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Au Nanoparticle-Catalyzed Insertion of Carbenes from α-Diazocarbonyl Compounds into Hydrosilanes

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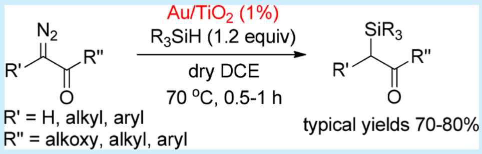
Supporting Information

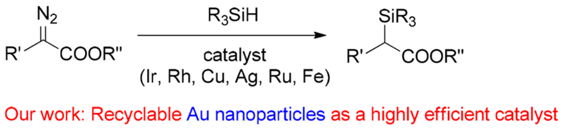
ABSTRACT: Supported Au nanoparticles on TiO_2 catalyze the insertion of carbenes from α-diazocabonyl compounds into hydrosilanes. It is proposed that the transformation involves two modes of catalytic activation: formation of nucleophilic Au carbenes on the surface of nanoparticle via expulsion of N_2 and activation of the Si−H bond of hydrosilane on Au nanoparticle, followed by coupling of the chemisorbed species. No external ligands or additives are required, while the process is purely heterogeneous, thus allowing the recycling and reuse of the catalyst.



The chemistry of metal carbenes, organometallic compounds bearing a neutral divalent carbon, has attracted the interest of organic chemists in recent years.[1] Several examples of metal carbenes are known involving a variety of cationic metals, among them not only ionic Au but metallic Au as well. Thus, R_2C: carbenes adsorbed on the surface of Au powder have been suggested as intermediates in the dimerization of diazoalkanes[2] or α-diazoketones[3] into alkenes and of alkenyl *gem*-dibromides into cumulenes.[4] In addition, *N*-heterocyclic carbenes adsorbed on adatoms of the Au surface have been recognized.[5] Recently, Leyva-Perez and Corma[6] established that electron-rich carbenes from diazoacetates [$Au_n{=}C(H)COOR$] can be formed on the surface of supported Au nanoparticles (Au_n) and were characterized spectroscopically. DFT calculations revealed that the carbene carbon atom bonds to two vicinal Au atoms, and there is an additional stabilizing interaction between an ester oxygen atom and a third vicinal Au atom. An exceedingly important feature of these Au carbenes is that they have a Schrock-type nucleophilic character through injection of electron density from the Au nanoparticle to the carbene carbon atom. It was established that these carbonyl group-stabilized electron-rich Au nanoparticle-adsorbed carbenes lack any reactivity with nucleophiles, such as alcohols, react slowly with electron poor alkenes, and in general, do not undergo any insertion reactions. Nucleophilic behavior was also shown in the so far only reported example of a Au(III)−carbene complex,[7] in contrast to the metal carbenes of cationic Au(I), which are electrophilic and react readily with nucleophiles.[8]

While Corma's work appeared in the literature,[6] concurrently, we were also working on the activation of α-diazocarbonyl compounds by Au nanoparticles supported on titania (Au/TiO_2) and have confirmed their results. Indeed, α-diazoesters cleanly and quantitatively undergo dimerization into alkenes. Yet, in contrast to the conclusion that these umpolung Au nanoparticle carbenes do not participate in insertion reactions, if a hydrosilane is present, insertion into the Si−H bond takes place to form α-silylesters in very good yields within short reaction times and low catalyst loading. Note that the formal insertion of carbenes into hydrosilanes[9] is a well-known reactivity mode (Scheme 1) and is catalyzed by a series of metals such as Rh(II),[10] Rh(I),[11] Cu(II),[10a,12] Cu(I),[13] Ir(III),[14] Ag(I),[15] Ru(II),[16] and Fe(II).[17]

