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Reactions of Aryl Azides with Cobaltadithiolenes. Substitution Reactions *via* Nitrene

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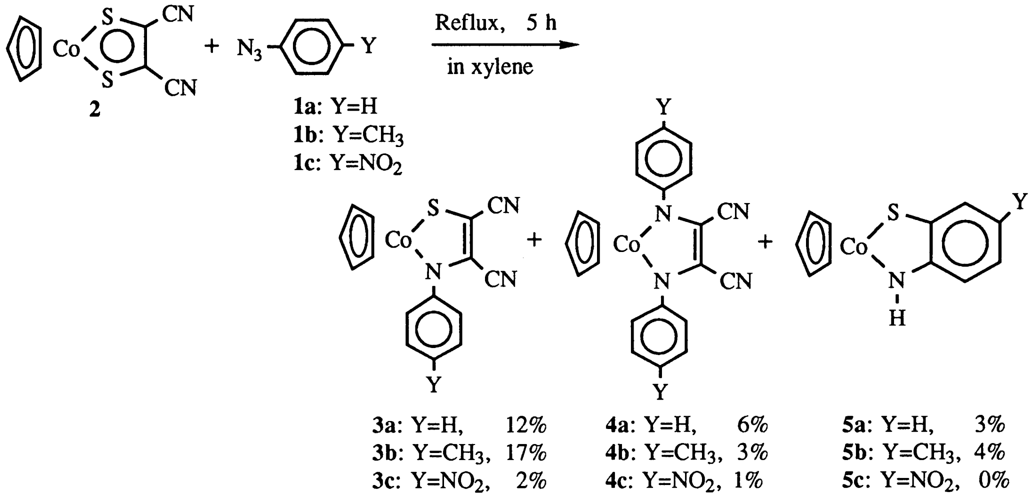
Two types of substitution reactions occur between arylnitrene from aryl azides (**1**) and a cobaltadithiolene, (η^5-cyclopentadienyl)(1,2-dicyano-1,2-ethenedithiolato)cobalt(III): 1) replacements of S by arylimino groups and 2) replacements of S-CX=CX moiety of a cobaltadithiolene by a biradical form of nitrene to give (η5-cyclopentadienyl)(2-imino-*κN*-arene-1-thiolato-*κS*)cobalt(III) (**5**). The reaction of **1** with a cluster compound [$Cp_4Co_4S_6$] gives also **5**.

A metalladithiolene ring is a very unique metallacycle. It behaves as an unsaturated ring. Alkylidene,$^{1)}$ alkyne,$^{2)}$ and quadricyclane$^{3)}$ 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, (η^5-cyclopentadienyl)(1,2-dicyano-1,2-ethenedithiolato)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 (η5-cyclopentadienyl)(2-imino-*κN*-arene-1-thiolato-*κS*)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 halogen$^{5)}$ or carbonyl$^{6)}$ 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=C$^{11)}$ bonds. The formation of tetraazendiyl complex in the reaction of [$Co(Cp)(CO)_2$] 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, (η^5-cyclopentadienyl)(1,2-dicyano-1,2-ethenedithiolato)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 arylnitrene species are generated. The reflux of a xylene solution of (**2**) and phenyl azide (**1a**) for 5 h gave (η5-cyclopentadienyl)[2-(phenylimino-*κN*)-1,2-dicyanoethene-1-thiolato-*κS*]cobalt(III) (**3a**), (η^5-cyclopentadienyl)[1,2-dicyano-1,2-bis(phenylimino)ethene-*κN*,*N*]cobalt(III) (**4a**), and (η5-cyclopentadienyl){2-imino-*κN*-benzene-1-thiolato-*κS*}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.



