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FACILE ELECTROGENERATION OF A 17-ELECTRON SPECIES FROM AN INERT HYDRIDOPHOSPHONITECOBALT(I) FOR CATALYTIC DOUBLE-BOND MIGRATION OF 3-PHENYLPROPENE

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A thermally inert hydridophosphonitecobalt(I) complex [CoH{PPh(OEt)$_2$}$_4$] was electrochemically oxidized to give a 17-electron Co(II) species, which catalyzed double-bond migration of 3-phenylpropene. On the other hand, the Co(III) species electrogenerated similarly showed only limited catalytic activity.

A hydridophosphonitecobalt(I) complex [CoH{PPh(OEt)$_2$}$_4$] (1) with an 18-electron configuration was thermally inert, and there have not been any descriptions on catalytic reactivities of the complex. On the other hand, Pyrex-filtered irradiation of 1 dissociated PPh(OEt)$_2$ from cobalt without cleavage of a hydrido-cobalt bond, yielding a coordinatively unsaturated active species "CoH{PPh(OEt)$_2$}$_3$."1,2) The species catalyzed double-bond migration of olefins1) and hydrogen transfer from secondary alcohols.3,4) In the present paper, we wish to report on electrochemical oxidation as an another facile method of activation for the thermally inert complex 1, and on double-bond migration of 3-phenylpropene with the resulting 17-electron Co(II) species. Sanders described preparations of [CoH(NCCH$_3$){PPh(OEt)$_2$}$_4$]-(PF$_6$)$_2$5) and [CoH{PPh(OEt)$_2$}$_4$]PF$_6$6) from 1 by use of some oxidizing chemicals. However, little has been known about their electrochemical properties and catalytic reactivities.

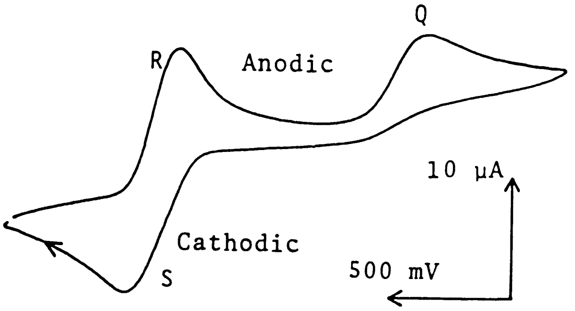

Fig. 1. Cyclic voltammogram of 1. 5×10^{-3} mol dm^{-3} in CH$_3$CN; scan rate, 100 mV/s.

An acetonitrile solution of 1 containing 0.1 mol dm^{-3} (n-Bu$_4$N)PF$_6$ as a supporting electrolyte, was served for electrochemical experiments. Working electrodes were a platinum disk and gauze. As the reference, a platinum wire was used in the CH$_3$CN solution of 0.01 mol dm^{-3} [Fe(C$_5$H$_5$)$_2$] and [Fe(C$_5$H$_5$)$_2$]PF$_6$ besides the supporting electrolyte. Cyclic voltammogram in Fig. 1 shows a redox-couple (R-S) and an irreversible anodic wave (Q) at potentials of ca. -880 and 240 mV, respectively. The couple R-S was assumed to be electrochemically reversible with diffusion-controlled one-electron transfer,[7)] and was attributed to the process of Co(I)⇄Co(II). On the other hand, the irreversible wave Q was ascribed to the oxidation process of Co(II)→Co(III), by means of controlled potential coulometry.

One-electron bulk oxidation of 1 at -350 mV afforded the green solution of the Co(II) species.[8)] Although the color of the solution turned pale yellow on exposure to air, the green solution under nitrogen did not show any significant change in the electronic absorption spectra for several hours. In addition, the Co(II) species was reduced again at -1300 mV to the univalent state, and the amount of electricity passed was close to one electron per molecule of the complex charged, indicating the fair stability of the species in the bulk electrolysis. It can also be stated that the basic structure such as the coordination number remained unchanged during the one-electron oxidation of 1. This is shown by the electrochemical reversibility of the couple R-S and by the maintenance of the redox potential during the electrolysis. Thus, the electrogenerated Co(II) species was the complex $[CoH\{PPh(OEt)_2\}_4]PF_6$, which was regarded as a 17-electron paramagnetic species. It is noted that the green solution of the electrogenerated Co(II) species showed practically the same absorption spectrum[8)] as that of an authentic sample of the complex prepared by the Sanders's method.[6)]

To the CH_3CN solution of the electrogenerated Co(II) species, 20-fold moles of

Table 1. Double-bond Migration of 3-Phenylpropene to 1-Phenylpropenes for 5 h[a)]

Run	Complex[b)]	Condition[c)]	Additive	1-Phenylpropenes Conversion/ %	1-Phenylpropenes E:Z
1	Co(II)	Dark	None	23.4±2.0	90:10
2	Co(II)	Irradiation	None	24.7±2.0	91:9
3	Co(II)	Dark	$PPh(OEt)_2$[d)]	10.0±3.0	84:16
4	Co(II)	Irradiation	$PPh(OEt)_2$[d)]	13.4±3.0	88:12
5	Co(I)	Dark	None	3.0±1.0	≈90:10
6	Co(I)	Irradiation	None	48.5±2.0	86:14
7	"Co(I)"	Irradiation	None	38.0±4.0	85:15
8	Co(III)	Dark	None	6.9±1.5	≈77:23
9	Co(III)	Irradiation	None	6.8±1.5	≈65:35

a) 3-Phenylpropene (0.5 mmol) was added to the deaerated CH_3CN solution (5 ml) of the complex 1 (0.025 mmol) or its electrochemically converted species with 0.1 mol dm^{-3} $(n\text{-}Bu_4N)PF_6$ as the supporting electrolyte. The reaction was performed for the solution at 30 °C for 5 h. b) Co(I), Complex 1; Co(II), The species after one-electron oxidation of 1; "Co(I)", The species after one-electron reduction of the Co(II) species; Co(III), The species after two-electron oxidation of 1. c) Irradiation was performed at a distance of 45 mm from a 400 W high-pressure Hg lamp with a Pyrex-filter. d) 0.05 mmol.

