

1 Two Copper-Carbene from One Diazo Compound

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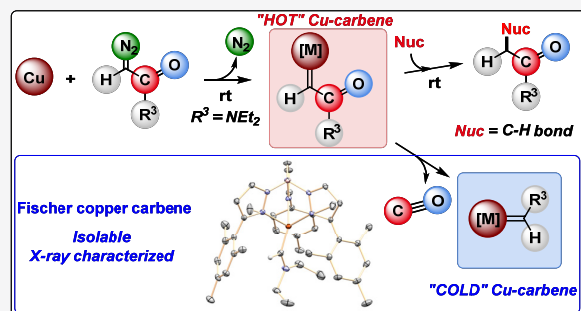


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Supporting Information

4 **ABSTRACT:** Many transition-metal complexes ML_n decompose
5 diazo compounds $N_2=CR^1R^2$ generating metal-carbenes $L_nM=$
6 CR^1R^2 which transfer the carbene group to other substrates,
7 constituting an important tool in organic synthesis. All previous
8 reports have shown that the CR^1R^2 fragment at the metal-carbene
9 remains intact from the parent diazo compound. Herein we report
10 the detection and isolation of a monosubstituted copper carbene
11 where the CR^1R^2 ligand has undergone a modification from the
12 initial diazo reagent. When $Tp^{Ms}Cu(THF)$ (Tp^{Ms} = hydrotris(3-
13 mesityl)pyrazolylborate ligand) was reacted with *N,N*-diethyl
14 diazoacetamide [$N_2=C(H)(CONEt_2)$], the stable copper carbene
15 $Tp^{Ms}Cu=C(H)(NEt_2)$ was isolated, resulting from a decarbon-
16 ylation process, with carbon monoxide being trapped as $Tp^{Ms}Cu-$
17 (CO) . The simultaneous observation of products derived from the intramolecular carbene insertion reaction into C–H bonds
18 demonstrates that the expected $Tp^{Ms}Cu=C(H)(CONEt_2)$ complex is also formed. Experimental data, DFT calculations, and
19 microkinetic models allow us to propose that the latter undergoes CO loss en route to the former.



20 ■ INTRODUCTION

21 More than a century after Buchner postulated the existence of
22 carbene CR_2 groups during the thermal decomposition of ethyl
23 diazoacetate,¹ the catalytic transfer of such moiety from diazo
24 compounds yet constitutes an area of continuous growth.^{2,3}
25 Such process consists of the metal-induced decomposition of
26 the diazo reagent in a process in which molecular N_2 is
27 extruded and a metalcarbene intermediate **MC** is formed
28 (Scheme 1a).⁴ This species is electrophilic⁵ in nature and
29 reacts with available nucleophiles transferring the carbene
30 group, thus liberating the metal to continue the catalytic cycle.
31 This strategy has been successfully employed in the addition of
32 carbene groups to unsaturated bonds or in its insertion into
33 C–H or other C–X bonds, both intra- and intermolecu-
34 larly.^{6–8}

35 With the appropriate tuning of the carbene substituent and
36 the metal complex, several metalcarbene complexes have
37 been detected, some of them being isolated and structurally
38 characterized. All metals from groups 8 to 11 are known to
39 catalyze the carbene transfer from diazo compounds (Scheme
40 1b), and at least one detected/isolated example of a metal-
41 carbene intermediate formed from a diazo compound has been
42 reported for each of them.^{8–18} In all cases, the CR^1R^2 moiety
43 in the initial diazo compound appears unmodified in the
44 subsequent metal-carbene intermediate (Scheme 1b), from
45 where it is further transferred to the nucleophile. From here, it
46 is always assumed that the carbene ligand is always transferred
47 without modification. One of the most popular diazo reagents

are diazocarbonyl compounds,⁴ with a CO group directly
bonded to the diazo functionality: the acceptor nature of the
–COR group favors the transfer of the carbene group toward
the nucleophile.

