A Novel Intramolecular Metallacycle-phosphine Reaction of an Electrochemically Oxidized Cobaltacyclopentadiene Complex

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A ferrocene-substituted cobaltacyclopentadiene complex, $C_5H_5(PPh_3)[Co{-}CH{=}CFc{-}CFc{=}CH]$ (**1**, Fc = ferrocenyl) undergoes quasi–reversible two-step one-electron oxidation reactions in 0.1 mol dm^{-3} $Bu_4NClO_4{-}CH_2Cl_2$ at room temperature, while irreversible two-electron oxidation (ECE reaction) of $C_5H_5(PPh_3)[Co{-}CFc{=}CH{-}CH{=}CFc]$ **2** causes intramolecular addition of PPh_3 fragments to the buta-1,3-dienediyl moiety, affording $PhCFc{=}CH{-}CH{=}CFcPOPh_2$ **7** and $PhCFc{=}CH{-}CFc{=}CHPPh_2$ **8**.

Metal-bound buta-1,3-dienediyl units in cobaltacyclopentadiene complexes are efficient synthetic skeletons convertible into various aromatic compounds by reaction with unsaturated molecules.[1] In this report, we present the electrochemical properties of the new ferrocene-substituted cobaltacyclopentadiene complexes, **1** and **2**, that show a remarkable difference in electrochemical reversibility between these geometric isomers and a novel intramolecular coupling reaction of the butadienediyl unit with triphenylphosphine ligand, induced by electrochemical oxidation of **2**.

The diferrocenylcobaltacyclopentadiene complexes, **1** and **2**, were obtained as brown and black crystals in 18 and 45% yield, respectively, by the reaction of $C_5H_5Co(PPh_3)_2\cdot\frac{1}{2}$ hexane[2] and $C_5H_5Fe(\eta^5\text{-}C_5H_4C{\equiv}CH)$[3] in the mole ratio 1 : 2 in benzene at 60 °C for 1 h.† Their cyclic voltammograms at a glassy carbon electrode in 0.1 mol dm^{-3} $Bu_4NClO_4{-}CH_2Cl_2$ are shown in Fig. 1. Three oxidation peaks appear at −0.20,

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† Satisfactory elemental analyses were obtained for compounds **1, 2, 7** and **8**. ^1H NMR data (in CD_2Cl_2): **1**: δ 7.33–7.03 (m, 15H), 4.71 (s, 5H), 4.19 (s, 4H), 4.08 (s, 4H), 4.01 (s, 10H), 3.93 (br, s, 1H), 3.13 (br, s, 1H); **2**: δ 7.38–7.16 (m, 15H), 6.50 (d, J_{HH} 2.9 Hz, 1H), 6.49 (d, 1H), 4.36 (m, 1H), 4.31 (m, 1H), 4.17 (m, 1H), 4.06 (s, 5H), 4.04 (m, 1H), 4.02 (s, 5H), 4.01 (m, 1H), 3.98 (m, 1H), 3.94 (m, 1H), 3.62 (m, 1H); **7**: δ 7.83–7.51 (m, 10H), 7.19–7.05 (m, 5H), 6.46 (d, J_{HH} 1.5 Hz, 1H), 6.40 (d, 1H), 4.27 (m, 2H), 4.21 (m, 2H), 4.14 (m, 2H), 4.13 (s, 5H), 4.05 (m, 2H), 4.03 (s, 5H); **8**: δ 7.27 (m, 10H), 7.08 (m, 5H), 6.87 (d, J_{HH} 0.9 Hz), 6.30 (m, 1H), 4.41 (m, 2H), 4.28 (m, 2H), 4.24 (m, 2H), 4.23 (s, 5H), 4.18 (m, 2H), 4.08 (s, 5H).

