Formation and Cleavage of a Dicobalt Complex Bridged with a Pentamethylene Group

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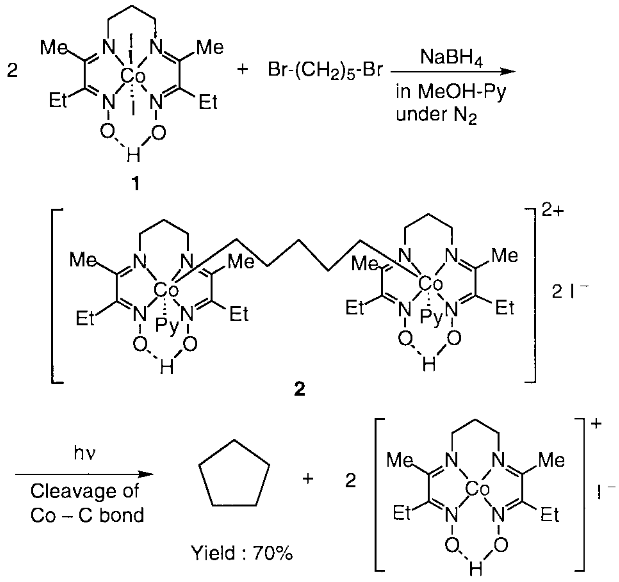
A new dicobalt complex bridged with a pentamethylene group was prepared and characterized by electronic and ESI mass spectroscopies. This cobalt complex gives cyclopentane via radical intermediates by anaerobic photolysis.

A compound with a cobalt–carbon bond, which was found as a key intermediate in vitamin B_{12} enzymic reaction, is a useful reagent for the generation of an organic radical species, because the cobalt–carbon bond cleaves readily to form a radical species by photolysis, electrolysis, or thermolysis.[1] Therefore, application of a cobalt complex with a cobalt–carbon bond, which is a radical-forming reagent, to organic synthesis in place of the conventional tin hydride method is quite interesting from the viewpoint of green chemistry.[2] In this paper, we report a radical cyclization reaction via a dicobalt complex bridged with a pentamethylene group as shown in Scheme 1. Dicobalt complexes bridged by an alkyl group were reported by several groups using natural vitamin B_{12} or cobaloxime,[3–5] but their reactivity and mechanism for the cleavage of cobalt–carbon bonds have never been reported.

Scheme 1.



New dicobalt complex **2** was prepared from the complex **1**, which has a mono-anionic ligand, as reported by Costa et al.[6–8] It is well known that **1** can form the cobalt–carbon bond and is used as a model compound of vitamin B_{12}. A typical experimental procedure is as follows: **1** (11.6 mg, 2.0×10^{-5} mol) was added to a nitrogen-saturated methanol solution (4.5 mL) containing pyridine (20.6 mg, 2.6×10^{-4} mol) and 1,5-dibromopentane (2.30 mg, 1.0×10^{-5} mol). The electronic spectrum of the solution showed line A in Figure 1. Then, $NaBH_4$ (3.78 mg, 1.0×10^{-4} mol) was added in portions, and the resulting dark-blue solution was stirred for 1 h at 298 K in the dark. The electronic spectrum of the reaction mixture was changed to line B in Figure 1. The spectrum B is characteristic of that for the corresponding alkylated complex with a cobalt–carbon bond that we previously prepared.[8] In addition, ESI-mass analysis showed the positive mass spectrum with a cluster of peaks at *m/z* 849 as a base peak (see Figure 2). The peaks were assigned to $[M - 2Py - I]^+$ ion derived from the complex **2**. Dicobalt complex **2** is stable at room temperature in the dark under anaerobic conditions, but it is unstable in the presence of oxygen. As the solution of **2** was exposed to air, the charge-trans-

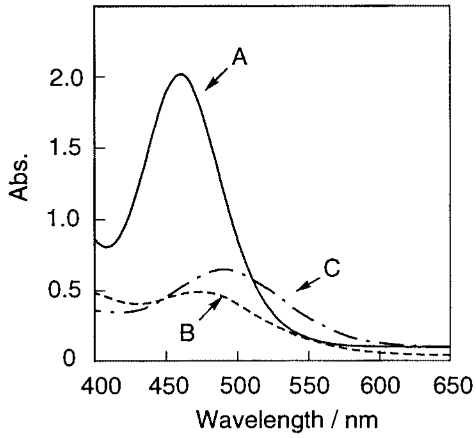


Figure 1. Electronic spectral change for the reaction. A, **1** in methanol; B, after stirred with $NaBH_4$ and 1,5-dibromopentane in the dark (the alkylated complex **2**); C, after anaerobic irradiation with visible light (the corresponding Co(II) complex).

