

## 論文の内容の要旨

### 論文題目

## Studies on Metastable Cobalt Complexes Trapped Inside of Bowl-Shaped [60]Fullerene Ligands

(ボウル型[60]フラーレン配位子に捕捉された準安定コバルト錯体に関する研究)

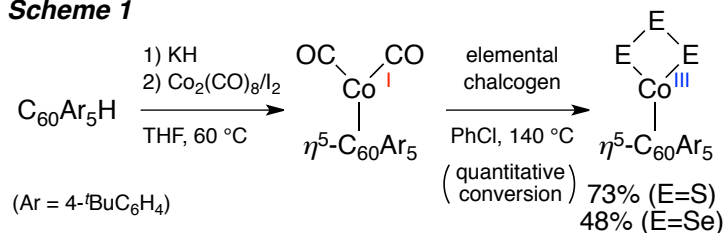
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The present thesis describes developments of the chemistry of metastable cobalt complexes, taking advantages of bowl-shaped [60]fullerene ligands.

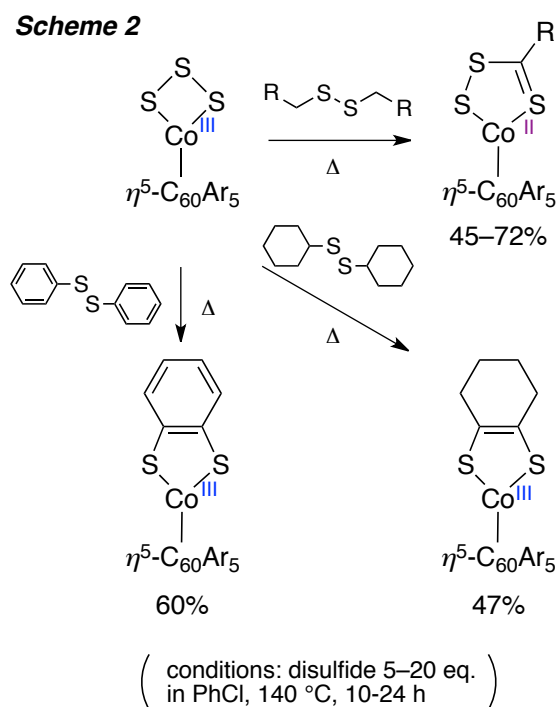
Sterically restricted reaction spaces are of great importance from the view points of stabilization of unstable species and achievements of unique reactivity. Chapter 1 describes the importance of steric restriction in developments of new reaction spaces. Half-open bowl-shaped ones are of particular interest in this thesis, and the merits and difficulties of them are described. Especially, penta(organo)[60]fullerene derivatives are focused on to give some introductions about them.

Chapter 2 describes the synthesis, isolation, and characterization of a series of novel metastable cobalt complexes, namely cobalt trichalcogenides, which were successfully prepared thanks to the bowl-shaped steric environments of  $C_{60}Ar_5$  ligands (Scheme 1). Characterization of the products suggested dominance of unique aromatic characters within the four-membered cobalt complexes.

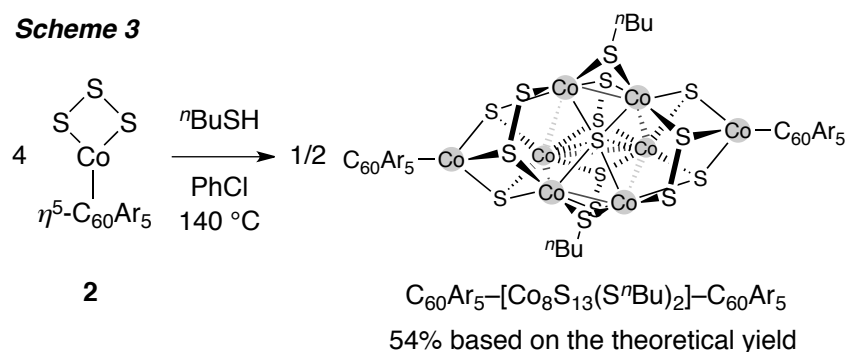
**Scheme 1**



Chapter 3 describes developments of unique C–H functionalization reactions using metastable cobalt trichalcogenide complexes (Scheme 2). Upon addition of sulfur radicals, cobalt trisulfide complexes were destabilized to promote various of C–H functionalization reactions, providing potential photofunctional motifs. The keys of those reactions were formations of reactive species by disruption of the metastability of the four-membered rings, which was achieved through addition of radicals. The photophysical properties of the resulting cobalt complexes were also characterized.



Chapter 4 describes the utilization of metastable cobalt trisulfide complexes as precursors for cluster complexes (Scheme 3). By taking advantages of the combination of metastable sulfide and large steric restriction, which satisfies the requirements of precursors for metal-sulfur clusters, selective synthesis of a  $\text{Co}_8\text{S}_{13}(\text{S}^n\text{Bu})_2$  cluster was demonstrated. The resulting complex possessed a quite rare geometry, which is slightly related to those of P-cluster and FeMo-cofactor. This exclusive formation was because of the steric templating effects of the bowl-shaped ligands.



Chapter 5 describes the overview of the present thesis. Chapters 6 and 7 are a data section and a reference section, respectively.