

E-beam Irradiation of Diyne-Cobaltcarbonyl Complexes for the Generation of Conjugated Alkyne in Gas Phase

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ABSTRACT: Substituted butadiyne cobalt complexes **1**, **2** were prepared and placed on the e-beam to study the fragmentation focused on diyne generation, in MS spectrometer. Phenyl or methyl substituted cobalt complexes generated the corresponding diyne with 100, 30% relative intensities under e-beam irradiation in gas phase.

Selectively immobilized alkyne group on a surface enable the attachment of diverse agents useful in nanopatterning,¹ lithography,² and diagnosis.³ The oligoynes or oligoenynes are especially attractive because of their electrical properties.⁴ The selective immobilization of alkyne on a surface can be achieved by photochemical conversion of a light-responding alkyne-precursors. For a practical application in industry, the functional group conversion should be clean, and requires simple mounting process of precursors onto the surface. As a photochemical alkyne-precursor, furoxanes⁵ and alkyne-cobalt complexes⁶ were reported by Hwang. Among both precursors, alkyne-cobalt complexes are considered quite attractive because of its fast conversion to alkyne in high efficiency.⁶ Inspired with the results derived from mono-alkyne cobalt complex, we expanded our interest to the oligoyne and its cobalt complex as a conjugated alkyne precursor. Here, we report the synthesis and fragmentation of diyne-cobalt complex(DC) **1**, **2** as potential diyne precursor.

The diyne-cobalt complexes were prepared by reaction of the corresponding diyne with dicobaltoctacarbonyl. The diyne compounds were obtained via Eglington coupling of alkyne under copper catalyst as follow.⁷

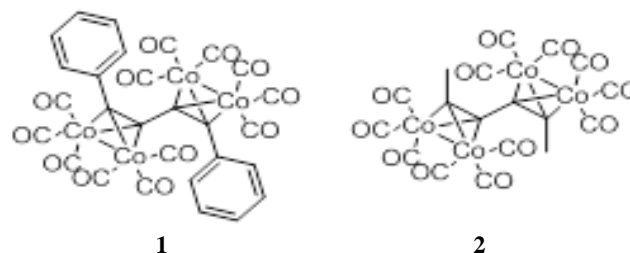


Figure 1. Chemical structure of diyne-cobalt complexes.

1,4-diphenylbutadiyne dicobaltdodecacarbonyl complex (**1**): The mixture of 1,4-diphenylbutadiyne (0.224 g, 1.107 mmol) and dicobalt octacarbonyl (0.78 g, 2.281 mmol) in THF(25 ml) was stirred for 1h at room temperature. To the brownish solution, water and EA was added then organic layer was separated, dried over MgSO₄. The concentrated residues are purified using column chromatography (10% EA/Hexane eluent) to give white DC **1**(780mg, 91%): MS (EI) m/z(rel. intensity); 745(M-1CO, 1.3), 717(M-2CO, 0.9), 689(M-3CO, 0.9), 661(M-4CO, 3.1), 633(M-5CO, 1.8), 605(M-6CO, 2.2), 577(M-7CO, 4.0), 549(M-8CO, 0.9), 521(M-9CO, 3.6), 494(M-10CO, 2.2), 466(M-11CO, 7.6), 438(M-12CO, 8.1), 320(SM+2Co, 62.5), 261(SM+1Co, 24.6), 202(SM, 100).

2,4-hexadiyne dicobaltdodecacarbonyl complex (**2**): Similar synthetic method used for DC **1** was applied to give DC **2** as yellow solid in 94% yield: MS (EI) m/z(rel. intensity); 621(M-1CO, 14.8), 593(M-2CO, 41.7), 565(M-3CO, 8.5), 537(M-4CO, 29.6), 510(M-5CO, 18.9), 482(M-6CO, 86.6), 454(M-7CO, 100.0), 426(M-8CO, 73.1), 398(M-9CO, 48.0), 370(M-10CO, 53.8), 342(M-11CO, 38.1), 314(M-12CO, 60.1), 196(SM+2Co, 31.1), 78(SM, 30.0).

The mass spectroscopic data of alkyne-cobalt complexes DC **1**, **2** was obtained using Autospec mass spectrometer (Micromass Inc, at Korea Research Institute of Chemical Technology) and the results are shown in Figure 2. In table 1, the relative intensities of the characteristic peaks of DC **1**, **2** are listed in table 1.

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Table 1. Relative intensities of intermediates derived from diyne-cobalt complexes **1**, **2** in mass spectrometer at 20eV. The values in () represent m/z value. SM means ligand- and metal-free diyne; and a represents not observed.

