

Catalytic Functionalization of Methane and Light Alkanes in Supercritical Carbon Dioxide

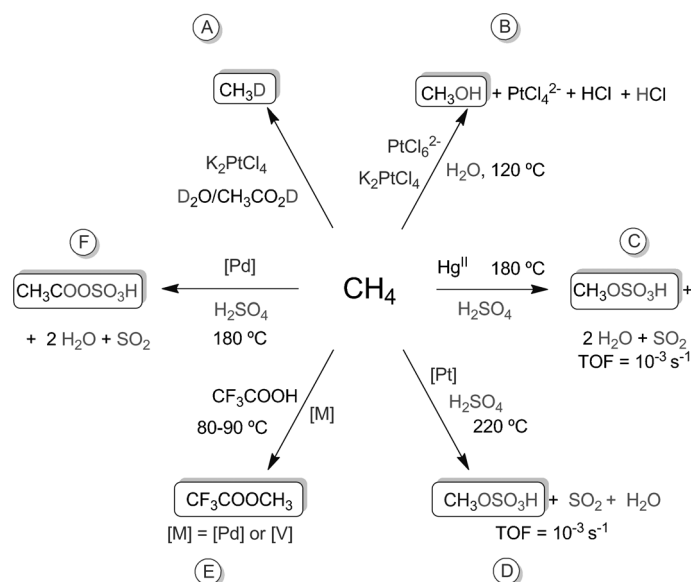
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Abstract: The development of catalytic methods for the effective functionalization of methane yet remains a challenge. The best system known to date is the so-called Catalytica Process based on the use of platinum catalysts to convert methane into methyl bisulfate with a TOF rate of 10^{-3} s. In this contribution, we report a series of silver complexes con-

taining perfluorinated tris(indazolyl)borate ligands that catalyze the functionalization of methane into ethyl propionate upon reaction with ethyl diazoacetate (EDA) by using supercritical carbon dioxide (scCO₂) as the reaction medium. The employment of this reaction medium has also allowed the functionalization of ethane, propane, butane, and isobutane.

Introduction

Methane is available in the earth's crust either in natural or shale gas and in ocean beds as clathrates in such amounts that it could be considered the ideal raw material for C1 chemistry.^[1,2] The main current use of methane from an industrial point of view consists of the preparation of syngas (synthesis gas), a mixture of carbon monoxide and hydrogen that can be further employed in the synthesis of methanol in the Fischer-Tropsch process for synthetic gasoline or in reactions requiring carbon monoxide and/or hydrogen (hydroformylation, hydrogenation, ammonia synthesis, or carbonylation among others).^[3] Alternatively, the direct, selective and low-energy conversion of methane into more valuable chemicals in homogeneous media yet constitutes a long-term challenge. Controlled oxidation of methane has been a major goal, given the importance of methanol as a fuel and an oxygenated inter-



Scheme 1. Different catalytic systems described to date based on the electrophilic activation of methane.

mediate. Significant advances are summarized in Scheme 1.^[4] In the late 1960s, Shilov and co-workers described the potential of platinum salts to promote the electrophilic activation of methane, first stoichiometrically (Scheme 1, route A) then catalytically (Scheme 1, route B).^[5] The main drawback of using platinum as a stoichiometric oxidant was addressed by Periana and co-workers who described the conversion of methane into methyl bisulfate in sulphuric acid as the reaction medium first with mercury (Scheme 1, route C),^[6] then with platinum salts as catalyst precursors in the so-called Catalytica process (route D).^[7] Very recently, main-group metals (Tl, Pb) were shown to oxidise the C–H bonds of methane and light alkanes

