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Transmetalation of Acyclic Tungsten Carbenes to Coinage Metals: Distinct Behavior of Silver toward Carbene Transfer and Hydrolysis

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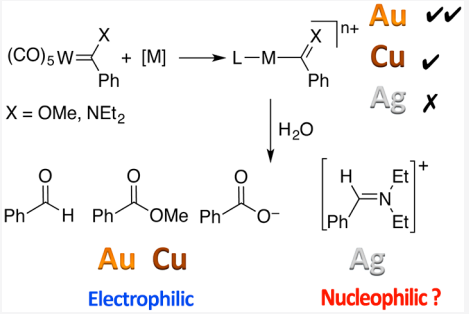
ABSTRACT: The transmetalation of acyclic monoamino and alkoxo carbenes from tungsten to group 11 metals has been studied for all three metals by analyzing the new metal carbenes formed and also their decomposition products in solution. The ease of transmetalation follows the trend Au > Cu > Ag, and the gold carbenes can be isolated: a copper carbene could be detected, but we found no experimental evidence of the formation of any silver carbene. The electrophilic character of copper and gold carbenes is supported by the identity of the products formed upon hydrolysis of the carbenes involved. Silver shows a distinct behavior, and the presence of Ag^+ ions in an acetonitrile solution of a tungsten aminocarbene leads to the formal protonation of the carbene fragment to give an iminium salt. This outcome, a seemingly nucleophilic behavior, is unexpected for group 11 carbenes, but DFT calculations show that the protonation of a putative cationic silver carbene is energetically accessible.



INTRODUCTION

The carbene chemistry of group 11 metals spans from the useful and robust spectator N-heterocyclic carbene (NHC),[1] diamino-type carbene (NAC),[2] and cyclic alkylamino carbene (CAAC) ligands,[3] widely used in catalysis, to the reactive carbene fragments from diazo derivatives or other precursors, used as reagents and incorporated into the products. All group 11 metals are involved in catalytic reactions that may form intermediate reactive metal carbenes in one of the steps of the process.[4] For example, the mechanisms of alkene cyclopropanation,[5] carbene insertion reactions into C−H bonds of alkanes,[6] coupling reactions of diazo compounds,[7] and the Wolff rearrangement[8] involve the formation of elusive metal−carbene species from the diazo derivatives used as reagents and this has been supported by DFT calculations.[9] Cycloheptatrienes as carbene precursors by a retro-Buchner reaction have been used in a gold-catalyzed cyclopropanation reaction with the likely participation of a gold carbene species.[10] Even if no reactant carbene source is present, many gold-catalyzed transformations of unsaturated compounds are explained by the formation of reactive species that can be considered gold−carbenes with more or less metal stabilized carbocation character.[11] This subject has been discussed in the literature, and efforts have been made to synthesize and study nonstabilized gold carbenes that could give information about the nature of those complexes.[12] As a result, a number of weakly stabilized AuCRR′ carbenes (R = R′ = hydrocarbyl, H) have been reported and their structures analyzed.[13] Nonstabilized carbenes of copper are even more elusive than gold carbenes, but nonetheless examples of CuCRR′ derivatives have been reported.[14] Only one example of a monomeric silver carbene has been disclosed.[14g] In general, those studies show that the M−C(carbene) bond length conforms to a single bond and that the metal to carbene back-bonding is quite small or often negligible.

There is still a lot to learn about reactive group 11 metal carbenes, and there are few studies that compare the behavior of the three metals toward the same carbene fragment and reaction conditions.[9a,14g,15] When there are enough data, structural or otherwise, to compare the three metals, significant differences between them and deviations from a periodic behavior are found. The work we describe here explores the formation of group 11 metal complexes with C(X)R carbenes (X = NR_2, OR) by transmetalation reactions from tungsten carbenes. Since the X group is electron donating and is capable of partially compensating the electron deficiency on the carbene carbon, an intermediate reactivity is expected for the M−C(X)R fragments, in comparison to NHCs or CRR′ groups (Scheme 1).[16] It might be useful to get information about the character and reactivity of the carbenes formed by all three metals. This strategy has been used before by us in the study of the reactivity of palladium carbenes and their migratory insertion reactions.[17] Transmetalation of monoamino or monoalkoxo carbenes between group 6 and another

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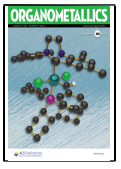

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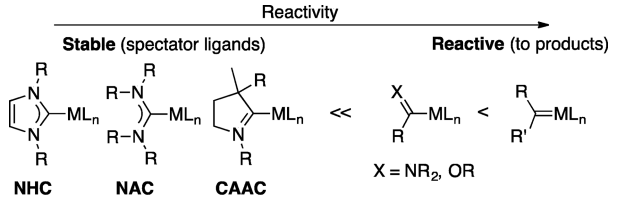
Scheme 1. Reactivity Trend for Metal Carbenes

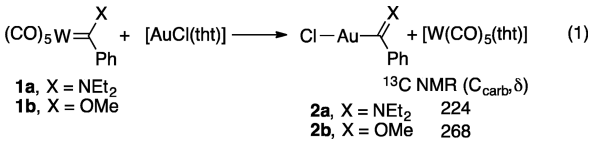


transition metal is often the synthetic method of choice for these unstable carbene fragments that are difficult to generate by other means.[18] There are some examples of this reaction involving group 11 metals that have led to the successful isolation of copper[19] and gold monoheteroatom-containing carbenes.[20] With these precedents we have analyzed and compared the behavior of analogous precursor complexes of Cu, Ag, and Au toward tungsten C(X)R′ carbenes (X = NR_2, OR), for both transmetalation and their hydrolysis reactions.

RESULTS AND DISCUSSION

The direct transmetalation of the tungsten carbenes was tested using neutral and cationic group 11 precursor complexes with weakly coordinated ligands that could favor the carbene for ligand substitution. [MCl(tht)] (M = Cu, Ag, Au; tht = tetrahydrothiophene) and $[Cu(MeCN)_4]PF_6$, $[Au(MeCN)_2]BF_4$, and $AgBF_4$ in acetonitrile were reacted with $[W(CO)_5\{C(X)Ph\}]$ (X = NEt_2, **1a**; X = OMe, **1b**). The results obtained for each metal are described below.