DC	M ⁺	M-1CO	M-2CO	M-3CO	M-4CO	M-5CO	M-6CO	M-7CO	M-8CO	M-9CO	M-10CO	M-11CO	M-12CO	SM+Co ₂	SM
1	<u>a</u>	1.3 (745)	0.9 (717)	0.9 (689)	3.1 (661)	1.8 (633)	2.2 (605)	4.0 (577)	0.9 (549)	3.6 (521)	2.2 (494)	7.6 (466)	8.1 (438)	62.5 (320)	100.0 (202)
2	4.9 (649)	14.8 (621)	41.7 (593)	8.5 (565)	29.6 (537)	13.9 (510)	86.6 (482)	100.0 (454)	73.1 (426)	48.0 (398)	53.8 (370)	38.1 (342)	60.1 (314)	31.1 (196)	30.0 (78)

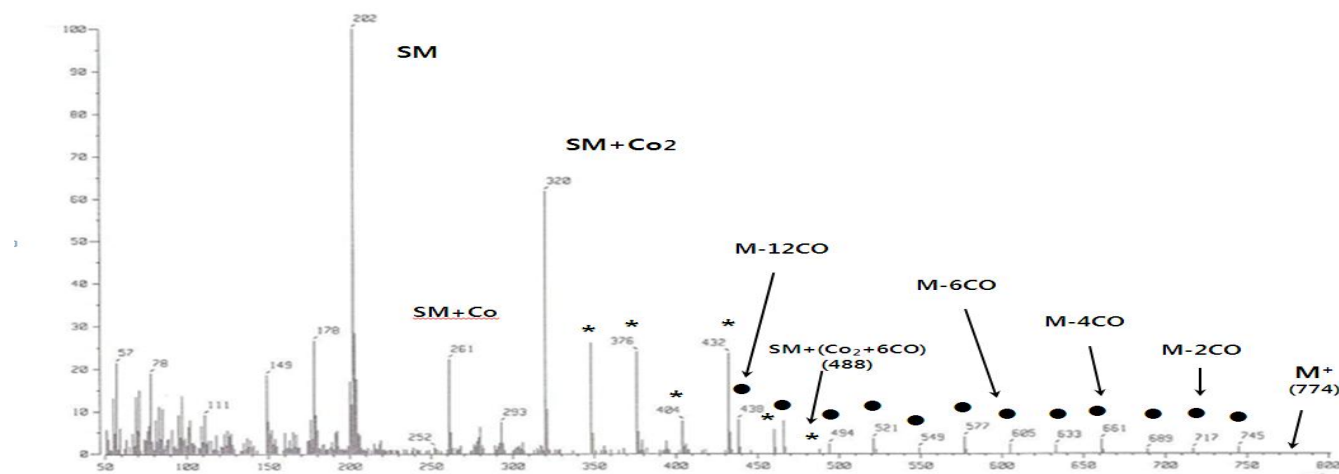


Figure 2. Mass spectrum of diyne-cobalt complex **1** at 20 eV. SM, parent alkyne; M-nCO, dissociation of nCO ligand. The ● represents peaks M-nCO; * is marked for (SM+Co₂+nCO) peaks resulted from the monoalkyne-dicobalthexacarbonyl intermediates at $m/z = 488, 460, 432, 404, 376,$ and 348 .

As shown in figure 1, M-n(CO) peaks appeared from $m/z=745$ (M-CO) to $m/z=202$ (M-12CO). Cobalt atom attached alkynes also observed at $m/z=320$ (SM+Co₂), and $m/z=261$ (SM+Co). It represents that CO ligand dissociation seems more facile over the cobalt-carbon bonding cleavage. However, the appearance of dicobalt-attached intermediates, [(SM+Co₂+nCO), * in figure 2], suggested that the cobalt-carbon bond cleavage at an alkyne could be proceed ahead to the CO dissociation from the other alkyne.

Interestingly, free alkyne(SM, $m/z=202$) appeared as a base peak which is attribute to release of 12 CO and 4 cobalt atoms from DC **1**. It is notable that the molecular ion peak(M⁺, $m/z=774$) of DC **1** was not observed under EI, even in FAB mass spectrum. It attribute presumably to labile evolution of CO ligand as in case of monoalkyne-cobalt complex.⁶

The mass spectrum of DC **2**, a methyl substituted butadiyne, showed similar fragmentation type to that of DC **1**. Release of CO ligands resulted M-nCO peaks from $m/z=621$ (M-CO) to 324 (M-12CO). The base peak appeared to $m/z=454$ representing M-7CO fragment. The free alkyne(SM, $m/z=78$) observed with 30% relative intensity.

As summary, diyne-cobalt complex was prepared and their fragmentation under e-beam in gas phase generated free diynes in high relative intensities, 100 and 30%, respectively. These results suggest that diyne-cobalt complex could be a photochemical alkyne precursor on the surface as well as in gas phase.

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KEYWORDS: conjugated alkyne, diyne, cobalt-alkyne complex, e-beam

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