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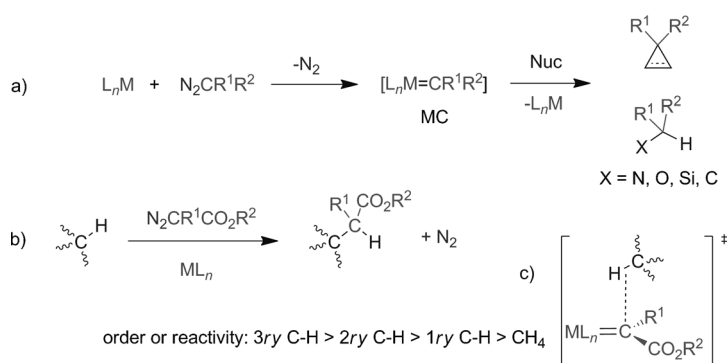
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in a stoichiometric manner.^[8] Other less effective examples of the functionalization of methane have been described by using trifluoroacetic acid as the reactant (route E).^[9,10,11] In addition to methyl bisulfate, acetic acid derivatives were observed under Catalytica-like conditions with a palladium-based catalyst (route F).^[12]

The need of harsh conditions for the functionalization of methane (and for alkanes in general)^[13] can be attributed to two thermodynamic and kinetic factors: the high C–H bond dissociation energy (BDE ca. 105 kcal mol⁻¹ for methane)^[14] and the very low polarity of the C–H bond derived from the similar electronegativity of C and H ($\chi_C = 2.55$, $\chi_H = 2.20$, Pauling scale). With a few exceptions, the activation of the weakly nucleophilic C–H bond of an alkane requires a powerful electrophile.^[15] Not surprisingly, the examples shown in Scheme 1 are termed electrophilic activation.

There are alternative ways of functionalizing methane with tuneable transition-metal catalysts. An attractive catalyst would be a metallocarbene complex (MC), generated in situ upon reacting the appropriate transition-metal complex and a diazo compound, a strategy that has ample precedents in organic synthesis.^[16] Complexes of metals from Groups 8 to 11 have been described for the transfer of CR¹R² units from N₂=CR¹R² (Scheme 2a) to a wide array of nucleophiles from olefins and



Scheme 2. a) General metal-catalyzed carbene transfer from diazo compounds. b) C–H bond functionalization by carbene insertion. c) Transition state for carbene insertion into C–H bonds.

alkynes to X–H bonds (X=N, O, Si, among others), in either inter- or intramolecular reactions. The reactive metallocarbenes MCs have been detected or isolated in a few cases.^[17,18] The functionalization of carbon–hydrogen bonds, including nonactivated C–H bonds such as those of alkanes, by this methodology is also known. Catalytic systems are based on rhodium, copper, silver, and gold, with a couple of examples on iron and ruthenium.^[19,20]

Diazo reagents of general formula N₂=CR¹CO₂R² were employed for C–H insertion reactions allowing the direct conversion of alkanes into esters upon chain homologation (Scheme 2b). This transformation has

been proposed to occur without any metal–alkane contact through a direct interaction of the C–H bond with the carbenic carbon atom (Scheme 2c). Therefore the trend in reactivity usually observed, tertiary > secondary > primary > methane C–H bonds, follows that of the bond-dissociation energies (BDEs).^[14] This trend has a tremendous impact when focussing on the functionalization of methane: the reaction must be carried out in the absence of any other C–H bond that would react more easily than that of methane. In this contribution, we report^[21] the use of a series of silver complexes bearing perfluorinated hydrotris(indazolyl)borate ligands that have been found to catalyse the reaction of methane and ethyl diazoacetate (N₂=CHCO₂Et, EDA) to give ethyl propionate in supercritical carbon dioxide (scCO₂) as the reaction medium.

