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Introduction

The conversion of carbon-hydrogen bonds into valuable products currently constitutes an area of continuous research.¹ One of the emerging strategies in the last few decades consists of the metal-catalyzed transfer of carbene groups from diazo compounds (Scheme 1, route a).² The same route has been scarcely applied to the silicon-hydrogen bond, in spite of the interest in silicon-containing reagents (Scheme 1, route b). First examples were independently described by Janssen^{3a} and Brook^{3b} with copper, at low conversions. Later, Doyle and



 $\label{eq:Scheme 1} \begin{array}{c} \mbox{The metal-catalyzed functionalization of C-H and Si-H bonds by carbone insertion from diazo compounds.} \end{array}$

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Silver-catalyzed silicon-hydrogen bond functionalization by carbene insertion + +

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The catalytic functionalization of silicon–hydrogen bonds by means of the insertion of carbene units : CHCO₂Et from ethyl diazoacetate (EDA) has been achieved using a silver-based catalyst, constituting the first example of this metal to promote this transformation. Competition experiments have revealed that the relative reactivity of substituted silanes depends on the bond dissociation energy of the Si–H bond (tertiary > secondary > primary for ethyl substituted). In the presence of bulky substituents such order reverts to secondary > primary \approx tertiary (for phenyl substituted). Screening with other diazo compounds has shown that N₂C(Ph)CO₂Et displays similar reactivity to that of EDA, whereas other N₂C(R)CO₂Et (R = Me, CO₂Et) gave lower conversions.

co-workers introduced $Rh_2(OAc)_4$ as an effective catalyst for the reaction of ethyl diazoacetate with silanes,4 which could be considered as the seminal work of this transformation. After this discovery, a series of contributions based on this metal appeared in the literature,^{5,6} including the asymmetric version.⁶ In addition to rhodium catalysts, only a few examples involving copper,⁷ iron⁸ or iridium⁹ have been reported to date to induce this silane functionalization. Given the interest in the chiral version,^{6,7,9} it seems appropriate to expand the yet reduced number of potential metals. On the basis of our previous work on the related C-H functionalization by carbene insertion with group 11 metal-based catalysts,¹⁰ we decided to test the catalytic capabilities of copper and silver complexes bearing the hydrotris(3,4,5-tribromopyrazolyl)borate ligand (Tp^{Br3}),¹¹ which have already been employed in the aforementioned C–H bond functionalization reaction.¹² As a result of this study, we found that both complexes induce the silane functionalization to a significant degree, in the first example of a silver-mediated Si-H derivatization by carbene insertion from diazo compounds.



Results and discussion

Catalytic activities of the complexes $Tp^{Br3}Cu(NCMe)$ (1) and $[Tp^{Br3}Ag]_2$ (2) in the reaction of silanes with ethyl diazoacetate

Given the well-known catalytic capabilities of the copper and silver complexes $Tp^{Br3}Cu(NCMe)^{12a}$ (1) and $[Tp^{Br3}Ag]_2^{12b}$ (2)



Scheme 2 Triethylsilane functionalization by carbene insertion from ethyl diazoacetate using complexes **1** or **2** as the catalyst precursor. ^aDiazo compound added in one portion. ^bSlow addition of diazo compound for 12 h.

toward the decomposition of ethyl diazoacetate (N_2CHCO_2Et , EDA) and the subsequent transfer of the :CHCO₂Et group to alkanes, we decided to expand their scope for silanes. As a probe substrate we have chosen Et_3SiH in order to compare the relative reactivity of C–H and Si–H bonds toward this transformation. As shown in Scheme 2, when this silane was reacted with EDA in the presence of catalytic amounts of the copper complex 1, the corresponding functionalized silane 3 was obtained in 68% yield, referred to the initial EDA. The reaction was performed using a 1:50:630 ratio of [catalyst]: [EDA]: [silane], adding the diazo compound in one portion at the beginning of the reaction (overall reaction time 12 h). That yield was enhanced up to 76% when adding the diazo compound with the aid of a syringe pump for 12 h. In addition to 3, diethyl fumarate and maleate accounted for all initial EDA.

