

**“*trans*-Dichlorobis(1,10-phenanthroline)cobalt(III) Chloride Hydrochloride Trihydrate” — Composition and Configuration**

JENS JOSEPHSEN and  
CLAUS ERIK SCHÄFFER

*Chemistry Department I (Inorganic Chemistry), University of Copenhagen, H. C. Ørsted Institute, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark*

In recent work<sup>1-4</sup> it was concluded that all known complexes of the type  $M(III)phen_2X_2^{n+}$  ( $M=Cr, Co, Rh, Ir$ ;  $X=F, Cl, Br, H_2O, OH$ ) had the *cis*-configuration. This conclusion was based on chemical evidence,<sup>1,2</sup> on X-ray powder photographs<sup>1,3</sup> indicating isomorphous series, and on comparisons of ligand field,<sup>1,2</sup> IR,<sup>3,4</sup> and PMR spectra.<sup>4,5</sup> The non-existence of *trans*-complexes was indicated by consideration of molecular models,<sup>2</sup> and other *trans*-configuration proposals in the literature have been shown to be unjustified.<sup>2</sup>

Recently another *trans*-configuration proposal,  $A=trans-[Cophen_2Cl_2]Cl, HCl, 3H_2O$ , has appeared.<sup>5</sup> We have now shown that this compound is actually  $B=cis-[Cophen_2Cl_2]_2[CoCl_4] \cdot 2H_2O$ .

The present sample was prepared according to Ref. 5 and shown by its PMR spectrum to be identical with the one studied there. The analytical data (Table 1) for our compound B are not very different

from those found in Ref. 5, except for the cobalt analysis.

The same compound was prepared (B' in Table 1) by precipitating *cis*- $[Cophen_2Cl_2]^+$  with cobalt(II) ions in 6 M hydrochloric acid. The identity of the compounds, prepared in the two different ways, was established from chemical analysis, from their identical X-ray powder photographs, and from the following spectral evidence. In 1.2 M hydrochloric acid both compounds showed a visible spectrum that was practically identical to that of *cis*- $[Cophen_2Cl_2]^+$  ( $Co(H_2O)_6^{2+}$  being little coloured) and a molecular weight corresponding to B could be determined for both complexes from the molar extinction coefficient at the absorption maximum of *cis*- $[Cophen_2Cl_2]^+$ . The spectra of the two compounds measured at the same concentration in nitromethane were also identical and showed the typical sharp peaks of chlorocobaltate(II) complexes. The PMR spectra in deuterated DMSO and in deuterium oxide were found to agree with those reported.<sup>5</sup> However, the spectrum<sup>5</sup> in DMSO was apparently given on a different scale, thereby obscuring the fact that apart from a line broadening it was identical with that of the *cis*-complex.

The fact that the PMR spectrum in water was found to be completely different from that in DMSO is understandable partly because in water one  $Cl^-$  of *cis*- $[Cophen_2Cl_2]^+$  is hydrolysed quite rapidly<sup>2</sup> while in DMSO it is not, and partly because in water the paramagnetic anion becomes the cationic hexaaquacobalt(II) ion while in DMSO it remains a chlorocobaltate(II) ion.

It is stated in Ref. 5 that the compound is diamagnetic, but as no supporting data are given, we conclude that the very existence of a resolved PMR spectrum led to this statement. The spectrum is, however, rather broad, as also stated in Ref. 5, just as would be expected for the diamagnetic cation accompanied by a paramagnetic anion.

We conclude again that all known octahedral bis{(1,10)-phenanthroline} and bis{(2,2')-bipyridine} complexes of chromium(III), cobalt(III), rhodium(III), and iridium(III) have the *cis*-configuration, and doubt whether *trans*-complexes are able to exist.

Table 1. Analytical data.

	Co	C	H	N	Cl
A calc.	9.6	49.0	3.8	9.1	23.1
Ref. 5 found	9.4	47.4	2.8	9.1	22.6
B found	14.58	47.48	2.98	9.19	23.78
B' »	14.41				
B calc.	14.53	47.33	2.96	9.20	23.33

We thank Kjeld Schaumburg for the measurement of the PMR spectra and for his helpful comments on them.