Synthesis and Reactions of Gold Carbene Complexes. The gold(I) carbenes **2a** and **2b** were synthesized in good yields by direct and smooth transmetalation from the tungsten(0) carbenes **1** to [AuCl(tht)] in either CH_2Cl_2 or acetonitrile at room temperature (eq 1).[16] On comparison of



2a and **2b**, the $^{13}C_{carbene}$ NMR resonance is 44 ppm higher for the alkoxocarbene, in agreement with the higher electrophilic character expected for this carbene (**2b**) vs the aminocarbene **2a**.

The X-ray crystal structures of **2a** and **2b** were determined, and they show two independent molecules in the unit cell (see the Supporting Information).[21] Both complexes show a linear coordination for the gold center, where the Au−$C_{carbene}$ bond distances conform to the typical range reported before for gold carbenes[20b−f,21] and are consistent with a single bond between an sp^2 carbon atom and the metal (Figure 1).[22] The C−X bond lengths are short and show a double-bond character as a result of the lone pair donation from X to the electrophilic carbene carbon. Therefore, the representation used for the group 11 carbenes in eq 1 and throughout the paper reflects these structural parameters and bonding situation.[16] Aurophilic interactions with an adjacent molecule are weak for **2b** (Au−Au distance 3.4481(2) Å) and even less important for **2a** (shortest Au−Au distance 3.6762 Å).[20f] The alkoxocarbene exhibits the so-called *anti* conformation, with the methyl group oriented toward the gold center, as observed before in other transition-metal Fischer alkoxocarbene complexes.[20f,23] The planar arrangement for the phenyl ring may indicate some

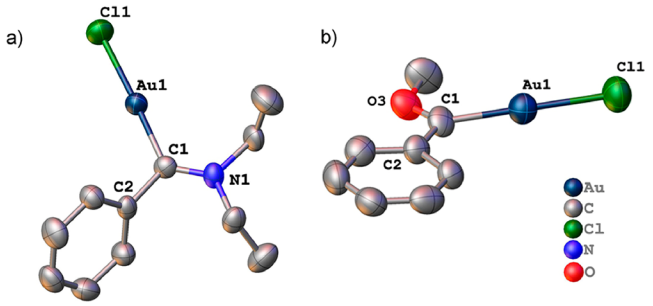
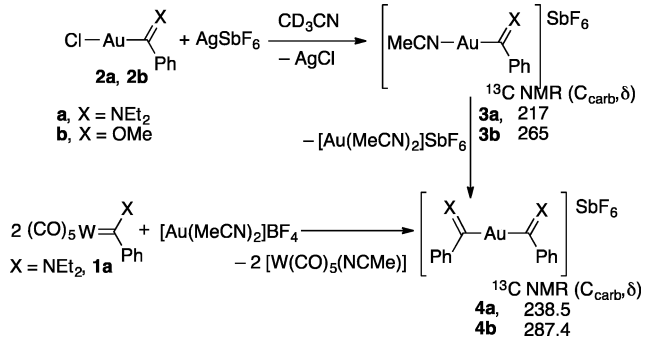


Figure 1. Molecular structures of complexes **2a** (a) and **2b** (b) (ORTEP plots; 40% probability ellipsoids). Hydrogens have been omitted for clarity. Selected distances (Å) and angles (deg): **2a**, Au1−C1, 1.985(5); C1−N1, 1.295(6); Cl1−Au1−C1, 177.62(14); **2b**, Au1−C1, 2.000(13); C1−O3, 1.277(13); Cl1−Au1−C1, 179.3(3).

involvement in the stabilization of the electrophilic carbene, but this is lost in solution, where free rotation of the ring occurs, as shown by its ^1H NMR pattern.

The reaction of the neutral gold carbenes **2a** and **2b** with $AgSbF_6$ in acetonitrile led to their complete conversion to the corresponding cationic Au(I) carbenes **3a** and **3b**. Unfortunately, their isolation was not possible, but they were stable enough to be characterized by NMR. Even at low temperature, both complexes slowly evolve in acetonitrile solution to new species which were identified as the cationic Au(I) bis-carbenes **4a** and **4b** (Scheme 2). A faster reaction rate for the

Scheme 2. Formation of Cationic Gold Carbene Derivatives



rearrangement to the bis-alkoxocarbene was observed in comparison to the amino analogue. The identity of the Au(I) bis-carbenes was supported by the reaction of different amounts of the tungsten monoaminocarbene **1a** with 1 equiv of the cationic Au(I) complex $[Au(MeCN)_2]BF_4$. When the reaction was carried out using equimolar amounts of Au and W complexes, both mono- and bis-carbenes were formed (100% conversion of **1a**; **3a**:**4a** = 5:1 molar ratio after 10 min in solution at 25 °C). On the other hand, only the bis-carbene complex **4a** was formed by the addition of 2 equiv of **1a** (Scheme 2). ^{13}C NMR reveals significant shifts in the carbenic carbon signals depending on the other ligand coordinated to the gold center, and thus, in comparison to the chloro (**2**) or acetonitrile (**3**) derivatives, the higher trans influence of the carbene fragment (**4**) is patent in the higher downfield shift observed (Schemes 1 and 2).

The formation of the bis-carbene complexes was also observed by the transmetalation of the alkoxocarbene from **1b** to the cationic gold(I) aminocarbene **3a** (generated in situ from **2a** as shown in Scheme 2). The reaction involves the

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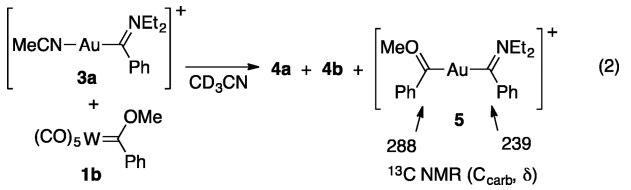
exchange of both carbene fragments and a mixture of the homoleptic biscarbenes **4a**, **4b** was observed along with the new mixed complex **5**, bearing two different carbene moieties (eq 2).



The reactivity of the neutral Au(I) monoamino- and alkoxocarbenes in the presence of acids or bases was studied (eq 3).