Scheme 1. Catalyzed Reaction Between α-Diazoesters and Hydrosilanes



Treatment of a premixed solution of ethyl diazoacetate (**1**) and 1.2 equiv of a hydrosilane (Et_3SiH, $ArMe_2SiH$, or Me_3SiOMe_2SiH) in dry 1,2-dichloroethane (DCE) with Au/TiO_2 (1 mol %) for 40 min at 70 °C results in the formation of α-silylacetates (**1a**−**e**) in >70% isolated yield (Figure 1). Under the same conditions, and in the absence of hydrosilane, quantitative dimerization into diethyl fumarate and diethyl maleate occurs.[6] The observation of insertion of a formal carbene from ethyl diazoacetate (**1**) into the Si−H bond of hydrosilanes urged us to examine the scope and limitations of this transformation in a series of α-diazocarbonyl compounds (Figure 1).[18] Thus, aryl- or alkyl-substituted α-diazoesters react smoothly, forming hydrosilylation products in very good isolated yields. The only possible side pathway is the replacement of the diazo group by two hydrogen atoms ($C{=}N_2 \rightarrow CH_2$). This pathway depends on the amount of moisture, and in nondried solvent, it may reach up to 30% in relative yield. Note that in the literature there are only a few reports of this reductive transformation using Pd/C-catalyzed hydrogenation.[19] An analogous reductive pathway, which requires a Au hydride and a proton, has been also observed in the nano Au-catalyzed reaction between hydrosilanes and π

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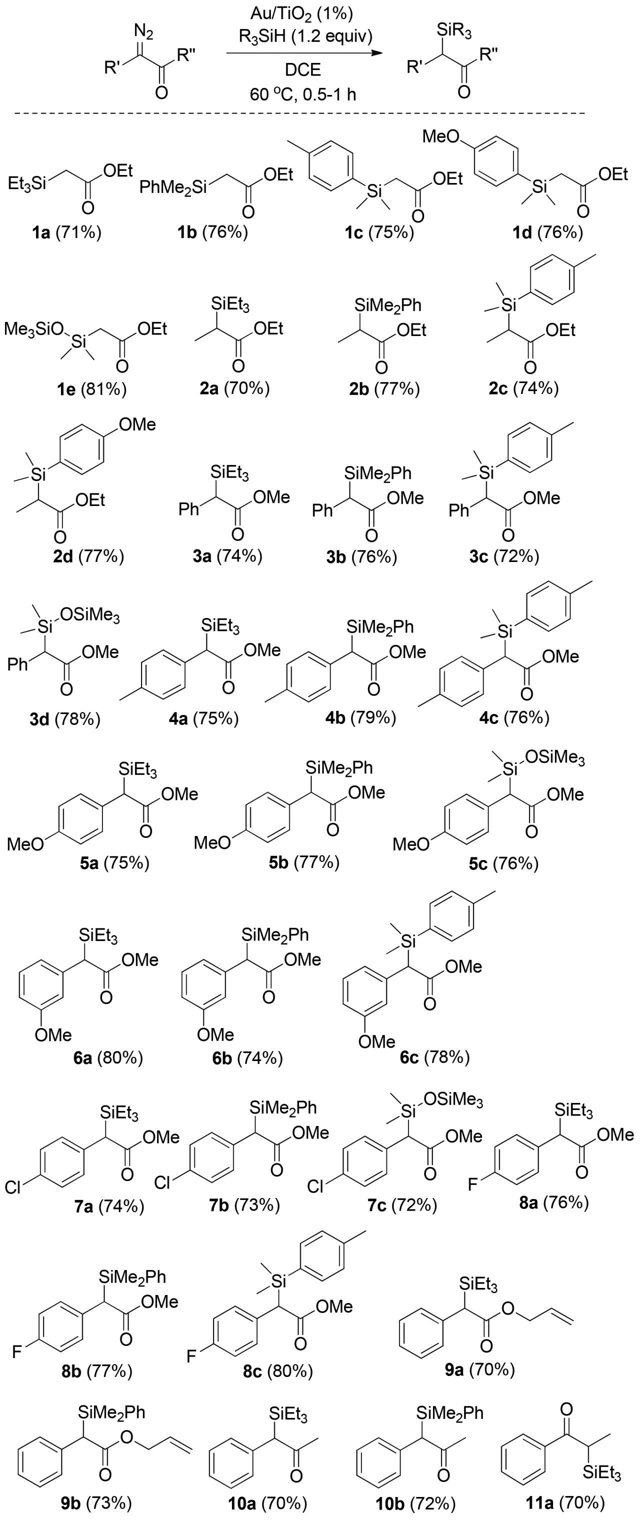


Figure 1. Reaction of hydrosilanes with α-diazocarbonyl compounds catalyzed by Au/TiO$_2$.