The silver-based catalyst 2 yielded 3 in 42% yield when adding EDA in one portion, with some other minor byproducts derived from the insertion of the carbene group into the ethyl C-H bonds being observed. However, when the reaction was performed using a slow addition device, only 3 was obtained in 72% yield, in addition to diethyl fumarate and maleate. The reaction was therefore quite selective toward the Si-H bond, in spite of a larger number of C-H bonds being available in the substrate. This is in agreement with the difference between the bond dissociation energies of silanes (*ca.* 90 kcal mol^{-1})¹³ and non-activated C-H bonds (ca. 94-97 kcal mol⁻¹).¹⁴ It is also worth mentioning that the tetrahedral environment forced by the Tp^x ligand seems to be crucial in the reaction outcome. The complexes bearing an N-heterocyclic carbene ligand such as IPr, either neutral or cationic, did not induce this transformation. The naked-silver precursor AgOTf did not catalyze this transformation either (Scheme 2).

After those preliminary results, we carried out a full set of experiments with a series of silanes bearing either alkyl or aryl substituents, and with primary, secondary and tertiary Si–H bonds (Scheme 3). The results are shown in Table 1. Diethyl silane was functionalized in a similar manner to triethylsilane, the silver-based catalyst being similar or slightly more active than the copper catalyst. A series of three mono-, di- and



Scheme 3 Alkyl- and aryl-silanes functionalization carried out in this work.

 $Table \ 1$ $\$ Catalytic functionalization of silanes with complexes 1 or 2 and ethyl diazoacetate (EDA)^a

| | | Catalyst/diazo addition ^b | | | | |
|-------|----------------------------------|--------------------------------------|--------------------------------------|----------------------------|------------------------------|--|
| Entry | Silane | 1 /one portion ^c | 1 /slow addition ^d | 2/one portion ^c | 2/slow addition ^d | |
| 1 | Et₃SiH | 68 | 76 | 42 | 72 | |
| 2 | Et ₂ SiH ₂ | 77 | 79 | 78 | 84 | |
| 3 | Ph ₃ SiH | 39 | 71 | 13 | 43 | |
| 4 | Ph_2SiH_2 | 81 | n.p. ^e | 94 | n.p. ^e | |
| 5 | PhSiH ₃ | 49 | 80 | 37 | 78 | |
| 6 | nPr ₃ SiH | 44 | 82 | 15 | 12 | |
| 7 | Me2 ^t BuSiH | 62 | 92 | 12 | 10 | |
| 8 | Me ₂ PhSiH | 74 | 80 | 11 | 72 | |
| 9 | MePh ₂ SiH | 75 | 70 | 7 | 40 | |

^{*a*} [catalyst]: [EDA]: [silane] = 1:50:630, 0.01 mmol of catalyst, 12 h of reaction time. ^{*b*} Percentage of the functionalization product, based on initial EDA. The remaining diazo compound was converted into diethyl fumarate and maleate. ^{*c*} EDA was added in one portion. ^{*d*} EDA was added for 12 h from a syringe pump. See the Experimental section for details. ^{*e*} Not performed.

tri-phenyl substituted silanes were also employed as the substrate. No reaction onto the aromatic ring (either addition to the double bond or insertion into the C-H bonds) was observed, only the modification of the Si-H and the corresponding formation of compounds 5-7 were detected. Yields were moderate to high both with copper and silver, with a very high value in the case of Ph₂SiH₂ being obtained with 2 as the catalyst and adding the EDA in one portion. A series of silanes with two different substituents (entries 6-9) have also being studied, with a reactivity pattern similar to that already commented on. Copper gave moderate to high yields whereas silver induced variable yields. Thus MePh2SiH was functionalized at 40% with 2 as the catalyst (entry 9), similarly to the value obtained with Ph₃SiH as the substrate (40%, entry 3). Analogously, Me₂PhSiH and Et₃SiH provided yields around 70%. These data support the proposal of a delicate balance between steric and electronic effects of the substituents. Finally, trialkyl-substituted silanes with bulky groups gave low conversions.