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Received July 30, 1969.

## On the Halogen-Metal Exchange Reaction between 2-Bromo-3-iodothiophene and Ethyllithium

SALO GRONOWITZ and BORIS HOLM

*Chemical Center, Division of Organic Chemistry, University of Lund, P.O. Box 740, S-220 07 Lund, Sweden*

Halogen-metal exchange between bromothiophenes and ethyllithium derivatives is a very rapid reaction even at  $-70^{\circ}\text{C}$ .<sup>1</sup> It is also known that 2-positioned bromine exchanges much more rapidly than 3-positioned bromine. For instance, this is demonstrated in the halogen-metal exchange reaction between 2,3-dibromothiophene or 2,4-dibromothiophene with butyllithium at  $-70^{\circ}\text{C}$  in which case only the  $\alpha$ -halogen is exchanged.<sup>1</sup> It is also well-known, from the classical investigations of Wittig *et al.* and Gilman *et al.* that iodides react more rapidly than bromides (for review, *cf.* Ref. 2). Therefore we were interested in studying the halogen exchange reaction of 2-bromo-3-iodothiophene with ethyllithium in order to find out which factor would be the most important.

The study of halogen-metal exchange with this substrate is also of interest in connection with the question of the existence of dehydrothiophene. One of us has earlier pointed out the high stability of *ortho* bromo-thienyllithium derivatives

such as 3-bromo-2-thienyllithium.<sup>3</sup> In contrast to *ortho* bromophenyllithium<sup>4</sup> these compounds showed no tendency to split out lithium bromide to give dehydrothiophenes.

It was also found that 3-fluoro-2-thienyllithium, obtained through metalation of 3-fluorothiophene was stable and no dehydrothiophene could be intercepted with furan.<sup>5</sup> Nor could the Grignard route from 3-fluoro-2-bromothiophene be used for the production of 2,3-dehydrothiophene.

A recent paper by Wittig and Rings describes extensive work to prove the intermediate formation of dehydrothiophene.<sup>6</sup> They used 3-bromo-2-thienyllithium and 2,5-diphenyl-4-iodo-3-thienyllithium as well as similar mercury compounds such as bis[3-iodo-2-thienyl]mercury as substrates. However, no evidence for the intermediate formation of dehydrothiophene was obtained. Reinecke and Adickes<sup>7</sup> have shown that the *ciné*-substitution, which occurs in the reaction of 2-bromothiophene with potassium amide in liquid ammonia does not proceed *via* a dehydrothiophene but occurs through a series of transbrominations similar to those observed by Gronowitz and coworkers in the reaction of 3-bromothiophene and the dibromothiophenes with butyllithium.<sup>1</sup> We therefore hoped that, if 2-bromo-3-thienyllithium was formed in the halogen-metal exchange reaction, this certainly should constitute the most suitable intermediate hitherto studied for the production of 2,3-dehydrothiophene.

2-Bromo-3-iodothiophene (b.p.  $106-109^{\circ}\text{C}/10$  mm Hg,  $\tau_{\text{OEt}}=2.83$  ppm,  $\tau_{\text{OEt}}=3.09$  ppm  $J_{45}=5.6$  cps) was obtained in 83% yield through reaction of 3-iodothiophene with *N*-bromosuccinimide in acetic acid.

Adding an ethereal solution of 2-bromo-3-iodothiophene to a 10% excess of ethereal ethyllithium at  $-70^{\circ}\text{C}$ , controlling the temperature below  $-60^{\circ}\text{C}$ , yielded upon reaction with ethanol, 20% 3-iodothiophene, 55% 3-bromothiophene, 5% 2-bromothiophene, and 20% 2,3-dibromothiophene. Carbonation of the reaction mixture yielded an acid mixture, which was esterified with diazomethane and analysed gas-chromatographically. The analysis indicated the formation of 26% of methyl 3-iodo-2-thiophenecarboxylate, 71% 3-bromo-2-thiophenecarboxylate, and 3% 2-bromo-3-thiophenecarboxylate. This indicates that the simple halothiophenes (except 2,3-dibromothiophene) obtained upon hydrolysis exist as lithiated derivatives. It would be attractive to