Supplemental Information – Activation of Alkyl Halides via a Silver-Catalyzed Carbene Insertion Process: H. V. R. Dias*, R. G. Browning, S. A. Polach, H. V. Diyabalanage, and C. J. Lovely*

Supporting Information: Experimental and Characterization data for all of the compounds (^{1}H and ^{13}C NMR) and

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General procedure for C-X insertion reactions (neat): The silver complex (40 mg, 0.05 mmol) was dissolved in $CHCl_3$ (1.5 mL) under N_2 in a light-shielded flask and stirred while purging with N_2 for 5 min. Ethyl diazoacetate (114 mg, 1.00 mmol) in $CHCl_3$ (5 mL) was added to the catalyst solution by automatic syringe over a period of ~0.5 h. The resulting solution was stirred overnight in the absence of light, diluted with $CHCl_3$ (15 mL), filtered through a short plug of Celite and concentrated. The residue was purified by flash chromatography (SiO_2, 9:1 hexanes/Et_2O), yielding the product as a colorless or slightly yellow oil.

Ethyl-2,3-dichloropropionate 6a: The product was obtained as a slightly yellow oil, 45 mg (26%). ^{1}H NMR (500 MHz, $CDCl_3$) = 4.41 (dd, *J* = 8.6, 5.2 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 3.96 (dd, *J* = 11.1, 8.6 Hz, 1H), 3.80 (dd, *J* = 11.1, 5.2 Hz, 1H), 1.33 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) 167.2, 62.8, 55.2, 44.0, 14.1.

Ethyl-2,3,3-trichloropropionate 14a: The product was obtained as a colorless oil, 123 mg (60%). ^{1}H NMR (500 MHz, $CDCl_3$) 6.01 (d, *J* = 7.6 Hz, 1H), 4.58 (d, *J* = 7.6 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) 165.3, 70.6, 63.3, 62.4, 14.0.

Ethyl-2,3,3,3-tetrachloropropionate 15a: The product was obtained as a colorless oil, 148 mg (62%). ^{1}H NMR (500 MHz, $CDCl_3$) = 4.95 (s, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$) 163.8, 95.5, 67.9, 63.3, 14.0.

Ethyl-2,3-dibromopropionate 6b: The product was obtained as a colorless oil, 169 mg (65%). ^{1}H NMR (500 MHz, $CDCl_3$) 4.41 (dd, *J* = 11.3, 4.4 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 3.91 (dd, *J* = 11.3, 9.9 Hz, 1H), 3.66 (dd, *J* = 9.9, 4.4 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H) ^{13}C NMR (125 MHz, $CDCl_3$) 167.6, 62.7, 41.2, 29.8, 14.0

General procedure for C-X insertions (solution): The silver complex (40 mg, 0.05 mmol) and CBr_4 (1.66 g, 5.0 mmol) were dissolved in CH_2Cl_2 (1 mL) under N_2 in a light-shielded flask and stirred while purging with N_2 for 5 min. Ethyl diazoacetate (114 mg, 1.00 mmol) in CH_2Cl_2 (2.5 mL) was added to the catalyst solution by automatic syringe over a period of ~0.5 h. The resulting solution was stirred overnight in the absence of light, diluted with CH_2Cl_2 (15 mL), filtered through a short plug of Celite and concentrated. The residue was purified by flash chromatography (SiO_2, 9:1 hexanes/Et_2O), yielding the product as a colorless oil.

Ethyl 2,3,3-tribromopropanoate 14b: The product was obtained as a colorless oil, which was an inseparable mixture (107 mg) of the title compound (27%) and ethyl 2,3-dichloropropanoate (9%).^{1}H NMR (500 MHz, $CDCl_3$) 5.81 (d, *J* = 9.8 Hz, 1H), 4.70 (d, *J* = 9.8 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 1H), 1.33 (t, *J* = 7.1 Hz, 3H) ^{13}C NMR (125 MHz, $CDCl_3$) 166.2, 63.2, 51.2, 40.0, 13.9.

Ethyl 2,3,3,3-tetrabromopropanoate 15b: The product was obtained as a colorless oil, which was an inseparable mixture (207 mg) of the title compound (48%), and ethyl 2,3-dichloropropanoate (3%). ^{1}H NMR (500 MHz, $CDCl_3$) 5.18 (s, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H) ^{13}C NMR (125 MHz, $CDCl_3$) 165.0, 63.1, 59.3, 33.7, 13.9.

GC Yield Determination for C-Cl and C-Br Addition/Elimination

The yields for both cyclohexene and the ethyl haloacetate products for each of the indicated reactions were determined by GC on a Varian 3300 gas chromatograph equipped with a Carbowax 20M column (2 m).

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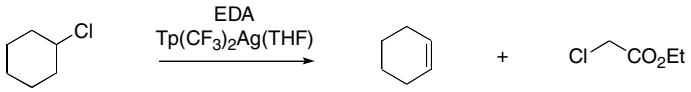
Method used for each run is as follows:
Injection volume: 0.5 L
Injector temperature: 175 ºC
Column temperature: 80 ºC to 200 ºC at 20 ºC/min, zero initial hold time
Detector: FID
Detector temperature: 175 ºC

Samples were taken directly from the reaction mixture after reaction was complete as evidenced by the cessation of nitrogen evolution.

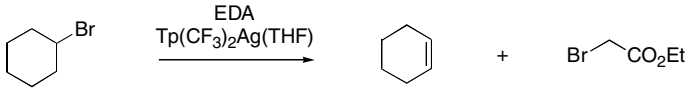
Concentration response curves were constructed using standards for each component and were measured at 1.0M, 0.6M, and 0.2M. Straight line plots were obtained with a zero intercept and correlations of $R^2 > 0.985$. Yields are based on the absolute number of mol per injection and back-calculated from the molarity of the reaction mixture.

Chlorocyclohexane 12a:



Cyclohexene yield (Retention Time – 0.57 min): 47%
Ethyl chloroacetate yield (Retention Time – 2.77 min): 63%

Bromocyclohexane 12b:



Cyclohexene yield: 57%
Ethyl bromoacetate yield (Retention Time – 3.34): 60%