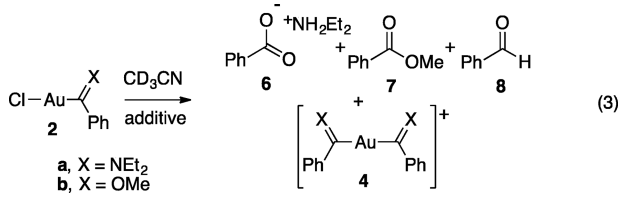


Table 1. Hydrolysis Reactions of Gold Carbenes[a]

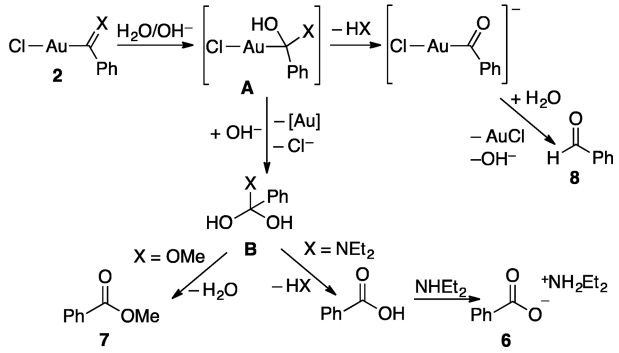
				conversion (%)			
entry	[Au]	additive	conditions	6	7	8	4
1	**2a**		days, 50 °C				
2	**2a**	H_2O[b]	days, 50 °C				
3	**2a**	NBu_4OH[c]	1.5 h, 25 °C	78			
4	**2a**	$HBF_4.OEt_2$	24 h, 25 °C				19
5	**2b**		48 h, 25 °C		5		
6	**2b**	H_2O[b]	5 min, 25 °C		15	64	
7	**2b**	NBu_4OH[c]	1.5 h, 25 °C		80		
8	**2b**	$HBF_4·OEt_2$	24 h, 25 °C		24		59

[a]Reaction conditions: 0.014 mmol of **2** in 0.6 mL of CD_3CN, 0.014 mmol of additive. Conversions were determined by ^1H NMR. [b]Addition of two drops of water. [c]Solution in MeOH.

Table 1 collects the phenyl-containing products formed, which give a complete account of the fate of the carbene fragment; the concomitant formation of other byproducts such as methanol of diethylamino derivatives also occurs (see below). **2a** is stable in solution and remains unchanged for days at 50 °C (entry 1, Table 1). No trace of hydrolysis products was detected even in the presence of water on heating at 50 °C (entry 2, Table 1). The addition of NBu_4OH to a solution of **2a** in CD_3CN led to the formation of benzoate (**6**) (entry 3, Table 1). On the other hand, the gold(I) alkoxocarbene **2b** is less stable and undergoes faster hydrolysis, leading to methyl benzoate (**7**), benzaldehyde (**8**), and MeOH as products (entries 5–7, Table 1). It is worth noting that a change in color of the solution from yellow to purple is usually observed with time, indicating the common decomposition to Au nanoparticles. The reactivity of the Au(I) carbenes toward a strong Brønsted acid such as HBF_4 was also explored, revealing that both alkoxo and amino carbenes lead to the corresponding cationic bis-carbenes **4** (entries 4 and 8, Table 1) with little or no decomposition of the carbene fragment; the higher reactivity of the alkoxocarbene leads to a higher conversion and eventually to some methyl benzoate as byproduct.

These reactions show the electrophilic character of the carbene carbon in these gold complexes, more pronounced for the alkoxocarbene than the aminocarbene. The hydrolysis of Fischer carbenes is well-documented in other transition-metal carbenes, and the mechanism for the hydrolysis of group 6 metal carbenes was deeply studied by Bernasconi et al. and others.[24] The results described in Table 1 suggest that a similar mechanism may operate for the electrophilic Au(I) Fischer carbenes. The reaction is believed to proceed in two stages involving a tetrahedral intermediate (**A**, Scheme 3) as a result

Scheme 3. Hydrolysis Processes for Gold Carbenes 2[26]



of a nucleophilic attack on the carbenic carbon. At this point, two different pathways are possible according to the concentration of OH^-. At low concentrations, the elimination of HX and the formation of the Au(I) acyl is faster than a second nucleophilic attack.[25] The subsequent hydrolysis with water provokes a demetalation, leading to benzaldehyde (**8**). At higher OH^- concentrations, the second nucleophilic attack on the former carbenic carbon is favored, resulting in the formation of the *gem*-diol **B** (Scheme 3). According to the nature of the substituent, when X = OMe, the elimination of water occurs, leading to methyl benzoate (**7**), while the formation of the carboxylate **6** indicates the elimination of HX as observed if X = NEt_2.

Reactions of Tungsten Carbenes with Ag and Cu Derivatives. A new carbene was detected during the reaction of the tungsten aminocarbene **1a** with [CuCl(tht)] in acetonitrile at room temperature (Scheme 4). The slow transmetalation (10% in 24 h at room temperature) prevented the isolation of the copper(I) carbene. Only a maximum conversion of 50% to **9** was achieved by heating at 50 °C due to its competing decomposition to benzaldehyde (**8**, 25%) and $NHEt_2$ under these conditions (entry 2, Table 2). NMR characterization of **9** revealed a ^{13}C shift at 239.8 ppm,

Scheme 4. Reactions of Cu and Ag Complexes with 1a

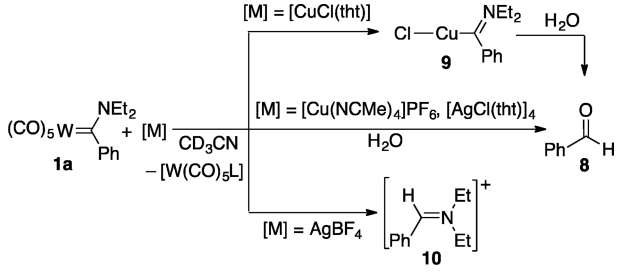


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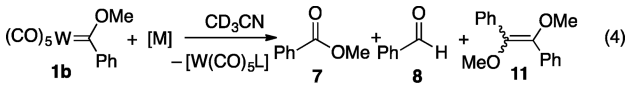
Table 2. Reactions of Carbenes 1 with Cu and Ag Complexes[a]

				conversion (%)				
entry	[W]	[M]	time	M-carb	7	8	10	11
1	**1a**		days			15		
2	**1a**	[CuCl(tht)]	4 h	50 (**9**)		25		
3	**1a**	$[Cu(MeCN)_4]PF_6$	24 h			51		
4[b]	**1a**	1/4 $[AgCl(tht)]_4$	24 h			13		
5	**1a**	$AgBF_4$	24 h				72	
6	**1b**		24 h		5	13		
7	**1b**	[CuCl(tht)]	24 h		19	4		77
8	**1b**	$[Cu(MeCN)_4]PF_6$	3 h		24	66		
9[b]	**1b**	1/4 $[AgCl(tht)]_4$	24 h		2	22		
10	**1b**	$AgBF_4$	30 h		9	18		

