Silver-catalyzed [2,3]-rearrangement of halonium ylides derived from allyl and propargyl halides and alkyl diazoacetates†

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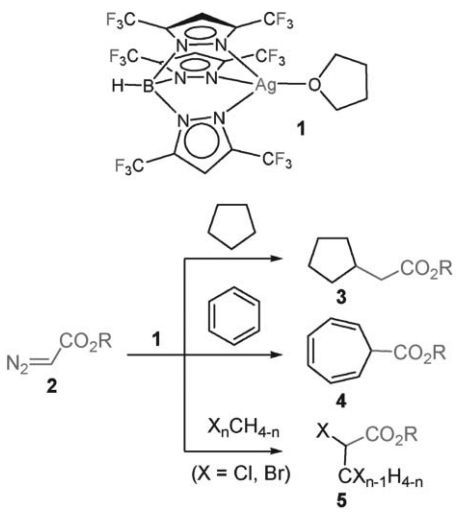
A silver(I) complex derived from a polyfluorinated tris(pyrazolyl)borate effectively catalyzes carbene transfer to allylic and propargylic halides, leading to the formation of α-haloacetate derivatives.

The use of metallacarbenes generated from diazo compounds and transition metals has been a fertile area of investigation leading to the invention and development of a number of robust synthetic methods.[1–3] Over the past few years, as a result of our ability to access of variety of well defined and thermally stable coinage metal (Cu, Ag, Au) complexes derived from polyfluorinated tris(pyrazoyl)borate (Tp) ligands,[4–10] we became interested in assessing the potential of these highly electron-deficient species as catalysts in nitrene, carbene and oxo transfer reactions.[11–14] Of the complexes investigated to date, silver complex $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(THF)$, **1** and ethyl diazoacetate (**2**, EDA) has displayed some very interesting and in some cases unusual reactivity patterns (Scheme 1).[15,16] For example, it catalyzes C–H insertion (**2** → **3**, Scheme 1),[13] the Büchner reaction (**2** → **4**, Scheme 1)[14] and, most interestingly, the insertion into C–Hal (Cl, Br) bonds of polyhalomethane derivatives (**2** → **5**, Scheme 1).[12]

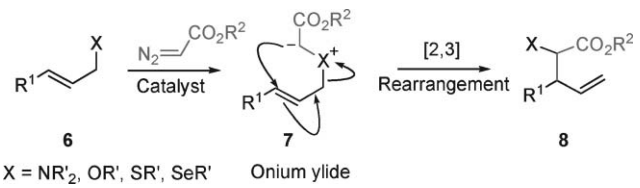


Scheme 1

Although we have no definitive evidence at this time for the precise mechanistic pathways of these reactions, the products obtained from these reactions are consistent with the formation of a silver carbenoid intermediate. In the case of the formation of **5**, as a working hypothesis, we proposed the intermediacy of a halonium ylide and a subsequent 1,2-shift.[12] With this in mind we began to search for other transformations that proceed *via* an ylide intermediate. Several metallacarbene species catalyze the generation of ylides with Lewis basic functional groups (X = NR'_2, OR′, SR′, SeR′), which if there is a pendent allyl moiety are poised to engage in a [2,3]-sigmatropic rearrangement (**6** → **7** → **8**, Scheme 2).[17] The corresponding rearrangement with allyl halides is much rarer, although some precedent does exist. Several rhodium and copper complexes have been shown to catalyze the formation and [2,3]-rearrangement of halonium ylides generated from a limited number of allylic halides and EDA.[18–20] Given the propensity of carbenoids generated with the aid of complex **1** to interact with halogen-containing substrates, this rearrangement appeared to offer a perfect opportunity for investigation.

We chose initially to investigate simple allyl halides as substrates and quickly established that the addition–rearrangement sequence was going to be viable. For example, when EDA was added *via* syringe pump to a solution of 2.5 mol% of **1** in allyl bromide (Table 1, entry 1), the expected product was obtained in 75% yield (Scheme 3). It should be noted that this product could also be formed *via* the 1,2-rearrangement pathway that had been previously proposed to account for the insertion into C–Hal bonds rather than the [2,3]-pathway.[12,21] In order to address this issue, crotyl chloride was employed under identical reaction conditions and this gave rise to a 1 : 1 mixture of *syn*- and *anti*-products, which clearly supports the sigmatropic rearrangement pathway (Table 1, entry 2).

As these initial reactions proceeded effectively, we investigated the scope and limitations of this reaction with a variety of chlorides and bromides, employing both EDA and *t*-butyl diazoacetate



Scheme 2

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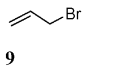
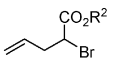
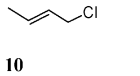
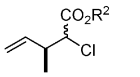
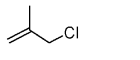
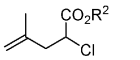
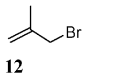
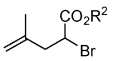
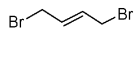
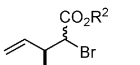
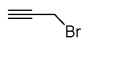
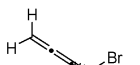
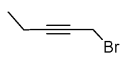
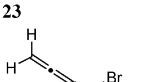
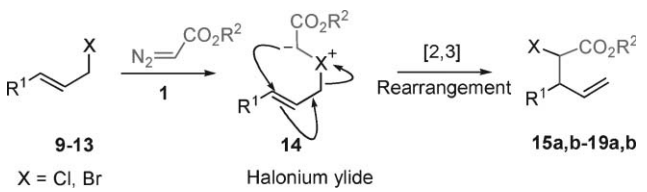
† Electronic supplementary information (ESI) available: Experimental details and full characterization data of all new compounds. See DOI: 10.1039/b608266a

