Further Studies on the Reactivity of π-Cyclo-octenyl-π-cyclo-octa-1,5-dienecobalt. Formation of π-Cycloheptadienyl-π-cyclo-octa-1,5-dienecobalt

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Treatment of π-cyclo-octenyl-π-cyclo-octa-1,5-dienecobalt, $Co(C_8H_{13})(C_8H_{12})$, with cyclo-heptatriene (C_7H_8) afforded the title compound, $Co(C_7H_9)(C_8H_{12})$, from which was derived $Co(C_7H_9)(CO)_2$. $Co(C_8H_{13})(P(n\text{-}C_4H_9)_3]_2$ and $Co(C_8H_{13})(PPh_3)_2$ were obtained from $Co(C_8H_{13})(C_8H_{12})$ and the corresponding phosphine. The formation of the title compound in n-heptane at 65 °C follows a composite rate equation, $R = k[Co][C_7H_8] + k'[Co]^{\frac{1}{2}}$. The kinetics, volatile products analysis, and isolation of a diamagnetic, dinuclear complex $[Co(C_7H_8)(C_8H_{12})]_2$ are used to infer the reaction pathways.

RECENTLY π-cyclo-octenyl-π-cyclo-octa-1,5-dienecobalt $Co(C_8H_{13})(C_8H_{12})$ [1] has been shown to be a very labile complex valuable for preparation of a variety of low-valent cobalt compounds.[2,3] We have now found that the reaction with cycloheptatriene (C_7H_8) leads to a novel complex, π-cycloheptadienyl-π-cyclo-octa-1,5-dienecobalt, $Co(C_7H_9)(C_8H_{12})$. Although existence of a hydride species $CoH(C_8H_{12})_2$ [4] as a tautomer of $Co(C_8H_{13})(C_8H_{12})$ has been excluded,[1] the ligand in $Co(C_8H_{13}(C_8H_{12})$ doubtless contains mobile hydrogen atoms responsible for easy formation of a hydride complex such as $CoHL_4$ [3] (L = tertiary phosphine) or $CoH(dp)_2$ [2] (dp = 1,2-diphenylphosphinoethane). The mechanism of formation of $Co(C_7H_9)(C_8H_{12})$ from $Co(C_8H_{13})C_8H_{12})$ also involving hydrogen transfer was studied by analysis of volatile products and kinetic measurements performed simultaneously during the reaction. The kinetics invoked participation of a dinuclear intermediate in the formation and we isolated a diamagnetic dicobalt complex relevant to the mechanism.

EXPERIMENTAL

All preparative work as well as physical measurements involving organometallic compounds were carried out under argon. I.r. spectra were recorded on a Hitachi–Perkin-Elmer model 225 as Nujol solution or mull, ^1H n.m.r. spectra on a 100 MHz model JNM 4H-100 with tetramethylsilane as internal reference unless otherwise stated, and mass spectra on a Hitachi RMU-7HR instrument. Analytical g.l.c. was carried out at a column temperature of 100 °C with helium as carrier gas at a flow rate of 40 ml/min on a Shimadzu GC-1C model chromatograph with hydrogen flame ionisation detector and 3 m × 5 mm² columns packed with a stationary phase of tricresyl phosphate (Shimalite) on Celite (60—80 mesh); calibrations were made with standard samples. Molecular weights were measured cryoscopically in benzene under argon.

Materials.—The preparation of $Co(C_8H_{13})(C_8H_{12})$ has been described.[1] Cycloheptatriene (Aldrich) was dried and distilled under argon before use; the purity (g.l.c.) was 96·0%. Hydrocarbon solvents were dried with sodium–potassium alloy and distilled under argon.

*π-Cycloheptadienyl-π-cyclo-octa-*1,5-*dienecobalt.*—A mixture of $Co(C_8H_{13})(C_8H_{12})$ (1·28 g, 4·54 mmol) and cycloheptatriene (1·5 ml, 13·9 mmol) in n-hexane (10 ml) was

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[1] S. Otsuka and M. Rossi, *J. Chem. Soc.* (*A*), 1968, 2630.
[2] S. Otsuka and M. Rossi, *J. Chem. Soc.* (*A*), 1969, 497.
[3] M. Rossi and A. Sacco, *Chem. Comm.*, 1969, 471.