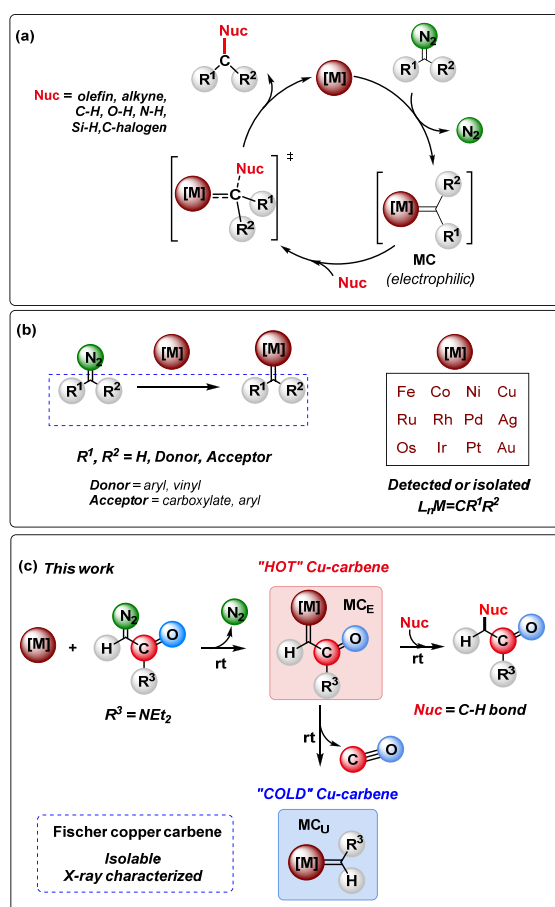
Herein we report the observation of the unprecedented
modification of the carbene unit during the course of a copper-
catalyzed transformation. The use of a diazoacetamide
compound (Scheme 1c) bearing a $CONR_2$ substituent leads
to the formation of the expected, undetected, *hot*, highly
reactive copper carbene MC_E (Scheme 1c) which promotes
the intramolecular C–H bond functionalization of the ethyl
groups of the amide fragment. In a parallel manner, MC_E
undergoes the loss of CO en route to the formation of the
unexpected, stable and isolable, *cold*, Fischer carbene complex
 MC_U (Scheme 1c), which has been structurally characterized.

63 ■ RESULTS AND DISCUSSION

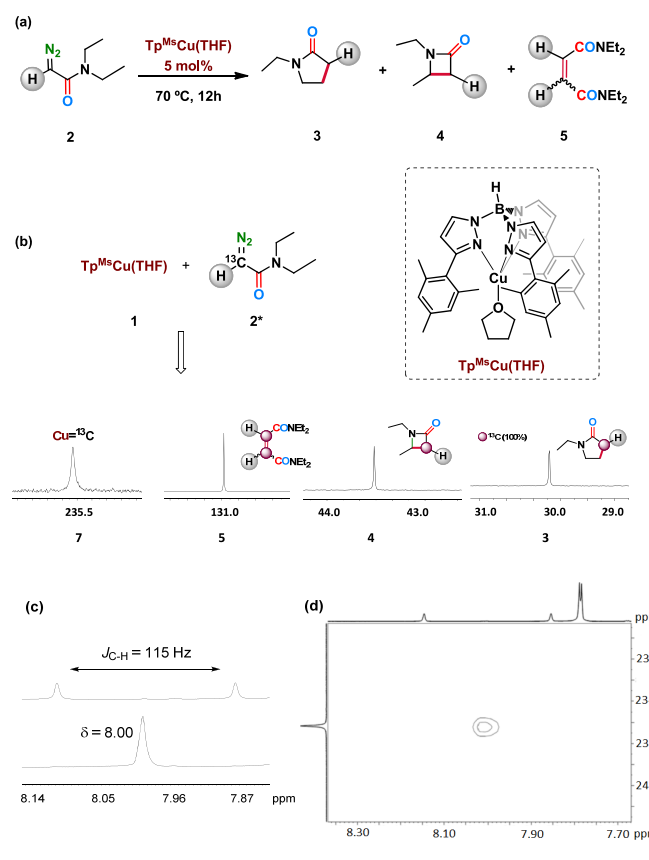
Reaction of $Tp^{Ms}Cu(THF)$ and $N_2=C(H)C(O)NEt_2$. Our
group has been involved in the area of carbene transfer from
diazo compounds, with emphasis on its application to the

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Scheme 1. Metal-Catalyzed Carbene Transfer from Diazo Compounds and the Formation of Metalcarbene Intermediates



Scheme 2. (a) Copper-Catalyzed Intramolecular C–H Bond Functionalization of *N,N*-Diethyldiazoacetamide; (b) $^{13}C\{^1H\}$ NMR Spectrum of the Reaction of Copper Complex 1 and ^{13}C -Labelled Diazoacetamide (2^*)



67 functionalization of C–H bonds of unmodified alkanes,^{6,19} for
 68 which the design of very active catalysts precluded the
 69 observation of intermediates. However, we recently detected
 70 copper-carbene species²⁰ in solution upon reacting $Tp^{Ms}Cu$ -
 71 (THF) (**1**) and ethyl phenyldiazoacetate (PheDA), which
 72 were stable at temperatures below 10 °C. After those findings,
 73 we aimed to detect copper-carbene intermediates with
 74 monosubstituted diazo compounds, which yet remains a
 75 challenge, particularly with the most popular catalysts within
 76 this field, i.e., rhodium and copper, for which only
 77 disubstituted carbene species have been detected or
 78 isolated.^{11,13,21} Toward that end we chose $Tp^{Ms}Cu(THF)$ ²²
 79 as the copper source, since the Tp^{Ms} ligand provides a high
 80 degree of steric protection to the metal center and, when
 81 formed, to the carbene ligand. Regarding the diazo reagent, we
 82 selected *N,N*-diethyl diazoacetamide (**2**), in view of the
 83 previously reported²³ intramolecular carbene insertion into
 84 the C–H bonds of the ethyl *N*-substituents in the presence of
 85 **1** as the catalyst (Scheme 2a), leading to mixtures of lactams **3**
 86 and **4**. Olefin **5** was also observed from the catalytic reaction of
 87 two molecules of **2**.²⁴ Since heating at 70 °C was needed to
 88 reach efficient ratios, we reasoned that perhaps the copper-
 89 carbene intermediate expected from the reaction of **1** and **2**,
 90 $Tp^{Ms}Cu=C(H)(CONEt_2)$ (**6**), could be stable enough at
 91 room temperature to be detected. Based on this idea, we
 92 started this study carrying out the reaction of $Tp^{Ms}Cu(THF)$
 93 (**1**) with 5 equiv of *N,N*-diethyl diazoacetamide (2^*), 100%