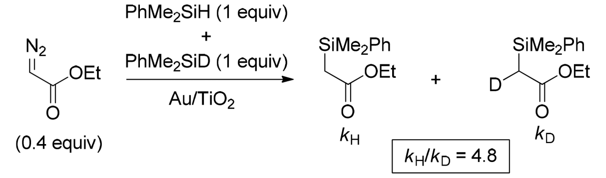
systems if a proton source (water or alcohol) is present.[20] Among the characteristics of the Au-catalyzed transformation is the clean reaction between hydrosilanes and allyl ester **9** forming products **9a** or **9b**, without observing any intramolecular insertion[13e] on the double bond. α-Diazoketones also undergo smooth insertion into hydrosilanes forming α-silylketones in good yields (Figure 1). Notably, although simple ketones readily undergo hydrosilylation in the presence of Au/TiO$_2$,[21] in α-diazoketones, the reaction occurs exclusively on the carbene carbon atom.

The catalytic system is reusable with no deterioration of its catalytic activity after three consecutive runs. Thus, after a simple filtration, washing with the reaction solvent and drying in the oven at 90 °C for 2 h, the catalyst can be used in a new run as active as before, which is indicative of the pure heterogeneous nature of the process. To the best of our knowledge, this is the first example of heterogeneous catalytic hydrosilylation of α-diazocarbonyl compounds. Additionally, we emphasize that, with one exception,[10b] all previous known analogous metal-catalyzed protocols require an excess of hydrosilane (up to 4 equiv), while the addition of the diazo compound into a solution of hydrosilane should be slow (using a syringe pump) and over the reaction time to avoid dimerization. In our case, we use almost stoichiometric amounts of reactants and they are immediately mixed.

In contrast to hydrosilanes, 1,2-disilanes, silylboranes, or diboranes, compounds that are readily activated by Au/TiO$_2$ and perform addition on π systems[22] do not undergo any reaction with Au nanoparticle carbenes on the basis of our attempts thus far.[23] Instead, α-diazoesters readily dimerize[6] under the reactions conditions or partially form hydrosilylation products in the case of disilanes and silylboranes if traces of moisture are present.

To draw mechanistic conclusions, we performed the kinetic competition between an equimolar mixture of PhMe$_2$SiH (1 equiv) and PhMe$_2$SiD (1 equiv) and 0.4 equiv of ethyl diazoacetate (**1**). The product analysis revealed a substantial kinetic primary isotope effect of $k_H/k_D = 4.8 \pm 0.4$ (Scheme 2).

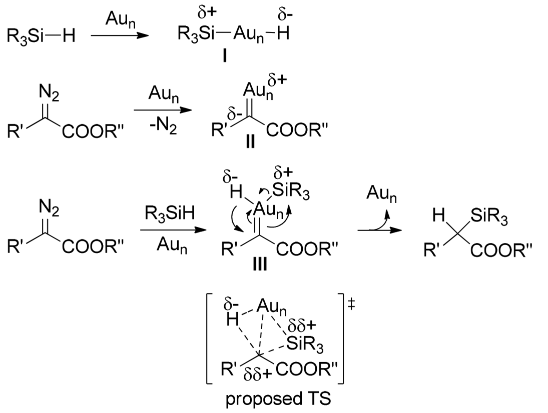
Scheme 2. Kinetic Isotope Effect Regarding the Insertion of Ethyl Diazoacetate into Si–H/Si–D Bonds



It was calculated as an average of four measurements at ~20% insertion of the isotopically competing hydrosilanes (Supporting Information). This value is significantly larger than the reported ones in analogous metal-catalyzed protocols, which range between k_H/k_D = 1.1–1.6,[13a,14a,17,24] and implies a different mechanism of insertion.[25] Additionally, the influence of the electronic nature of aryl substituents on kinetics was examined (Supporting Information). As a general trend, donors at the para position of aryl-substituted diazoesters and acceptors at the para position of aryldimethylsilanes increase the reaction rate. The linear correlation of the Hammett plots is not often ideal. We indicate, however, that in heterogeneous Au nanoparticle-catalyzed reactions such data should be treated with care because adsorption–desorption phenomena of reactants on the catalyst's surface, as well as the support, largely affect the reaction's kinetics.[26] The measured isotope effect and the profile of Hammett kinetics will be further analyzed in the accompanying mechanistic discussion.