[4] G. Wilke, Proc. 10th Internat. Conf. Co-ord. Chem., Tokyo, 1967; *Chem. and Chem. Ind.* (*Japan*), 1967, **20**, 1308.

stirred at 60—70 °C for 3 h. The solvent and volatile olefins were distilled off leaving a brown oil which was treated with a little n-pentane and chilled at −78 °C to give, after recrystallisation from n-pentane, reddish-brown *needles* (0·9 g, 77%), m.p. 63—65° (under argon in sealed tube) (Found: C, 69·7; H, 8·2. $C_{15}H_{21}Co$ requires C, 69·2; H, 8·1%); i.r.: 2808s, 1428s, 1348m, 1319s, 1304m, 1238m, 1172m, 1146m, 1082m, 1073m, 990m, 958m, 859s, 851s, 819m, 789m, and 691m cm^{-1}. The mass spectrum. measured at an ionisation potential of 70 eV and an ionisation chamber temperature of 100 °C contained the following peaks (*m/e*, relative intensity, and ion): 260, 14·3, $Co(C_7H_9)(C_8H_{12})^+$; 164, 7·1, $Co(C_8H_9)^+$; 151, 6·4, $Co(C_7H_8)^+$; 150, 45·0, $Co(C_7H_7)^+$; 138, 4·9, $Co(C_6H_7)^+$; 137, 4·9, $Co(C_6H_6)^+$; 124, 8·8, $Co(C_5H_5)^+$; 113, 4·9, —; 108, 3·8, $C_8H_{12}^+$; 91, 31·4, $C_7H_7^+$; 79, 37·9, $C_6H_7^+$; 78, 33·0, $C_6H_6^+$; 77, 19·8, $C_6H_5^+$, *etc.*

Attempted Deuteriation.—(*a*) $Co(C_8H_{13})(C_8H_{12})$ was treated with cycloheptatriene in a similar manner but under deuterium; we expected deuteriation of $Co(C_7H_9)(C_8H_{12})$ formed. Rapid absorption of deuterium was accompanied by prevalent decomposition of $Co(C_8H_{13})(C_8H_{12})$ into metallic cobalt. (*b*) A solution of $Co(C_7H_9)(C_8H_{12})$ in n-hexane prepared separately was refluxed under a deuterium atmosphere for 3 h. Neither absorption of D_2 nor decomposition of $Co(C_7H_9)(C_8H_{12})$ takes place and ^1H n.m.r. spectrum (in $[^2H_8]$toluene) indicated no change in intensity of any signal of $Co(C_7H_9)(C_8H_{12})$.

π-Cycloheptadienyldicarbonylcobalt.—A solution in n-pentane of $Co(C_7H_9)(C_8H_{12})$ (1·16 g, 4·46 mmol) was stirred at room temperature under carbon monoxide. During 1 h about 20 ml (9 mmol) of CO were absorbed. After removal of the solvent the residue was subjected to molecular distillation at 10^{-3} mmHg and a bath temperature of 40—45 °C to afford dark red *needles* on the cold finger (0·5 g; 56%). Recrystallisation from cold n-pentane gave an analytical sample, m.p. 0—5 °C (Found: C, 52·0; H, 4·6. $C_9H_9CoO_2$ requires C, 51·9; H, 4·4%); i.r.: 3010s, 2835s, 2050vs, 1988vs, 1950w, 1652w, 1602w, 1427s, 1417m, 1402m, 1359s, 1310s, 1260m, 1183s, 1027m, 958m, 870s, 842m, 822s, 795s, and 710s cm^{-1}. The n.m.r. spectrum measured in $[^2H_6]$benzene at room temperature showed three complex broad peaks (a half-height width of *ca.* 20 Hz for all) centred at δ (p.p.m. from external $SiMe_4$) 0·90 (2H), 1·65 (2H), and 4·65 (5H). The two higher-field signals, both of which appear to be sextets, are assigned to the methylene protons and the lowest-field peaks centred at δ 4·65 p.p.m. to the five olefinic protons.

