

Reactions of Aryl Azides with Cobaltadithiolenes. Substitution Reactions *via* NitreneHideaki KATSUTA, Naoko NOGUCHI, Yohsuke INOMATA, Masatsugu KAJITANI,
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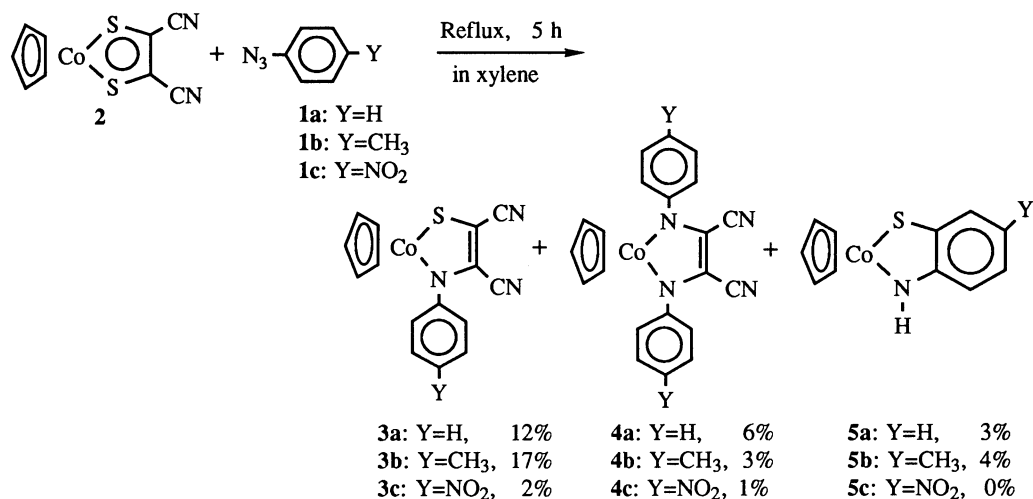
Two types of substitution reactions occur between aryl nitrene from aryl azides (**1**) and a cobaltadithiolene, $(\eta^5\text{-cyclopentadienyl})(1,2\text{-dicyano-1,2-ethenedithiolato})\text{cobalt(III)}$ (**III**): 1) replacements of S by arylimino groups and 2) replacements of S-CX=CX moiety of a cobaltadithiolene by a biradical form of nitrene to give $(\eta^5\text{-cyclopentadienyl})(2\text{-imino-}\kappa\text{V-arene-1-thiolato-}\kappa\text{S})\text{cobalt(III)}$ (**5**). The reaction of **1** with a cluster compound $[\text{Cp}_4\text{Co}_4\text{S}_6]$ gives also **5**.

A metalladithiolene ring is a very unique metallacycle. It behaves as an unsaturated ring. Alkylidene,¹⁾ alkyne,²⁾ and quadricyclane³⁾ add between metal and chalcogen of the metalladichalcogenolene ring. The addition of an alkylidene group in the reaction with a diazo compound is a typical example of such a reaction.¹⁾ A similar reaction, the bridging between cobalt and chalcogen atoms by imino groups, occurs in the reaction of *p*-toluenesulfonyl azide or ethyl azidoformate with a cobaltadithiolene.⁴⁾ We report here other two types of reactions *via* nitrene between aryl azides and a cobaltadithiolene, $(\eta^5\text{-cyclopentadienyl})(1,2\text{-dicyano-1,2-ethenedithiolato})\text{cobalt(III)}$: 1) the replacement of S by arylimino groups and 2) the replacement of S-CX=CX moiety of a cobaltadithiolene by a biradical form of nitrene to give $(\eta^5\text{-cyclopentadienyl})(2\text{-imino-}\kappa\text{V-arene-1-thiolato-}\kappa\text{S})\text{cobalt(III)}$.

