

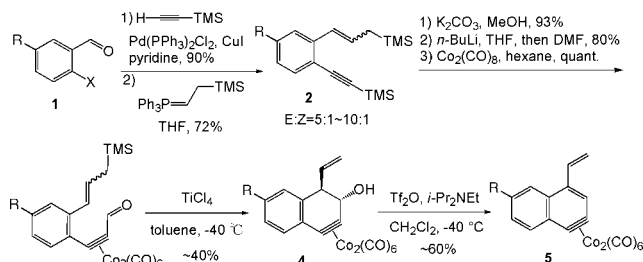
Synthesis, Structure, and Reactivity of Naphthalene–Co<sub>2</sub>(CO)<sub>6</sub> ComplexesNobuharu Iwasawa,\* Maiko Otsuka, Satomi Yamashita, Masao Aoki, and Jun Takaya  
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Arynes are well-known, highly reactive transient species, which have been employed for the preparation of various aromatic compounds.<sup>1</sup> Interestingly, these highly reactive arynes can be stabilized and sometimes become isolable by making a complex with transition metals, and a variety of such complexes have been reported so far.<sup>2</sup> However, it is a little surprising that the corresponding alkyne–Co<sub>2</sub>(CO)<sub>6</sub> complexes, probably one of the most common and stable alkyne complexes of transition metals,<sup>3</sup> have not yet been synthesized.<sup>4,5</sup> In this paper, we would like to report the first example of isolation and X-ray analysis of this type of complex, that is, naphthalene–Co<sub>2</sub>(CO)<sub>6</sub> complex and its unique reactivity as an alkyne–Co<sub>2</sub>(CO)<sub>6</sub> complex.

After extensive fruitless trials for the preparation of aryne–Co<sub>2</sub>(CO)<sub>6</sub> complexes from acyclic alkyne–Co<sub>2</sub>(CO)<sub>6</sub> precursors utilizing cyclization reactions, such as coupling reactions, metathesis reactions, and so on,<sup>6</sup> we have succeeded in preparing the naphthalene–Co<sub>2</sub>(CO)<sub>6</sub> derivatives according to the following procedure utilizing cyclization of benzene derivatives having an allylsilane and an alkynal–Co<sub>2</sub>(CO)<sub>6</sub> moiety at the ortho-position,<sup>4b</sup> followed by dehydration of the produced alcohols (Scheme 1).

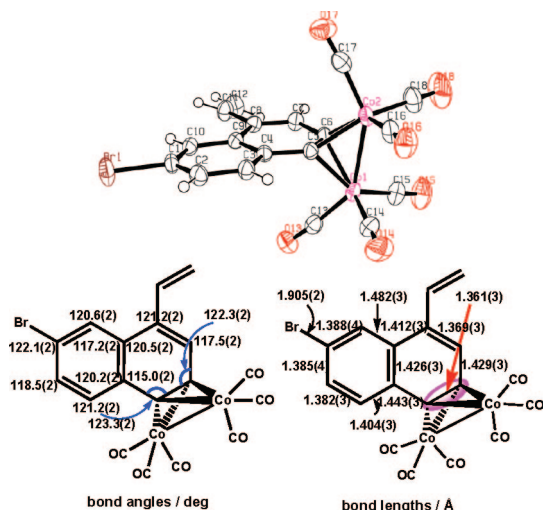
Thus, the cyclization precursor **3a** (R = H) was prepared in five steps from *o*-iodobenzaldehyde **1a** (R = H, X = I), and the cyclization was carried out under strictly controlled conditions using 3.5 mol amounts of TiCl<sub>4</sub> at –40 °C followed by purification by silica gel column chromatography under argon using precooled solvent. The yield of the cyclized product **4a**, a dark-red solid, is around 40% in a small-scale experiment, but on a larger scale, the yield of the product became lower probably due to decomposition of the product during purification.<sup>7</sup> This dihydronaphthalene–Co<sub>2</sub>(CO)<sub>6</sub> complex **4a** decomposed within 1 or 2 days in the air at room temperature, but the decomposition could be mostly suppressed under Ar. Then dehydration was examined under several conditions and was found to proceed smoothly by carrying out the reaction using Tf<sub>2</sub>O and Hunig's base in CH<sub>2</sub>Cl<sub>2</sub> at –40 °C. The dehydration reaction itself was clean by direct measurement of the reaction mixture by low-temperature <sup>1</sup>H NMR,<sup>8</sup> but by increasing the temperature to 20 °C, decomposition of the complex occurred in the reaction mixture. The most difficult point is the instability of the final product, in particular, to oxygen during isolation, and finally, we have succeeded in isolating the desired naphthalene–Co<sub>2</sub>(CO)<sub>6</sub> complex **5a**, a brownish yellow solid, by rapidly carrying out a silica gel column chromatograph cooled to –10 °C using degassed, precooled solvent under Ar and removing the solvent around 0 °C with sufficient care to the air. Roughly estimated isolated yield is around 60%. We have also prepared MeO- and Br-substituted naphthalene–Co<sub>2</sub>(CO)<sub>6</sub> complexes (**5b**: R = OMe; **5c**: R = Br) in a similar manner,<sup>9</sup> but the stability of the complexes did not change to a great extent. Under strict exclusion of oxygen, the complexes were stable even at room temperature in a solid state, but mostly decomposed in the air at room temperature in 1 or 2 h, and furthermore, when a hexane solution of naphthalene–Co<sub>2</sub>(CO)<sub>6</sub> was left open in the air for 10 min at 0 °C, decomposition occurred rapidly and insoluble red solids appeared. The structure of the products was first determined by <sup>1</sup>H, <sup>13</sup>C, and HMBC spectra, and finally, we have succeeded in obtaining a single crystal suitable for X-ray analysis for the Br-substituted complex **5c** by carefully recrystallizing from pentane (Figure 1).<sup>10</sup>

