Carbene versus Carbenoid Hot Paper

International Edition: DOI: 10.1002/anie.201504117
German Edition: DOI: 10.1002/ange.201504117

Copper and Silver Carbene Complexes without Heteroatom-Stabilization: Structure, Spectroscopy, and Relativistic Effects**

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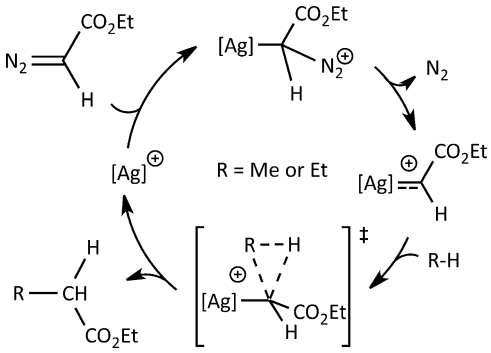
Abstract: *Salts of a copper and a silver carbene complex were prepared from dimesityl diazomethane, made possible by the steric shielding of the N-heterocyclic carbene (NHC) ancillary ligand IPr**. The mint-green complex $[IPr^{**}Ag{=}CMes_2]^+[NTf_2]^-$ is the first isolated silver carbene complex without heteroatom donor substituents. Single-crystal X-ray diffraction provides evidence for a predominant carbenoid character, and supports the postulation of such reactive species as intermediates in silver-catalyzed C–H activation reactions. The greenish yellow copper carbene complex $[IPr^{**}Cu{=}CMes_2]^+[NTf_2]^-$ has spectroscopic properties in between the isostructural silver complex and the already reported emerald green gold carbene complex. A comparison in the Group 11 series indicates that relativistic effects are responsible for the strong σ bond and the significant π back-bonding in the gold carbene moiety.*

The coinage metals copper, silver, and gold have influenced history, mythology, and religions of mankind for millennia.[1] Group 11 elements and their alloys are of tremendous technological and monetary importance owing to their unique physical and chemical properties.[2] As in no other group in the periodic table, relativistic effects play a decisive role in the chemistry of the copper triad elements.[3] The velocity of electrons in proximity to the gold nucleus is close to the speed of light, thereby increasing the mass of the electron, and leading to more compact s-orbitals with lowered energy.[4] As a consequence, the d orbitals of a gold atom are more diffuse and higher in energy than in the hypothetical non-relativistic case. The literally golden-yellow color of metallic gold is the result of the absorption of violet and blue light caused by the relativistically decreased energy gap between the 5d band and the Fermi level with 6s orbital character.[5] The comparison of copper, silver, and gold compounds sheds light on the impact of relativistic effects.[6] Isostructural mononuclear hexyne complexes of copper(I), silver(I), and gold(I) have already been prepared and structurally characterized by Dias and Kroll.[7] Carbene complexes display larger structural and spectroscopic differences than alkyne complexes, because carbene ligands without stabilization by heteroatom donor substituents interact more strongly with metal fragments. Some silver complexes catalyze the elimination of dinitrogen from diazoalkanes.[8] Silver carbene complexes are proposed as highly reactive intermediates in organic-synthetic catalysis, but they have remained elusive so far. The assumed mechanism for the silver(I)-catalyzed alkane functionalization by ethyl diazoacetate involves a highly electrophilic silver carbene complex that mediates the carbene transfer (Scheme 1).[9] Such



Scheme 1. Silver carbene complex as proposed intermediate in the silver(I)-catalyzed carbene insertion into an alkane C–H bond.[8a,9]

intermediates are also proposed for the carbene insertion in arenes to yield cycloheptatrienes.[10] Experimental and theoretical studies imply a silver carbene complex is responsible for the silver(I)-catalyzed [3+2] cycloaddition of several nitriles and diazoacetate to disubstituted oxazoles.[11] To our knowledge, only silver carbene complexes with strong donor substituents have been characterized in the condensed phase to date.[12] Concordantly, Pérez, Maseras and co-workers stated recently that such "highly reactive metallocarbene intermediates"… "are difficult to observe experimentally."[13]