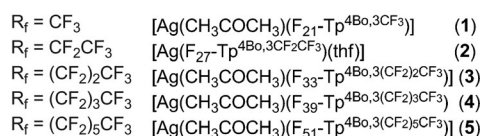
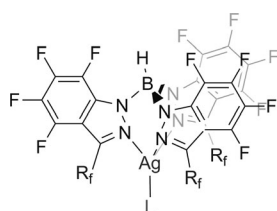
Results and Discussion

Catalytic functionalization of methane with silver-based catalysts

As mentioned above, the election of methane as the target substrate brings the need of the absence of other, more reactive, C–H bonds in the reaction mixture. Therefore, we decided to develop a catalytic system for the transfer of carbene units

from ethyl diazoacetate (EDA) to methane by using supercritical carbon dioxide (scCO₂) as the reaction medium, leaving methane as the only compound bearing C–H bonds available to react. In addition to the requirement of an electrophilic metal centre for the catalyst, we must add the capability of the latter to dissolve in scCO₂. Both features could be fulfilled with the series of complexes [Ag(F_N-Tp^{4Bo,3C_nF_{2n+1})](L) (N = 6n + 15; n = 1, L = acetone, **1**; n = 2, L = THF, **2**; n = 3, L = acetone, **3**; n = 4, L = acetone, **4**; n = 6, L = acetone, **5**),^[22] bearing a perfluoroalkyl chain C_nF_{2n+1} in the 3-position of the indazolyl ring as well as four additional fluorine atoms per indazolyl group (Scheme 3). It is well known that a high degree of fluorination of the catalyst facilitates dissolution in scCO₂.^[23] In addition, the donor capabilities of the N atoms in those ligands are considerably lowered due}

to the presence of the fluorine substituents. Actually, the corresponding [Ag(CO)(F_N-Tp^{4Bo,3C_nF_{2n+1})] complexes display $\nu(\text{CO})$ values within the very narrow range of 2166–2167 cm⁻¹, which indicates not only an electron-deficient metal centre,^[24] but also a very limited electronic effect of the length of the fluorinated chain at the 3-position.}



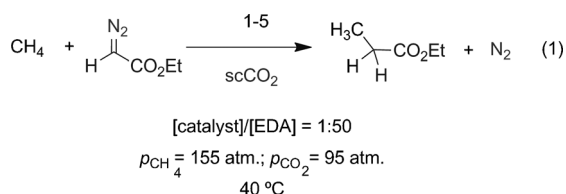
Scheme 3. Silver complexes employed as catalysts in this work.

Complexes 1–5 have been tested as catalysts for the reaction of EDA with methane in $scCO_2$ as the reaction medium. In a high-pressure vessel, EDA (0.35 mmol) was placed in a polypropylene open container, whereas the catalyst (0.007 mmol of compounds 1–5) was introduced in a polypropylene cylinder with two parallel filters. The reactor was then heated and maintained at 40 °C before pressurizing with methane at 155 atm. Carbon dioxide was then pumped in that temperature to reach a final pressure of 250 atm. This mixture corresponded to a 0.96 molar ratio of CH_4/CO_2 (experimentally determined by weight). Under these conditions of temperature and pressure, a homogeneous fluid resulted within a few minutes. The mixture was stirred for 14 h before being analyzed with the aid of a GC connected on-line to the reactor. The GC trace showed the formation of ethyl propionate [Eq. (1)] as the result of the silver-mediated insertion of the $CHCO_2Et$ unit from EDA into the C–H bond of methane. As shown in Table 1,

R	Cat.	Ethyl propionate [mmol]	Yield [%] (EDA-based) ^[b]
CF_3	1	0.103	29
CF_2CF_3	2	0.080	22
$CF_2CF_2CF_3$	3	0.067	19
$CF_2CF_2CF_2CF_3$	4	0.063	18
$CF_2CF_2CF_2CF_2CF_3$	5	0.064	18

[a] 0.007 mmol of catalyst. [b] By GC analysis using calibration curves. See the Supporting Information.

the amount of ethyl propionate slightly decreased when moving from 1 to 5, corresponding to yields within the range of 29–18% (EDA-based). The remaining of the initial EDA was converted into a mixture of diethyl fumarate and maleate (from metal-mediated diazo coupling),^[25] along with some ethyl 2-hydroxyacetate (from adventitious water functionalization).