Scheme 1. Preparation of Naphthalene–Co<sub>2</sub>(CO)<sub>6</sub> Complexes **5**

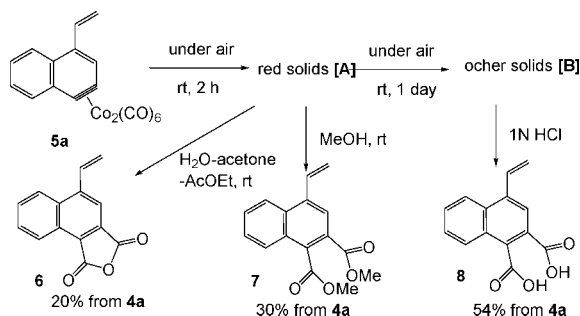
The yields were shown for compounds with R = H.

The characteristic features of the complex are as follows. The complex has a planar naphthalene core, and the Co complex moiety is mostly symmetrical concerning this plane. Furthermore, this naphthalene–Co<sub>2</sub>(CO)<sub>6</sub> complex clearly showed no naphthalene character but substituted benzene character, as obviously seen from the bond length of the noncomplexed benzene part of the naphthalene–Co<sub>2</sub>(CO)<sub>6</sub> complex. Usually, bond alternation is observed for naphthalene derivatives, but in this complex, three consecutive bonds had almost the same length around 1.38–1.39 Å and the other three had longer length of 1.40–1.43 Å, probably due to the influence of the strained alkyne–Co<sub>2</sub>(CO)<sub>6</sub> moiety. Another feature is the bond angle of 122–123° around the alkyne–Co<sub>2</sub>(CO)<sub>6</sub> moiety, which is highly deviated from the standard bond angle of around 140° for acyclic alkyne–Co<sub>2</sub>(CO)<sub>6</sub> complexes.

We next examined the reactivity of the complex.<sup>11</sup> First, the reactivity to oxygen was scrutinized (Scheme 2). When the complex **5** was left in the air at room temperature, it changed its brownish yellow color to red within 1 or 2 h and then to ochre after 1 day.<sup>12</sup> Treatment of the red solids **A** with H<sub>2</sub>O/acetone/AcOEt at room temperature in the air gave naphthalene dicarboxylic acid anhydride **6**, while treatment with MeOH gave the corresponding dimethyl ester **7**. On the other hand, treatment of the ochre solids **B** under the same reaction conditions

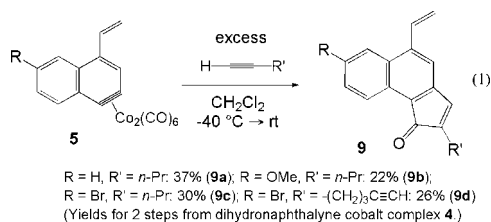
Figure 1. X-ray structure of naphthalene–Co<sub>2</sub>(CO)<sub>6</sub> complex **5c**.

**Scheme 2.** Reaction of Naphthalene- $\text{Co}_2(\text{CO})_6$  Complex **5a** under Air



gave none of the above products, but on treatment with 1 N HCl, dicarboxylic acid **8** was obtained in good yield. Although the exact mechanism of the reaction is not clear, we currently suppose that carbonyl insertion occurred by oxidation of the complex **5** with molecular oxygen to give acylcobalt intermediate,<sup>12–14</sup> which gave acid anhydride or dimethyl ester as described above.<sup>15</sup> Further exposure to the air induced the reaction of acylcobalt intermediate with oxygen to give other dicarboxylic acid cobalt salt **B**,<sup>12</sup> which gave dicarboxylic acid on treatment with 1 N HCl.

