Re(CO)₅Br-catalyzed addition of carboxylic acids to terminal alkynes: a high *anti*-Markovnikov and recoverable homogeneous catalyst

Ruimao Hua*, Xin Tian

Department of Chemistry, Tsinghua University, Key Laboratory of Organic Optoelectronics & Molecular Engineering of Ministry of Education, Beijing 100084, China

ruimao@mail.tsinghua.edu.cn

Supporting Information:

- 1. Experimental Procedure**
- 2. The ORTEP structure of the recovered Re(CO)₅Br**
- 3. The charts of ¹H and ¹³C NMR of 3a ~ 3i**

1. Experimental Section

The addition reactions were carried out in a thick-walled Pyrex tube which was sealed under an air atmosphere. ¹H NMR spectra were recorded on a Bruker-300 spectrometer at 300 MHz in CDCl₃. IR spectra were recorded on a PERKIN ELMER FT/IR-2000 spectrometer (with KBr pellet). Gas chromatographic analyses were performed on an Agilent Technologies 1790 GC with an OV-1701 capillary column (30 m). GC-MS was performed on a HEWLETT 5890 PACKARD SERIES II GC/MS spectrometer with an OV-1701 (30 m) capillary column. All the chemicals were reagent grade and used as received without further purification.

A typical procedure for the addition reaction of terminal alkynes with carboxylic

acids

The reaction of **1a** with **2a** in *n*-heptane is representative. A mixture of **1a** (220 μ l, 2.0 mmol), **2a** (150 μ l, 2.5 mmol) and Re(CO)₅Br (8.2 mg, 0.02 mmol) in toluene (1.0 mL) was heated with stirring in a sealed tube at 110 °C for 15 h. After cooling, the reaction was diluted with toluene to 4.0 mL and *n*-C₁₈H₃₈ (56.0 mg, as internal standard) was added. The resulting mixture was then analyzed by GC and GC-MS. Volatiles were removed in vacuum and the residue was purified by column chromatograph (silica gel, eluted with hexane, and then with a 10 : 1 hexane-diethyl ether mixture). **3a** (a mixture of adducts, 195.0 mg, 1.2 mmol, 60 %) was obtained as colorless oil.

3a ~ 3g are known compounds. The literatures in which these compounds were reported are shown below.

- (1) Doucet, H.; Martin-Vaca, B.; Bruneau, C.; Dixneuf, P. H. *J. Org. Chem.*, **1995**, *60*, 7247-7255 (adducts: **3a** and **3b**)
- (2) Murata, M.; Satoh, K.; Watanabe, S.; Masuda, Y. *J. Chem. Soc., Perkin Trans. 1*, **1998**, 1465-1466 (adducts: **3d** and **3g**)
- (3) Park, H.-g.; Kim, D.-H.; Yoo, M.-S.; Park, M.-k.; Jew, S.-s. *Tetrahedron Lett.*, **2000**, *41*, 4579-4582 (adduct: **3c**)
- (4) Melis, K.; Samulkiewicz, P.; Rynkowski, J.; Verpoort, F., *Tetrahedron Lett.*, **2002**, *43*, 2713-2716 (adducts: **3a**, **3d** and **3g**)
- (5) Nakagawa, H.; Okimoto, S.; Sakaguchi, S.; Ishii, Y. *Tetrahedron Lett.*, **2003**, *44*, 103-106 (adducts: **3a**, **3d**, **3e** and **3f**)
- (6) Melis, K.; Verpoort, F. *J. Mol. Catal. A: Chem.* **2003**, *194*, 39-47 (adducts: **3a**, **3d**, and **3g**)

The spectroscopic data of **3h** and **3i** are concluded as follows.

Z-3h: ^1H NMR (CDCl_3) δ 7.04 (d, 1H, $J = 6.5$ Hz), 4.75 (td, 1H, $J = 7.4, 6.5$ Hz), 2.31 – 2.22 (m, 4H), 2.10 (s, 3H), 1.73 – 1.64 (m, 2H); ^{13}C NMR (CDCl_3) δ 168.9, 136.9, 120.4, 112, 25.9, 24.2, 21.7, 17.4; GC-MS m/z (% relative intensity): 153 (M^+ , 0.3), 125 (7.6), 82 (23.9), 57 (10.4), 43 (100), 27 (16.0). **E-3h**: ^1H NMR (CDCl_3) δ 7.06 (d, 1H, $J = 12.4$ Hz), 5.28 (dt, 1H, $J = 12.4, 7.5$ Hz), 2.32 – 2.26 (m, 2H), 2.05 (s, 3H), 1.71 – 1.66 (m, 2H). GC-MS m/z (% relative intensity): 153 (M^+ , 0.4), 82 (3.0), 57 (13.5), 43 (100), 39 (18.1), 27 (17.0).

E-3i: ^1H NMR (CDCl_3) δ 8.23.04 (d, 1H, $J = 12.5$ Hz), 5.65 (d, 1H, $J = 12.5$ Hz), 3.71 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (CDCl_3) δ 166.6, 166.5, 149.5, 105.3, 51.5, 20.4; GC-MS m/z (% relative intensity): 144 (M^+ , 1.0), 113 (6.0), 102 (3.2), 69 (12.1), 43 (100), 29 (18.0).

2. The ORTEP structure of the recovered $\text{Re}(\text{CO})_5\text{Br}$

Crystallographic data for $\text{ReBr}(\text{CO})_5$: orthorhombic, space group $Pnma$, $a = 11.865$ (2) Å, $b = 11.624$ (2) Å, $c = 6.1750$ (12) Å; $\alpha = \beta = \gamma = 90.00^\circ$, $V = 851.6$ (3) Å³, $Z = 4$.

Molecular structure of $\text{Re}(\text{CO})_5\text{Br}$ drawn at the 30% probability level.

3. The charts of ^1H and ^{13}C NMR of 3a ~ 3i

tx-040427-5-C-single pulse dec2
single pulse decoupled gated NOE

tian-040424-3-H-single_pulse2
single_pulse

tan-040424-3-C-single_pulse_dec2
single pulse decoupled gated NOE

TX-040428-66-C—single pulse dec2
single pulse decoupled gated NOE

13C-040430-53-C-single pulse dec2
single pulse decoupled gated NOE

ftir-040424-1-C—single pulse dec2
single pulse decoupled gated NOE

tian-040424-2-H-single_pulse2
 single_pulse

tian-040424-2-C-single pulse dec2
single pulse decoupled gated NOE

TX-040427-172-H-single-pulse.2
single_pulse

tx-040427-172-C—single_pulse_dec2
single_pulse decoupled gated NOE

15-040428-63-1Hsingle_pulse2
single_pulse

h-040328-63-C-single_pulse_dec.2
single_pulse decoupled gated NOE

tx-040428-63a-H-single_pulse2
single_pulse

15-040428-63a-C-sample pulse dec2
single pulse decoupled gated NOE

TX-040428-64-H-single_pulse.2
single_pulse

1x-040428-64-C—single pulse, dec 2
single pulse decoupled gated NOE