

## Stereospecific Electrochemical Synthesis: Preparation of Isomers of $(\text{CF}_3)_6\text{C}_6\text{Co}_2(\text{CO})_2[\text{P}(\text{OMe})_3]_2$

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Selective stereochemical synthesis of certain metal-metal bonded organometallic compounds can be achieved *via* their radical anions; the catalytic preparation of isomers of  $(\text{CF}_3)_6\text{C}_6\text{Co}_2(\text{CO})_2[\text{P}(\text{OMe})_3]_2$  is described.

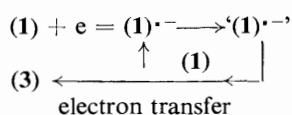
Recently we reported<sup>1</sup> the formation of radical anions from various acetylene complexes of cobalt, and demonstrated<sup>2</sup> that these anions show enhanced activity towards nucleophiles. While exploring the synthetic catalytic consequences of the enhanced reactivity of radical anions<sup>3</sup> we have found that compounds which can exist as stereoisomers can be selectively synthesised by taking advantage of their different redox properties. In this communication we illustrate this generality by considering the synthesis of Lewis base derivatives of the 'flyover' complex  $(\text{CF}_3)_6\text{C}_6\text{Co}_2(\text{CO})_4$ .

The 'flyover'<sup>4</sup> complex  $(\text{CF}_3)_6\text{C}_6\text{Co}_2(\text{CO})_4$  (**1**) is readily reduced (chemically or electrochemically) to its radical anion  $(\mathbf{1})^{\cdot-}$ , which has a half-life of several minutes under  $\text{N}_2$ . Controlled potential electrolysis of **1** at  $-0.1$  V (MeCN or  $\text{CH}_2\text{Cl}_2$ , supporting electrolyte  $\text{Bu}_4\text{N}^+\text{ClO}_4^-$ ) in the presence of  $\text{P}(\text{OMe})_3$  immediately produced a solution containing two new derivatives:† the purple  $(\text{CF}_3)_6\text{C}_6\text{Co}_2(\text{CO})_3[\text{P}(\text{OMe})_3]$  (**2**) and a blue compound of stoichiometry  $(\text{CF}_3)_6\text{C}_6\text{Co}_2(\text{CO})_2[\text{P}(\text{OMe})_3]_2$  (**3**). 100% conversion of **1** into **2** and **3** is achieved *within 2 min* and, with a 10 molar excess of ligand, yields of >90% of **3** are achieved. Thermal methods only give small yields (<10%) of **3** from **1** and this electrochemical method is the most direct rapid general route to 'flyover' derivatives. Most significant however, is the observation that only a trace of reducing agent is required to achieve this conversion and the reaction is essentially catalytic once  $(\mathbf{1})^{\cdot-}$  is produced.

Compound **3** undergoes a quasi-reversible one-electron reduction to its radical anion  $(\mathbf{3})^{\cdot-}$  at  $E_{\frac{1}{2}} = -0.7$  V vs. Ag/AgCl. Electrolysis of an acetonitrile solution of **3** at  $-0.7$  V instantaneously produces a colour change from blue to purple and a purple isomer (**4**) of  $(\text{CF}_3)_6\text{C}_6\text{Co}_2(\text{CO})_2[\text{P}(\text{OMe})_3]_2$  can be isolated in 100% yield. Again, only a trace of reducing agent is required for the conversion **3** → **4** and it is not possible to reverse the transformation by chemical, thermal or electrochemical means. Therefore, by selecting the appropriate potential for electrolysis, it is possible to synthesise selectively either isomer in yields in excess of 90%.

An ECE mechanism<sup>3,3</sup> can be invoked for the conversions **1** → **2** + **3** and **3** → **4** but the rapidity of these reactions is believed to be due to the enhanced electrophilicity of a species  $(\mathbf{1})^{\cdot-}$  derived from the radical anions  $(\mathbf{1})^{\cdot-}$  and  $(\mathbf{3})^{\cdot-}$  by cleavage of the Co-Co bond [the odd electron in  $(\mathbf{1})^{\cdot-}$  occupies an antibonding orbital centred on the Co-Co bond] (Scheme 1).

Spectroscopic data and X-ray crystal structure analyses‡

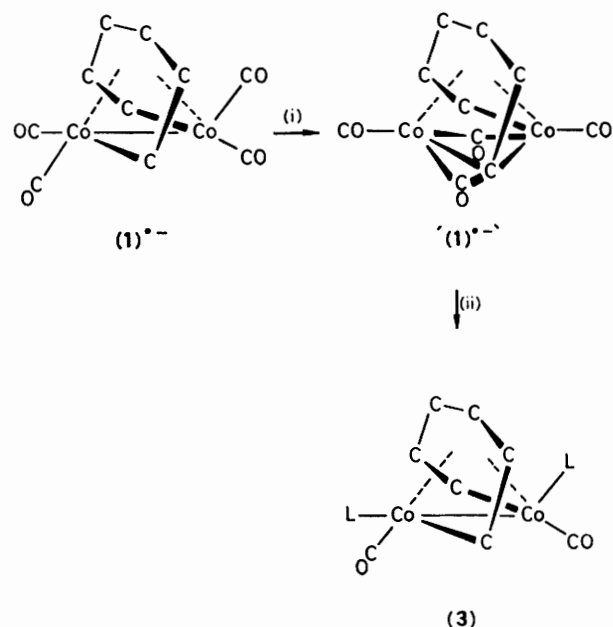


Scheme 1

† All new compounds had satisfactory analyses and spectroscopic data.

‡ At the present stage of refinement  $R = 6.3\%$  for **3** and  $7.0\%$  for **4**. Full details will be published elsewhere.

show that the difference between **3** and **4** lies in the position of the phosphite ligands with respect to the 'flyover' backbone (Figure 1). Two interesting points arise from the structural analysis. (a) Why is the ligand configuration adopted by **3** preferred and is selective in the electrochemical preparation? (b) Why is the conversion **3** → **4** so facile when both a  $90^\circ$  rotation and reflection about the Co-Co bond bridged by a



Scheme 2. (i) Bond cleavage; (ii) electron transfer to **1** and substitution.

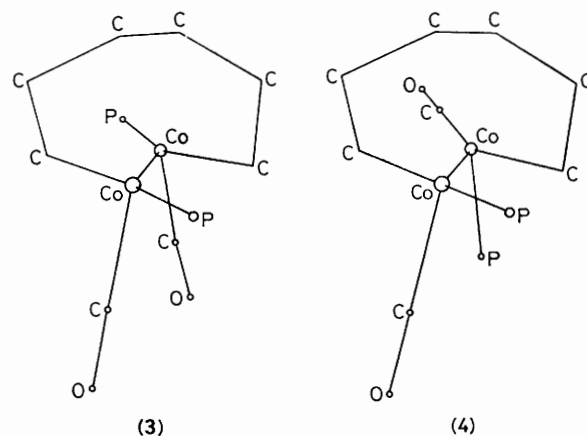


Figure 1. Structures of **3** and **4** showing the different positions of the phosphite ligands.

rigid 'flyover' back bone is required? We suggest that stereochemical selectivity is achieved because of the specific conformation of the intermediates '(1)<sup>•-</sup>' and '(3)<sup>•-</sup>'. A detailed analysis will be presented elsewhere but Scheme 2 shows how the specific formation of (3) arises from a CO-bridged radical anion '(1)<sup>•-</sup>'.

Electrochemical syntheses of the type described here are versatile and have been successfully adapted for the preparation of 'flyover' derivatives and other organometallic and cluster compounds.

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