampen bond shortening with increasing bond order in digold complexes **3**. Otherwise, digold complexes **3** react in a manner very similar to that of monogold complexes **2** in different substitution patterns.

While sharing one carbon π-orbital, the majority of diaurated allylic carbocations **3** show stronger π-backbonding and shorter bonds compared to their monoaurated analogs **2** and to reference carbene complex **6**. Gold's weaker electron σ-donating properties compared to hydrogen results in an electron-poor C^1. This leads to the rise of carbene character of digold complexes **3**. Apart from oxo-substituted **3f**, interestingly, the *cis* C^1−Au bonds in **3** are almost not influenced by different substitution patterns. This implies that the stronger coupling to the *trans* gold center buffers the electronic impact of substitution.

Most of the gold complexes have stronger π-backbonds than carbene complex $[(\text{IPr})\text{AuCPh}_2]^+$ **6**. This holds true for the example $[(\text{Cy}_3\text{P})\text{AuCPh}_2]^+$ that was calculated similarly in the literature. The found π-backbond is weaker than that in the *o*-carborane diphosphine ligated carbene complex $[(\text{DPCb})\text{AuCPh}_2]^{+}$.[47,49]

Analysis of chromium complexes **4**, **5**, and **7** gave a very different picture (Figures 15b and S3). With decreasing bond

length, stronger bonding is required to introduce further shortening of the C−Cr bonds. Vice versa, the bond lengths merely elongate any further on the decreases of the backbond strengths at the lower end of the observed spectrum; the carbene character is considerably weakened in ketene-containing complex **5f**. Complexes **4** show short bonds and strong carbene characters, while major σ-donation and saturation of the π-system cause weak π-backdonation and long bond lengths in **5**. Each of the chromium atoms only donate around half of the electron density compared to the one in $[(\text{CO})_5\text{CrCPh}_2]$, **7**.[47,53,55] Compared to the gold analogs, dichromium complexes **5** react largely symmetrically to electronic changes in the system. At the same time, they show a much stronger dampening of the correlation between π-backbond and bond shortening. With a slope of m = −1.42, dichromium complexes **5** have less than half of the decrease of bond length with increasing π-donation as monochromium complexes **4** with a slope of m = −3.51 (coefficients of determination R^2 = 0.87 and 0.99). Their ligands are in intimate proximity of the ligands of the neighboring octahedral metal center, which explains the strong counterforce against bond shortening.

Interestingly, fitting this correlation for the whole ensemble of mono- and dimetal complexes demonstrates common trends. A linear fit describes the bond length−π-donation correlation in gold complexes **2**, **3**, and **6** (coefficient of determination R^2 = 0.68, Figure S2). The bonds of the *trans* gold centers in **3** seem to show the onset of a saturation effect with decreasing π-donation having marginally less impact on the length of the bond in the frontier region. Both monogold complexes **2** and **6** as well as digold complexes **3** show a comparable correlation of the bond lengths to π-backdonation. A third degree polynomial gives a good fit for chromium complexes **4**, **5**, and **7** (coefficient of determination R^2 = 0.96, Figure S3). This indicates a saturation effect: The bonding in dichromium complexes **5** is converging toward single bonds, while monochromium complexes **4** approach increasing repulsion caused by the carbonyl ligands. More importantly, this conceivable ensemble behavior hints at the similarity and comparability of carbene and sesquicarbene complexes once again. Both M−C bonds in sesquicarbenes largely act like carbene metal bonds. Saturation of the π-system and steric bulk lead to a flattened bond shortening response to increasing π-backdonation.

■ CONCLUSION

The electronic structures of the $[\text{M}_2\text{C(vinyl)}]^+$ (M = Au(IPr) and Cr(CO)$_5^-$) complexes investigated in this work is on the interface between M−C single bonds and M=C double bonds. The coordinating carbon atom acts as a significantly stronger σ-donor than the IPr ligand toward both metal centers. With these strong σ-donor properties available for two dative bonds, C^1 has similarity to carbodiphosphoranes and carbodicarbenes. The coordinating atom is an allylic carbon atom that donates σ-bonds to bridge two metal centers as a double L-type ligand. An empty π-orbital accepts π-backdonation from both metal centers and, in many cases, further resonance stabilization by the vinyl function (Figure 16). Incorporating two carbene-type dative bonds to both metal centers with only one carbon p-atom orbital accepting π-backbonds, these compounds can be described as sesquicarbene complexes.
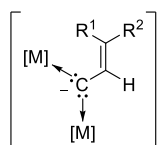
Figure 16. Simplified coordination scheme of sesquicarbene complexes.

A known reaction pattern of the digold complexes that first involves nucleophilic addition to C^1 is supported by the polarity of the π-system and leads to a tetrahedral sp³-carbon atom with two M—C single bonds which can be used for further transformations.[28] The electronic structure of sesqui-carbene complexes also implies promise for typical metathesis reactions. The adaptive behavior of the π-bonds should allow the substitution of one metal center either by a carbenoid or an alkylation pathway, making the respective transferred fragment an alkyl or a carbene complex that is ready for subsequent functionalization. We look forward to further experimental and computational investigation regarding the scope of the sesquicarbene concept toward further metals and substitution patterns and their application in the functionalization of allylic carbon atoms.

■ COMPUTATIONAL SECTION

Optimizations and single-point calculations were performed with the Q-Chem 5.2 quantum chemistry package.[50] Geometries were optimized at the PBEh-3c/def2-mSVP level of theory.[51] Single-point calculations at the ωB97M-V/def2-TZVP level of theory were then employed.[52,53] The effective core potential (ECP) def2-ECP was employed for the computational treatment of metal complexes and the solvent influence of methylene chloride ($\varepsilon = 8.51$) was modeled using the integral equation formalism polarizable continuum model (IEFPCM).[54−56] The canonical orbitals generated this way were then used as input for the generation of IBOs (exponent 2).[45,46]

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00102.00

    Computational details, optimized geometries, and intrinsic bond orbital data (PDF)
    Optimized geometries (XYZ)

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Notes

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