π-Cyclo-octenyl-bis(tri-n-butylphosphine)cobalt.—A solution in n-pentane of $Co(C_8H_{13})(C_8H_{12})$ (0·67 g, 2·42 mmol) and tri-n-butylphosphine (8·5 mmol) was stirred under argon at room temperature for 10 min. After concentration of the dark red solution a small amount of n-pentane was added and the mixture was chilled to −78 °C to give *ca.* 0·60 g (40%) of mauve *needles*, m.p. 60—62°, decomp. 90° (Found: C, 67·4; H, 11·9%; *M*, 561. $C_{32}H_{67}CoP_2$ requires C, 67·1; H, 11·8%; *M*, 572·7); i.r.: 1332s, 1297s, 1274m, 1217m, 1200s, 1150s, 1087vs, 1065s, 1034s, 1011m, 1000m, 960m, 899vs, 885vs, 860s, 789s, 766vs, and 718vs; ^1H n.m.r. (in $[^2H_6]$benzene at room temperature): δ 4·63br (1H, central protons of the allyl group), 4·06br (2H, allyl-H), 1·23br (46H, $-CH_2-$), and 0·77br (18H, Me) p.p.m.

π-Cyclo-octenyl-bis(triphenylphosphine)cobalt.— To a solution of $Co(C_8H_{13})(C_8H_{12})$ (0·36 g, 1·3 mmol) in toluene was added a solution of PPh_3 (0·68 g, 2·6 mmol) in toluene (5·2 ml) and the mixture was stirred under argon at room temperature; a mauve solution resulted from which was isolated, upon addition of n-pentane and cooling at 5 °C, *mauve prisms* (0·63 g, 70%), m.p. 105° (sealed tube) (Found: C, 77·1; H, 5·4. $C_{44}H_{43}CoP_2$ requires C, 77·3; H, 5·0%); ^1H n.m.r. (in $[^2H_8]$toluene): 7·5br (12H, Ph), 7·0br 18H, Ph), 5·62 (1H, complex t, central proton of the allyl group), 3·60br (2H, allyl-H), 1·45 (2H, $-CH_2-$ methylene), 1·23 (4H, $-CH_2-$), and 0·88 (4H, $-CH_2-$).

Isolation of a Dinuclear Complex, $[Co(C_7H_8)(C_8H_{12})]_2$.—A solution of $Co(C_8H_{13})(C_8H_{12})$ (1·82 g, 6·6 mmol) and cycloheptatriene (0·3 g, 3·3 mmol) in n-heptane was stirred at 65 °C under argon for 4 h. A fine black precipitate gradually appeared in very small amounts. After cooling, the precipitate was separated from the brown solution which contained high-boiling hydrocarbons in addition to the more soluble complex, $Co(C_7H_9)(C_8H_{12})$. The solid was washed with n-hexane, dissolved in toluene, and ether was added affording black, fine crystals (*ca.* 150 mg; 8·8%), m.p. 150° (decomp.) (Found: C, 68·7; H, 7·3%; *M*, 460. $C_{30}H_{40}Co_2$ requires C, 69·4; H, 7·8%; *M*, 518); ^1H n.m.r. (in $[^2H_6]$benzene): 5·0 (4H, complex q), 3·7 (16H, complex), 2·0br (16H, complex), and 1·1 (4H, complex q) p.p.m. The complex, dissolved in benzene, was decomposed with dilute aqueous hydrochloric acid. G.l.c. analysis of the organic layer indicated the presence of C_7 and C_8 fractions in approximately equal amount. The C_7 fraction contained C_7H_8 (over 80%) and a small amount of C_7H_{10} and the C_8 fraction contained mainly cyclo-octa-1,5-diene together with a small amount of C_8H_{14} and cyclo-octa-1,3-diene. Similarly, decomposition of the complex in benzene with air afforded comparable amounts of C_7 and C_8 (solely cyclo-octa-1,5-diene) fractions. Hence the ligands for each cobalt atom are likely to be C_7H_8 and 1,5-C_8H_{12}.