Interestingly, we observed through the sapphire windows of the reactor (see the Supporting Information) that most of the initial solid remained in the polypropylene vessel at the end of the reaction. A control experiment in which only $scCO_2$ was introduced in the reactor showed that catalysts completely dissolved in the supercritical fluid, which indicated that methane is a very poor solvent for these compounds. To evaluate the actual concentration of the catalyst dissolved in the reaction medium, the reactor was slowly depressurized through a cold

trap to condense reactants, products, and some dissolved catalyst. In addition, the residue inside the reactor (and outside the catalyst container) was collected with methylene chloride. Both samples (from the trap and the reactor) were investigated by ICP-MS, showing the presence of silver in the supercritical phase, with most of it remaining inside the reactor after depressurization. A plot of the total amount of silver dissolved in the reaction mixture as a function of the percentage of fluorine in the catalyst is shown in Figure 1. In spite of initially adding

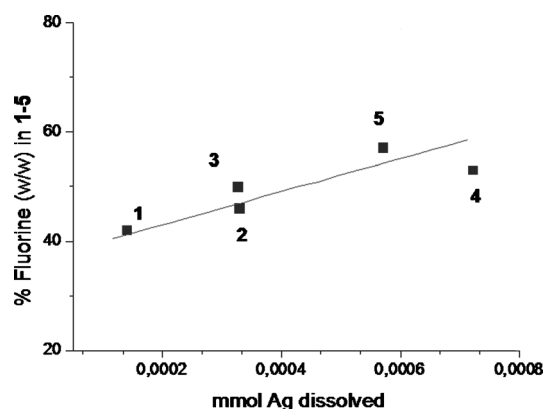


Figure 1. Solubility of complexes 1–5 in a 155:95 atm. mixture of methane/carbon dioxide at 40 °C as a function of the percentage of fluorine.

the same quantity of the different catalysts (7×10^{-3} mmol), their concentration in solution varied within the range 1×10^{-4} to 7×10^{-4} mmol. Also, the homogeneous nature of the catalytic reaction under supercritical conditions was assessed with pentane as the substrate and 2 as the catalyst [Eq. (2)]. It is seen that very similar regioselectivity for carbene insertion into the various CH bonds of pentane is observed either in pure pentane acting as a solvent (and a substrate) or in $scCO_2$, which indicates an identical mechanism for both processes. Additional evidence has been obtained with a competition experiment between methane and ethane [Eq. (3)]. A respective 2.81:1 molar ratio of both gases in $scCO_2$ was reacted with EDA in the presence of 2 as the catalyst was fully soluble under these conditions. Ethyl propionate and butyrate were obtained leading to a corrected relative reactivity $C-H_{ethane}/C-H_{methane}$ of 14.^[21] On the basis of the available data, we believe that the homogeneous nature of this transformation is well established.

Once the amounts of dissolved catalysts in $scCO_2$ were determined, we could estimate the turnover number (TON) of the series of catalysts for the functionalization of methane, on the basis of the amount of ethyl propionate formed (Table 1) and of silver available in solution (data from Figure 1). Table 2 shows the corresponding data, from which the highest TON of 734 was obtained for complex 1, a remarkable number for the functionalization of methane with a metal-based catalyst in homogeneous medium. The TON was observed to decrease when the amount of dissolved silver was increased (Figure 2), again complex 1 being the more active of the series under

	1	2	3	4	5
TON ^[b]	734	242	204	87	112
TOF ^[c]	0.014	0.004	0.003	0.001	0.002

[a] From the data in Table 1 and Figure 1 (see the Supporting Information). [b] As mmol product/mmol catalyst. [c] As mmol product/(mmol catalysts x h).