enriched in ^{13}C at the $^{13}C=N_2$ site, in toluene- d_8 (Scheme 94
 2b). Monitoring of the reaction by $^{13}C\{^1H\}$ NMR spectroscopy
 95 showed the appearance of a resonance centered at 235.6
 96 ppm. This is within the typical region of $Cu=C$ moieties
 97 reported by Hofmann²⁵ for the complexes $[^tBu_2P(NSiMe_3)_2-$
 98 $\kappa_2N]Cu=C(Ar)C(O)R]$ (235.8–219.0 ppm), by Warren¹³
 99 for $[\beta\text{-diketiminate}]Cu=CPh_2$ (253.1 ppm), or by our group
 100 for complexes $Tp^xCu=C(Ph)(CO_2Et)$ ($Tp^x = Tp^{iPr_2}$, Tp^* ,
 101 Tp^{Ms} ; 233.9, 236.8, and 248.5 ppm, respectively).²⁰ Under
 102 these conditions, the resonances for **3**, **4**, and **5** were also
 103 observed, the latter being the major product. The reaction was
 104 immediate, and no free diazo compound 2^* was observed after
 105 5 min. Successive registration of $^{13}C\{^1H\}$ NMR spectra for
 106 hours showed no change in the composition of the mixture. 107

In view of the apparent stability of the species bearing the
 108 $Cu=C$ unit, we repeated the reaction at a bench scale (see
 109 Supporting Information (SI) for optimization conditions). 110
 111 When 0.25 g of **1** was reacted with 5 equiv of diazo **2** in
 112 toluene at room temperature for 1 h, a yellowish solution was
 113 formed from which, after workup, the new compound **7** was
 114 isolated as crystalline material in 30% yield. The 1H NMR
 115 spectrum of **7** showed three equivalent pyrazolyl rings, two
 116 inequivalent ethyl groups, and a singlet at 8.0 ppm (Scheme
 117 2c), which corresponds to one proton that correlates in the
 118 2D-HSQC experiment with the aforementioned signal at 236.6
 119 ppm (Scheme 2d). In the sample derived from the ^{13}C -labeled
 120 diazo compound, the singlet at 8.0 in the 1H NMR spectrum
 121 split into a doublet with $J_{C-H} = 115$ Hz (Scheme 2c).

122 Albeit the above data could support the assignment of
 123 complex 7 as the pursued $\text{Tp}^{\text{Ms}}\text{Cu}=\text{C}(\text{H})(\text{CONEt}_2)$, some
 124 other experimental data were not in agreement with that
 125 proposal: neither the FT-IR spectrum showed the expected
 126 absorption for the CO group nor the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum
 127 displayed any resonance within the carbonyl region. We
 128 suspected that a decarbonylation process could have occurred,
 129 an idea that was confirmed when single crystals of this complex
 130 were grown, and the molecular structure determined by X-ray
 131 studies showed the formulation $\text{Tp}^{\text{Ms}}\text{Cu}=\text{CH}(\text{NEt}_2)$ (7).²⁶
 132 As shown in Figure 1, this complex contains the Tp^{Ms} ligand

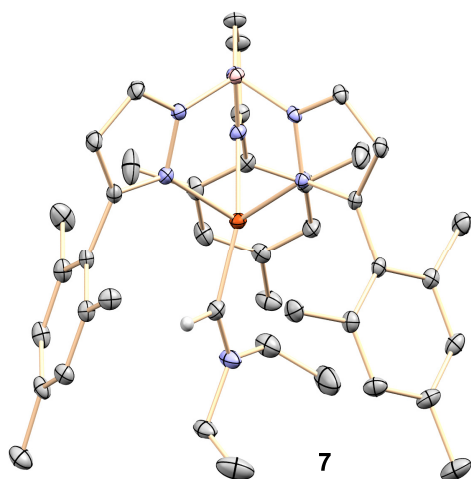


Figure 1. Molecular structure of the molecules for complex 7. Hydrogens have been omitted for clarity.