Regarding the proposed mechanism that is presented in Scheme 3, we invoke two well-established activation modes by Au nanoparticles (Au$_n$): the insertion of the σ Si–H bond of hydrosilanes on Au$_n$ to form intermediate **I**[27] and the

Scheme 3. Proposed Mechanism in the Au/TiO$_2$-Catalyzed Insertion of Carbenes from α-Diazoesters into Hydrosilanes



formation of adsorbed electron-rich carbenes on the Au nanoparticle from α-diazoesters (**II**).[6] Any of these two activation modes may initiate the process to form a Au adatom on the nanoparticle surface.[5] The electron-deficient adatom is most likely the necessary catalytic site of the second, product-leading, activation (either of diazocarbonyl compound or hydrosilane) to form **III**. In intermediate **III**, coadsorbed carbene and hydrosilane are proximal[28] and couple to form the final product. It is suggested that the rate-determining step of the whole process is most likely the collapse of intermediate **III** into the final hydrosilylation product. Indeed, the magnitude of k_H/k_D is consistent with H or D transfer from **III** to the carbene and is substantial because hydrogen is bonded to a nucleus with a very high reduced mass (Au) and is transferred to a carbon atom which has a significantly smaller reduced mass.[29] In the case of direct hydrogen atom transfer from neutral hydrosilane to the carbene, as proposed in the so far presented examples in the literature,[13a,14a,17,24] a much smaller kinetic isotope effect should be anticipated, as indeed found. The transition state of this step is more likely unsymmetrical with silyl transfer slightly progressing hydride transfer and a partial positive charge developing on the carbon atom, which justifies the profile of the kinetic experiments of p-aryl-substituted diazoesters, already mentioned above. Additionally, a partial positive charge renders on the silicon atom in the transition state but apparently is less than that appearing in intermediate **III**, which also justifies the fact that electron-withdrawing substituents on ArMe$_2$SiH enhance the reaction rate.

In conclusion, we present herein a novel property of supported Au nanoparticles and their ability to catalyze the insertion of carbenes from α-diazocarbonyl compounds into hydrosilanes. The reaction takes place using co-mixed and almost stoichiometric amounts of reagents at low catalyst loading, in short reaction times, and in very good yields, while the catalytic system is recyclable and reusable. It is proposed that the transformation occurs by chemisorption of both reactants on proximal sites on the Au nanoparticle.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b01638.

^{1}H and ^{13}C NMR of all products (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Recent review articles: (a) Xia, Y.; Qiu, D.; Wang, J. *Chem. Rev.* **2017**, *117*, 13810. (b) Cheng, Q.-Q.; Yu, Y.; Yedoyan, J.; Doyle, M. P. *ChemCatChem* **2018**, *10*, 488.

(2) Zhou, Y.; Trewyn, B. G.; Angelici, R. J.; Woo, L. K. *J. Am. Chem. Soc.* **2009**, *131*, 11734.

(3) Liu, L.; Klaasen, H.; Timmer, A.; Gao, H.-Y.; Barton, D.; Monig, H.; Neugebauer, J.; Fuchs, H.; Studer, A. *J. Am. Chem. Soc.* **2018**, *140*, 6000.

(4) Sun, Q.; Tran, B. V.; Cai, L.; Ma, H.; Yu, X.; Yuan, C.; Stohr, M.; Xu, W. *Angew. Chem., Int. Ed.* **2017**, *56*, 12165.

(5) (a) Wang, G.; Ruhling, A.; Amirjalayer, S.; Knor, M.; Ernst, J. B.; Richter, C.; Gao, H.-J.; Timmer, A.; Gao, H.-Y.; Doltsinis, N. L.; Glorius, F.; Fuchs, H. *Nat. Chem.* **2017**, *9*, 152. (b) Zhukhovitskiy, A. V.; Mavros, M. G.; van Voorhis, T.; Johnson, J. A. *J. Am. Chem. Soc.* **2013**, *135*, 7418.

(6) Oliver-Meseguer, J.; Boronat, M.; Vidal-Moya, A.; Concepcion, P.; Rivero-Crespo, M. A.; Leyva-Perez, A.; Corma, A. *J. Am. Chem. Soc.* **2018**, *140*, 3215.

(7) Pujol, A.; Lafage, M.; Rekhroukh, F.; Saffon-Merceron, N.; Amgoune, A.; Bourissou, D.; Nebra, N.; Fustier-Boutignon, M.; Mezailles, N. *Angew. Chem., Int. Ed.* **2017**, *56*, 12264.

