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Pd-catalyzed Dithiolene–Aryl Cross-coupling Reaction of Aromatic Cyclopentadienylcobalt Dithiolene Complex

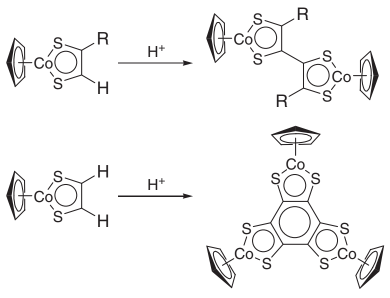
Mitsushiro Nomura,*,† Kosuke Terada, Akihide Onozawa, Yoshiro Mitome, Toru Sugiyama, and Masatsugu Kajitani*
Department of Materials and Life Sciences, Faculty of Science and Technology, Sophia University,
7-1 Kioi-cho, Chiyoda-ku, Tokyo 102-8554

(Received December 11, 2009; CL-091102; E-mail: m-nomura@sophia.ac.jp, kajita-m@sophia.ac.jp)

[CpCo(dithiolene)] complex with a boronate group, which is formulated as [CpCo{S_2C_2(Ph)(Bpin)}] (**1**, Bpin = 4,4,5,5-tetramethyl-1,3,2-dioxaboronate), was prepared from the one-pot reaction of [CpCo$(CO)_2$], elemental sulfur, and boronated alkyne. **1** underwent Pd-catalyzed Suzuki–Miyaura cross-coupling reactions with 3-bromopyridine or 9-bromoanthracene.

Metal dithiolene complexes can be attractive molecular materials because of conductive,[1] magnetic,[2] and optical properties of their π-electron contributions.[3] The five-membered metalladithiolene ring involving one metal, two sulfurs, and two unsaturated carbons, has 6π-conjugated electrons, thus this is an aromatic metallacycle due to Hückel's rule. Eventually, π-extended dithiolene system provides a low energy HOMO–LUMO gap.[1] The aromaticity of the metalladithiolene ring has been supported by the ring current effect during the NMR measurement[4] and theoretical DFT calculation.[5] We have also proved it by chemical reactivities of [CpCo(dithiolene)] (Cp = η^5-cyclopentadienyl) complexes. The hydrogen atom of the [CpCo{S_2C_2(R)(H)}] complexes can be replaced by electrophilic substitution (Friedel–Crafts acylation) and radical substitution reactions.[6] Metallabenzenes and metallabenzenoids (M = Os, Ir, Pt, and Ta) also behave as aromatic metallacycles and they show some electrophilic substitution reactions on the ring.[7]

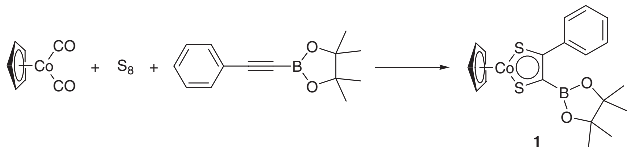
Previously, some interesting dithiolene–dithiolene *homo-coupling* reactions have been observed in [CpCo{S_2C_2(R)(H)}][8] and [CpCo$(S_2C_2H_2)$][9] under acidic conditions, as shown in Scheme 1. On the basis of this background, we have decided to study a dithiolene–aryl *cross-coupling* reaction due to the aromaticity of the metalladithiolene ring. As many organic chemists know, one representative aryl–aryl cross-coupling reaction is the Suzuki–Miyaura reaction[10] whose reactive precursor is an aryl boronic acid or an aryl boronate. Accordingly, the first task of this work is the synthesis of boronated [CpCo(dithiolene)] complex, which is available to react with aryl halide in the presence of Pd catalyst. In addition, this paper describes some examples of dithiolene–aryl cross-coupling reaction by using the boronated [CpCo(dithiolene)] complex.



Scheme 1. Dithiolene–dithiolene homo-coupling reactions.

Typically, most [CpCo(dithiolene)] complexes can be prepared from one-pot reaction of [CpCo$(CO)_2$], elemental sulfur, and an alkyne.[11] As shown in Scheme 2, alkynylboronate (Ph–C≡C–Bpin)[12] could be used for the one-pot reaction in refluxing toluene for 6 h to form [CpCo{S_2C_2(Ph)(Bpin)}] (**1**) in 3% yield (Bpin = 4,4,5,5-tetramethyl-1,3,2-dioxaboronate).[21] Although the reaction time increased up to 18 h, **1** was obtained in only 4% yield. **1** was identified with spectroscopic data and elemental analysis.[21] One reason for low yield of **1** is due to the weak electrophilicity of alkynylboronate, because the nucleophilic [$Cp_4Co_4S_n$] (n = 4 or 6) cluster initially forms from [CpCo$(CO)_2$] and elemental sulfur.[13] In fact, one-pot reaction using DMAD (dimethyl acetylenedicarboxylate), which is a strongly electrophilic alkyne, has previously produced [CpCo{$S_2C_2(COOMe)_2$}] in more than 80% yield.[11]

Figure 1 shows the molecular structure of **1**.[14] Needless to say, this structure confirms that the boron atom of the Bpin group is directly bound to the cobaltadithiolene ring. The C–B bond length of **1** is 1.566(5) Å, which is shorter than those of typical organic aryl boronate compounds (1.58–1.63 Å).[15] There is a typical two-legged piano-stool geometry. Indeed, Cp ligand is located at a perpendicular position with respect to the cobaltadithiolene ring. The cobaltadithiolene ring of **1** is extremely planar because the largest deviation of atoms in metallacycle from its best plane is 0.0254 Å. The bond lengths in the metallacycle (Co–S = 2.1063(11), 2.0991(11) Å, S–C =



Scheme 2. One-pot reaction for boronated [CpCo(dithiolene)].