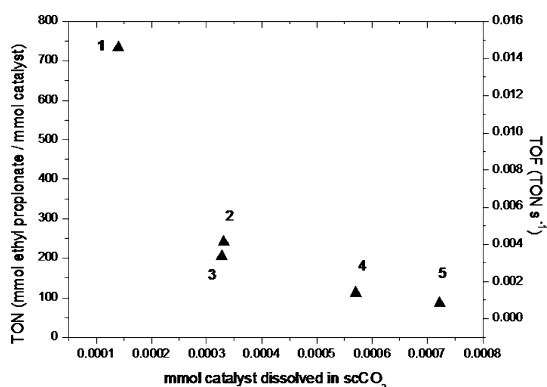
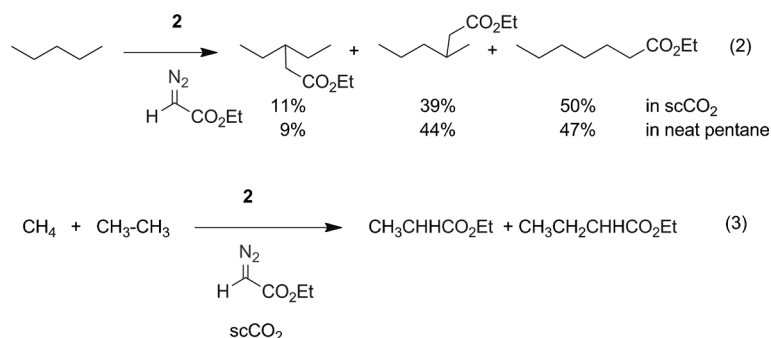


Figure 2. TON and TOF values of the reaction of methane with EDA with 1–5 as the catalysts.



these reaction conditions. This TON corresponds to a TOF of 0.014 s⁻¹. As a general trend, the catalytic functionalization of methane is favoured by high pressures of the hydrocarbon and by low catalyst concentrations. The latter is the result of a decrease in the deleterious EDA dimerization that gives diethyl fumarate and maleate, as demonstrated from our previous work.^[25]

Overall, elimination of other more reactive C–H bonds from the reaction medium by using scCO₂ as the solvent allows the functionalization of methane following a methodology previously described for more reactive C–H bonds.

Catalytic functionalization of ethane, propane, and butanes: Relative reactivity toward methane

After having demonstrated the catalytic capabilities of the silver complexes 1–5 to transfer CHCO₂Et units from EDA to

the C–H bonds of methane, we decided to explore the next members of the homologous series C_nH_{2n+2} with n=2–4, which have been scarcely employed with this methodology.^[26] The hydrocarbon (ethane, propane, *n*-butane, or *iso*-butane, large excess, see the Supporting Information for exact amounts) was reacted with EDA (0.5 mmol) in scCO₂ for 4 h with [Ag(F₂₇-Tp^{4Bo,3CF₂CF₃})(thf)] (5 × 10⁻³ mmol) as the catalyst to give the insertion products shown in Scheme 4. This time was enough to achieve full consumption of EDA (>98%). It is worth mentioning that the catalyst was completely soluble in the C₂–C₄ alkane/scCO₂ mixtures. The yields in functionalized products were 84% for ethane and >95% (EDA-based) for propane and both linear and branched butanes. This contrasts with the functionalization of methane that only consumed 31% of EDA to give ethyl propionate with 7% yield under these conditions (different from those employed in the previous section). Propane, *n*-butane and *iso*-butane each led to a mixture of two products as the result of the existence of two distinct reaction sites. The relative reactivity (per CH bond) found for primary versus secondary C–H bonds in propane and *n*-butane was 1.0:3.6 and 1.0:2.1, respectively. This difference must be related to the distinct steric hindrance of both secondary C–H bonds, since their BDE values are nearly identical. For *iso*-butane the ratio for primary versus tertiary sites increased to 1.0:4.0.