Thus, we aimed at the synthesis of copper and silver carbene complexes that are isostructural to the recently published first gold carbene without heteroatom donor substituents.[14] We present herein the characterization of such transient species to advance the mechanistic understanding of homogeneous coinage-metal-catalyzed reactions, to help to unravel the ongoing "carbene versus carbenoid" controversy,[14,15] and to provide data for the quantification of relativistic effects. The sterically demanding IPr** ancillary ligand is perfectly suited as an ancillary ligand, because it efficiently shields reactive metal fragments.[16] The copper and silver bistriflimide complexes $\mathbf{1}_{Cu}$ and $\mathbf{1}_{Ag}$ are isostructural to

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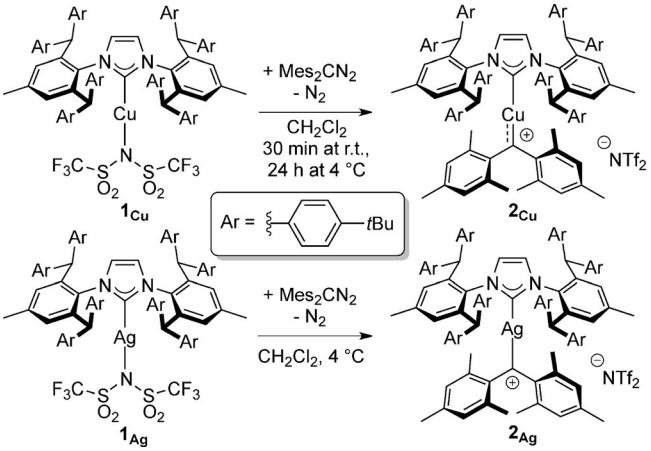
[+] Responsible for single-crystal X-ray diffraction analyses.

[**] Financial support by the Universität Heidelberg and the DFG is gratefully acknowledged.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201504117.

[IPr**AuNTf$_2$] ($\mathbf{1_{Au}}$)[14,16a] in the solid state, and react analogously with dimesityl diazomethane to give dinitrogen and the carbene complexes $\mathbf{2_{Cu}}$ and $\mathbf{2_{Ag}}$. The reaction of red dimesityl diazomethane[17] with colorless, air-sensitive [IPr**-CuNTf$_2$] ($\mathbf{1_{Cu}}$) in dichloromethane leads to the formation of a greenish yellow, diamagnetic, thermolabile, and water-sensitive copper carbene complex $\mathbf{2_{Cu}}$ (Scheme 2, first reaction). The analogous reaction of Mes_2CN_2 with colorless [IPr**AgNTf$_2$] ($\mathbf{1_{Ag}}$) in dichloromethane yields a mint-green, diamagnetic, light-sensitive, water-sensitive, and even more thermolabile silver carbene complex $\mathbf{2_{Ag}}$ (Scheme 2, second reaction). In contrast to the remarkable stability of the recently reported gold carbene complex $\mathbf{2_{Au}}$, the copper and silver analogues rapidly decompose under the conditions of column chromatography. Owing to competing decomposition processes, we were unable to find reaction conditions with a clean and quantitative conversion of diazoalkane substrate and bistriflimide complexes $\mathbf{1_{Cu}}$ and $\mathbf{1_{Ag}}$. The unstable carbene complexes generate species that catalyze the decomposition of the diazoalkane substrate. Despite these obstacles, optimized reaction conditions resulted in high concentrations of the carbene complexes $\mathbf{2_{Cu}}$ and $\mathbf{2_{Ag}}$ that were characterized by HR-ESI+ mass spectrometry, UV/Vis spectroscopy, and NMR spectroscopy.



Scheme 2. Preparation of copper and silver carbene complexes $\mathbf{2_{Cu}}$ and $\mathbf{2_{Ag}}$ without heteroatom stabilization.

