

E-beam Irradiated Fragmentation of Thio-Alkyne Cobaltcarbonyl Complex in Gas Phase as Alkyne Precursor

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ABSTRACT: Arylalkyne cobalt complexes **5**, **6** were prepared and irradiated with e-beam to study their fragmentation focused in alkyne formation. Thioaryl complex **6** showed facile CO ligand release and generated parent alkyne in 89% relative intensity. Meanwhile, hydroxyaryl complex **5** gave alkyne in 6% relative intensity.

Arrayed alkyne group on a surface plays a role of attachment of diverse functionalities applicable in nanopatterning,¹ lithography,² diagnosis,³ and microelectrode.⁴ Selective array of alkyne on a surface can be achieved by photochemical conversion of a alkyne-precursors such as furoxanes⁵ and alkyne-cobalt complexes.⁶ For a practical fabrication of an alkyne on a surface, the functional group conversion should be clean, and requires simple anchoring process. In regard of this sense, alkyne-cobalt complexes are considered quite attractive light-sensitive alkyne-precursor because of its fast and efficient conversion to alkyne.^{6,7} For the attachment of alkyne-functionality to gold surface, the substance requires thiol group and should be inert under irradiation. Thus, we prepared thiol containing alkyne-cobalt complex as a potential alkyne precursor and studied their fragmentation. Here, we report the synthesis and fragmentation of alkyne-cobalt complexes (AC) **5**, **6** under e-beam in mass spectrometer.

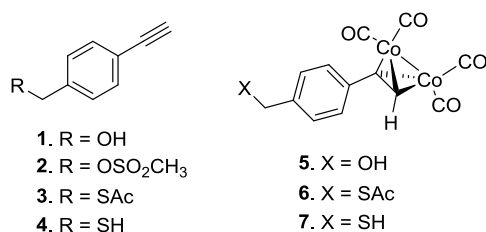


Figure 1. Chemical structure of alkyne-cobalt complexes.

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Table 1. Relative intensities of fragments derived from AC **5**, **6** in mass spectrometer at 20eV. SM; parent alkyne. The values in () represent m/z value: a, detected in neglect.

Compound	M ⁺	M-1CO	M-2CO	M-3CO	M-4CO	M-5CO	M-6CO	SM+Co	SM
5	3.8 (418)	34.2 (390)	49.5 (362)	50.8 (334)	42.2 (3061)	41.6 (278)	100.0 (250)	15.2 (191)	5.5 (132)
6	10.8 (476)	21.6 (448)	88.5 (420)	100 (392)	10.0 (364)	6.1 (336)	a (308)	a (249)	88.5 (190)

The thio-alkyne cobalt complex **6**, was prepared by the reaction of corresponding alkyne **3** with dicobaltocta-carbonyl.⁶ To a solution of thioacetate **3** (30 mg, 0.2 mmol) in THF(5 ml) was added dicobalt octacarbonyl (68.4 mg, 0.2 mmol) then stirred for 3h at room temperature. After usual workup and isolation using column chromatography (hexane) gave complex **6** as deep brown solid (110 mg, 70%).⁸ Similarly, cobalt complex **5** was obtained from alcohol **1** as brown solid in 77% yield.⁸ Thioalkyne complex (TC) **7**, however, was not affordable from thiol **4** under the same method used for complex **6**. It was considered presumably due to strong affinity between thiol and cobalt atom resulting thio-cobalt complex.

Benzyl alcohol **1** was converted to thiol **4** by sequential functional group conversion as follow. In the first step, 4-vinylbenzaldehyde was reduced with NaBH₄ to give alcohol **1** in quantitative yield. Reaction of alcohol **1** with methanesulfonyl chloride followed by displacement with potassium thioacetate in MeOH and basic hydrolysis with K₂CO₃ in MeOH generated thiol **4** as dimer because of self-oxidation in overall 64% yield.⁹

The mass spectroscopic data of AC **5**, **6** was obtained using Autospec mass spectrometer (Micromass Inc, at Korea Research Institute of Chemical Technology) and are shown in table 1 and Figure 2.

As shown in Figure 2, M-nCO peaks of thioalkyne complex **6** appeared from m/z , 448(M-CO) to 308(M-6CO). The M-3CO peak (m/z , 392) appeared as base peak. It represents that the CO ligand dissociation proceed facile over other bond cleavage of complex **6** as reported.^{6,7} Cobalt atom detached alkyne (SM, m/z 190) was shown with high intensity (89%) which is attribute to release of 6CO and 2 cobalt atoms without cleavage of carbon-sulfur bond. It suggested that AC **6** could be a potential alkyne precursor on gold surface. It is notable that the complex **5** containing OH group, however, showed very low intensity of SM fragment (5.5%, m/z , 132). The fragments resulted from the cleavage of acetyl group are marked as * peaks from m/z 432 to 147 in figure 2. Because of the acylium ion is so stable that its cleavage seems favored as well as the CO release.