These results constitute, to the best of our knowledge, the first example of a silver-based catalyst capable of inducing the catalytic functionalization of silanes by carbene insertion. Given the aforementioned reduced number of metals yet^{4–9} reported for this transformation (rhodium, iridium, copper), the incorporation of another metal could be interesting *per se*. It has to be pointed out that the catalytic activity of this catalyst is not as high as those of the above metals. However, we believe that the use of silver integrates some value added to the field. First, it does not oxidize to the +2 oxidation state as copper does, a wellknown decomposition route for most of the Cu-based catalysts. Second, there are several silver-based chiral complexes and salts that could be employed to develop the chiral version of this reaction, which could make them suitable as potential catalysts and, if positive, would challenge chiral rhodium⁶ and iridiumbased⁹ catalysts from an economical point of view.

Relative reactivity of silane bonds toward carbene insertion

It is a well-known feature in the related carbon-hydrogen bond functionalization reaction with diazo compounds that the relative reactivity follows the trend tertiary C-H > secondary C-H > primary C-H, *i.e.*, it is coincident with the bond dissociation energy (BDE).¹² This is in good agreement with a transition state in which the C-H bond interacts with the metallocarbene carbon atom, with the concerted breaking of such C-H bonds and the concomitant formation of the new C-C and C-H bonds.¹⁵ In order to ascertain if such behavior can be extrapolated to the Si-H bonds, we have run a competition experiment with the three silanes bearing the phenyl rings, using a 2:1:0.67 molar mixture of Ph₃SiH: Ph₂SiH₂: PhSiH₃, respectively, which ensures the same number of potential Si-H reaction sites for each reagent. At the end of the reaction, a mixture of compounds 5-7 was obtained (Scheme 4), the resonance of the CH2 group of the Si-CH2-CO2Et moiety in the ¹H NMR spectrum of the reaction mixture providing the exact ratio of products obtained (Fig. 1). The 5:6:7 ratio was quite similar for both the copper and silver catalysts: 1.0:1.4:1.2 for the former and 1.0:1.2:1.1 for the latter. In both cases, the secondary > primary \approx tertiary trend seems to be distinct from that described for the related C-H functionalization reaction. However, there is a significant difference between C-H and

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equimolar in Si-H bonds



Si-H bond dissociation energies.^{13,14,16} The incorporation of a phenyl ring attached to the C-H moiety induces, by conjugation, a decrease in the BDE by 17 kcal mol^{-1} (89 kcal mol^{-1} in toluene vs. 105 kcal mol⁻¹ in methane);¹⁴ on the other hand, such substitution barely originates a substantial decrease of the BDE of a Si-H bond attached to a Ph ring: the 91.8 kcal mol⁻¹ of a Si-H attributed to SiH₄ dropped to 91.3 in PhSiH₃ and 88.7 in Ph₃SiH.¹³ Thus, the narrow interval of less than 3 kcal mol⁻¹ and the considerable difference in bulkiness within the three silanes employed could explain that steric effects influence to a larger extent the Si-H functionalization reaction. To verify our hypothesis, we have run a second competition experiment using Et₃SiH and Et₂SiH₂, and complex 1 as the catalyst, from which a 1.8:1 relative reactivity for tertiary: secondary Si-H bonds has been obtained. It seems clear that the decrease of the steric pressure around the functionalization site shows that the reaction is electronically-driven.

Functionalization with other diazo compounds

Other diazo compounds have also been tested with both catalysts in order to check the effect of the substituents at the



Fig. 1 Selected region of the ¹H NMR spectrum corresponding to competition experiments with different silanes. Left: Experiment carried out with Ph₃SiH, Ph₂SiH₂ and PhSiH₃ leading to a mixture of **5–7**. Right: Experiment carried out with Et₃SiH, Et₂SiH₂ affording **3** and **4** (see Scheme 4 for numbering).