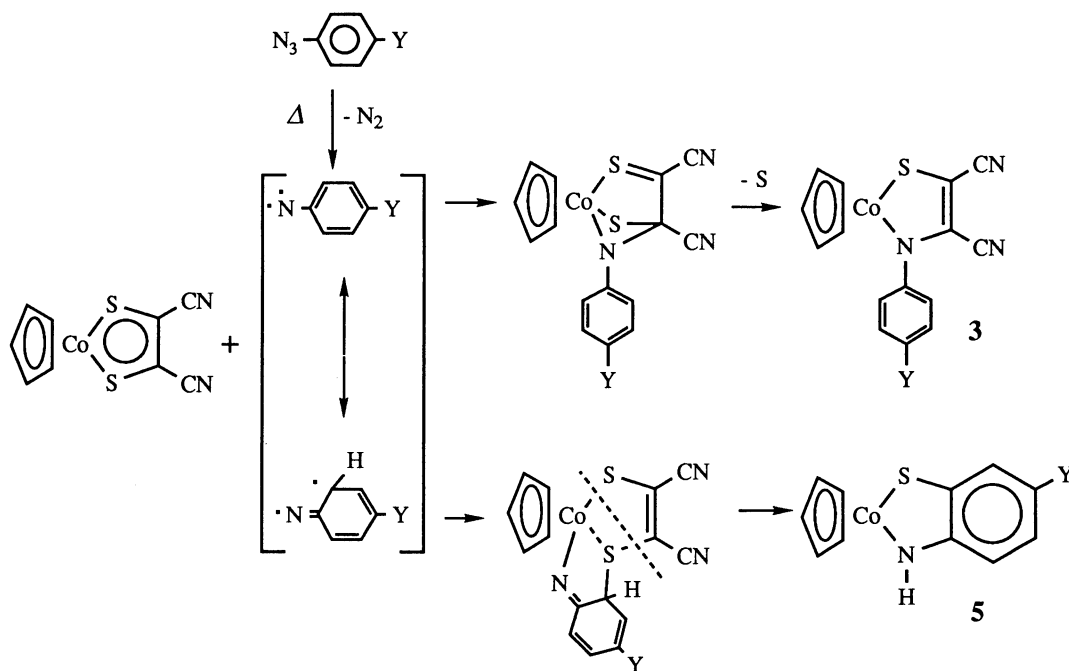
The hitherto known reactions of azides with organometallic compounds are classified in two categories. The first one is *via* nitrene formed from azides and second one is *via* 1,3-dipolar cycloaddition. The first category involves the replacement of coordinated halogen⁵⁾ or carbonyl⁶⁾ by imino groups, and the insertion of imino group to M-(CO)(M=Pd,Pt)⁷⁾ or V-V bond.⁸⁾ The second category involves the cycloadditions to Ge=C,⁹⁾ W=C,¹⁰⁾ and Co=C¹¹⁾ bonds. The formation of tetraazendiyl complex in the reaction of $[\text{Co}(\text{Cp})(\text{CO})_2]$ with phenyl azide may belong to the category.¹²⁾ More vigorous conditions are needed for the reactions *via* nitrene than those *via* 1,3-dipole.

The reaction of aryl azides (1.65 mmol) with a cobaltadithiolene, $(\eta^5\text{-cyclopentadienyl})(1,2\text{-dicyano-1,2-ethenedithiolato})\text{cobalt(III)}$ (**2**) (0.30 mmol) was carried out under the conditions (at 140 °C, under reflux in xylene) where the azides decompose thermally and aryl nitrene species are generated. The reflux of a xylene solution of (**2**) and phenyl azide (**1a**) for 5 h gave $(\eta^5\text{-cyclopentadienyl})[2\text{-}(\text{phenylimino-}\kappa\text{V})\text{-1,2-dicyanoethene-1-thiolato-}\kappa\text{S}]\text{cobalt(III)}$ (**3a**), $(\eta^5\text{-cyclopentadienyl})[1,2\text{-dicyano-1,2-bis}(\text{phenylimino})\text{ethene-}\kappa\text{V},\text{N}]\text{cobalt(III)}$ (**4a**), and $(\eta^5\text{-cyclopentadienyl})\{2\text{-imino-}\kappa\text{V-benzene-1-thiolato-}\kappa\text{S}\}\text{cobalt(III)}$ (**5a**).¹³⁾ *p*-

methylphenyl azide and *p*-nitrophenyl azide undergo similar reactions. The azide with an electron-donating substituent gives higher yield of the substitution products than an azide with an electron-attracting substituent.