133 bonded to copper in a κ^3 -fashion, and a carbene ligand with
 134 two substituents: a hydrogen and a diethylamido group, the
 135 latter resulting from the loss of the CO present in the initial
 136 diazo compound. The distance $\text{Cu1}-\text{C1}$, 1858(5) Å, is similar
 137 to that reported by Warren for $[\beta\text{-diketiminate}]\text{Cu}=\text{CPh}_2$
 138 (1.834(3) Å).¹³ Complex 7 constitutes the first example of a
 139 metal-carbene complex formed from a diazo compound in
 140 which the CR^1R^2 moiety in the latter is different from that in
 141 the former. Additionally, it is also the first example of a
 142 monosubstituted copper carbene complex.²⁷

143 Further investigation of the ^1H NMR spectrum of the
 144 experiment carried out with a 1:3 ratio (excess of diazo is
 145 employed since C–H bond insertion also occurs in a catalytic
 146 manner to some extent) of 1 and 2* showed that, in addition
 147 to 7, another $\text{Tp}^{\text{Ms}}\text{Cu}$ -containing species was formed, both
 148 accounting for all detectable $\text{Tp}^{\text{Ms}}\text{Cu}$ cores. Such compound
 149 has been identified as $\text{Tp}^{\text{Ms}}\text{Cu}(\text{CO})$ (8) (Scheme 3), as the
 150 result of the trapping of carbon monoxide by 1.²² To gain
 151 further information, we have prepared the doubly isotopically
 152 enriched $\text{N}_2=^{13}\text{C}(\text{H})^{13}\text{C}(\text{O})\text{NEt}_2$ (2**) diazo compound and
 153 monitored the reaction with complex 1, observing the
 154 resonances of carbene and carbonyl ligands of 7 and 8,
 155 respectively (see Supporting Information also). Thus, this
 156 observation unambiguously demonstrates the existence of a
 157 decarbonylation process.

158 The yield in complex 7 is dramatically affected by
 159 temperature, as shown in Figure 2a. The reaction of 1 and 2
 160 (1:5 ratio) has been performed within the -30 to $+70$ °C
 161 range, showing an increase in the reaction yield from 2% to
 162 78%, respectively, in 1 h time experiments. The high yield
 163 preparation and isolation of 7 is better performed at 70 °C (see

Scheme 3. Reaction of $\text{Tp}^{\text{Ms}}\text{Cu}(\text{THF})$ with Doubly Isotopically Labeled 2** and Region of the $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum Showing the Labeled Carbene and Carbonyl Groups of 7* and 8*

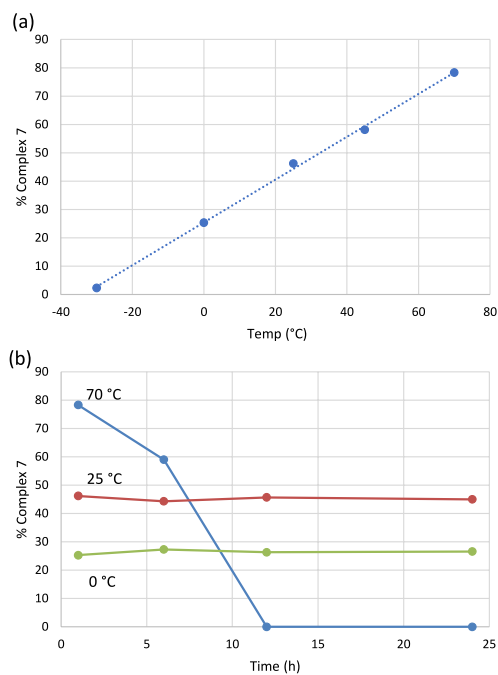
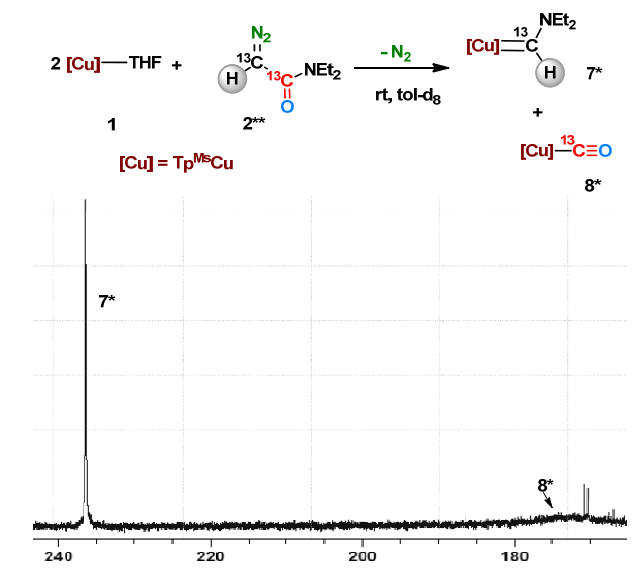
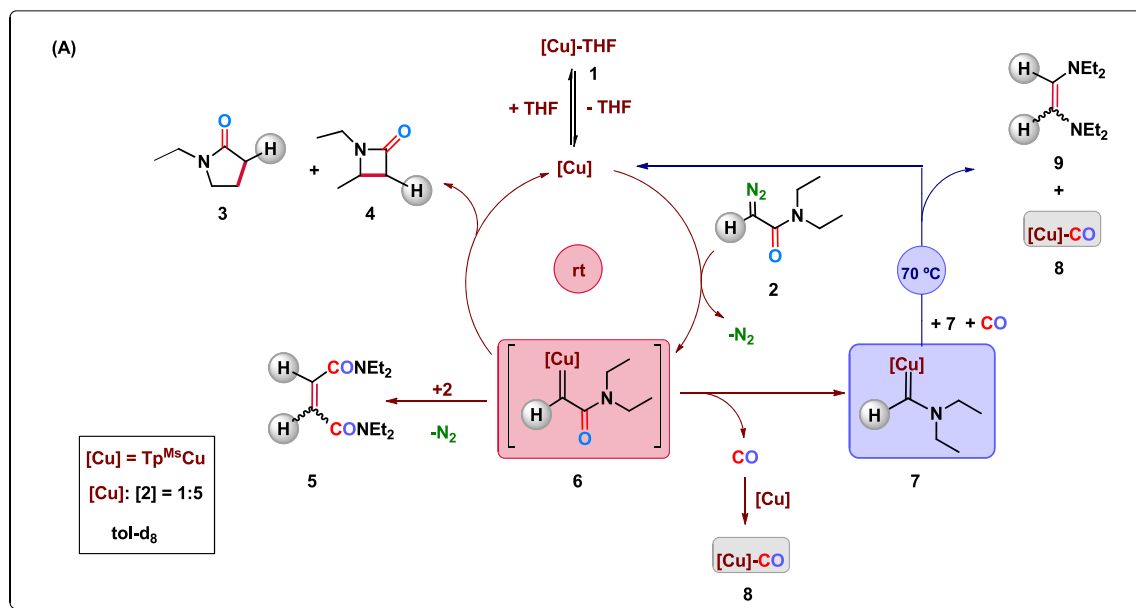


