Supporting Information

Highly Efficient Atom Transfer Radical Addition Reactions with a Ru^{III} Complex as a Catalyst Precursor

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General procedure for the ATRA of CCl₄ to olefins: 690 µL of a freshly prepared toluene stock solution of AIBN, CCl₄, and the internal standard 1,4-bis(trifluoromethyl)benzene were introduced into a 1.5 mL vial. The olefin (1.38 mmol) was then added, as well as 50 µL of a toluene stock solution of the catalyst, and the total volume was completed to 1000 µL with toluene (final conc.: [AIBN] = 69 mM, [olefin] = 1.38 M, [CCl₄] = 5.52 M, [internal standard] = 270 mM). The resulting solution was placed in an oil bath tempered at 60 °C. After the time given, a sample (20 µL) was removed from the reaction mixture, diluted with CDCl₃ (500 µL), and analyzed by ¹H NMR spectroscopy. The preparative reactions were performed on a 5 times larger scale without internal standard to facilitate purification.

General procedure for the ATRA of CHCl₃ to olefins: 440 µL of a freshly prepared CHCl₃ stock solution of AIBN and the internal standard 1,4-bis(trifluoromethyl)benzene were introduced into a 1.5 mL vial. The olefin (1.38 mmol) was then added, as well as 300 µL of a CHCl₃ stock solution of the catalyst, and the total volume was completed to 1000 µL with CHCl₃ (final conc.: [AIBN] = 69 mM, [olefin] = 1.38 M, [internal standard] = 270 mM). The resulting solution was placed in an oil bath tempered at 60 °C. After 24 h, a sample (20 µL) was removed from the reaction mixture, diluted with CDCl₃ (500 µL), and analyzed by ¹H NMR spectroscopy. The preparative reactions were performed on a 5 times larger scale without internal standard to facilitate purification.

General procedure for the ATRA of CXCl₂CO₂Et to olefins: The desired amount of a freshly prepared toluene stock solution of AIBN, the ester, the olefin and the internal standard 1,4-bis(trifluoromethyl)benzene were introduced into a 1.5 mL vial. 50 μ L of a toluene stock solution of the catalyst was then added and the total volume was completed to 1000 μ L with toluene (final conc.: [AIBN] = 69 mM, [olefin] = 1.38 M, [CXCl₂CO₂Et] = 4.14 M, [internal standard] = 270 mM). The resulting solution was placed in an oil bath tempered at 60 °C. After 24 h, a sample (20 μ L) was removed from the reaction mixture, diluted with CDCl₃ (500 μ L), and analyzed by ¹H NMR spectroscopy.

General procedure for the ATRA of TsCl to olefins: *p*-Tosylchloride (0.52 mmol) was placed in a 1.5 ml vial. Then the necessary amount of a freshly prepared toluene stock solution of AIBN, the olefin and the internal standard 1,4-bis(trifluoromethyl)benzene or mesitylene and a stock solution of the catalyst were introduced. The total volume was 1000 μ L (final conc.: [AIBN] = 22 mM, [TsCl] = 520 mM, [olefin] = 440 mM, [internal standard] = 100 or 120 mM). The resulting solution was placed in an oil bath tempered at 60 °C. After 24 h, a sample (20 μ L) was removed from the reaction mixture, diluted with CDCl₃ (500 μ L), and analyzed by ¹H NMR spectroscopy.

Mechanistic Investigations: In order to obtain more information about the mechanism of the catalytic reaction, we have studied the decomposition of AIBN (69 mM) under different conditions. When a toluene-*d*⁸ solution of AIBN was heated to 60 °C for 24 h, the expected decomposition products tetramethylsuccinic dinitrile and dimethyl-*N*-(2-cyano-2-propyl) ketenimine could be observed by ¹H NMR spectroscopy. Neither the presence of 80 equivalents of CCl₄ nor that of 0.2 % of complex **2** did affect the decomposition reaction, whereas in the presence of both, CCl₄ and complex **2**, additional compounds were formed. A GC-MS analysis revealed that the main new products were chloroisobutyronitrile, C₂Cl₆ and trichloromethylisobutyro-nitrile. This data is in agreement with the assumption that the isobutyronitrile radical formed from AIBN is able to abstract a chloro atom from complex **2**. The resulting Ru(II) species reacts with CCl₄ to give complex **2** and a •CCl₃ radical, which can either dimerize or react with another isobutyronitrile radical. In the presence of an olefin, however, the •CCl₃ radical preferentially attacks the double bond to form the new C-C bond of the final

product. A likely side reaction is the addition of the isobutyronitrile radical to the olefin followed by abstraction of a chloro atom or by further addition of olefins (oligo- or polymerization) but the high yields obtained for the ATRA products show that these reactions are of minor importance.