The extreme reactivity and the thermodynamic lability of silver carbene complexes has been deduced from the nonformation of a silver methoxymethylidene complex in the collision-induced dissociation (CID) of *cis*-1,2-dimethoxycyclopropane with [IMesAg]$^+$ in the gas phase by Batiste and Chen.[18] Copper and gold cations yielded the analogous electronically stabilized methoxymethylidene complexes in the gas phase, supporting the quantum-chemically derived trend Ag < Cu < Au for the stability of Group 11 element carbene complexes.[18] Any attempt towards the crystallization of the thermolabile silver carbene complex $\mathbf{2_{Ag}}$ thus appeared to be a bold undertaking. We removed dichloromethane solvent in vacuo from the cold reaction mixture comprising $\mathbf{1_{Ag}}$ and $\mathbf{2_{Ag}}$, dissolved the residue in toluene, and added hexamethyldisiloxane to create a supersaturated solution. We obtained a single crystal of carbene salt $\mathbf{2_{Ag}}$ that was satisfactory for an X-ray diffraction study (Figure 1).

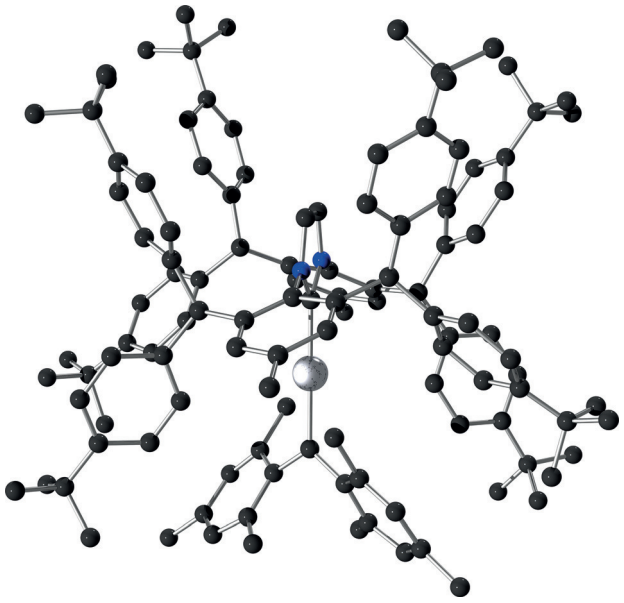


Figure 1. Simplified ball-and-stick model of the cationic silver carbene complex in salt $\mathbf{2_{Ag}}$ in the solid state.[19] Bistriflimide counterion, hydrogen atoms and two toluene solvent molecules have been omitted for clarity (CCDC 1050688). Bond lengths [pm]: Ag-C(IPr**) 199(3), Ag-CMes$_2$ 205(2). Bond angles [°]: C-Ag-C 177.7(8), N-C-Ag 131.9(15), 131.6(15), N-C-N 97(2), C(Mes)-C-C(Mes) 113(2). Angle sum [Ag]CMes$_2$ 359.8°.

As in the solid-state structure of the gold analogue $\mathbf{2_{Au}}$,[14] the mesityl substituents in $\mathbf{2_{Ag}}$ are twisted out of the silver carbene plane, thereby diminishing the resonance stabilization of the carbene by the aromatic π systems. The Ag–C(IPr**) bond is shorter than the Ag–CMes$_2$ bond by approximately 6 pm. This stands in sharp contrast to the isostructural gold carbene complex $\mathbf{2_{Au}}$, in which the Au–CMes$_2$ bond is slightly shorter than the Au–C(IPr**) bond ($\Delta d_{CAu} = 1.6$ pm). This situation reflects the marginal back bonding of silver to the dimesitylcarbene moiety, while gold features a significant [Au]=CMes$_2$ double bond character. Bent's rule applies to the carbene complexes **2** of all three metals M = Cu, Ag, and Au.[20] The more electronegative nitrogen atoms in the IPr** ancillary ligand and the larger M–C–N bond angles lead to a higher carbon 2s orbital percentage in the M–C(IPr**) σ bond than in the M–CMes$_2$ σ bond. We have already postulated these hybridization effects for gold complex $\mathbf{2_{Au}}$.[14] Complexes $\mathbf{1_{Ag}}$ and $\mathbf{2_{Ag}}$ show a characteristic $^{13}C\{^1H\}$ NMR pattern of the carbene signals resulting from the coupling of carbon-13 to the silver isotopes ^{107}Ag and ^{109}Ag (Figure 2). This coupling substantiates our line of argumentation for the analogous interactions of the IPr** ancillary ligand with the silver(I) ion and of the silver(I) ion with the dimesitylcarbene fragment. The carbenes' hybridization, that is, the 2s/2p ratio in the Ag–C bond, and silver's 5s percentage in the C–Ag σ bond correlate with the values of the respective $^1J_{CAg}$ coupling constants. Because of the weakly coordinating bistriflimide ligand, the silver ion in the precursor complex $\mathbf{1_{Ag}}$ donates more 5s character to the