We next examined the reactivity of the complex **5** with several kinds of alkenes and alkynes. Although the complexes did not react cleanly with alkenes, such as norbornene, styrene, maleic anhydride, etc., they reacted with terminal alkynes in a [2 + 2 + 1] manner to give 1H-cyclopenta[a]naphthalen-1-one derivatives **9** in good yield by carrying out the reaction using an excess of alkynes in  $\text{CH}_2\text{Cl}_2$  at  $-40^\circ\text{C}$  to room temperature (eq 1).<sup>11,16</sup> The same type of reaction with alkenes is the Pauson-Khand reaction, a well-known transformation of the alkyne- $\text{Co}_2(\text{CO})_6$  complex, but the reaction with alkynes to give cyclopentadienone derivatives has rarely been achieved.<sup>17</sup> Furthermore, this reaction is specific to the naphthalene- $\text{Co}_2(\text{CO})_6$  complexes, and the corresponding dihydronaphthalene- $\text{Co}_2(\text{CO})_6$  complex did not give the same kind of product under similar conditions. Thus, the naphthalene- $\text{Co}_2(\text{CO})_6$  complexes showed unique reactivities, which have not been achieved by the standard alkyne- $\text{Co}_2(\text{CO})_6$  complexes.



In conclusion, we have succeeded in preparing and isolating naphthalene- $\text{Co}_2(\text{CO})_6$  complexes for the first time. Their unique reactivities are also disclosed. We are currently trying to prepare other arylene- $\text{Co}_2(\text{CO})_6$  complexes.