Figure 2. (a) Plot of the yields into complex 7 vs temperature (°C). (b) Variation of the yield of complex 7 with time at different temperatures.

Supporting Information). We have also monitored the 164 concentration of complex 7 with time at three different 165 temperatures (Figure 2b) and have found that at 0 or 25 °C 166 such concentration remains constant after 24 h. However, at 167 70 °C, a process involving the disappearance of 7 takes place 168 with time in such a way that after 12 h it cannot be detected in 169 solution. NMR studies have also shown that the olefin 170 $(\text{Et}_2\text{N})(\text{H})\text{C}=\text{C}(\text{H})(\text{NEt}_2)$ (9) derived from the coupling 171 of two of the carbene units in 7 is formed. 172

The reactivity of isolated copper carbene 7 has also been 173 investigated. On one hand, no reaction was observed with 174

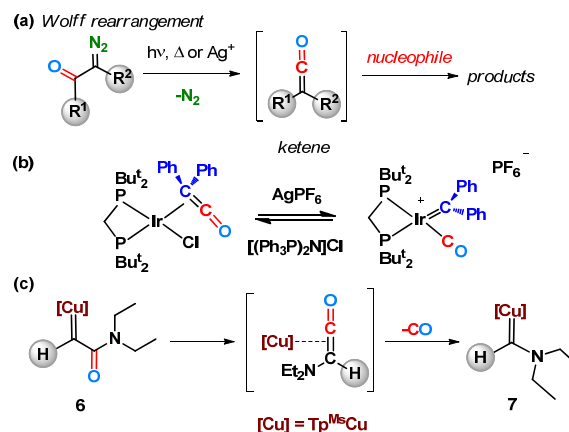
Scheme 4. General Picture of the Reactivity Derived from the Interaction of $\text{Tp}^{\text{Ms}}\text{Cu}(\text{THF})$ (1) and $\text{N}_2=\text{C}(\text{H})\text{CONEt}_2$ (2)

175 styrene, *tert*-butanol, benzene, or cyclohexane from room
 176 temperature to 70 °C. It seems clear that the loss of the CO
 177 group modifies the electronic behavior of the carbene
 178 $\text{C}(\text{H})\text{NEt}_2$ ligand decreasing the electrophilicity from
 179 $\text{Tp}^{\text{Ms}}\text{Cu}=\text{C}(\text{H})(\text{CONEt}_2)$ (6) to $\text{Tp}^{\text{Ms}}\text{Cu}=\text{C}(\text{H})\text{NEt}_2$ (7).
 180 Interestingly, heating toluene solutions of isolated 7 at 70 °C
 181 for hours/days did not lead to any transformation, whereas the
 182 same experiment under a CO atmosphere (4 bar) for 6 h
 183 induced a clean conversion of 7 into $\text{Tp}^{\text{Ms}}\text{Cu}(\text{CO})$ (8) and
 184 olefin 9. This result agrees with the lack of observation of
 185 copper-carbene 7 in the reaction of 1 and 2 at 70 °C for several
 186 hours, because of the presence of CO from the decarbon-
 187 ylation process.

