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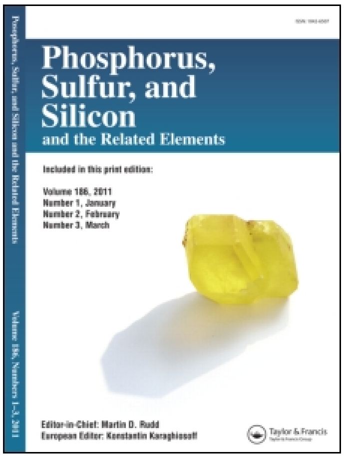

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Substitution in Metalladithiolene Rings by Sulfur-Centered Radicals

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A hydrogen atom in quasi-aromatic cobaltadithiolene rings is replaced by sulfur-centered radicals such as benzoylthio and arylthio radicals.

Keywords: radical substitution; cobaltadithiolene; sulfur radical

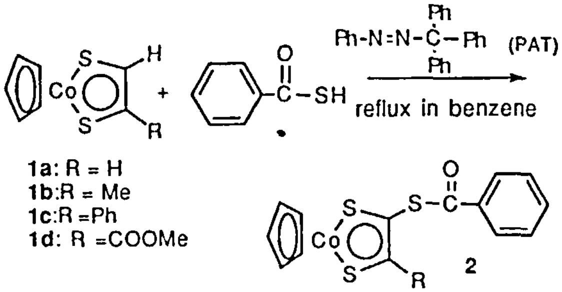
INTRODUCTION

Previously we have reported the first example of radical substitution reaction in metalladithiolene rings, quasi-aromatic metal chelate ring, in the reaction with 1-cyano-1-methylethyl radical derived from azobis-(isobutyronitrile).[1,2] Here we report the substitution in the cobaltadithiolene ring by sulfur-centered radicals.

RESULTS AND DISCUSSION

Sulfur-centered radicals are produced by two methods: 1) hydrogen abstraction by radical species from S-H and 2) homolytic cleavage of disulfides. Thiobenzoic acid reacts slightly with (η^5-cyclopentadienyl)(1-phenyl-1,2-ethenedithiolato)cobalt(III) (**1c**) in the absence of radical initiators. The initiation of the reaction with (phenylazo)triphenylmethane (PAT) as a radical source, the benzoylthio-substitution proceeds efficiently and more selectively. The cobaltadithiolene complexes **1a** (R = H) and **1b** (R = Me) give benzoylthio-substituted complexes.

However, **1d** (R = COOMe) does not undergo the substitution reaction. This shows the electrophilic character of the radical substitution reaction.



1a: R = H
1b: R = Me
1c: R = Ph
1d: R = COOMe

Several sulfur-centered radicals formed in the homolytic S-S cleavage undergo substitution reactions. The thermal reaction of **1c** with dibenzoyl disulfide (BDS) gives **2c**.[3] Similarly the reaction of **1c** with bis(2,4-dinitrophenyl) disulfide gives the 2,4-dinitrophenylthio-substituted product. Among disulfides, di(benzothiazolyl) disulfide is most effective for arylthio-subtitution. The benzothiazolylthio-substitution occurs in the UV-irradiation or in γ-irradiation in benzene. In these cases, excited di(benzothiazolyl) disulfide undergoes homolytic cleavage of S-S bond and the formed sulfur radical causes the substitution.

References

[1] M. Kajitani, G. Hagino, M. Tamada, T. Fujita, M. Sakurada, T. Akiyama, and A. Sugimori, *J. Am. Chem. Soc.*, **118**, 489 (1996).
[2] A. Sugimori, N. Tachiya, M. Kajitani, and T. Akiyama, *Organometallics*, **15**, 5564 (1996).
[3] In the reaction with dibenzoyl peroxide (BPO), 1c gives benzoyloxy-substituted product. The product from BPO is similar to that from dibenzoyl disulfide but the reaction mechanism is different: A. Sugimori, K. Yanagi, G. Hagino, M. Tamada, M. Kajitani, and T. Akiyama, *Chem. Lett.*, **1997**, 807.