These types of reactions by aryl azides are different from those by *p*-toluenesulfonyl azide or ethyl azidoformate. In the latter reactions, the bridging by imino groups between Co and S occurs.⁴⁾ The bridging by imino groups is similar to that by alkylidene groups in the reactions of cobaltadithiolenes with diazo compounds. (The bridging by alkylidene groups has been concluded not *via* carbene species but *via* the nucleophilic attack of diazo compounds to the cobaltadithiolenes.^{1b)})



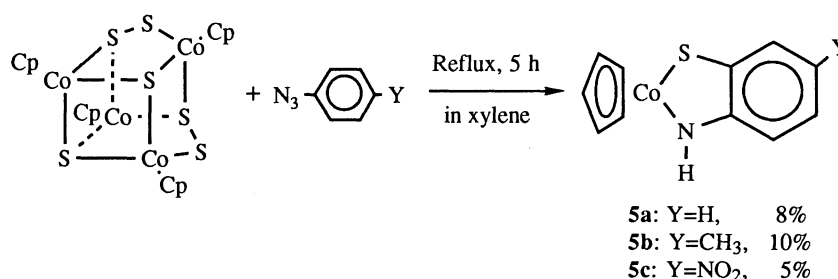
Scheme 1.

The formation of **3a** is explained by a mechanism in which nitrene bridges between Co and C atoms as a biradical species at the N atom and then a sulfur atom is eliminated. The complex **5a** should be formed by the attack of an aryl nitrene having a biradical character at N and at the *o*-position of an aryl group to Co and S atoms of a cobaltadithiolene ring.

As byproducts, we identified aniline and azobenzene. This shows the intermediacy of nitrene species. When we tried the reactions under milder conditions at 80 °C where azides do not decompose thermally, we obtained neither **3**, **4**, nor **5**.

A possible mechanism for the formation of **3** and **5** is shown in Scheme 1.

When a cluster complex, $[\text{Cp}_4\text{Co}_4\text{S}_6]$,¹⁴⁾ reacts with aryl azides, the complexes **5** are formed. In this case, the azide with an electron-donating substituent gives higher yield of **5** than that with an electron-attracting substituent. This substituent effect is similar to that in the reaction between cobaltadithiolene and aryl azides.



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References

- 1) a) M. Kajitani, M. Sakurada, K. Dohki, T. Suetsugu, T. Akiyama, and A. Sugimori, *J. Chem. Soc., Chem. Commun.*, **1990**, 19 ; b) M. Sakurada, M. Kajitani, K. Dohki, T. Suetsugu, T. Akiyama, and A. Sugimori, *J. Organomet. Chem.*, **423**, 144 (1992); c) M. Sakurada, J. Okubo, M. Kajitani, T. Akiyama, and A. Sugimori, *Chem. Lett.*, **1990**, 1837; d) M. Sakurada, J. Okubo, M. Kajitani, T. Akiyama, and A. Sugimori, *Phosphorus, Sulfur, and Silicon*, **67**, 145 (1992).
- 2) M. Kajitani, T. Suetsugu, R. Wakabayashi, A. Igarashi, T. Akiyama, and A. Sugimori, *J. Organomet. Chem.*, **293**, C15 (1985).
- 3) M. kajitani, H. Hatano, T. Fujita, T. Okumachi, H. Nagao, T. Akiyama, and A. Sugimori, *J. Organomet. Chem.*, **430**, C64 (1992).
- 4) M. Sakurada, M. Kajitani, T. Akiyama, and A. Sugimori, *Chemistry Express*, **6**, 759 (1991).
- 5) W. A. Herrmann, B. Menjon, and E. Herdtweck, *Organometallics*, **10**, 2134 (1991).
- 6) M. Dekker and G. R. Knox, *J. Chem. Soc., Chem. Commun.*, **1967**, 1243 ; B. L. Haymore, E. A. Maata, and R. A. D. Wentworth, *J. Am. Chem. Soc.*, **101**, 2063 (1979).
- 7) W. Beck, W. Rieber, S. Cenini, F. Porta, and G. La Monica, *J. Chem. Soc., Dalton Trans.*, **1974**, 298.
- 8) T. S. Haddad, A. Aistars, J. W. Ziller, and N. M. Doherty, *Organometallics*, **12**, 2420 (1993).

- 9) N. Wiberg and C. -K. Kim, *Chem. Ber.*, **119**, 2980 (1986).
- 10) W. Schütt, E. Herdtweck, and F. R. Kreißl, *J. Organomet. Chem.*, **456**, C15 (1993).
- 11) G. Hörlin, N. Mahr, and H. Werner, *Organometallics*, **12**, 1775 (1993).
- 12) S. Otsuka and A. Nakamura, *Inorg. Chem.*, **7**, 2542 (1968).
- 13) The products were identified on the basis of spectral data and elemental analyses.