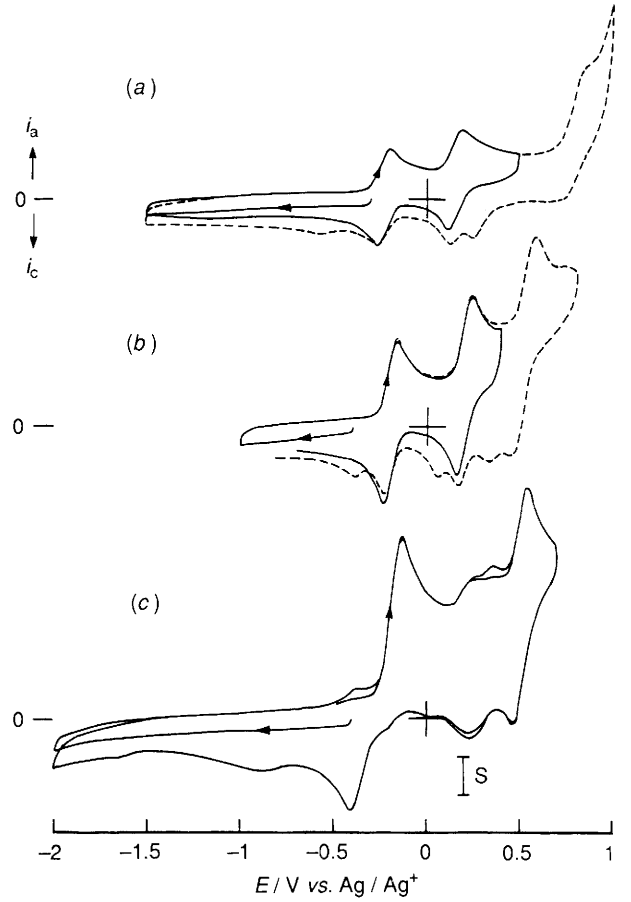


Fig. 1 Cyclic voltammograms of diferrocenylcobaltacylcopentadienes at a glassy carbon disk electrode (area: 0.20 cm^{-2}) in 0.1 mol dm^{-3} Bu_4NClO_4-CH_2Cl_2 at 0.1 V s^{-1}: (*a*) 0.20 mmol dm^{-3} of **1** at room temp., (*b*) 0.33 mmol dm^{-3} of **2** at −64 °C, (*c*) 0.34 mmol dm^{-3} of **2** at room temp. S = 10 μA for (*a*) and (*c*), and 5 μA for (*b*).

+0.19 and +0.86 V *vs.* Ag/Ag$^+$ in the voltammogram of **1** at room temp., and the first two 1e$^-$ oxidation reactions are quasi-reversible and the third one is irreversible. Kelly and Geiger have reported that η^5-cyclopentadienyl(triphenylphosphine)cobaltacyclopentadiene complexes undergo two-step one-electron oxidation under mild conditions (at low temperatures in tetrahydrofuran or CH_2Cl_2) and differences in $E^{0\prime}$ between the first and second oxidation are 0.7–0.9 V.[4] Thus, the first wave shown in the voltammogram in Fig. 1(*a*) can be ascribed to the first oxidation of cobaltacyclopentadiene and the second one to oxidation of one ferrocenyl moiety judging from their formal potentials. The third oxidation peak at +0.86 V might be due to second oxidation of the cobaltacyclopentadiene unit and/or oxidation of the second ferrocenyl group.

An isomeric cobaltacyclopentadine of **1**, **2** also shows quasi-reversible two-step one-electron oxidation reactions at $E^{0\prime}$ = −0.19 and +0.20 V *vs.* Ag/Ag$^+$, which are similar potentials to those of **1**, at −64 °C [see Fig. 1(*b*)]. However, it gives a complicated voltammogram with an irreversible oxidation of metallacycle at −0.13 V *vs.* Ag/Ag$^+$ at room temp. [see Fig. 1(*c*)]. Bulk coulometry of **2** at 0 V *vs.* Ag/Ag$^+$ at room temperature resulted in the release of two electrons, consistent with the ECE process. Kelly and Geiger have already reported an occurrence of ECE reaction for a cobaltacyclopentadiene complex, but the reaction products have not been identified.[4] In the bulk electrolysis of **2**, cobalt-free compounds **7** and **8** were obtained in the yields 12 and 38%, respectively.† The molecular structure of **8** was determined by the X-ray crystallographic study and the