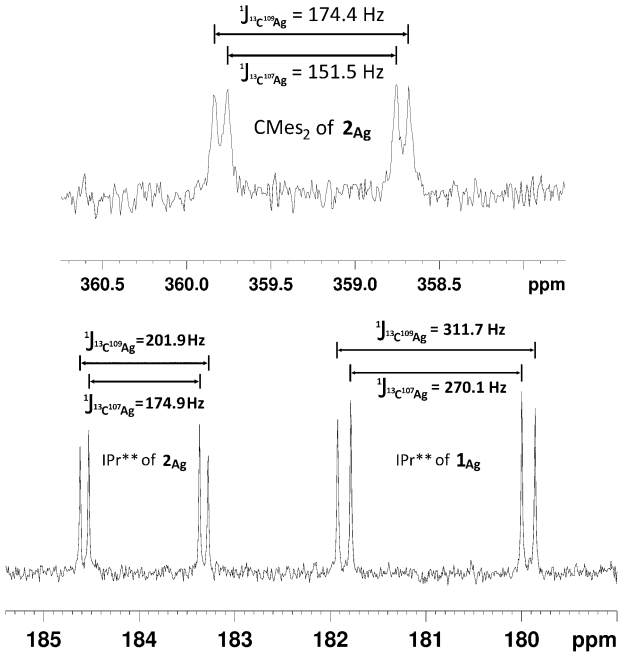


Figure 2. Sections of a $^{13}C\{^1H\}$ NMR spectrum (150.93 MHz, 283 K, CD_2Cl_2): dimesitylcarbene ligand signal of complex $\mathbf{2_{Ag}}$ with $^1J_{CAg}$ coupling of both silver isotopes ^{109}Ag and ^{107}Ag (top spectrum), and IPr** carbene signals of $\mathbf{2_{Ag}}$ (two doublets in bottom spectrum, left side) and of the residual precursor $\mathbf{1_{Ag}}$ (two doublets in bottom spectrum, right side)

IPr**-Ag bond than the silver ion in the carbene complex $\mathbf{2_{Ag}}$. This situation explains the increase of $^1J_{CAg}$ coupling constants in the order $Mes_2C{-}Ag$ ($\mathbf{2_{Ag}}$) < IPr**–Ag ($\mathbf{2_{Ag}}$) ≪ IPr**–Ag ($\mathbf{1_{Ag}}$).

The $^{13}C\{^1H\}$ NMR spectrum of $\mathbf{2_{Ag}}$ reflects the extreme electronic difference of the iminio ylide-type N-heterocyclic carbene ligand ($\delta = 184.0$ ppm) and the dimesitylcarbene ($\delta =$ 359.3 ppm, Figure 2). The carbon nucleus of the dimesitylcarbene is even more deshielded than that of the isostructural gold carbene complex $\mathbf{2_{Au}}$ ($\delta = 321.3$ ppm).[14]

The carbene signal of copper complex $\mathbf{2_{Cu}}$ at $\delta = 332$ ppm resides between those of the isostructural silver and gold complexes (Figure 3), providing evidence for the elimination of the diazoalkane substrate's dinitrogen. In contrast, Mankad and Peters have observed the coordination of the terminal nitrogen atom of dimesityl diazomethane to an uncharged bisphosphane copper(I) complex.[21]

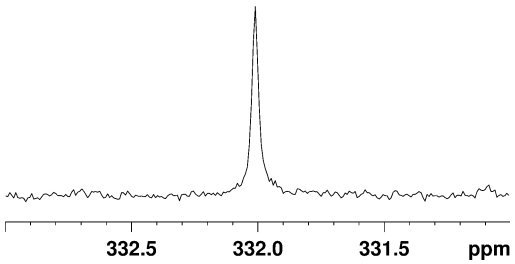


Figure 3. Section of the $^{13}C\{^1H\}$ NMR spectrum (150.93 MHz, 295 K, CD_2Cl_2) showing the dimesitylcarbene signal of copper salt $\mathbf{2_{Cu}}$.