(8) Selected examples: (a) Harris, R. J.; Widenhoefer, R. A. *Chem. Soc. Rev.* **2016**, *45*, 4533. (b) Wang, Y.; Muratore, M. E.; Echavarren, A. M. *Chem. - Eur. J.* **2015**, *21*, 7332. (c) Seidel, G.; Mynott, R.; Furstner, A. *Angew. Chem., Int. Ed.* **2009**, *48*, 2510. (d) Benitez, D.; Shapiro, N. D.; Tkatchouk, E.; Wang, Y.; Goddard, W. A.; Toste, F. D. *Nat. Chem.* **2009**, *1*, 482. (e) Joost, M.; Estevez, L.; Mallet-Ladeira, S.; Miqueu, K.; Amgoune, A.; Bourissou, D. *Angew. Chem., Int. Ed.* **2014**, *53*, 14512. (f) Nunes dos Santos Comprido, L.; Klein, J. E. M. N.; Knizia, G.; Kastner, J.; Hashmi, A. S. K. *Angew. Chem., Int. Ed.* **2015**, *54*, 10336.

(9) Keipour, H.; Carreras, V.; Ollevier, T. *Org. Biomol. Chem.* **2017**, *15*, 5441.

(10) Selected examples: (a) Bagheri, V.; Doyle, M. P.; Taunton, J.; Claxton, E. E. *J. Org. Chem.* **1988**, *53*, 6158. (b) Andrey, O.; Landais, Y.; Planchenault, D.; Weber, V. *Tetrahedron* **1995**, *51*, 12083. (c) Bulugahapitiya, P.; Landais, Y.; Parra-Rapado, L.; Planchenault, D.; Weber, V. *J. Org. Chem.* **1997**, *62*, 1630. (d) Qu, Z.; Shi, W.; Wang, J. *J. Org. Chem.* **2001**, *66*, 8139. (e) Sambasivan, R.; Ball, Z. T. *J. Am. Chem. Soc.* **2010**, *132*, 9289.

(11) Chen, D.; Zhu, D.-X.; Xu, M.-H. *J. Am. Chem. Soc.* **2016**, *138*, 1498.

(12) Landais, Y.; Planchenault, D. *Tetrahedron* **1997**, *53*, 2855.

(13) Selected examples: (a) Dakin, L. A.; Ong, P. C.; Panek, J. S.; Staples, R. J.; Stavropoulos, P. *Organometallics* **2000**, *19*, 2896. (b) Zhang, Y. Z.; Zhu, S.-F.; Wang, L.-X.; Zhou, Q.-L. *Angew. Chem., Int. Ed.* **2008**, *47*, 8496. (c) Wu, J.; Chen, Y.; Panek, J. S. *Org. Lett.* **2010**, *12*, 2112. (d) Hyde, S.; Veliks, J.; Liegault, B.; Grassi, D.; Taillefer, M.; Gouverneur, V. *Angew. Chem., Int. Ed.* **2016**, *55*, 3785. (e) Keipour, H.; Jalba, A.; Delage-Laurin, L.; Ollevier, T. *J. Org. Chem.* **2017**, *82*, 3000.

(14) (a) Yasutomi, Y.; Suematsu, H.; Katsuki, T. *J. Am. Chem. Soc.* **2010**, *132*, 4510. (b) Wang, J.-C.; Xu, Z.-J.; Guo, Z.; Deng, Q.-H.; Zhou, C.-Y.; Wan, X.-L.; Che, C.-M. *Chem. Commun.* **2012**, *48*, 4299.

(15) (a) Iglesias, M. J.; Nicasio, M. C.; Caballero, A.; Perez, P. J. *Dalton Trans.* **2013**, *42*, 1191. (b) Liu, Z.; Li, Q.; Yang, Y.; Bi, X. *Chem. Commun.* **2017**, *53*, 2503.

(16) Nakagawa, Y.; Chanthamath, S.; Fujisawa, I.; Shibatomi, K.; Iwasa, S. *Chem. Commun.* **2017**, *53*, 3753.

(17) Keipour, H.; Ollevier, T. *Org. Lett.* **2017**, *19*, 5736.