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| Entry | \mathbb{R}^{1} | 1 | 2 |
|-------|------------------|----|----|
| 1 | Н | 72 | 76 |
| 2 | Me | 15 | 0 |
| 3 | Ph | 70 | 33 |
| 4 | CO_2Et | 36 | 14 |
| | | | |

 a See the Experimental section for details. Although previously reported, the NMR data of the products are given in the ESI‡ for the sake of completeness.

diazo functionality. Thus, in addition to EDA, three more diazo compounds bearing common CO₂Et substituents have been studied, varying the other group among Me, Ph and CO_2Et [eqn (1)], and with triethylsilane as the substrate. As shown in Table 2, the group of diazo reagents induced quite distinct yields. This is related to the different electronic behavior of the substituents.¹⁷ It seems that for this transformation, the preferred diazo compounds are those bearing H or Ph groups, that is, an acceptor or a donor-acceptor diazo source, respectively. The acceptor-acceptor diazomalonate is less reactive due to the stability of the diazo compound.^{2,17} Interestingly, the donor-acceptor CH₃C(N₂)CO₂Et does not work in a similar manner to that containing a Ph group. The role of the phenyl substituent in these transformations has been extensively studied by Davies and co-workers in a number of transformations.17

Conclusions

We have found that the complexes $Tp^{Br3}Cu(NCMe)^{12a}$ (1) and $[Tp^{Br3}Ag]_2^{12b}$ (2) catalyze the transfer of carbene units from diazo compounds, to Si-H bonds, with moderate to high yields, the silver case being the first example based on this metal for such transformation. The relative reactivity seems to be strongly influenced by steric factors, although in their absence the observed trend seems to follow the bond dissociation energy order. The discovery of silver as a metal to promote this transformation could be of interest to increase the knowledge of the chiral version of this reaction.

Experimental

General

All preparations and manipulations were carried out using Schlenk techniques or a glovebox. The solvents were dried using a Solvent Purification System (MBraun). All the reagents

were purchased from Aldrich and used without further purification. GC data were collected with a Varian 3900 instrument. NMR spectra were recorded on a Varian Mercury 400 MHz. The complexes $Tp^{Br3}Cu(NCMe)$ (1) and $[Tp^{Br3}Ag]_2$ (2) were prepared according to the literature.^{12a,b}

General procedure for the silane functionalization reaction

Complexes 1 or 2 (0.01 mmol) were dissolved in a mixture of dichloromethane (3 mL) and the corresponding silane (6.3 mmol). Ethyl diazoacetate (52.6 μ L, 0.5 mmol) was added in one portion or dissolved in dichloromethane (3 mL) and added for 12 h with the aid of a syringe pump, at room temperature. No ethyl diazoacetate was detected by GC after 12 h in both cases. The solvent was removed under reduced pressure and the residue was dissolved in CDCl₃ to be analyzed by ¹H NMR spectroscopy. 2-Iodoanisole as an internal standard was added (39.1 μ l, 0.3 mmol), the conversion and yields being estimated by ¹H NMR. Although previously reported, the NMR data of the products are given in the ESI[‡] for the sake of completeness.

Competition experiments with Ph₃SiH, Ph₂SiH₂ and PhSiH₃

0.01 mmol of complexes **1** or **2** were dissolved in CH_2Cl_2 (3 mL) and the solution was charged with 2 mmol of Ph_3SiH , 1 mmol of Ph_2SiH_2 and 0.67 mmol of $PhSiH_3$. Ethyl diazoacetate (52.6 µl, 0.5 mmol) was added, in one portion, to the above solution. The ratio of products was determined by ¹H NMR spectroscopy (see Fig. 1) as 1.0:1.4:1.2 with **1** and 1.0:1.2:1.1 with **2**.

Competition experiment with Et₃SiH and Et₂SiH₂

Following a similar procedure to that described above, 0.01 mmol of complex 1 was dissolved in CH_2Cl_2 and the solution was charged with 2 mmol of Et_3SiH and 1 mmol of Et_2SiH_2 . A solution of ethyl diazoacetate (52.6 µl, 0.5 mmol) in dichloromethane (5 mL) was slowly added for 12 h with the aid of a syringe pump into the above solution. The ratio of products 3:4 was determined by ¹H NMR spectroscopy (see Fig. 1) as 1.8:1.

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