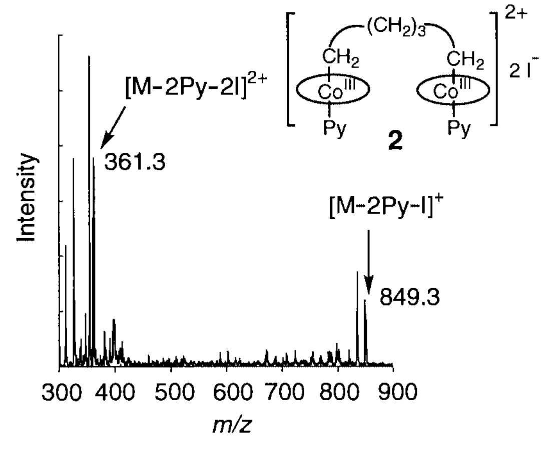


Figure 2. ESI mass spectrum of **2**.

fer band at 475 nm disappeared and the ESI-mass spectrum mentioned above was no longer observed. Dioxygen insertion into the cobalt–carbon bonds must induce the decomposition of the complex **2**.[9]

After anaerobic irradiation of visible light with a 500-W tungsten lamp at a distance of 30 cm, the spectrum of the solution was changed to line C in Figure 1, which is typical for the corresponding Co(II) complex. The reaction mixture was analyzed by GLC and GC–MS after the photolysis. Cyclopentane was obtained in 70% yield as a major product. There was little consumption of 1,5-dibromopentane in the absence of the complex **1**. Peters et al. have reported the direct reduction of 1,5-dibromopentane using an electrochemical procedure, but the yield of cyclopentane was less than 30%.[10] The yield of the cyclic compound in this system was markedly dependent on the length of the methylene chain in the substrate. The highest yield for cycloalkane was obtained by using 1,5-dibromopentane, and the yield decreased in the order of the length of the methylene chain. When we used 1,6-dibromohexane, the major products detected were hexane, hexene, and hexadiene, while only 3% cyclohexane was detected. Such reactions do not proceed without irradiation of visible light; therefore, the cleavage of the cobalt–carbon bond by the photolysis must induce the reaction.

In order to clarify the reaction mechanism, the reaction was followed by the spin-trapping technique with α-phenyl *N*-(*t*-butyl)nitrone (PBN).[11] An ESR signal attributable to the PBN spin adducts ($g = 2.006$, $A^N = 15.3$ G, $A^H = 3.6$ G) was observed in the presence of PBN, and the yield of cyclopentane was decreased to 14%. This result indicates that the radical species are generated as the reaction intermediates under the present conditions. On the other hand, no cyclic compound was obtained when 1,5-dibromopentane was treated with tributyltin hydride under the conditions for generating the free radicals.[12]

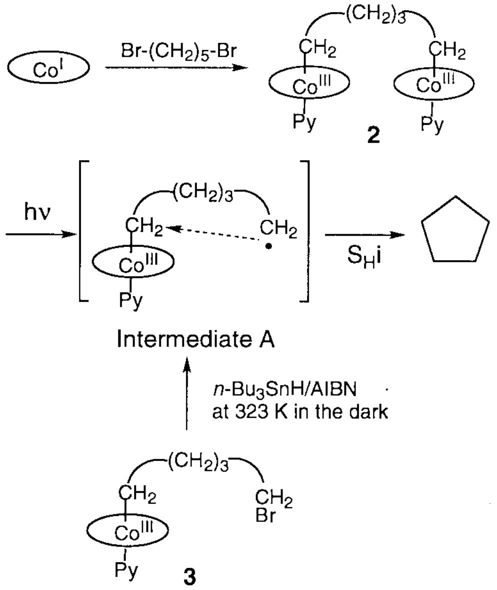


Figure 3. Proposed mechanism for the cleavage of cobalt-carbon bonds and the formation of cyclopentane.

A proposed reaction mechanism is shown in Figure 3. Pentamethylene-bridged dicobalt complex **2** is formed by the reaction of the Co(I) species and 1,5-dibromopentane, and one of the cobalt–carbon bonds in the dicobalt complex homolytically cleaves to form the intermediate A. And then, an intramolecular homolytic substitution (S$_{\rm H}$i),[13] in which the radical species tethered to the cobalt attacks the cobalt–carbon bond, will occur, so that the expulsion of the Co(II) species is accompanied with the cyclopentane-ring formation. The formation of the Co(II) species was confirmed by ESR ($g_\perp = 2.26$, $g_{//} = 2.01$, $A_{//}^{N} = 15.0$ G, $A_{//}^{Co} = 94.7$ G) as well as the electronic spectrum described above.

The following experiment also supported the S$_{\rm H}$i mechanism. We prepared the alkylated complex **3**, which has a bromopentamethylene group on the cobalt, by the reaction of **1** (11.6 mg, 2.0×10^{-5} mol), pyridine (20.6 mg, 2.6×10^{-4} mol), 1,5-dibromopentane (460 mg, 2.0×10^{-3} mol), and $NaBH_4$ (15.1 mg, 4.0×10^{-4} mol). The electronic spectrum and ESI-mass analysis indicated the formation of the complex **3**; λ_{max} 475 nm in methanol, *m/z* 477 for $[M - Py - I]^+$. The complex **3** was treated with tributyltin hydride and AIBN in the dark under the conditions for generating the radical species as shown in Figure 3. The products were analyzed by GC and GC–MS to form cyclopentane as a major product. Therefore, we conclude that the cyclization reaction mainly proceeds via the S$_{\rm H}$i mechanism. Detailed mechanistic study is now in progress in our laboratory.

References and Notes

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11 Reaction conditions: Solvent, MeOH; [complex] = 4.4×10^{-3} M, [$NaBH_4$] = 2.2×10^{-2} M, [1,5-dibromopentane] = 2.2×10^{-3} M, [PBN] = 8.9×10^{-1} M at 298 K.

12 Reaction conditions: Solvent, benzene; [*n*-Bu_3SnH] = 2.2×10^{-1} M, [AIBN] = 1.4×10^{-4} M, [1,5-dibromopentane] = 2.2×10^{-3} M at room temperature with irradiation of visible light. Pentane was obtained in 86% yield.

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