Table 1 Products and yields from the rearrangement[a]

Entry	Substrate	Product	Yield (%) R^2 = Et (**a**)	Yield (%) R^2 = *t*-Bu (**b**)
1	 **9**	 **15**	75	65
2	 **10**	 **16**	86 (1 : 1)[b]	96 (1 : 1)[b]
3	 **11**	 **17**	59	84
4	 **12**	 **18**	57	89
5	 **13**	 **19**	70 (1 : 1)[b]	80 (1 : 1)[b]
6	 **20**	 **23**	—	66
7	 **21**	 **24**	71	74

[a] The reactions are conducted in neat halide with the exception of entry 5, in which the substrate is dissolved in CH_2Cl_2. [b] *Syn*/*anti* ratio, determined by ^{1}H NMR spectroscopy.

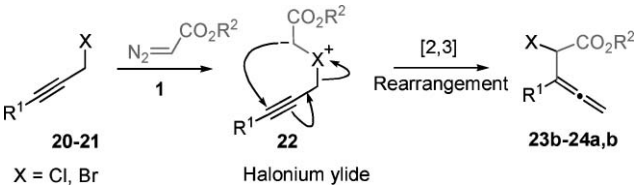


Scheme 3

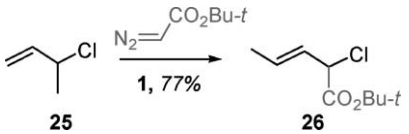
(BDA). As can be seen from the Table 1, a variety of substrates participate in this rearrangement reaction affording the α-haloester in good to excellent yield. Generally speaking, the reactions with BDA afford better yields, but this is most likely due to reduced volatility which renders product isolation more convenient. All of these reactions occur with allylic transposition, which is completely consistent with the formation of a halonium ylide and subsequent sigmatropic rearrangement.

It was found that propargylic systems **20** and **21** reacted similarly under these reaction conditions, giving rise to the corresponding allene (Scheme 4). The formation of the allene is consistent with the formation and rearrangement of a halonium ylide (Table 1, entries 6 and 7).

Primary cinnamyl systems were investigated in this chemistry, but only complex products were obtained. In this case, there is the potential for addition to the aromatic moiety (or the vinyl moiety), as well as rearrangement, leading to a variety of products. We have also investigated one secondary allyl halide: this engages in the



Scheme 4



Scheme 5

rearrangement chemistry, providing α-chloroester **26** as a single isomer (Scheme 5).

In each substrate, there are potentially two sites where reaction of the metallacarbene can occur: at the halogen (leading to the α-haloester) or at the double or triple bond (leading to the cyclopropane or cyclopropene respectively), and thus there are chemoselectivity issues to consider. In all cases with **1**, reaction at the halogen is the major or exclusive site of reaction which is in contrast with other catalysts (Rh and Cu) used for this reaction.[22] Copper catalysts favor higher proportions of rearrangement *versus* cyclopropanation than rhodium catalysts, but the relative ratios are substrate- and halogen-dependent.[18] With the present system **1**, the rearrangement product is the major product irrespective of the substrate, or halide, employed. The differences between the rhodium and copper catalysts have been interpreted in terms of the electrophilicity of the metallacarbene;[18] in the present case, the silver center is highly electron deficient, which presumably renders the carbene center highly electrophilic.[23] The effects of this high electrophilicity have been observed previously.[12,16]

In summary, we have demonstrated that primary allylic and propargylic halides undergo a net addition–rearrangement sequence on treatment with diazoacetate derivatives in the presence of a silver(I) tris(pyrazolyl)borate catalyst (**1**). The reaction has reasonably broad scope and provides the rearranged products in moderate to good yield, and with low diastereoselectivities.

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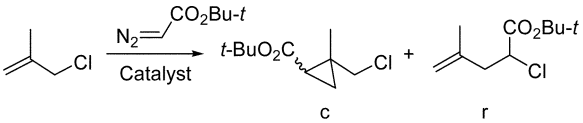
21 It is also conceivable that this product can be formed *via* nucleophilic substitution of bromide to generate a carbocation and subsequent nucleophilic capture with bromide, see: D. D. Philips, *J. Am. Chem. Soc.*, 1954, **76**, 5385–5388. For a related example, see: M. Vincens, A. Dussage and M. Vidal, *Tetrahedron*, 1977, **33**, 2937–2948.
22 For example, with methylallyl chloride and *t*-butyl diazoacetate, $Cu(OAc)_2$ provides a mixture of cyclopropanation (*c*) and rearrangement (*r*) products (*c* : *r* = 4.6 : 1), $Rh_2(OAc)_4$ provides essentially only cyclopropanation, whereas with with **1**, a mixture favoring the rearrangement product (*c* : *r* = 1 : 3.6) is obtained



23 Other silver salts that we have examined (AgOTf, and $AgSbF_6$) do not catalyze ylide formation and rearrangement.