[a]Reaction conditions: 0.022 mmol of **1a** and 0.022 mmol of [M] in 0.6 mL of CD_3CN at 50 °C. Conversions were determined by ^1H NMR. [b]The same results were obtained using $[AgBr(tht)]_4$.

deshielded by 16 ppm in comparison to the analogous neutral gold(I) carbene **2a** (224 ppm). Attempts to isolate **9** or to obtain suitable crystals for X-ray diffraction from the reaction mixture failed, and the two-coordinated Cu(I) complex represented in Scheme 4 is tentative. DFT calculations show that the formation of **9** and $[W(CO_5(tht)]$ is thermodynamically favored and the associated free energies for the process are very similar for the two-, three- or four-coordinated Cu(I) complexes $[CuCl(carbene)(MeCN)_n]$ (n = 0, 1, 2; ΔG = −6, −6.4, and −7.5 kcal mol^{-1}, respectively, see Table S4 in the Supporting Information). Therefore, the formation of solvento three- or four-coordinated complexes, most probably in equilibrium with the dicoordinated complex in acetonitrile solution, cannot be ruled out. The lability of the ligands in three-coordinated cationic copper carbene complexes has been studied before.[27]

The reaction of **1a** with $[Cu(MeCN)_4]PF_6$ led to hydrolysis products (Scheme 4 and entry 3, Table 2) with no detection of a cationic Cu(I) carbene intermediate. Similarly, no trace of new carbenes was observed when the tungsten alkoxocarbene **1b** was reacted with Cu(I) complexes (eq 4). The addition of

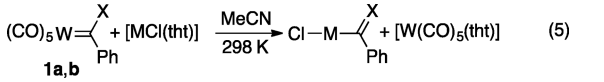


$[Cu(MeCN)_4]PF_6$ leads to decomposition to the hydrolysis products, by the same routes depicted in Scheme 3. The carbene dimerization derivative **11** (mixture of cis and trans isomers) was obtained as the major product if $[ClCu(tht)]$ was used (eq 4 and entries 7 and 8, Table 2). It is known that some Cu complexes,[18b,19,28] as well as other transition-metal derivatives,[18a,29,30] promote this carbene homocoupling in good to excellent yields.

No trace of a new metal carbene complex was observed by direct transmetalation from the tungsten(0) carbenes **1** to $[AgCl(tht)]_4$ or $AgBF_4$ in acetonitrile. Moreover, the decomposition data in Table 2 shows that the presence of $[AgCl(tht)]_4$ does not affect the decomposition rate of **1a** (cf. entries 1 and 4, Table 2), and a similar behavior was observed for the reaction of either $[AgCl(tht)]_4$ or $AgBF_4$ and **1b** (cf. entries 6, 9, and 10, Table 2). In contrast, the presence of copper strongly affects the decomposition of the tungsten derivatives **1** (cf. entries 1−3 and 6−8, Table 2), which points to the transfer of the carbene fragment to Cu (observed in the formation of **9** or undetected for other precursor complexes) and the lack of transmetalation for silver.

However, the reaction of **1a** with $AgBF_4$ revealed an interesting reactivity because of the unexpected formation of the iminium salt **10** when the mixture was heated at 50 °C in acetonitrile (Scheme 4 and entry 5, Table 2). Other silver salts AgY with weakly coodinating anions led to the same product but, in general, proved to be less efficient in the decomposition of the carbene fragment. Under the same conditions of entry 5, Table 2: AgOTf, 69% **10**; $AgSbF_6$, 45% **10**; AgOTs, 34% **10**; AgTFA, 27% **10**, 28% **8**. The formation of the iminium salt **10** from a metal carbene is a formal protonation of the carbene carbon, a very unusual reaction for the electrophilic Fischer carbenes involved in these reactions, as will be discussed below.

Comparison of the Behavior of Group 11 Metals toward Transmetalation. The experimental results described above indicate a clear trend in the ease of transmetalation from tungsten to group 11 metals: Au > Cu > Ag. The same trend is observed in the thermodynamic parameters of the whole transmetalation processes, as shown in eqs 5 and



6, calculated by DFT and collected in Table 3 (see the Experimental Section for details). The formation of the dicoordinated group 11 carbene complex was considered in all cases for comparison. Other coordination numbers were also explored in the reagents ($[M(MeCN)_n]^+$) and products, but the resulting energy values do not alter the observed trend (see above and Tables S4 and S5 in the Supporting Information). The transmetalation of the amino carbene group from complexes **1a** to both neutral and cationic group 11 metal complexes is thermodynamically more favored than the transmetalation of the alkoxo carbene group from **1b**. For every combination of analogous reactants, the values in Table 3 show that, as far as thermodynamics is concerned, the ease of transmetalation follows the trend Au > Cu > Ag. These results are in agreement with the complete carbene transfer

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Table 3. Calculated Free Energies for the Formation of the Group 11 Metal Carbenes[a]

entry	X	[M]	ΔG (kcal mol^{-1})	M-carb[b]
1	NEt_2	[CuCl(tht)]	−6	**9**
2	NEt_2	[AgCl(tht)]	−0.23	
3	NEt_2	[AuCl(tht)]	−9.3	**2a**
4	OMe	[CuCl(tht)]	+1	
5	OMe	[AgCl(tht)]	+7.4	
6	OMe	[AuCl(tht)]	−2.9	**2b**
7	NEt_2	$[Cu(NCMe)_2]^+$	−3.9	
8	NEt_2	$[Ag(NCMe)_2]^+$	−2.1	
9	NEt_2	$[Au(NCMe)_2]^+$	−16.3	**3a**
10	OMe	$[Cu(NCMe)_2]^+$	+4.3	
11	OMe	$[Ag(NCMe)_2]^+$	+5.3	
12	OMe	$[Au(NCMe)_2]^+$	−9.2	**3b**

[a]DFT calculations according to eq 5 and 6. [b]Isolated (**2**) or characterized in solution (**3**, **9**).

experimentally observed for gold in every case, whereas the formation of a copper carbene complex is observed in only one of the examples corresponding to the reaction in entry 1, Table 3. Nonetheless, the more reluctant formation of carbene **9** (M = Cu, 10% in 24 h) in comparison to **2a** (M = Au, complete conversion in 30 min) must have a kinetic origin, since the free energy values for both reactions are not too far apart (entries 1 and 3, Table 3). No silver carbene was detected and, as shown in Table 2 (entries 4, 9, and 10), the extent and rate of decomposition of the starting tungsten carbenes do not indicate the intermediacy of a more reactive metal carbene. One exception is the reaction of $AgBF_4$ with **1a** (entry 5, Table 2), which shows a distinct and faster decomposition pattern and corresponds to the energetically most favorable transmetalation process calculated for silver (entry 8, Table 3).