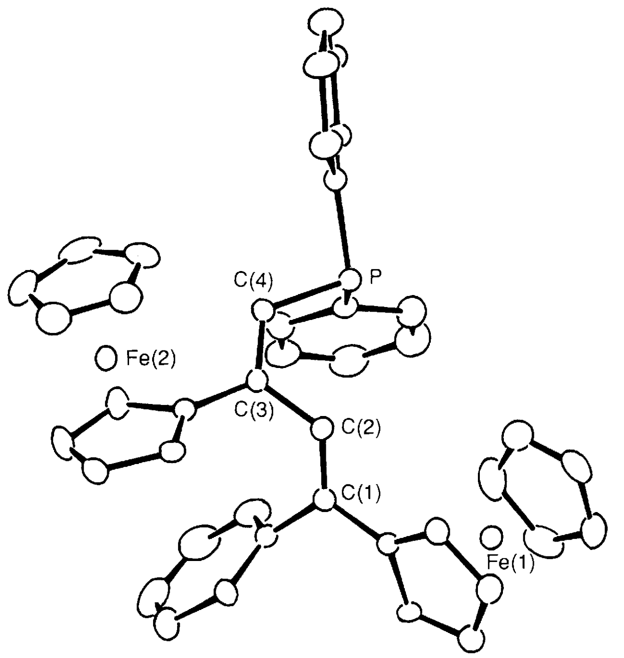
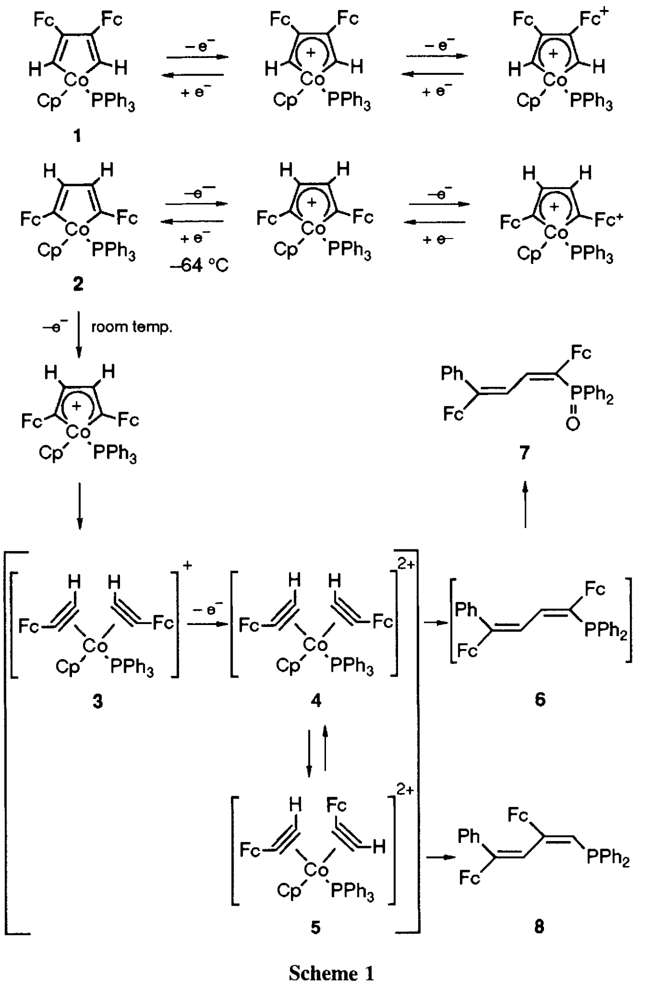


Fig. 2 ORTEP diagram of phosphine **8**. Hydrogen atoms were neglected in the analysis. Selected mean distances (Å) and angles (°): C(1)–C(2) 1.347(8), C(2)–C(3) 1.480(9), C(3)–C(4) 1.365(7), C(4)–P 1.815(6), C(1)–C(2)–C(3) 124.6(6), C(2)–C(3)–C(4) 122.7(5).