We have established the bathochromic shift of the long-wave absorption band of gold carbene complexes as a good measure of their electronic carbenoid character, compared to complexes with an ylide-type carbene ligand or compared to the respective carbocation.[14] The formal replacement of the gold ion in carbene complex $\mathbf{2_{Au}}$ with a copper ion leads to a bathochromic shift of the absorption maximum from 642 nm to 730 nm in $\mathbf{2_{Cu}}$ (Figure 4). The silver analogue $\mathbf{2_{Ag}}$ even

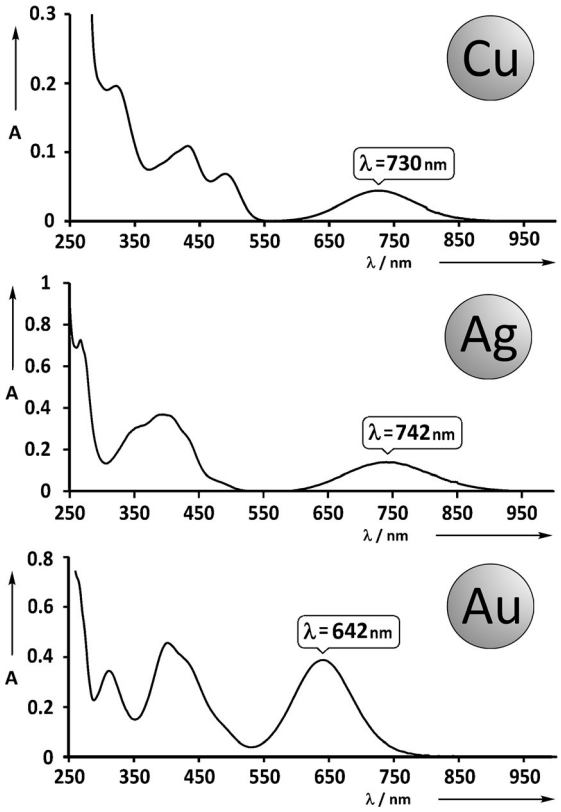


Figure 4. UV/Vis spectra of the reaction mixtures in dichloromethane of copper carbene complex $\mathbf{2_{Cu}}$ (top), silver carbene complex $\mathbf{2_{Ag}}$ (middle), and of gold carbene complex $\mathbf{2_{Au}}$ (bottom).[14]

features a broad absorption maximum at 742 nm. Absorption maxima, chemical shifts in ^{13}C NMR spectroscopy, and metal–carbon bond lengths concur with the carbenoid character of Group 11 element carbene complexes increasing in the order Au ≪ Cu < Ag.

We have performed TDDFT[22] calculations on optimized structures of the C_2-symmetric 1,3-dimethylimidazol-2-ylidene Group 11 element dimesitylcarbene cations in the gas phase at the M06/LACV3P** ++ level of theory[23] with the Jaguar software package.[24] The quantum-chemically computed absorption maxima reproduce the trend of the experimental values: the computed values are 591 nm for gold, 619 nm for copper, and 651 nm for silver. As already reported for the gold carbene complex,[14] the bathochromic absorptions for the copper and silver analogues essentially correspond to the electronic transition from the HOMO, which is based on an antibonding σ interaction of an sp^2-hybridized singlet carbene with a metal d orbital, into the LUMO, which

is dominated by the carbene's empty p orbital. For the simplified cationic copper and gold model complexes, the M=CMes$_2$ bond is slightly shorter than the NHC metal bond, while it is longer for silver—consistent with the crystal structures of the carbene complexes $\mathbf{2}_{Ag}$ and $\mathbf{2}_{Au}$.