Heterobimetallic intermediates with bridging carbenes have been experimentally detected and/or isolated by Fürstner et al. during the transmetalation of chromium or tungsten carbenes to gold[13b,20d] and calculated by Sierra et al. for the transmetalation of carbene fragments from chromium to palladium, copper, or rhodium.[18b] Thus, we decided to calculate the analogous heterobimetallic intermediates for the transmetalation of **1a** to $[M(CH_3CN)_2]^+$, where M = Ag, Au. This is the process that shows the lowest free energy among those transmetalations that involve silver and also a distinct reactivity pattern. The reactivity observed for the carbene fragment could derive from a complete transfer of the carbene to silver or from an arrested transmetalation to give a bimetallic intermediate with a bridging carbene. The intermediates **1a-M** (M = Ag, Au) depicted in Figure 2 were found, where M interacts with the carbenic carbon and one of the carbonyl groups of the tungsten center. The Au−$C_{carbene}$ distance in the calculated **1a-Au** (2.784 Å) is longer than the Au−CO distance (2.245 Å), indicating an important interaction of the gold center with one of the carbonyl groups. In comparison with this derivative, the intermediate **1a-Ag** shows similar distances between the metal and both fragments (Ag−$C_{carbene}$, 2.594 Å; Ag−C(O), 2.544 Å). The calculated energy values for **1a-M** (M = Au, Ag) are not very different but suggest again that the transmetalation of the tungsten monoaminocarbene to silver is less favored in comparison to gold since the silver heterobimetallic intermediate is about 3 kcal mol^{-1} higher in energy than the gold analogue.[31]

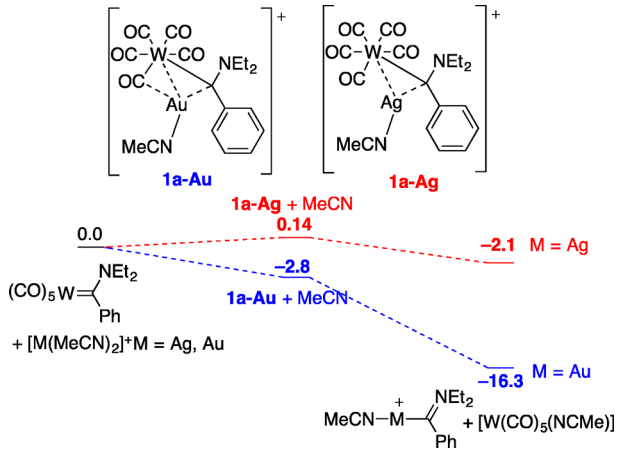

Figure 2. Calculated bimetallic intermediates in the transmetalation pathway (ΔG, kcal mol^{-1}).

Electrophilic Character of the Group 11 Metal Carbenes and the Role of Silver in the Formation of the Iminium Salt 10. The hydrolysis products observed for the gold carbenes or the reactions of the copper derivatives with **1** are consistent with the expected reactivity of an electrophilic carbene: i.e., a carbene fragment bound to a late-transition-metal fragment with no or very weak back-donation ability. We calculated the three analogous cationic metal carbenes $[M\{CPh(NEt_2)\}(NCMe)]^+$ (M = Cu, Ag, Au (**3a**)), and indeed, the frontier orbitals for all three metal carbenes show similar electron distributions. However, the decomposition of **1a** in the presence of $AgBF_4$ leads cleanly to the iminium salt **10**, which is formally the result of the carbene protonation, a reaction pathway unexpected for a putative silver carbene. The generation of a free carbene by dissociation from silver could produce a nucleophilic center amenable to protonation. However, a less selective reaction should be expected from such reactive species and DFT calculations show a high dissociation energy, not very different from the copper or tungsten carbenes which do not show that reactivity pattern under the same conditions (see Table S6 in the Supporting Information).

We carried out decomposition reactions of **1a** in the presence and absence of $AgBF_4$ under different conditions to corroborate that silver is playing a genuine role (eq 7 and

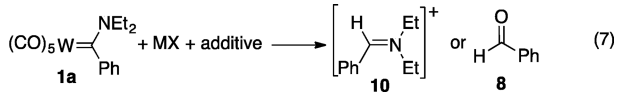

Table 4). Despite the plausible presence of water due to the highly hygroscopic character of the silver salt, this is not responsible for the reactivity observed by itself, since no trace of the iminium salt was detected when water was deliberately added to a solution of **1a** (entry 3, Table 4). Water does not accelerate the reaction in the presence of silver (entry 4, Table 4), and just an increase in the hydrolysis of the iminium salt to **8** was observed, as was tested independently. When D_2O was used, the deuterated aldehyde **8**-D was observed, indicating that the source of the proton in **10** is water.[32] Only a couple of reports can be found in the literature describing the protonation of a tungsten carbene with HCl or HBr.[33] Indeed, the addition of $HBF_4{\cdot}OEt_2$ to complex **1a** led to the iminium salt, a reaction that is still faster if $AgBF_4$ is additionally present

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Table 4. Decomposition Reactions of 1a According to Eq 7[a]

				conversion (%)	
entry	MX	additive	conditions	**10**	**8**
1			6 days, 50 °C		15
2	$AgBF_4$		26 h, 50 °C	72	
3		H_2O[b]	26 h, 50 °C		4
4	$AgBF_4$	H_2O[b]	20 h 50 °C		36
5		HBF_4	24 h, 25 °C	67	
6	$AgBF_4$	HBF_4	5 h, 50 °C	90	
7	$ZnCl_2$		24 h, 50 °C		17
8	$Zn(OTf)_2$		20 h, 50 °C		9
9	AgOTf		24 h, 50 °C	69	

[a]Reaction conditions: 0.022 mmol of **1a**, 0.022 mmol of $AgBF_4$ or zinc salt, and 0.022 mmol of additive in 0.6 mL of CD_3CN. Conversions were determined by ^1H NMR. [b]Two drops of water.

