Nuclear Magnetic Resonance Evidence for the Formation of *cis*- and *trans*-σ-But-2-enyl and *syn*-π-(1-Methylallyl) Complexes in the Hydrogenation of Butadiene by Pentacyanocobaltate(II)

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Summary Formation of similar amounts of *cis*- and *trans*-σ-but-2-enyl pentacyanocobaltate(III) and of *syn*-π-(1-methylallyl)tetracyanocobaltate(III) in the hydrogenation of butadiene by pentacyanocobaltate(II) is demonstrated from the i.r. spectrum and the n.m.r. spectra at 60, 100, and 220 MHz.

IN the hydrogenation of butadiene by pentacyanocobaltate(II), but-1-ene is selectively produced in the presence of excess of CN^- (CN : Co > 5) and *trans*-but-2-ene in the presence of a smaller amount of CN^- (CN : Co < 5), but the mechanism is still obscure. While Kwiatek and Seyler[1] proposed a mechanism in which σ-but-2-enyl pentacyanocobaltate(III) (σ_1) and π-(1-methylallyl)tetracyanocobaltate(III) were intermediates in the formation of but-1-ene and *trans*-but-2-ene respectively, Burnett *et al.* proposed that the intermediate in the formation of but-1-ene was σ-1-methylprop-2-enyl pentacyanocobaltate. In an attempt to clarify the mechanism we report here the n.m.r. and i.r. spectra of the complexes in the reaction process.

The reaction was performed both in D_2O and H_2O at 0 °C and with a Co concentration of 0·2 M under an atmosphere of H_2 and butadiene. Without isolation of the complexes, the n.m.r. and i.r. spectra of the solution were obtained at room temperature.

As shown in Figure 1, the solution at CN : Co > 5 showed different spectra at 60, 100, and 220 MHz. The signal near τ 8·45 changed from a doublet (60 MHz) to a quartet (100 MHz) and to a triplet (220 MHz). The spectra revealed that the solution contained two complexes with very similar configurations. We assigned them to the *cis*- and *trans*-isomers of σ_1, although we could not determine which signals corresponded to the *cis*- or *trans*-isomer. τ 8·43 [d, Me, $J_{3,4}$ 7·0 Hz (a)], 8·46 [d, Me, $J_{3,4}$ 6·5 Hz (b)], 7·60 [d, CH_2, $J_{1,2}$ 9·4 Hz (c)], 7·67 [d, CH_2, $J_{1,2}$ 8·6 Hz (d)], 4·30 [m, =CH (3)], and 4·01 [m, =CH(2)]. The similar intensity of the two CH_2 doublets suggests that the two isomers are formed

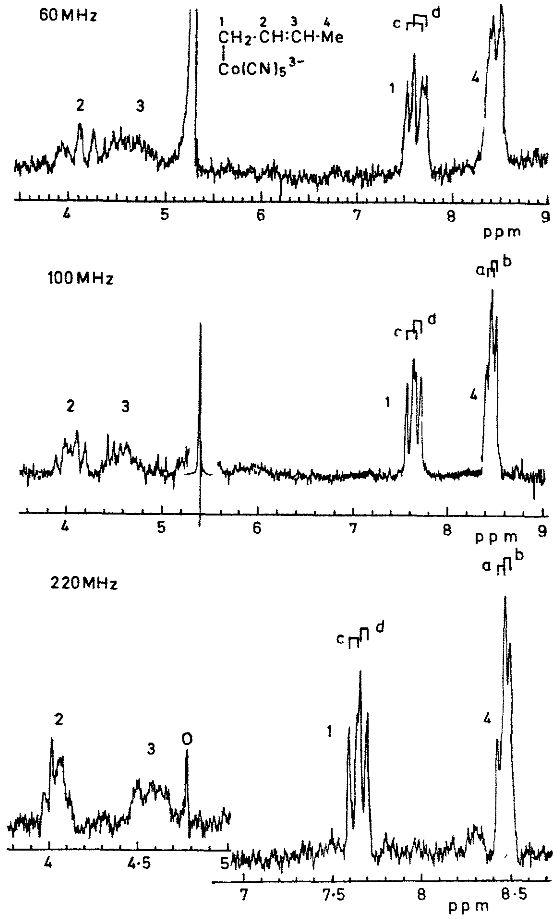

FIGURE 1. *N.m.r. spectra of σ-But-2-enylpentacyanocobaltate*(III) *in* D_2O *at* 60, 100, *and* 220 *MHz*. 0, *Side band of* H_2O.

in similar amounts, and the results may be explained either by the equilibrium $\sigma_1 \rightleftharpoons \sigma_2$ or by *cis*- and *trans*-1,4-addition. From our i.r. study, the former seems preferable.

The n.m.r. spectrum at CN : Co < 5 (Figure 2) shows that the complex formed is a *syn*-π-(1-methylallyl) complex, τ 8·50 (d, CH_3, *J* 6·2 Hz), 7·53 (d, 3-H, $J_{1,3}$ 12·3 Hz), 6·68 (d, 2-H, $J_{1,2}$ 7·8 Hz), 6·23 (dq, 4-H, $J_{1,4}$ 12·3 Hz), 4·89 (dt, 1-H). The spectrum also revealed that the solution contains no *anti*-complex. The i.r. spectrum showed $\nu_{C\equiv N}$ 2104 cm^{-1} (σ-but-2-enyl complex) and 2110 cm^{-1} (π-methylallyl complex). In addition, a band shift from the latter to the former was observed when excess of KCN was added to the solution. This is the first demonstration of the conversion of a π-methylallyl complex into a σ-but-2-enyl complex. By observation of the characteristic bands, the formation of the complex could be followed. Preliminary comparison of the rate with the rate of the butene formation[3] suggests that σ-but-2-enyl complexes are not direct intermediates for the but-1-ene formation and that the π-methylallyl complex is the most probable intermediate for the *trans*-but-2-ene formation.

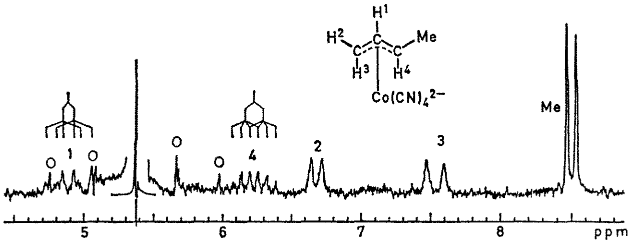

FIGURE 2. *N.m.r. spectrum of* syn-π-(1-*methallyl*)*tetracyanocobaltate*(III) *in* D_2O (100 MHz).
0, *Side bands of* H_2O.

At present, the i.r. and n.m.r. studies of aqueous solutions support the mechanism proposed by Burnett, but details of the mechanism based on the i.r. study will be discussed later.

(*Received, June* 14*th*, 1971; *Com.* 976.)

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