Conclusion

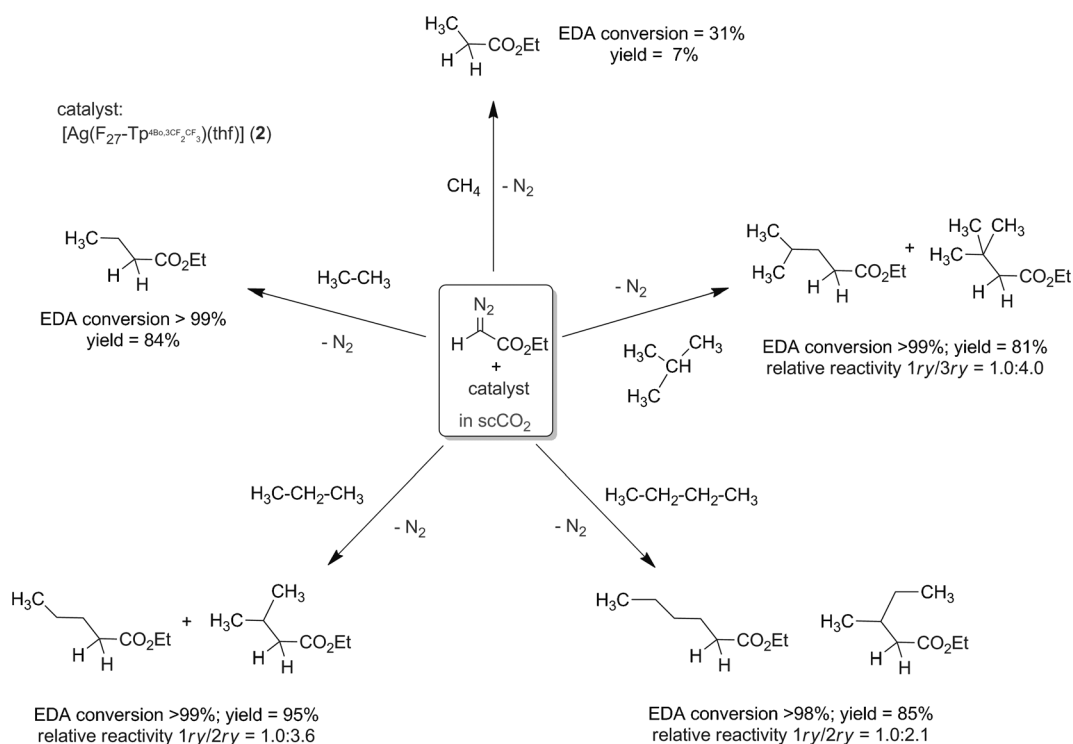
We have developed a family of perfluorinated tris(indazolyl)borate silver complexes that are capable of catalyzing the transfer of carbene units from ethyl diazoacetate to the very poorly nucleophilic carbon–hydrogen bond of methane. TON and TOF values of 734 and 1.4 × 10⁻² s⁻¹, respectively, have been achieved with the most active catalyst. Other light alkanes (ethane, propane, *n*-butane, and *iso*-butane) have also been functionalized

and the relative intramolecular reactivity values for the C–H bonds in those alkanes have been obtained. This contribution has also demonstrated the potential of using an inert phase, such as scCO₂, as a reaction medium to isolate the C–H bonds of methane from other more reactive bonds, favoring the aforementioned catalytic functionalization.

Experimental Section

General methods

All substrates were purchased from Aldrich. Substrates and solvents were rigorously dried prior to their use. The complexes [Ag(acetone)(F₂₁-Tp^{4Bo,3CF₂CF₃})] (1),^[27] [Ag(F₂₇-Tp^{4Bo,3CF₂CF₃})(thf)] (2),^[21] [Ag(acetone)(F₃₃-Tp^{4Bo,3(CF₂)₂CF₃})] (3),^[22] [Ag(acetone)(F₃₉-Tp^{4Bo,3(CF₂)₃CF₃})] (4)^[22] and [Ag(acetone)(F₅₁-Tp^{4Bo,3(CF₂)₅CF₃})] (5),^[22] were prepared ac-



Scheme 4. Functionalization of C_1 – C_4 alkanes with EDA by using complex **2** as the catalyst in $scCO_2$.

according to the literature from the respective hydrotris(indazolyl)borate salts.^[28] The supercritical experiments were carried out in a commercial THAR Technologies R100SYS supercritical plant or in Phenomenex empty 33 mL HPLC columns 21.2 mm ID×1 in OD×100 mmL connected to a HIP valve through 1/16" stainless steel tubes. A Varian GC 450 was directly connected to the supercritical reactor vessels for online product analysis. Ag was analyzed by inductively coupled plasma mass spectrometry (ICP-MS) with an HP4500 instrument with detection limit of 0.01 $\mu\text{g L}^{-1}$.