188 The reactivity observed from the initial mixture of 1 and 2
 189 (1:5 ratio) is rationalized in Scheme 4. The $\text{Tp}^{\text{Ms}}\text{Cu}$ core is
 190 generated upon decooordination of THF and reacts with the
 191 diazo compound 2 to generate the transient copper carbene 6.
 192 This species undergoes either the intermolecular reaction with
 193 a second molecule of 2 or the intramolecular insertion of the
 194 carbene group into the secondary or primary C–H bonds of
 195 the ethyl groups of the NEt_2 fragment, thus yielding lactams 3
 196 and 4, these catalytic cycles taking place at room temperature.
 197 Intermediate 6 can alternatively undergo a decarbonylation
 198 process which generates the isolable copper carbene 7, a
 199 process which occurs, at least, within the -30 to $+70$ °C
 200 interval. Evolved CO can be trapped by $\text{Tp}^{\text{Ms}}\text{Cu}$ cores leading
 201 to the formation of $\text{Tp}^{\text{Ms}}\text{Cu}(\text{CO})$ (8). At 70 °C, copper-
 202 carbene 7 originates olefin 9 and carbonyl 8 in a process
 203 requiring carbon monoxide. This proposal agrees with the
 204 initial observation of the need for heating at 70 °C to induce
 205 catalysis by 1,²³ since the copper–carbonyl 8 under the
 206 reaction conditions in the presence of 2 also generates $\text{Tp}^{\text{Ms}}\text{Cu}$
 207 cores to catalyze the C–H bond functionalization reaction.

208 The transformation of 6 into 7 somehow resembles the
 209 Wolff rearrangement of diazo compounds (Scheme 5a), which
 210 originate short-lived ketenes^{4,28} which further react with
 211 nucleophiles, in a process triggered by light, heating, or
 212 silver(I) salts. Grotjahn and co-workers described a ketene
 213 iridium complex which undergoes the reversible conversion of
 214 the coordinated ketene into a metalcarbene which contains a

Scheme 5. (a) Wolff Rearrangement of Diazo Compounds; (b) Reversible Formation of Ketenes from Carbene and CO Ligands Described by Grotjahn; (d) Plausible Intermediate for the Conversion of 6 into 7



215 CO ligand (Scheme 5b).²⁹ Based on these precedents, it could
 216 be possible that copper-carbene 6 undergoes a related
 217 rearrangement in the coordination sphere of copper, followed
 218 by CO extrusion (Scheme 5c). As mentioned above, the
 219 reverse reaction is not observed in our case, at least apparently,
 220 as inferred from the experiment carried out with 7 and CO.

221 **DFT Studies and Microkinetic Model.** Given the
 222 unexpected formation of 7, we further explored the process
 223 with DFT studies (B3LYP-D3 optimizations in solution; see
 224 details in the Supporting Information) and microkinetic
 225 simulations. Computational results are summarized in Figure
 226 3. Figure 3a shows the free energy profile for the conversion
 227 from the starting $\text{Tp}^{\text{Ms}}\text{Cu}(\text{THF})$ complex (1) to compound 7.
 228 The initial steps follow the usual mechanism up to the
 229 formation of metal-carbene 6, with the highest barrier
 230 corresponding to nitrogen extrusion ($17.3 \text{ kcal/mol}^{-1}$).
 231 Species such as metal-carbene 6 have been previously shown
 232 to be very reactive toward homocoupling or C–H
 233 activation.^{19,23,24} The novelty in this system is the availability