(18) CAUTION NOTE: While the reactions in Figure 1 were performed using approximately 0.2 mmol of the diazo compounds (see SI), we also performed the reaction of **1** with $PhMe_2SiH$ on a larger scale (4 mmol), and product **1b** was isolated in 61% yield (unoptimized). At a such scale, however, precautions have to be taken because violent gas evolution occurs in the reaction flask.

(19) (a) Pellicciari, R.; Natalini, B.; Cecchetti, S.; Fringuelli, R. *J. Chem. Soc., Perkin Trans. 1* **1985**, 493. (b) Zhou, L.; Liu, Z.; Liu, Y.; Zhang, Y.; Wang, J. *Tetrahedron* **2013**, *69*, 6083.

(20) (a) Yan, M.; Jin, T.; Ishikawa, Y.; Minato, T.; Fujita, T.; Chen, L.-Y.; Bao, M.; Asao, N.; Chen, M.-W.; Yamamoto, Y. *J. Am. Chem. Soc.* **2012**, *134*, 17536. (b) Yan, M.; Jin, T.; Chen, Q.; Ho, H. E.; Fujita, T.; Chen, L.-Y.; Bao, M.; Chen, M.-W.; Asao, N.; Yamamoto, Y. *Org. Lett.* **2013**, *15*, 1484. (c) Louka, A.; Gryparis, C.; Stratakis, M. *ARKIVOC* **2015**, *iii*, 38.

(21) Vasilikogiannaki, E.; Titilas, I.; Gryparis, C.; Louka, A.; Lykakis, I. N.; Stratakis, M. *Tetrahedron* **2014**, *70*, 6106.

(22) (a) Gryparis, C.; Kidonakis, M.; Stratakis, M. *Org. Lett.* **2013**, *15*, 6038. (b) Gryparis, C.; Stratakis, M. *Org. Lett.* **2014**, *16*, 1430. (c) Kidonakis, M.; Stratakis, M. *ACS Catal.* **2018**, *8*, 1227.

(23) Selected examples of insertion of in situ generated metal carbenes on σ Si−Si, Sn−Sn, B−B, or Si−B bonds: (a) Liu, Z.; Tan, H.; Fu, T.; Xia, Y.; Qiu, D.; Zhang, Y.; Wang, J. *J. Am. Chem. Soc.* **2015**, *137*, 12800. (b) Cuenca, A. B.; Cid, J.; Garcia-Lopez, D.; Carbo, J. J.; Fernandez, E. *Org. Biomol. Chem.* **2015**, *13*, 9659. (c) Li, H.; Shangguan, X.; Zhang, Z.; Huang, S.; Zhang, Y.; Wang, J. *Org. Lett.* **2014**, *16*, 448. (d) Abu Ali, H.; Goldberg, I.; Kaufmann, D.; Burmeister, C.; Srebnik, M. *Organometallics* **2002**, *21*, 1870.

(24) Landais, Y.; Parra-Rapado, L.; Planchenault, D.; Weber, V. *Tetrahedron Lett.* **1997**, *38*, 229.

(25) For a review article on kinetic isotope effects in organometallic reactions including hydrosilanes, see: Gomez-Gallego, M.; Sierra, M. A. *Chem. Rev.* **2011**, *111*, 4857.

(26) (a) Kumar, G.; Tibbitts, L.; Newell, J.; Panthi, B.; Mukhopadhyay, A.; Rioux, R. M.; Pursell, C. J.; Janik, M.; Chandler, B. D. *Nat. Chem.* **2018**, *10*, 268. (b) Miura, H.; Tanaka, Y.; Nakahara, K.; Hachiya, H.; Endo, K.; Shishido, T. *Angew. Chem., Int. Ed.* **2018**, *57*, 6136.

(27) Selected examples from our group: (a) Stratakis, M.; Garcia, H. *Chem. Rev.* **2012**, *112*, 4469. (b) Lykakis, I. N.; Psyllaki, A.; Stratakis, M. *J. Am. Chem. Soc.* **2011**, *133*, 10426. (c) Kidonakis, M.; Stratakis, M. *Org. Lett.* **2015**, *17*, 4538.

(28) For STM images of bis-adsorbed organic species on adatoms of a metal surface, see ref 3.

(29) For the influence of metal on the kinetic isotope effects of reductive transformations by metal hydrides, see: Ashby, E. C.; Boone, J. R. *J. Am. Chem. Soc.* **1976**, *98*, 5524.