Functionalization of methane in supercritical carbon dioxide with $[\text{Ag}(\text{acetone})(\text{F}_{21}\text{-Tp}^{4\text{Bo},3\text{CF}_3})]$ to $[\text{Ag}(\text{acetone})(\text{F}_{51}\text{-Tp}^{4\text{Bo},3(\text{CF}_2)_2\text{CF}_3})]$ series

These reactions were performed in a 100 mL stainless steel reactor mechanically stirred by paddles. The corresponding complex (**1–5**, 0.007 mmol) was placed into a polypropylene tube, and both sides were closed with a permeable cap. A second polypropylene container was charged with ethyl diazoacetate (0.35 mmol). Both containers were fixed to the mixer axis of the reactor (see the Supporting Information for details). The reactor was closed and pressurized first with 155 atm. of methane and then with carbon dioxide up to a total pressure of 250 atm. at a constant temperature of 40 °C (computer controlled). Through a sapphire window we could observe differences in the solubility of the reaction components, EDA completely dissolved in the reaction medium while the major part of the catalyst seemed to remain in the polypropylene container (see the Supporting Information). After 14 h of stirring at 40 °C, the reaction was analyzed by gas chromatography. The gas mixture was directly injected into the GC column by opening the valve connecting the reactor and the GC analysis. The exact amounts of the products were determined using calibration curves previously recorded with commercial samples.

Quantification of the amount of silver complex dissolved

After analysis of the reaction mixture by gas chromatography, the reactor was depressurized slowly through a trap cooled at –78 °C. Once atmospheric pressure was reached, the reactor was opened and, after removing the catalyst container, it was washed with dichloromethane (3×10 mL). The trap was allowed to warm to room temperature and it was washed with dichloromethane in the same manner. All solutions were collected and the solvent was removed and the residue was dissolved in 2 mL of aqueous HNO_3 (5%) and diluted to a final volume of 10 mL with Milli-Q water. The samples were analyzed by ICP-MS. See the Supporting Information for data collected.

Functionalization of light alkanes C_1 – C_4 in supercritical carbon dioxide with $[\text{Ag}(\text{F}_{27}\text{-Tp}^{4\text{Bo},3\text{CF}_2\text{CF}_3})(\text{thf})]$ (**2**)

These reactions were performed in a supercritical reactor consisting of an empty 33 mL HPLC column connected to a high-pressure valve through a 1/16" stainless steel tube. To ensure the homogenization of the reaction mixture, the reactors were immersed in an ultrasound bath thermostated at 40 °C. Two polypropylene receptacles were placed inside the column containing EDA (0.5 mmol) and the catalyst **2** (0.005 mmol). The first container was opened on one side while the second one was closed with permeable caps on both sides. The reactor was then closed and weighted. For reactions with methane the column was connected to a methane bottle and pressurized to 150 atm. For reactions with ethane, the reactor was connected to an ethane bottle and pressurized to 30 atm. For reactions with propane, butane, and isobutane, the reactor was cooled to 0 °C and connected to a pressurized bottle of the desired alkane for a period of time long enough to charge 3 to 5 g of the alkane. The exact amount of alkane was determined by weight difference before and after pressurization (see the Supporting Information). The reactor was then placed in an ultrasonic bath

thermostated at 40 °C. After temperature stabilization the reactor was pressurized with CO₂ until a total pressure of 250 atm. was reached. The reactor was sonicated for 4 h before connecting it to the GC and the analysis of the reaction mixture. The exact amount of the different products was determined using calibration curves obtained with commercial samples (see the Supporting Information).

Acknowledgements

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Keywords

carbene insertion • C–H activation • diazo compounds
• methane activation • silver catalysts

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