(cf. entries 5 and 6, Table 4). According to this, the role of a metal cation could be to increase the acidity of the water present, by coordination, and therefore increase the decomposition rate. However, the Lewis acidic character of silver does not explain the formation of the iminium salt, since no trace of **10** was observed when a Lewis acid of higher acidity such as Zn(II) was added, even in the presence of water (cf. entries 7–9, Table 4).[34]

These experiments show that silver is important to trigger the decomposition observed. Since the carbene transmetalation from **1a** to a cationic acetonitrile silver complex is the thermodynamically most favored process for this metal, according to the data in Table 3, we explored the possibility of the protonation of the putative silver carbene $[Ag\{CPh(NEt_2)\}(NCMe)]^+$ (**c1**) by water. An energetically accessible pathway was found through a transition state that involves the simultaneous interaction of water with silver and the carbene carbon (Figure 3). The process has an activation energy of 25.3 kcal mol^{-1}, which could be overcome under the reaction conditions used: the formation of the iminum salt is a slow reaction that requires heating for hours. The products formed from **TS1**, **10** and Ag(OH)NCMe, are not very stable, but the evolution of the silver species to the insoluble silver oxide can provide the thermodynamic driving force of the process.

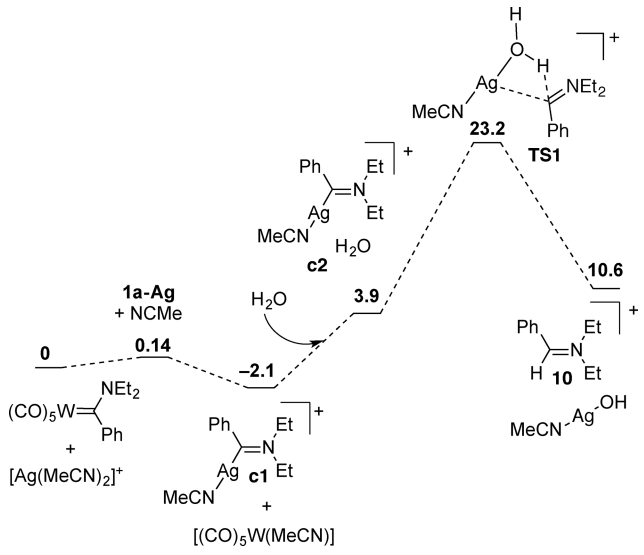

Figure 3. Free energy profile for the protonation of a silver carbene by water. Energies are given in kcal mol^{-1}.

This means that a nucleophilic behavior for silver carbenes might be possible. Fürstner at al. have suggested this type of behavior for silver polymetallic complexes with bridging nonstabilized diarylcarbene fragments, recently disclosed by this group.[35]

According to this, we also explored if the interaction of water with bimetallic silver complexes could lead to the direct protonation of the bridging carbene. No intermediate was found from the interaction of H_2O with the calculated bimetallic Ag–W complex **1a-Ag** (Figure 2). The calculated dimeric complex $[(MeCN)Ag\{\mu\text{-}CPh(NEt_2)\}Ag(NCMe)]^{2+}$ evolves in the presence of a water molecule to the monomeric silver carbene $[Ag\{CPh(NEt_2)\}(NCMe)]^+$ and $[Ag(NCMe)(H_2O)]^+$ (see the Supporting Information for details).

CONCLUSION

The reaction of tungsten(0) Fischer carbenes with neutral and cationic complexes of the group 11 metals revealed different behavior for each metal. Direct transmetalation to gold occurs leading to the instantaneous formation of the carbene complexes, and a series of neutral and cationic Au(I) carbenes have been prepared and characterized. Transmetalation to Cu(I) may occur, but only one copper monoaminocarbene species has been detected during our studies due to their lower stability. No experimental evidence of the formation of silver carbenes was found. DFT calculations mirror the experimental results and show that the formation of group 11 carbenes by direct transmetalation of tungsten(0) Fischer carbenes is thermodynamically favored for gold(I), possible for copper(I), and endergonic for most silver(I) precursors.

The hydrolysis of the isolated gold carbenes reveals the typical behavior of an electrophilic metal carbene. The same type of reactivity is observed by an analysis of the carbene decomposition products in the reactions of the tungsten(0) carbenes with copper complexes.

On the other hand, the presence of silver does not induce the decomposition of the tungsten methoxycarbene **1b** in all cases or the monoamino carbene for the neutral silver precursors. This is an indirect indication that transmetalation of the carbene fragment to silver is not taking place. However, the reaction of the tungsten(0) monoaminocarbene **1a** with silver salts with weakly coordinating anions, and specially $AgBF_4$ in acetonitrile, leads to an unprecedented carbene demetalation reaction by the formation of an iminium salt. This is a formal protonation of the carbene acting as a nucleophilic center. The transmetalation of the carbene from **1a** to a silver acetonitrile complex is thermodynamically favored, and we found by DFT calculations that the protonation of the resulting putative cationic silver carbene with water is possible, although energetically demanding. This shows a distinct behavior for silver among group 11 metals and the possibility of a mirror reactivity (carbene as a nucleophile) for the elusive silver complexes with less stabilized carbenes.

EXPERIMENTAL SECTION

General Methods. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on Bruker AV-400, Agilent MR400, and Agilent MR500 spectrometers (LTI-UVa). Chemical shifts (in δ units, ppm) were referenced to $SiMe_4$ (^1H and ^{13}C) and H_3PO_4 (85%, ^{31}P). The spectral data were recorded at 293 K unless otherwise noted. Heteronuclear ^1H–^{13}C HSQC and HMBC experiments were used to

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help with the signal assignments. All reactions were carried out under an atmosphere of N_2. Tungsten carbenes **1a**[36] and **1b**,[37] [AuCl(tht)],[38] $[Au(CH_3CN)_2]BF_4$,[39] $[Cu(CH_3CN)_4]PF_6$,[40] [CuCl(tht)],[41] [AgBr(tht)]$_4$, and [AgCl(tht)]$_4$[42] were synthetized according to the literature methods. Solvents were dried using an SPS PS-MD-5 solvent purification system prior to use. Silver salts, tetrabutylammonium hydroxide (1 M solution in MeOH), tetrafluoroboric acid etherate, zinc chloride, and zinc triflate are commercially available and were purchased from commercial sources. The reactions using the light-sensitive silver compounds were carried out in the absence of light.