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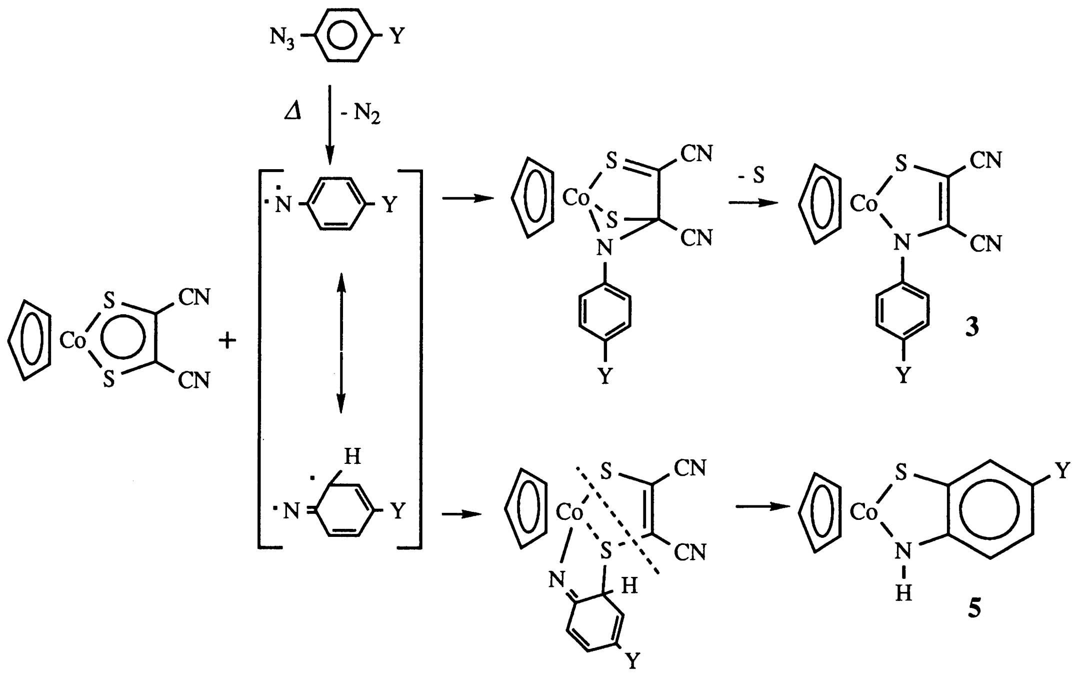
1a: Y=H
1b: Y=CH_3
1c: Y=NO_2

3a: Y=H, 12%
3b: Y=CH_3, 17%
3c: Y=NO_2, 2%

4a: Y=H, 6%
4b: Y=CH_3, 3%
4c: Y=NO_2, 1%

5a: Y=H, 3%
5b: Y=CH_3, 4%
5c: Y=NO_2, 0%

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])



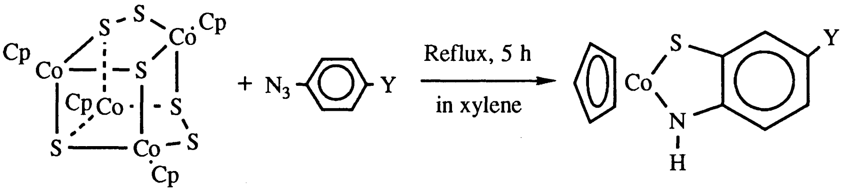
Scheme 1.

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 arylnitrene 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, [$Cp_4Co_4S_6$],[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.



5a: Y=H, 8%
5b: Y=CH_3, 10%
5c: Y=NO_2, 5%

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13) The products were identified on the basis of spectral data and elemental analyses.

($\eta5$-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 cm^{-1} mol^{-1} dm^{3}), 290 (21000), 376 (5100), and 568 nm (5800); IR (KBr) 3105, 2360, 2198, 1635, 1523, 1508, 1489, 1053, and 729 cm^{-1}; ^{1}H 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, and 158.8; MS (EI 70 eV) *m/z* (rel intensity) 323 (100, M^{+}), 253 (28, M^{+}-SCCN), 232 (36, M^{+}-NPh), and 124 (16, CpCo). Found: C, 56.40; H, 3.07; N, 13.04%; M^{+}=323. Calcd for $C_{15}H_{10}N_3SCo$: 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 spectral data and elemental analysis. Mp (decomp.); UV-vis (CH_2Cl_2) 234 (ε, 17400 cm^{-1} mol^{-1} dm^{3}), 1419, and 741 cm^{-1}; ^{1}H 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, 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%; M^{+}=382. Calcd for $C_{21}H_{15}N_4Co$: C, 65.98; H, 3.95; N, 14.65%.

($\eta5$-Cyclopentadienyl){2-imino-κN-benzene-1-thiolato-κS}cobalt(III) (**5a**) was identified on the spectral data and elemental analysis. Mp 164 °C; UV-vis (CH_2Cl_2) 241 (ε, 15000 cm^{-1} mol^{-1} dm^{3}), 274 (19300), 571 (14600), and 793 nm (1000); IR (KBr) 3305, 3050, 1651, 1558, 1539, 1508, 1454, 756, and 729 cm^{-1}; ^{1}H 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 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, and 163.6; MS (EI 70 eV) *m/z* (rel intensity) 247 (100, M^{+}), 182 (34, M^{+}-Cp), 124 (9, CpCo), and 123 (7, M^{+}-CpCo). Found: C, 53.64; H, 4.03; N, 5.70%; M^{+}=247. Calcd for $C_{11}H_{10}NSCo$: 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 $[Co_4(Cp)_4S_6]$ 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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