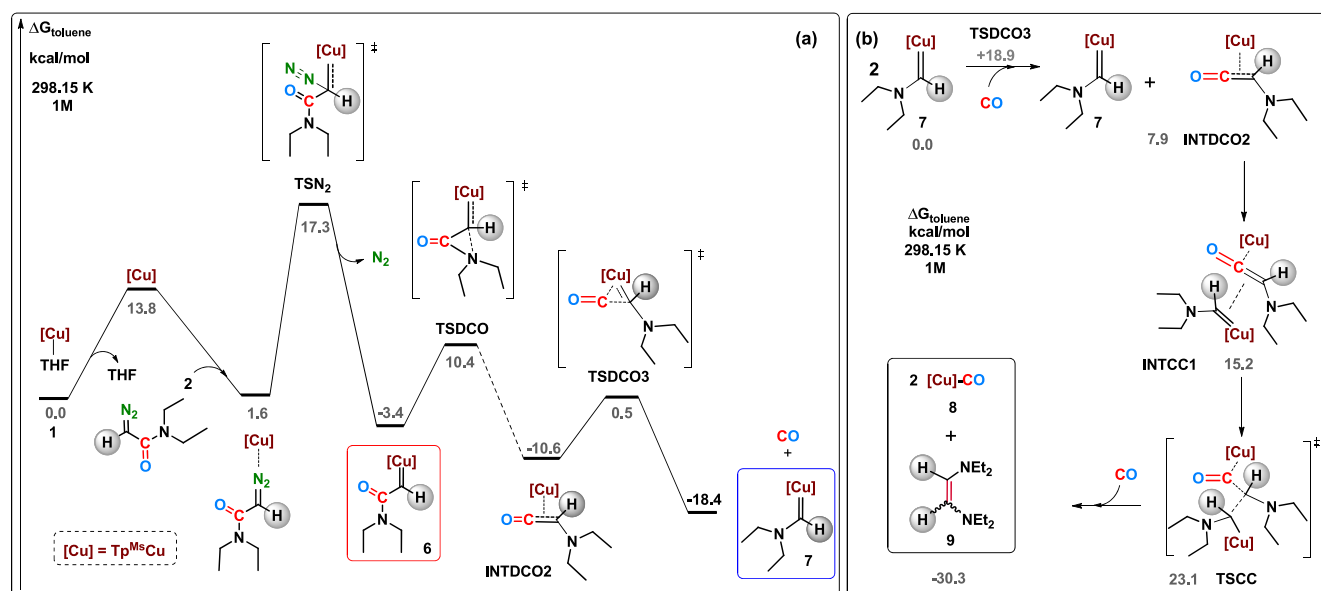


Figure 3. (a) Simplified reaction free energy profile from DFT calculations for the generation of copper carbenes **6** and **7**. (b) Simplified reaction mechanisms for the formation of olefin **9**.

234 of an alternative low energy path via decarbonylation. The
 235 latter proceeds through a rather stable ketene intermediate
 236 **INTDCO₂**, with a linear arrangement between the CO and the
 237 former carbene carbon (see [Supporting Information](#) for more
 238 details). The barrier for the decarbonylation process is low at
 239 298.15 K (13.8 kcal/mol) while the reverse barrier is 28.0 kcal-
 240 mol⁻¹, too high to take place significantly at ambient
 241 temperature. At 343.15 K the profile is similar to decarbon-
 242 ylation barriers of 13.9 and 30.3 kcal/mol for the reverse
 243 process. The lack of observation of the reverse pathway when
 244 reacting complex **7** and CO at 70 °C is due to the more
 245 favorable path of formation of olefin **9** and carbonyl adduct **8**
 246 (see below). Further calculations were carried out for the case
 247 where the toluene solvent is replaced by dichloromethane, also
 248 reproducing the experimental observation of pyrrolidinone (**3**)
 249 and azetidinone (**4**). The detailed computational results for
 250 these cases are given in the [Supporting Information](#).

251 The formation of **9** has also been investigated. Several paths
 252 previously reported for such carbene coupling have been
 253 discarded based on their high energy barriers: (a) direct
 254 interaction of two molecules of **7**;²⁴ (b) carbene C(H)NEt₂
 255 dissociation and reaction with **7**;²⁴ and (c) coupling of two
 256 dissociated carbene units³⁰ (see [Supporting Information](#)). At
 257 variance with that, we have found an accessible route which
 258 involves two molecules of **7** and one of CO. The simplified
 259 mechanism for the formation of olefin **9** is depicted in [Figure](#)
 260 **3b**. The mechanism starts with one molecule of the metal-
 261 carbene **7** adding a molecule of CO to form the above-
 262 mentioned intermediate **INTDCO₂** which further reacts with a
 263 second molecule of **7**. The formation of the olefin **9** must
 264 overcome a barrier of 23.1 kcal/mol. Thus, albeit olefin **9** is
 265 more stable than metal-carbene **7**, its formation involves a
 266 higher barrier (see [Supporting Information](#) for further details).

267 The third possible product from the interaction between the
 268 precursor **1** and *N,N*-diethyl diazoacetamide is olefin **5**, which
 269 is also experimentally observed. We also computed the
 270 mechanism of its formation from **6**, which is detailed in the
 271 [Supporting Information](#). The key result is that the free energy
 272 barrier for C=C bond formation leading to **5** is 8.9 kcal/mol.

This value is significantly lower than the 13.8 kcal/mol 273
 reported above for decarbonylation, which from a simplistic 274
 view would indicate that decarbonylation should not take 275
 place. However, for convoluted mechanisms such as the one 276
 present here, it is better to translate the computed free energy 277
 barriers to rate constants and use those to estimate reaction 278
 times through microkinetic modeling.³¹ We performed such 279
 microkinetic modeling with additional energy adjustment³² 280
 (see [Supporting Information](#) for details), and we obtained the 281
 results shown in [Figure 4](#). The agreement between calculations 282
 and experimental data (displayed in [Figure 2](#)) is certainly 283
 remarkable, and this strongly supports the validity of our 284
 mechanistic proposal. 285

286 ■ CONCLUSION

We herein report the first example of the modification of a 287
 carbene group during its metal-catalyzed transfer from a diazo 288
 functionality, a discovery that should result in further 289
 consideration from the community involved in this area. 290
 From now on, the belief that the carbene moiety remains 291
 undisturbed in this type of processes must be reconsidered 292
 when analyzing reaction outcomes, particularly in those 293
 catalytic systems which either seem deactivated or require 294
 anomalous heating. Additionally, the chemistry of these 295
 isolated metal-carbenes is yet to be developed and could find 296
 important applications as surrogates of well-known midtransition 297
 metal Fischer carbene complexes 298