Synthesis of 2a. [AuCl(tht)] (0.26 g, 0.83 mmol) was added to a solution of the tungsten carbene **1a** (0.4 g, 0.83 mmol) in 30 mL of CH_2Cl_2. The yellow solution was stirred for 20 min and filtered through Celite and activated carbon. The solvent was evaporated to ca. 2 mL, and pentane (5 mL) was added. The yellow solid was filtered, recrystallized in CH_2Cl_2/pentane, and dried under vacuum (0.28 g; 86% yield). ^{1}H NMR (400 MHz, δ, CD_3CN): 7.47 (m, 2H, H_{meta}), 7.36 (m, 1H, H_{para}), 7.09 (m, 2H, H_{ortho}), 4.23 (q, J = 7.25 Hz, 2H, CH_2CH_3), 3.53 (q, J = 7.25 Hz, 2H, CH'_2CH_3), 1.55 (t, J = 7.25 Hz, 3H, CH_2CH_3), 1.17 (t, J = 7.25 Hz, 3H, $CH_2CH'_3$). ^{13}C{^{1}H} NMR (100.61 MHz, δ, CD_3CN): 223.8 ($C_{carbene}$), 144.7 (C_{ipso}), 129.9 (C_{meta}), 129.3 (C_{para}), 123.8 (C_{ortho}), 57.9 (CH_2CH_3), 49.2 ($C'H_2CH_3$), 14.6 (CH_2CH_3), 13.9 ($CH_2C'H_3$). Anal. Calcd for $C_{11}H_{15}AuClN$: C, 33.56; H, 3.84; N, 3.56; Found: C, 33.66; H, 3.62; N, 3.50.

Synthesis of 2b. This complex was synthesized using a procedure similar to that described above for **2a** but using the tungsten carbene **1b**. Red solid (0.26 g; 88% yield). ^{1}H NMR (400 MHz, δ, CD_3CN): 8.35 (m, 2H, H_{ortho}), 7.88 (m, 1H, H_{para}), 7.62 (m, 2H, H_{meta}), 4.94 (s, 3H, OCH_3). ^{13}C{^{1}H} NMR (100.61 MHz, δ, CD_3CN): 267.9 ($C_{carbene}$), 143.2 (C_{ipso}), 139.4 (C_{para}), 136.0 (C_{ortho}), 130.5 (C_{meta}), 72.6 (OCH_3). Anal. Calcd for C_8H_8AuClO: C, 27.26; H, 2.29; Found: C, 27.33; H, 2.32.

Characterization of 3a and 4a. A vial was charged with $AgSbF_6$ (0.04 g, 0.116 mmol), and a solution of **2a** (0.03 g, 0.076 mmol) in 0.6 mL of CD_3CN was added under an atmosphere of nitrogen at 243 K. The gray suspension was warmed to room temperature for 30 min and filtered through a pad of Celite. The colorless solution, containing complexes **3a** and **4a** in a 20:1 mole ratio, was introduced in a 5 mm NMR tube and characterized by NMR. Data for **3a** are as follows. ^{1}H NMR (400 MHz, δ, CD_3CN, 243 K): 7.51 (m, 2H, H_{meta}), 7.41 (m, 1H, H_{para}), 7.12 (m, 2H, H_{ortho}), 4.22 (q, J = 7.33 Hz, 2H, CH_2CH_3), 3.62 (q, J = 7.33 Hz, 2H, CH'_2CH_3), 1.55 (t, J = 7.33 Hz, 3H, CH_2CH_3), 1.19 (t, J = 7.33 Hz, 3H, $CH_2CH'_3$). ^{13}C{^{1}H} NMR (100.61 MHz, δ, CD_3CN, 243 K): 216.9 ($C_{carbene}$), 143.1 (C_{ipso}), 130.1 (C_{para}), 130 (C_{meta}), 124.2 (C_{ortho}), 58.9 (CH_2CH_3), 49.7 ($C'H_2CH_3$), 14.9 (CH_2CH_3), 14 ($CH_2C'H_3$). Data for **4a** are as follows. ^{1}H NMR (400 MHz, δ, CD_3CN, 243 K): 7.46 (m, 2H, H_{meta}), 7.38 (m, 1H, H_{para}), 7.05 (m, 2H, H_{meta}), 4.18 (q, J = 7.31 Hz, 2H, CH_2CH_3), 3.57 (q, J = 7.31 Hz, 2H, CH'_2CH_3), 1.52 (t, J = 7.31 Hz, 3H, CH_2CH_3), 1.17 (t, J = 7.31 Hz, 3H, $CH_2C'H_3$). ^{13}C{^{1}H} NMR (100.61 MHz, δ, CD_3CN, 243 K): 239 ($C_{carbene}$), 143.7 (C_{ipso}), 129.9 (C_{para}), 129.5 (C_{meta}), 123.9 (C_{ortho}), 57.5 (CH_2CH_3), 49.7 ($C'H_2CH_3$), 15.2 (CH_2CH_3), 14.1 ($CH_2C'H_3$).

Characterization of 3b and 4b. A vial was charged with $AgSbF_6$ (0.03 g, 0.087 mmol), and a solution of **2b** (0.02 g, 0.057 mmol) in 0.6 mL of CD_3CN was added under an atmosphere of nitrogen at 243 K and stirred for 10 min. The yellowish solution was transferred to a 5 mm NMR tube and the mixture (**3b**:**4b** = 10:1 mol ratio) characterized by NMR at 243 K. Data for **3b** are as follows. ^{1}H NMR (500 MHz, δ, CD_3CN, 243 K): 8.31 (m, 2H, H_{ortho}), 7.92 (m, 1H, H_{para}), 7.64 (m, 2H, H_{meta}), 4.94 (s, 3H, OCH_3). ^{13}C{^{1}H} NMR (125.76 MHz, δ, CD_3CN, 243 K): 264.6 ($C_{carbene}$), 141.5 (C_{ipso}), 140.2 (C_{para}), 135.9 (C_{ortho}), 130.2 (C_{meta}), 73.4 (OCH_3). Data for **4b** are as follows. ^{1}H NMR (500 MHz, δ, CD_3CN, 243 K): 8.42 (m, 2H, H_{ortho}), 7.93 (m, 1H, H_{para}), 7.70 (m, 2H, H_{meta}), 5.10 (s, 3H, OCH_3). ^{13}C{^{1}H} NMR (125.76 MHz, δ, CD_3CN, 243 K): 287.4 ($C_{carbene}$), 142.2 (C_{ipso}), 140 (C_{para}), 135.4 (C_{ortho}), 130.2 (C_{meta}), 72.2 (OCH_3).

