Supporting Information

Selectfluor promoted NHC-Oxazoline gold(I) complexes catalyzed cycloaddition/oxidation reaction of enynones with alkenes

Qin Xu,\textsuperscript{b} Peng Gu,\textsuperscript{b} Fei-jun Wang\textsuperscript{a,*} and Min Shi\textsuperscript{a,*}\textsuperscript{b}

\textsuperscript{a} State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Road, Shanghai 200032, China. Mshi@mail.sioc.ac.cn.
Fax 86-21-64166128

\textsuperscript{b} Key Laboratory for Advanced Materials and Institute of Fine Chemicals, School of Chemistry & Molecular Engineering, East China University of Science and Technology, 130 Mei-Long Road, Shanghai 200237 China.

Content

1) \textsuperscript{1}H NMR and \textsuperscript{13}C NMR spectra of compounds 2-7 S2-S8
2) \textsuperscript{1}H NMR and \textsuperscript{13}C NMR spectra of complexes 8 S9-S10
3) \textsuperscript{1}H NMR and \textsuperscript{13}C NMR spectra of complexes 10 S11-S13
4) \textsuperscript{1}H NMR and \textsuperscript{13}C NMR spectra of product 13 S14-S20
5) Controlled experiments S21-S23
6) Crystal structure data for complex 8a S24
7) Crystal structure data for complex 10c S25
1. NMR spectra of compounds 2-7

$^1$H NMR and $^{13}$C NMR spectra of compound 2
$^1$H NMR and $^{13}$C NMR spectra of compound 3
$^1$H NMR and $^{13}$C NMR spectra of compound 4
$^1$H NMR and $^{13}$C NMR spectra of compound 5a
$^1$H NMR and $^{13}$C NMR spectra of compound 5b
$^1$H NMR and $^{13}$C NMR spectra of compound 6a
$^1$H NMR and $^{13}$C NMR spectra of compound 6b
2. NMR spectra of NHC-gold complex 8

$^1$H NMR, $^{13}$C NMR spectra of NHC-gold complex 8a
$^1$H NMR, $^{13}$C NMR spectra of NHC-gold complex 8b
3. NMR spectra of NHC-gold(I) complex 10

$^1$H NMR, $^{13}$C NMR spectra of NHC-gold complex 10a
$^1$H NMR, $^{13}$C NMR spectra of NHC-gold complex 10b
$^1$H NMR, $^{13}$C NMR spectra of NHC-gold complex 10c
4. NMR spectra of product 13

$^1$H NMR spectra of compound 13a

![NMR Spectrum Image]
$^1$H NMR and $^{13}$C NMR spectra of compound 13b
$^1$H NMR and $^{13}$C NMR spectra of compound 13c
$^1$H NMR and $^{13}$C NMR spectra of compound 13d
$^1$H NMR and $^{13}$C NMR spectra of compound 13e
$^1$H NMR spectra of compound 13f
$^1$H NMR and $^{13}$C NMR spectra of compound 13g
5. Controlled experiments

A. The synthesis of active complex 14 with AgBF₄

To a solution of the NHC-oxazoline gold(I) complex 8a in DCM at room temperature was added AgBF₄ (1.1 eq.) in one portions. The white precipitate was formed immediately and the mixture was stirred at that temperature for 0.5 h. After that, the mixture was filtered through the celite pad twice to remove the AgI and the excess amount of AgBF₄ and washed three times with DCM. The combined organic solvents were removed in vacuo to afford the crude chelated NHC-oxazoline gold(I) complex 14 as a white solid.

Fig. 1. The ¹⁹F NMR spectra of the generated complex 14
B. The reversed synthesis of NHC-oxazoline gold(I) complex 8a

To a solution of synthesized crude ionic chelated NHC-oxazoline gold(I) complex 14 in acetone was added tetrabutylammonium iodide (2 eq.) (TBAI) in one portion. The mixture was stirred at room temperature for 2 hours. After that, the salt was filtered off and the solvent was removed under reduced pressure to afford the crude NHC-oxazoline gold(I) complex 8a. The ratio of the isomer was changed into 1:1.7. The synthesized complex 8a was confirmed by its ^1H NMR and ESI-Mass spectra.
Fig. 3. The characteristic $^1$H NMR spectra of the generated complex 8a

Fig. 4. The ESI-Mass spectra of the generated complex 8a
6. Crystal structure data for complex 8a

The crystal data of 8a have been deposited in CCDC with number 973292. Empirical Formula: C_{23}H_{19}AuIN_{3}O, Formula weight: 677.28, Temperature: 293(2) K, Crystal system, space group: Orthorhombic, P2(1)2(1)2(1), Unit cell dimensions: a = 10.3025(5) Å, alpha = 90 deg. b = 16.0231(8) Å, beta = 90 deg. c = 26.3966(14) Å, gamma = 90 deg. Volume: 4357.5(4) Å^{3}, Z, Calculated density: 8, 2.065 Mg/m^{3}, F(000): 2544, Crystal size: 0.176 x 0.164 x 0.112 mm^{3}, Final R indices [I>2sigma(I)], R1 = 0.0368, wR2 = 0.0704.
The crystal data of 10c have been deposited in CCDC with number 950237. Empirical Formula: C_{25}H_{23}AuIN_{3}O; Formula Weight: 705.33; Crystal Color, Habit: colorless, Crystal Dimensions: 0.156 x 0.123 x 0.085 mm; Crystal System: Monoclinic; Lattice Parameters: a = 32.577(6)Å, b = 10.964(2)Å, c = 15.077(3)Å, α = 90°, β = 101.267(6)°, γ = 90°, V = 5281.1(18)Å³; Space group: C2/c; Z = 8; D_{calc} = 1.774 g/cm³; F_{000} = 2672; Final R indices [l>2σ(I)] R1 = 0.0430, wR2 = 0.1081.