(η^5 -Cyclopentadienyl)[2-(phenylimino- κN)-1,2-dicyanoethene-1-thiolato- κS]cobalt(III) (**3a**) was identified on the basis of its spectral data and elemental analysis. Mp 167 °C; UV-vis (CH_2Cl_2) 236 (ϵ , $11800 \text{ cm}^{-1} \text{ mol}^{-1} \text{ dm}^3$), 290 (21000), 376 (5100), and 568 nm (5800); IR (KBr) 3105, 2360, 2198, 1635, 1523, 1508, 1489, 1053, and 729 cm^{-1} ; ^1H NMR (CDCl_3) $\delta = 5.08$ (5H, s, Cp), 7.57 (3H, m, aromatic), 7.68 (2H, m, aromatic); ^{13}C NMR (CDCl_3) $\delta = 80.1, 112.1, 118.2, 120.7, 124.0, 128.0, 129.1, 139.8, \text{ and } 158.8$; MS (EI 70 eV) m/z (rel intensity) 323 (100, M^+), 253 (28, $\text{M}^+ - \text{SCCN}$), 232 (36, $\text{M}^+ - \text{NPh}$), and 124 (16, CpCo). Found: C, 56.40; H, 3.07; N, 13.04%; $\text{M}^+ = 323$. Calcd for $\text{C}_{15}\text{H}_{10}\text{N}_3\text{SCo}$: C, 55.73; H, 3.12; N, 13.00%.

(η^5 -Cyclopentadienyl)[1,2-dicyano-1,2-bis(phenylimino)ethene- $\kappa N, N$]cobalt(III) (**4a**) was identified on the basis of its spectral data and elemental analysis. Mp (decomp.); UV-vis (CH_2Cl_2) 234 (ϵ , $17400 \text{ cm}^{-1} \text{ mol}^{-1} \text{ dm}^3$), 1419, and 741 cm^{-1} ; ^1H NMR (CDCl_3) $\delta = 4.59$ (5H, s, Cp), 7.53 (6H, m, aromatic), 7.75 (4H, m, aromatic); ^{13}C NMR (CDCl_3) $\delta = 78.6, 113.3, 121.9, 123.5, 127.4, 129.0, \text{ and } 156.8$; MS (EI 70 eV) m/z (rel intensity) 382 (100, M^+), 129 (89, NPhCCN), and 124 (6, CpCo). Found: C, 65.13; H, 3.78; N, 13.94%; $\text{M}^+ = 382$. Calcd for $\text{C}_{21}\text{H}_{15}\text{N}_4\text{Co}$: C, 65.98; H, 3.95; N, 14.65%.

(η^5 -Cyclopentadienyl){2-imino- κN -benzene-1-thiolato- κS }cobalt(III) (**5a**) was identified on the basis of its spectral data and elemental analysis. Mp 164 °C; UV-vis (CH_2Cl_2) 241 (ϵ , $15000 \text{ cm}^{-1} \text{ mol}^{-1} \text{ dm}^3$), 274 (19300), 571 (14600), and 793 nm (1000); IR (KBr) 3305, 3050, 1651, 1558, 1539, 1508, 1454, 756, and 729 cm^{-1} ; ^1H NMR (CDCl_3) $\delta = 5.28$ (5H, s, Cp), 6.97 (1H, m, aromatic), 7.39 (2H, m, aromatic), 7.66 (1H, d $J = 8.42 \text{ Hz}$, aromatic), 11.3 (1H, broad, N-H); ^{13}C NMR (CDCl_3) $\delta = 77.4, 118.7, 118.8, 124.7, 130.2, 148.7, \text{ and } 163.6$; MS (EI 70 eV) m/z (rel intensity) 247 (100, M^+), 182 (34, $\text{M}^+ - \text{Cp}$), 124 (9, CpCo), and 123 (7, $\text{M}^+ - \text{CpCo}$). Found: C, 53.64; H, 4.03; N, 5.70%; $\text{M}^+ = 247$. Calcd for $\text{C}_{11}\text{H}_{10}\text{NSCo}$: C, 53.45; H, 4.08; N, 5.67%.

The other complexes, **3b**, **3c**, **4b**, **4c**, **5b**, and **5c** were identified by the comparison of their spectral data with those of **3a**, **4a**, and **5a**.
- 14) The cluster complex $[\text{Co}_4(\text{Cp})_4\text{S}_6]$ was synthesized according to Uchtman and Dahl (V. A. Uchtman and L. F. Dahl, *J. Am. Chem. Soc.*, **91**, 3756 (1969)).

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