Characterization of 5. A vial was charged with $AgSbF_6$ (0.027 g, 0.077 mmol), and a solution of **2a** (0.02 g, 0.051 mmol) in 0.6 mL of CD_3CN was added under an atmosphere of nitrogen at −30 °C. After 2 min, the tungsten carbene **1b** (0.023 g, 0.051 mmol) was added to the mixture. The yellowish suspension was filtered, transferred to a 5 mm NMR tube, and characterized by NMR at 293 K. It contained the mixture **4a**:**4b**:**5** = 1.6:1:3.6 mol ratio. Data for **5** are as follows. ^{1}H NMR (400 MHz, δ, CD_3CN): 8.32 (m, 2H, H^b_{ortho}), 7.90 (m, 1H, H^b_{para}), 7.67 (m, 2H, H^b_{meta}), 7.55 (m, 2H, H^a_{meta}), 7.43 (m, 1H, H^a_{para}), 7.23 (m, 2H, H^a_{ortho}), 4.99 (s, 3H, OCH_3), 4.30 (q, J = 7.32 Hz, 2H, CH_2CH_3), 3.68 (q, J = 7.32 Hz, 2H, CH'_2CH_3), 1.62 (t, J = 7.32 Hz, 3H, CH_2CH_3), 1.25 (t, J = 7.32 Hz, 3H, $CH_2CH'_3$). ^{13}C{^{1}H} NMR (100.61 MHz, δ, CD_3CN): 288.8 ($C^b_{carbene}$), 239.1 ($C^a_{carbene}$), 143.8 (C^a_{ipso}), 143.1 (C^b_{ipso}), 140.3 (C^b_{para}), 135.6 (C^b_{ortho}), 130.7 (C^b_{meta}), 130.2 (C^a_{meta}), 130 (C^a_{para}), 124.4 (C^a_{ortho}), 72.5 (OCH_3), 57.8 (CH_2CH_3), 50.1 ($C'H_2CH_3$), 15.6 (CH_2CH_3), 14.3 ($CH_2C'H_3$).

Detection and Characterization of 9. [CuCl(tht)] (0.023 g, 0.123 mmol) was added under an atmosphere of nitrogen to a solution of **1a** (0.015 g, 0.031 mmol) in 0.6 mL of CD_3CN. The yellowish solution was heated for 1 h at 50 °C and characterized by NMR at 293 K. ^{1}H NMR (400 MHz, δ, CD_3CN): 7.43−7.32 (m, 3H, H_{meta} + H_{para}), 7.02 (m, 2H, H_{ortho}), 4.10 (q, J = 7.23 Hz, 2H, CH_2CH_3), 3.50 (q, J = 7.23 Hz, 2H, CH'_2CH_3), 1.52 (t, J = 7.23 Hz, 3H, CH_2CH_3), 1.17 (t, J = 7.23 Hz, 3H, $CH_2CH'_3$). ^{13}C{^{1}H} NMR (100.61 MHz, δ, CD_3CN): 239.8 ($C_{carbene}$), 144.3 (C_{ipso}), 128.2 (C_{para}), 129 (C_{meta}), 122.8 (C_{ortho}), 58.7 (CH_2CH_3), 47.7 ($C'H_2CH_3$), 15.4 (CH_2CH_3), 14.4 ($CH_2C'H_3$).

General Procedure for the Decomposition of the Carbene Complexes. For gold complexes, a 5 mm NMR tube was charged with the neutral Au(I) carbene (**2a** or **2b**, 0.014 mmol) and 0.6 mL of CD_3CN, and finally stoichiometric amounts of the additive were added if necessary. For copper and silver complexes, under a N_2 atmosphere a 5 mm NMR tube was charged with the silver or copper salt or complex (0.02−0.03 mmol), 0.6 mL of CD_3CN, equimolar amounts of the tungsten carbene (**1a** or **1b**), and the additive when needed. The decomposition products of the carbene fragment were characterized by NMR by comparison with authentic samples (**6**−**8**). The identity of **10** was independently corroborated by treatment of PhCH=NEt with $(OEt_3)BF_4$ (see the Supporting Information).

Data for **10** are as follows. ^{1}H NMR (500 MHz, δ, CD_3CN): 8.83 (s, 1H, $H_{iminium}$), 7.85 (m, 1H, H_{para}), 7.83 (m, 2H, H_{ortho}), 7.76 (m, 2H, H_{meta}), 4.09 (q, J = 7.36 Hz, 2H, CH_2CH_3), 4.04 (q, J = 7.36 Hz, 2H, CH'_2CH_3), 1.51 (t, J = 7.36 Hz, 6H, CH_2CH_3 + $CH_2CH'_3$). ^{13}C{^{1}H} NMR (125.76 MHz, δ, CD_2Cl_2): 171.2 ($C_{iminium}$), 137.3 (C_{para}), 132.6 (C_{ortho}), 130.4 (C_{meta}), 125.7 (s, C_{ipso}), 57.1 (CH_2CH_3), 49.3 (s, $C'H_2CH_3$), 12.5 (s, CH_2CH_3 + $CH_2C'H_3$).

Computational Methods. The DFT studies were performed with the M06 functional,[43,44] as implemented in the Gaussian09 program package.[45] The 6-31+G(d) basis set was used for C, O, S, Cl, N, and H,[46,47] and LANL2TZ(f) for Cu, Ag, A, and W[48,49] (basis set I). Solvation was introduced in all optimizations, and frequency calculations and potential energy refinement were carried out through the SMD model, where we applied the experimental solvent, acetonitrile, as the solvent (ε = 27.9). All structure optimizations were carried out in the solvent phase with no symmetry restrictions. Free energy corrections were calculated at 298.15 K and 10^5 Pa pressure, including zero-point energy corrections (ZPE), and the energies were converted to 1 M standard state in solution (adding/subtracting 1.89 kcal mol^{-1} for nonunimolecular processes). Vibrational frequency calculations were performed in order to confirm that the stationary points were minima (without imaginary frequencies) or transition states (with one imaginary frequency). The connectivity of the transition state structure was confirmed by relaxing the transition state geometry toward both the reactant and the product. Final potential energies were refined by performing additional single-point energy calculations (also in solution); Cu, Ag, Au, and W were still described with the LANL2TZ(f) basis set, and the remaining atoms were treated with the 6-311++G(d,p) basis set (basis set II). All energies presented correspond to free energies in solution, obtained

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from potential energies (including solvation) with basis set II plus Gibbs energy corrections with basis set I and are given in kcal mol^{-1}.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00675.

Additional experimental data, selected spectra, and computational details (PDF)

Cartesian coordinates of the calculated structures (XYZ)

Accession Codes

CCDC 2038426 and 2038428 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Author Contributions

The manuscript was written through contributions of all authors./All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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