

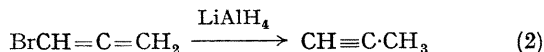
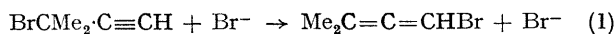
## A $\sigma$ -Bonded Cobalt Allene

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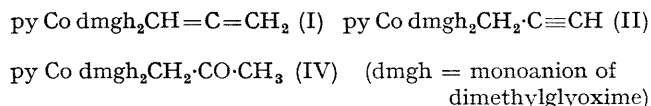
**Summary** A  $\sigma$ -bonded cobalt allene has been prepared by the reaction of the bis(dimethylglyoximate)pyridine-cobalt(I) anion with prop-2-ynyl bromide. Although another  $\sigma$ -bonded allenyl-metal compound had been prepared previously, it is incorrectly described as a  $\sigma$ -prop-2-ynyl compound.

PROP-2-YNYL and ALLENYL HALIDES react with nucleophiles by  $S_N2$  or  $S_N2'$  mechanisms to give mixtures of prop-2-ynyl- and allenyl compounds. For example, prop-2-ynyl bromides react with bromide ion to give allenyl bromides<sup>1</sup> [*e.g.* equation (1)] and allenyl bromide reacts with lithium aluminium hydride to give up to 98.3% of propyne, depending on the conditions [equation (2)].<sup>2</sup>

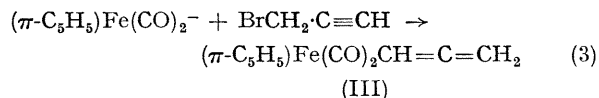


We anticipated, therefore, that, as bis(dimethylglyoximate)cobaltate(I) ions may apparently behave as reactive nucleophiles,<sup>3</sup> reaction with prop-2-ynyl bromide might lead to the  $\sigma$ -prop-2-ynyl and/or the  $\sigma$ -allenylcobalt complex.

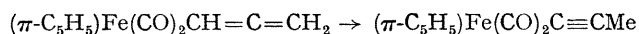
The only organometallic product which was isolated from the reaction of methanolic prop-2-ynyl bromide with a solution of the cobaltate(I) ion, prepared from sodium borohydride and hexakis(dimethylglyoximate)dipyridine-dicobalt(II), was the  $\sigma$ -bonded bis(dimethylglyoximate)-allenylpyridine cobalt(III) (I). This allene is characterised by the  $\text{AB}_2$   $^1\text{H}$  n.m.r. spectrum in  $\text{CDCl}_3$  ( $\tau$  5.15,  $\alpha$  = CH; 5.57,  $\gamma$ - $\text{CH}_2$ ;  $J_{\alpha\gamma}$  6.1 c. sec.; 1.46, pyridine  $\alpha$ -CH; 7.85, dimethylglyoxime) and by the C=C=C stretch at 1927  $\text{cm}^{-1}$ . These values are comparable with those for other allenes [ $\tau$ (=CH<sub>2</sub>) *ca.* 5.3;  $J_{\alpha\gamma}$  -6.1 to 7.0 c. sec.;<sup>4</sup>  $\nu$ (C=C=C) 1950  $\text{cm}^{-1}$ ]<sup>5</sup> and are quite different from those expected for the prop-2-ynyl compound (II) [ $\tau$ (=CH) *ca.* 7.5;  $\tau$ (CH<sub>2</sub>) *est.* 8 + 1;  $J_{\alpha\gamma}$  2.6  $\pm$  0.3 c. sec.].<sup>6</sup> Furthermore the absence of the  $\sigma$ -prop-2-ynyl cobalt is demonstrated<sup>7</sup> by the lack of any C $\equiv$ C stretching absorption at *ca.* 2200  $\text{cm}^{-1}$ .



However, though the only other  $\sigma$ -allenyl transition-metal complex that has been described in the literature is a perfluoroallenylrhenium carbonyl,<sup>8</sup> we believe that the product of reaction of prop-2-ynyl bromide with the dicarbonyl- $\pi$ -cyclopentadienyliron anion, which was first described<sup>9</sup> as the  $\sigma$ -prop-1-ynyl- and later<sup>10</sup> as the  $\sigma$ -prop-2-ynyl compound, is in fact the  $\sigma$ -allenyl compound (III) [equation (3)]. This compound also has characteristics of an allenyl rather than a prop-2-ynyl complex, *i.e.*  $^1\text{H}$  n.m.r.:  $\tau$  5.11,  $\alpha$ -CH;  $\tau$  6.03,  $\gamma$ -CH<sub>2</sub>;  $J_{\alpha\gamma}$  6.5 c./sec. The i.r. absorption characteristic of the allenyl group of this compound is unfortunately in the C $\equiv$ O stretching region and may have been obscured or misinterpreted, but no C $\equiv$ C stretching absorption was described.



Treatment of this compound with acid gave the prop-1-ynyl-iron derivative, which was interpreted by a four-step mechanism involving two hydrogen shifts with the  $\sigma$ -allenyliron complex as a transitory intermediate. In view of the true structure of the compound, a single hydrogen-shift is appropriate [equation (4)].



On treatment of the allenylcobalt complex (I) with aqueous-methanolic hydrochloric acid, the allenyl group is hydrated to give the  $\sigma$ -bonded acetyliron complex (IV).

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