Scheme 1

ORTEP diagram is displayed in Fig. 2.‡ The formation of **7** and **8** implies an unusual reaction pathway of the oxidized form of **2**, involving rearrangement of the 1,4-diferrocenylbuta-1,3-dienediyl backbone, fragmentation of PPh_3 into PPh_2 and Ph and their intramolecular addition to the buta-1,3-dienediyl unit. A possible mechanism is given in Scheme 1, in which the $18e^-$–$17e^-$–$19e^-$–$18e^-$ configuration changes take place in the ECE process. A bis(acetylene)cobalt complex **4** is proposed as the $18e^-$ complex formed in the ECE reaction, since the equilibrium of this configuration with an isomer **5** can be used to rationalize the formation of both **7** and **8**. Phosphine oxide, **8** should be formed by the aerobic oxidation of phosphine, **7**, during the isolation and purification by column chromatography carried out in air.

Cyclic voltammograms of **7** and **8** exhibit two reversible and slightly split one-electron oxidation waves due to the ferrocenyl moieties at +0.27 and +0.36 V *vs.* Ag/Ag^+. Thus, the small redox waves seen at the same potentials as noted above in the voltammogram of **2** in Fig. 1(*c*) are assignable to those of phosphines, **6** and **8**. A reduction peak also appears at −0.41 V *vs.* Ag/Ag^+ after oxidation of **2** in the cyclic voltammogram. Any compounds showing this reduction peak have not been isolated, but the $18e^-$ complxes **4** and **5** should be the most stable intermediates in the reaction path written in Scheme 1, and thus the most likely candidates of the origin of the reduction peak.

The intramolecular metallacycle-phosphine reaction induced by electrochemical oxidation presented in this paper may lead to a new synthetic route of organophosphorus compounds from acetylenes.

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‡ *Crystal data for*: **8** $C_{42}H_{35}Fe_2P$, $M = 682.4$, triclinic, space group $P\bar{1}$, $a = 15.777(3)$, $b = 20.008(2)$, $c = 11.303(2)$ Å, $\alpha = 106.14(1)$, $\beta = 99.94(2)$, $\gamma = 96.76(2)°$, $V = 3323.9(9)$ Å^3, $T = 299$ K, $D_c = 1.36$ g cm^{-3}, $Z = 4$, $\mu(\text{Mo-K}\alpha) = 9.48$ cm^{-1}, $R(F) = 0.057$, $R_w = 0.073$ for 7229 independent reflections with $|F_o| > 3\sigma(|F_o|)$, $2\theta_{max} = 55°$. There exist two independent molecules in the crystal, and their structures are the same.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

References

1 Y. Wakatsuki, T. Kuramitsu and H. Yamazaki, *Tetrahedron Lett.*, 1974, 4549; H. Bönnemann, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 248; P. W. Jolly and G. Wilke, in *Comprehensive Organometallic Chemistry,* ed. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon Press, Oxford, 1982, vol. 8, p. 613.

2 P. V. Rinze, J. Lorberth, H. Nöth and B. Stutte, *J. Organomet. Chem.*, 1969, **19**, 399.

3 M. Rosenblum N. Brawn, J. Papenmeier and M. Applebaum, *J. Organomet. Chem.*, 1966, **6**, 173.

4 R. S. Kelly and W. E. Geiger, *Organometallics*, 1987, **6**, 1432.