The peak at $m/z = 220$, attribute to (phenylacetylene + 2Co), is quite interesting. Because the stronger Ph-CH₂ bond of AC **6** is expected to give less cleavage than C-S bond cleavage resulting the fragment $m/z = 234$. Meanwhile hydroxyalkyne complex **5** did not give the peak at $m/z = 220$.

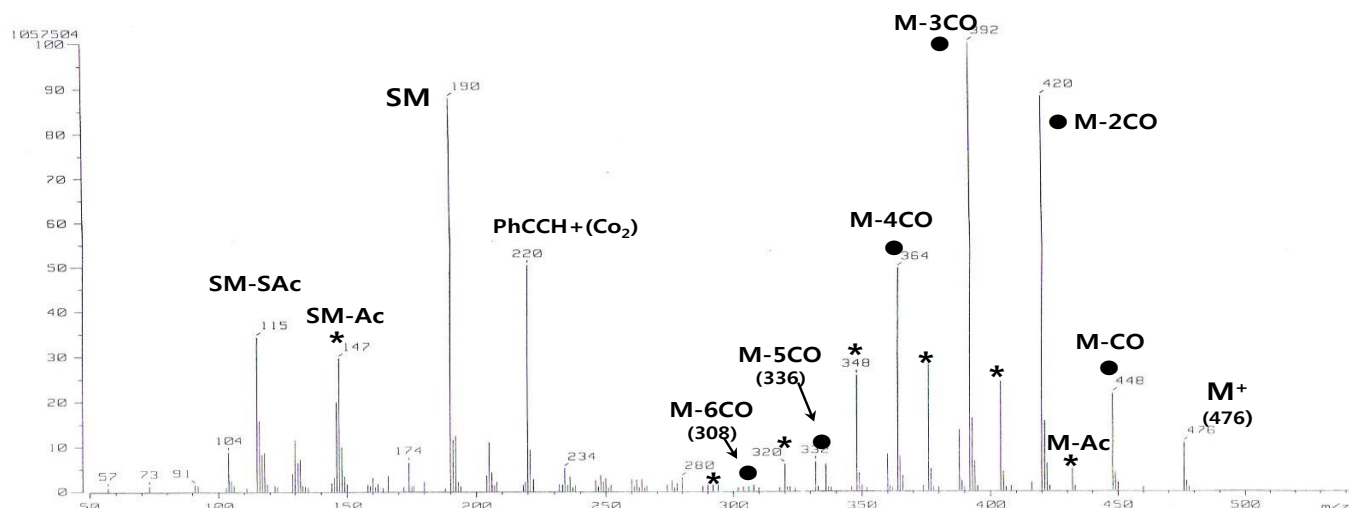


Figure 2. Mass spectrum of thioalkyne cobalt complex **6** at 20eV. SM, parent alkyne; M-nCO, dissociation of nCO ligand. ● represents the peaks M-nCO; * marked for the fragments derived from the acetyl group off resulting in intermediates at $m/z = 432, 404, 376, 348, 320, 292,$ and 147.

AC **5**, a hydroxyl group substituted complex, showed similar fragmentation-pattern with those of AC **6**. Release of CO ligands resulted M-nCO peaks from m/z , 390 (M-CO) to 250 (M-6CO). The base peak appeared at $m/z = 250$ corresponding to M-6CO fragment. The parent alkyne (SM, m/z 132) of AC **5** observed in less relative intensity (5.5%) than that of AC **6** (88.5%). The relative ratio of SM/ M^+ for AC **5**, **6** (1.5 and 8.2 respectively) also represented that thioalkyne **6** generated SM more efficiently than AC **5** by e-beam.

As summary, the irradiation of thio- and oxy-aryl-cobalt complexes **5** and **6** with e-beam in gas phase generated parent alkynes in 89 and 6% relative intensities, respectively. These results suggest that thiol group containing aryl-alkyne cobalt complex could be a photochemical alkyne precursor on a gold surface as in gas phase.

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KEYWORDS: Thioalkyne, cobalt-alkyne complex, e-beam, fragmentation.

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8. (a) Spectroscopic data of **6**: $^1\text{H-NMR}$ δ (CDCl_3 , ppm); 2.3-2.4 (s, 3H, COCH_3), 3.5-3.6 (m, 2H, CH_2), 6.3-6.4 (s, 1H, spC-H), 7.1-7.3 (m, 2H, Ar-H), 7.4-7.5 (m, 2H, Ar-H); MS m/z (relative intensity); see table 1. (b) Spectroscopic data of **5**: $^1\text{H-NMR}$ δ (CDCl_3 , ppm); 1.6-1.7(s, 1H, O-H) 4.6-4.8(m, 2H, CH_2) 6.3-6.4 (s, 1H, C-H), 7.3-7.4 (m, 2H, Ar-H), 7.5-7.6 (m, 2H, Ar-H); MS m/z (relative intensity); 417.9 (M^+ , 3.8), 389.9 (M-CO, 34), 361.9 (M-2CO, 49), 333.9 (M-3CO, 50), 305.9 (M-4CO, 42), 277.9 (M-5CO, 41), 249.9 (M-6CO, 100), 190.9 (M-6CO-Co, 15), 131.9 (M-6CO-2Co, 5.5).
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