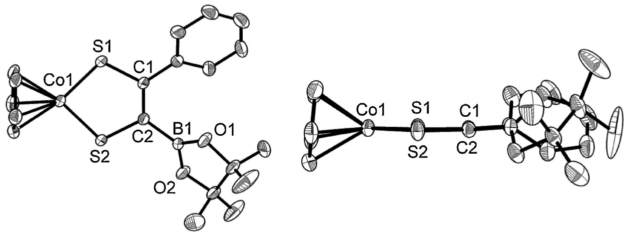
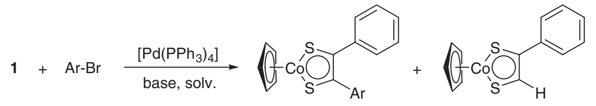


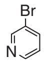
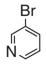
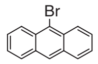
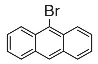
Figure 1. ORTEP drawing of **1**. Thermal ellipsiods are drawn at 30% probability. Selected bond lengths (Å): Co1–S1 = 2.1063(11), Co1–S2 = 2.0991(11), S1–C1 = 1.724(3), S2–C2 = 1.726(3), C1–C2 = 1.370(5), C2–B1 = 1.566(5).



2: Ar = 3-Py
3: Ar = 9-Anth
4

Scheme 3. Dithiolene–aryl cross-coupling reactions.

Table 1. Summarized results of cross-coupling reactions

Entry	Ar–Br	Base	Solvent	Temp	Time/h	Yield/% of **2** or **3**	Yield/% of **4**
1		Na$_2$CO$_3$	THF	reflux	3	trace (**2**)	49
2		NEt$_3$	1,4-dioxane	reflux	24	6 (**2**)	13
3		Na$_2$CO$_3$	THF	reflux	4	9 (**3**)	49
4		NEt$_3$	THF	reflux	30	9 (**3**)	12

1.724(3), 1.726(3) Å, C=C = 1.370(5) Å) are similar to those of aromatic [CpCo(dithiolene)] complexes.[16]

The Pd-catalyzed reactions of **1** with aryl halides[21] (Scheme 3) are summarized in Table 1. **1** reacted with 10 equiv of 3-bromopyridine (3-PyBr) in the presence of [Pd(PPh$_3$)$_4$] (0.13 equiv) and excess Na$_2$CO$_3$ aq. in refluxing THF for 3 h to form the cross-coupling product [CpCo{S$_2$C$_2$(Ph)(3-Py)}] (**2**), but unfortunately it was a trace amount (Entry 1). The main product of this reaction was the hydrogenated [CpCo{S$_2$C$_2$-(Ph)(H)}] (**4**) (49% yield). A hydrogen source of **4** is probably from aqueous solution of Na$_2$CO$_3$. **1** was reacted completely and not recovered at all.

When excess triethylamine was used as a base instead of Na$_2$CO$_3$, higher yield of **2** (6% yield) and lower yield of **4** (13% yield) were obtained, although the reaction time required 24 h in refluxing 1,4-dioxane (Entry 2). We consider that a little amount of H$_2$O in the solvents affects for the hydrogenation. These results suggest that use of a strong base leads to deprotection of the Bpin group and cannot ensure effective formation of the cross-coupling product. In fact, the treatment of **1** with Na$_2$CO$_3$ in THF gave the hydrogenated product **4** in 30% yield.

1 also reacted with 10 equiv of 9-bromoanthracene (9-AnthBr) in the presence of [Pd(PPh$_3$)$_4$] (0.12 equiv) and excess Na$_2$CO$_3$ to produce [CpCo{S$_2$C$_2$(Ph)(9-Anth)}] (**3**) in 9% yield but formed a large amount of **4** in 49% yield (Entry 3). While excess triethylamine was added instead of Na$_2$CO$_3$, the same yield of **3** (9% yield) but less of **4** (12% yield) was obtained (Entry 4). Although this is an ineffective cross-coupling reaction because of low yield, this is the first case of Suzuki–Miyaura cross-coupling reaction for aromatic metallacycles.

In conclusion, the Suzuki–Miyaura cross-coupling reaction on the metalladithiolene ring supports the aromaticity of the ring afresh. We also conclude why the cross-coupling reaction gives low yield, because the metalladithiolene ring is *pseudo aromatic*.[5] In other words, the ring is slightly unsaturated. Therefore, [CpCo(dithiolene)] complexes have shown coexistence of aromaticity and unsaturation for diverse chemical reactions on the ring so far.[8]

Finally, we describe some good applications using the dithiolene–aryl system as follows. (1) Dithiolene–thienyl system:[17] this can be electropolymerizable for conductive polymeric dithiolene complex. (2) Dithiolene–pyridyl system:[18,19] the dithiolene complex itself can be metalloligand for polymetallic systems, coordination polymers, and supramolecular complexes. (3) Dithiolene–alkylphenyl system:[20] the complex can have thermal bistability and can be metallomesogen (liquid crystalline complex).

References and Notes

† Present address: Condensed Molecular Materials Laboratory, RIKEN, 2-1 Hirosawa, Wako 351-0198. E-mail: mitsushiro@riken.jp

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