3-phenylpropene was added, and double-bond migration of the olefin was monitored by GLPC. Even without irradiation, the migration proceeded well to (E)- and (Z)-1-phenylpropenes, in a sharp contrast to the case of the photoassisted migration with 1.[1)] In the present system, additional irradiation did not accelerate the migration practically. Similar results of the double-bond migration were obtained also by use of the authentic sample of the Sanders's complex $[CoH\{PPh(OEt)_2\}_4]PF_6$. The reciprocal initial-rate of the migration in the dark with the electrogenerated Co(II) species was plotted in Fig. 2 against the various reciprocal concentrations of 3-phenylpropene charged, and a linear relationship was observed between them. By analogy with interpretation of the Michaelis-Menthen rate equation[9)] and in

$$\left[\frac{dP}{dt}\right]^{-1}_{t=0} = a \times [S]^{-1}_{t=0} + b$$

P=1-Phenylpropenes, S=3-Phenylpropene, t=Time.
$a = 3.7\ h$, $b = 51\ h\ mol^{-1}\ dm^3$, Correlation coefficient=0.996.

consideration of the above-described fair stability of the Co(II) species, the linear relationship observed was associated with coordination equilibrium of the olefin to the species and with subsequent release of the isomerized olefin from the Co(II) intermediate formed transiently. The 17-electron Co(II) species was probably allowed to form the short-lived six-coordinate Co(II) intermediate through contact with the olefin. Metal carbonyl complexes $[M(CO)_n]$ (n=5 for Fe and n=6 for Mo) were suggested previously to undergo irreversible oxidation, where the initial products of 17-electron metal-centered radicals $[M(CO)_n]^{+\cdot}$ were highly susceptible to nucleophilic attack.[10)] In addition, there were reports on the high lability of some neutral radicals such as $V(CO)_6$ and photogenerated $Re(CO)_5\cdot$, which favored an associative pathway for thermal ligand-substitution.[11,12)] These matters probably support the above-described reaction-process. To our knowledge the present study seemed to be the first example of catalytic reactions using the electrochemically generated 17-electron radical i.e. paramagnetic cations with tertiary phosphorus compounds.

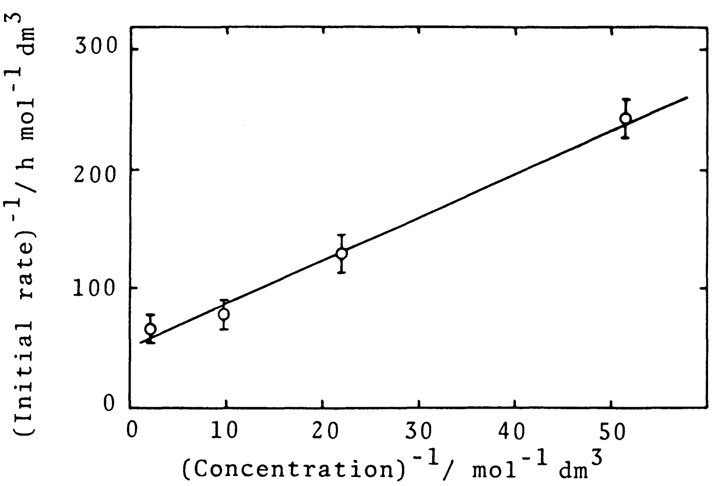

Fig. 2. The plots of reciprocal of the initial rate of the migration against the reciprocal of the substrate concentration.
Co(II), $5\times10^{-3}\ mol\ dm^{-3}$; At 30 °C; In the dark.

For runs 8 and 9 in Table 1, 3-phenylpropene was treated with the electrogenerated Co(III) species. However, only small amounts of 1-phenylpropenes were obtained. In consideration of the totally irreversible anodic wave Q and Sanders's complex $[CoH(NCCH_3)\{PPh(OEt)_2\}_4](PF_6)_2$, the electrogenerated Co(III) species was six-coordinate with the 18-electron configuration, and showed only limited catalytic activity both in the dark and under irradiation with the present conditions.

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7) When the couple R-S was observed in the sweeps of the potential range from -1400 to -300 mV, the peak current ratio of i_{pc}/i_{pa} remained close to unity for the sweep rate v from 200 to 30 mV/s, and the current function (proportional to $i_p/\sqrt{v}$) was also independent of the rate. The potential separation between R and S was almost constant at *ca*. 97 mV, which was a little larger than the theoretical 59 mV. In addition, the bulk electrolysis at -350 mV gave an anodic current, which upon integration yielded charge consistent with one-electron per molecule of 1.
8) Data of the electronic absorption bands (CH_3CN): the authentic sample of [CoH{PPh(OEt)$_2$}$_4$]PF$_6$, λ_{max} 960 nm (ε 200); the electrogenerated Co(II) species, λ_{max} 960 nm (ε 190, based on 1 charged).
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