299 ■ EXPERIMENTAL SECTION

Synthesis and Characterization of Complexes **7 and **7***.** In a 300
 250 mL Schlenk flask, Tp^{M_s}Cu(THF) (**1**, 0.450 g, 0.64 mmol) was 301
 dissolved in 75 mL of toluene, and a solution of 2-diazo-*N,N*- 302
 diethylacetamide (**2**, 0.451 g, 3.2 mmol) in the same solvent (37 mL) 303
 was added via canula. The mixture was stirred at 70 °C for 1 h before 304
 the volatiles were removed under reduced pressure. The residue was 305
 washed with dry acetone (5 mL) and cold Et₂O (3 × 5 mL) and dried 306
 under vacuum, to afford 0.35 g of a yellow solid corresponding, 307
 according to NMR studies, to a mixture of complexes **7** and **8** (yields 308
 of 47% and 10% referred to initial **1**). Crystallization from a mixture 309
 of toluene/hexane (4:4 mL) at -30 °C led to the isolation of complex 310

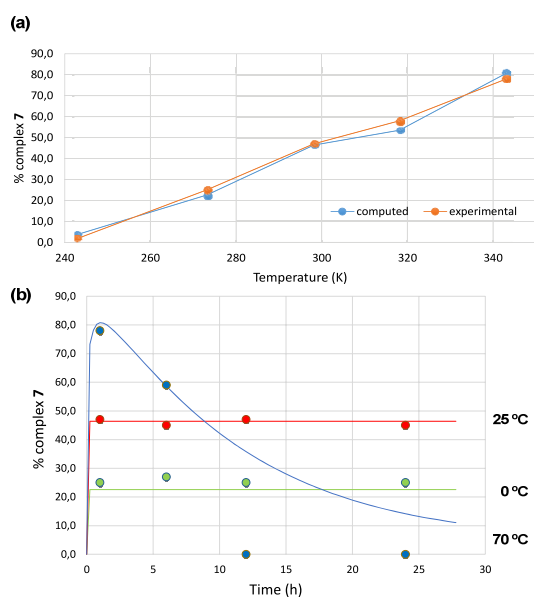


Figure 4. (a) Computed yield (%) of metallocarbene **7** at 1 h of reaction for different reaction temperatures (K). (b) Evolution over time (h) of the yield (%) of metallocarbene **7** at different temperatures (continuous line obtained from DFT and microkinetic simulations; dots obtained from experiment).

311 **7** as yellow crystals in 35% yield (combined crops). Analytically
 312 calculated for $C_{41}H_{51}BCuN_7$ (**1**): C, 68.75; H, 7.18; N, 13.69%.
 313 Found: C, 69.41; H, 7.12; N, 13.66%. Complex **7*** was prepared
 314 following the same procedure, with the corresponding labeled diazo
 315 compound (see SI) with an isolated yield of 28%.
 316 1H NMR (C_6D_6 , 500 MHz): δ 0.28 (t, $J_{HH} = 7.3$ Hz, 3H,
 317 NCH_2CH_3), 0.44 (t, $J_{HH} = 7.3$ Hz, 3H, NCH_2CH_3), 2.12 (s, 27H,
 318 CH_3), 2.23 (q, $J_{HH} = 7.3$ Hz, 2H, NCH_2CH_3), 2.41 (q, $J_{HH} = 7.3$ Hz,
 319 2H, NCH_2CH_3), 6.01 (d, $J_{HH} = 2.0$ Hz, 3H, CH), 6.71 (s, 6H, CH),
 320 7.80 (d, $J_{HH} = 2.0$ Hz, 3H, CH), 8.02 (s, 1H, $Cu=CH$). $^{13}C\{^1H\}$
 321 NMR (C_6D_6 , 125 MHz): δ 12.9 (CH_3), 13.6 (CH_3), 20.9 ($CH_{3,Ms}$),
 322 21.1 ($CH_{3,Ms}$), 53.1 (NCH_2), 54.9 (NCH_2), 104.5 (CH_{pz}), 127.8
 323 (CH_{Ms}), 133.6 ($C_{q,Ms}$), 134.9 (CH_{pz}), 136.2 ($C_{q,Ms}$), 138.3 ($C_{q,Ms}$),
 324 150.9 ($C_{q,pz}$), 236.6 ($Cu=C$).

325 ■ ASSOCIATED CONTENT

326 **SI** Supporting Information

327 The Supporting Information is available free of charge at
 328 <https://pubs.acs.org/doi/10.1021/jacs.1c01483>.

329 All procedures and characterization data, computational
 330 data, and Cartesian coordinates of the optimized
 331 structures (PDF)

332 Accession Codes

333 CCDC 2057177 contains the supplementary crystallographic
 334 data for this paper. These data can be obtained free of charge
 335 via www.ccdc.cam.ac.uk/data_request/cif, or by emailing
 336 data_request@ccdc.cam.ac.uk, or by contacting The Cam-
 337 bridge Crystallographic Data Centre, 12 Union Road,
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