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**Supporting Information Available:** Preparative methods and spectral and analytical data of compounds **1–9**, X-ray data and a CIF file for **5c**, and IR data for oxidation intermediates **A** and **B**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- (1) For recent reviews, see: (a) Pellissier, H.; Santelli, M. *Tetrahedron* **2003**, *59*, 701. (b) Dyke, A. M.; Hester, A. J.; Lloyd-Jones, G. C. *Synthesis* **2006**, 4093.
- (2) For examples of transition metal complexes of arynes, see: (a) Jones, W. M.; Klosin, J. *Adv. Organomet. Chem.* **1998**, *42*, 147. (b) Hughes, R. P.; Laritchev, R. B.; Williamson, A.; Incarvito, C. D.; Zakharov, L. N.; Rheingold, A. L. *Organometallics* **2002**, *21*, 4873. (c) Hughes, R. P.; Laritchev, R. B.; Williamson, A. L.; Incarvito, C. D.; Zakharov, L. N.; Rheingold, A. L. *Organometallics* **2003**, *22*, 2134. (d) Wada, K.; Pamplin, C. B.; Legzdins, P.; Patrick, B. O.; Tsyba, I.; Bau, R. *J. Am. Chem. Soc.* **2003**, *125*, 7035. (e) Kabir, S. E.; Begum, N.; Manjur, H. M.; Iqbal, H.; Nur, H.; Bennett, D. W.; Siddique, T. A.; Haworth, D. T.; Rosenberg, S. A. *J. Am. Chem. Soc.* **2004**, *126*, 1569. (f) Keen, A. L.; Johnson, S. A. *J. Am. Chem. Soc.* **2006**, *128*, 1806, and references cited therein.
- (3) Kimmitt, R. D. W.; Russell, D. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, 1982; Vol. 5, pp 195–209.
- (4) For preparation of six-membered alkyne- $\text{Co}_2(\text{CO})_6$  complexes, see: (a) Hunt, R. L.; Wilkinson, G. *Inorg. Chem.* **1965**, *4*, 1270. (b) Schreiber, S. L.; Sammakia, T.; Crowe, W. E. *J. Am. Chem. Soc.* **1986**, *108*, 3128. (c) Magnus, P.; Carter, R.; Davies, M.; Elliott, J.; Pittner, T. *Tetrahedron* **1996**, *52*, 6283.
- (5) It was reported that decomposition of  $\text{C}_6\text{F}_5\text{MgBr}$  in dioxane in the presence of  $\text{Co}_2(\text{CO})_8$  gave a tetranuclear  $\text{C}_6\text{F}_5\text{Co}_4(\text{CO})_{10}$  complex, although no X-ray analysis was carried out. See: Roe, D. M.; Massey, A. G. *J. Organomet. Chem.* **1970**, *23*, 517.
- (6) For a previous trial, see: Iwasawa, N.; Satoh, H. *J. Am. Chem. Soc.* **1999**, *121*, 7951.
- (7) In general, 50 mg (0.095 mmol) of **3** was cyclized to give about 15–20 mg of **4** (around 40% yield) after chromatography. Complex **4** was stable for a short period of time even in the air at room temperature in a solid state, but a solution of **4** was more sensitive to the air, in particular, on silica gel.
- (8) The yield of the complex **5** in the NMR tube was around 90% based on the internal standard method.
- (9) The overall yield of **5** from **1**: 13% for **5a**; 19% for **5b**; 13% for **5c**.
- (10) Crystal data and structure refinement for **5a**.  $T = 173(2)$  K, space group =  $P2_1/n$ , unit cell dimensions =  $a = 15.931(5)$  Å,  $\alpha = 90^\circ$ ,  $b = 7.498(3)$  Å,  $\beta = 110.193(13)^\circ$ ,  $c = 16.677(6)$  Å,  $\gamma = 90^\circ$ ,  $Z = 4$ , reflections collected = 17 486, Data/restraints/parameters = 4241/0/272, final  $R$  indices [ $I > 2\sigma(I)$ ],  $R1 = 0.0307$ ,  $R2 = 0.0700$ ,  $R$  indices (all data),  $R1 = 0.0366$ ,  $R2 = 0.0733$ , Goodness-of-fit on  $F^2 = 1.046$ .
- (11) In a solid state, the naphthalene- $\text{Co}_2(\text{CO})_6$  complex **5** could be handled in the air at room temperature for a few minutes; however, to avoid the decomposition of the complex due to its inherent instability to oxygen, examination of the reactions of the naphthalene- $\text{Co}_2(\text{CO})_6$  complex **5** was carried out without the exact weight of **5** directly using the chromatographed and concentrated complex obtained from about 15–20 mg of **4**. Thus the yields were based on the dihydronaphthalene- $\text{Co}_2(\text{CO})_6$  complex **4**.
- (12) We have not yet succeeded in characterizing these complexes, partly due to their insolubility in most solvents. The red solid **A** has IR absorptions around  $2000\text{ cm}^{-1}$  for carbonyl ligands but does not seem to have an absorption around  $1600\text{ cm}^{-1}$  corresponding to acyl carbonyl. Thus, at present, we suppose the red solid **A** is the precursor of acylcobalt intermediate and treatment of **A** with  $\text{H}_2\text{O}$  or  $\text{MeOH}$  in the air induced acylcobalt formation followed by nucleophilic addition. In fact, no reaction occurred on treatment of **A** with  $\text{H}_2\text{O}$  or  $\text{MeOH}$  under argon. The other solids **B** have an IR absorption at  $1560\text{ cm}^{-1}$  which could be that of carboxylate salt and no absorption for carbonyl ligands.
- (13) For the reaction of alkyne- $\text{Co}_2(\text{CO})_6$  complex with  $\text{O}_2$ , see: Hamajima, A.; Nakata, H.; Goto, M.; Isobe, M. *Chem. Lett.* **2006**, *35*, 464.
- (14) For acyl cobalt intermediates, see: (a) Liebeskind, L. S.; Jewell, C. F., Jr. *J. Organomet. Chem.* **1985**, *285*, 305. (b) Kovacs, I.; Ungvary, F. *Coord. Chem. Rev.* **1997**, *161*, 1.
- (15) It was reported that acid anhydrides were obtained on treatment of cyclic alkyne- $\text{Co}_2(\text{CO})_6$  complexes with CAN, although its mechanism has not been made clear. See: Tanino, K.; Shimizu, T.; Miyama, M.; Kuwajima, I. *J. Am. Chem. Soc.* **2000**, *122*, 6116.
- (16) A small amount of regioisomer was also produced in most cases. The regiochemistry of the major products was determined by NOE. As the yield of the first dehydration step was about 60%, the [2 + 2 + 1] cycloaddition proceeded in about 40–60% yield. The remainder was mainly the oxidized product.
- (17) Only a few examples are known for this type of reaction utilizing alkyne- $\text{Co}_2(\text{CO})_6$  complexes. See: (a) Rajesh, T.; Periasamy, M. *Organometallics* **1999**, *18*, 5709. (b) Hong, S. H.; Kim, J. W.; Choi, D. S.; Chung, Y. K.; Lee, S.-G. *Chem. Commun.* **1999**, 2099. (c) Shibata, T.; Yamashita, K.; Takagi, K.; Ohta, T.; Soai, K. *Tetrahedron* **2000**, *56*, 9259–9267. (d) Sugihara, T.; Wakabayashi, A.; Takao, H.; Imagawa, H.; Nishizawa, M. *Chem. Commun.* **2001**, 2456.

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