The color of all three carbene complexes **2** with their d^{10} ML_2 electronic structure is green or greenish (Figure 5).

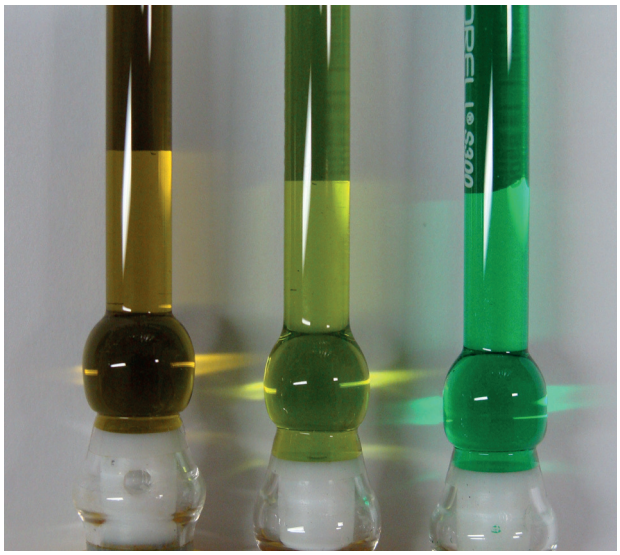


Figure 5. Characteristic colors of dichloromethane solutions of the new copper carbene complex $\mathbf{2}_{Cu}$ (left), of the new silver carbene complex $\mathbf{2}_{Ag}$ (middle) and of the already published gold carbene complex $\mathbf{2}_{Au}$ (right).[14]

Interestingly, imidophosphamidato and β-diketiminato copper carbene complexes[25] and a bisphosphane gold carbene complex[26] of the d^{10} ML_3 type are all violet or purple. The correlation of deshielded carbene carbons and high carbenoid character is equivalent to the correlation of shielded carbene carbon atoms and strong metal-to-carbene back-bonding. The ^{13}C NMR chemical shifts of uncharged copper carbene complexes feature more-shielded carbene signals ($\delta = 229.9$ ppm,[25a] $\delta = 253.1$ ppm,[25b] $\delta = 264.5$, 239.7, and 266.4 ppm,[25c] and six carbene complexes with α-carbonyl substituents and $219.0\ \text{ppm} \le \delta \le 235.8\ \text{ppm}$[25d]) than the copper complex $\mathbf{2}_{Cu}$ ($\delta = 332.0$ ppm) with its positive charge and its lower coordination number at copper. The identity of the Group 11 element, its coordination number, the nature and the charge of the ancillary ligand, and the π-donor strength of the carbene's substituents determine reactivity, stability, and the spectral properties of carbene complexes.

In summary, we have prepared and characterized the first d^{10} ML_2-type copper and silver carbene complexes without heteroatom stabilization.[27] The proposal of their role as short-lived and highly reactive intermediates in catalytic carbene transfer reactions is in accordance with the properties of the sterically stabilized carbene complexes observed in this study. The carbenoid character of Group 11 metal carbene complexes increases in the order Au ≪ Cu < Ag. The carbenoid reactivity of the copper and silver dimesitylcarbene complexes is reflected in their thermolability, their bathochromic light absorption, and in their carbenes' deshielded NMR chemical shifts compared to the isostructural gold complex. The strong Au–C σ bond and the significant Au=C back-bonding is consistent with a major impact of relativistic effects on gold's valence shell, that is, higher energy for gold's 5d orbitals and a lower energy for gold's 6s orbital. The copper carbene complex combines a still significant back-bonding and a weak σ bond, while the weak Ag–C σ bond and the marginal Ag=C back-bonding classify silver carbene complexes as metal-stabilized singlet carbene species.

Keywords: carbene · carbenoid · copper · relativistic effects · silver

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 10331–10335
Angew. Chem. **2015**, *127*, 10472–10476

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[27] Single-crystal X-ray diffraction analyses for $\mathbf{1}_{Cu}$, $\mathbf{1}_{Ag}$, and $\mathbf{2}_{Ag}$ CCDC 1050686 – 1050688.

Received: May 5, 2015
Published online: July 15, 2015