Higher-boiling hydrocarbons were isolated from the foregoing brown solution. Thus, concentration *in vacuo*, removal of solvents and C_7—C_8 fractions, and subsequent hydrolysis with aqueous hydrochloric acid followed by usual work-up and vacuum distillation afforded a few drops of colourless oils, b.p. 50—60° (bath) at 10^{-4} mmHg. The u.v. (broad maximum at 245—255 nm) and n.m.r. spectrum (a number of complex peaks in olefinic proton regions) suggested the presence of diene and triene. Although the colour indicated absence of heptafulvalene [5,6] (cycloheptatrienylidene dimer), the b.p. lies within those of a range of dimers of C_7 and C_8 polyenes.

Kinetic Studies.—The reaction vessel was a 30 ml flask accommodating a sealed stirrer, a gas inlet arm, and a neck for sampling. It was attached *via* a condenser to a vacuum system. The apparatus was evacuated and flushed three times with argon. The weighed cobalt complex and carefully degassed solvent (n-heptane) were introduced into the flask under argon. After the solution had attained the desired temperature (±0·5 °C), cycloheptatriene was admitted at once with stirring. At appropriate intervals 1 ml aliquot portions were taken

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[5] W. von E. Doering and L. H. Knox, *J. Amer. Chem. Soc.*, 1957, **79**, 352.

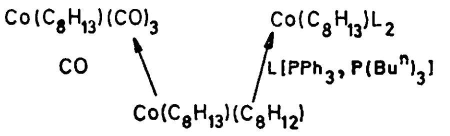
[6] R. C. Joines, A. B. Turner, and W. M. Jones, *J. Amer. Chem. Soc.*, 1969, **91**, 7754.

from the homogeneous solution with a syringe and chilled to −78 °C. Each aliquot portion was distilled into a trap cooled in a liquid-nitrogen bath to collect all the volatile materials for analysis of $C_7$and C_8 hydrocarbons by g.l.c. The rate was thus followed on the basis of consumptions of cycloheptatriene. G.l.c. analysis of the volatile products was carried out simultaneously with rate measurements for the typical runs indicating that cyclo-octene, cyclo-octa-1,3-diene, and cyclo-octa-1,5-diene constituted over 98% of the volatile product, a minor component being cyclo-octa-1,4-diene.

RESULTS AND DISCUSSION

Preparative Chemistry.—When π-cyclo-octenyl-π-cyclo-octa-1,5-dienecobalt $Co(C_8H_{13})(C_8H_{12})$ was treated with an excess of cycloheptatriene in a hydrocarbon solvent at 60—70 °C, diamagentic reddish-brown crystals, m.p. 63—65°, were obtained in *ca.* 80% yield. The complex is formulated as $C_{15}H_{21}Co$ from elemental analysis and the mass spectrum which showed the molecular ion (*m*/*e* 260). It is very soluble in hydrocarbons and relatively thermally stable, compared with $Co(C_8H_{13})(C_8H_{12})$, in the solid state as well as in solution. It is not very sensitive to air. The i.r. spectrum is complex; it lacks bands in the region 1800—1450 cm^{-1} suggesting absence of unco-ordinated olefinic bonds. The mass spectrum contained prominent peaks ascribable to such fragment ions as $Co(C_7H_7)^+$, $Co(C_8H_9)^+$, and $C_7H_7^+$. The complex could then be formulated either as π-cyclo-octenyl-π-cyclo-heptatrienecobalt $Co(C_8H_{13})(C_7H_8)$ or π-cycloheptadienyl-π-cyclo-octa-1,5-dienecobalt $Co(C_7H_9)(C_8H_{12})$. The latter formulation was strongly supported by the following observations.

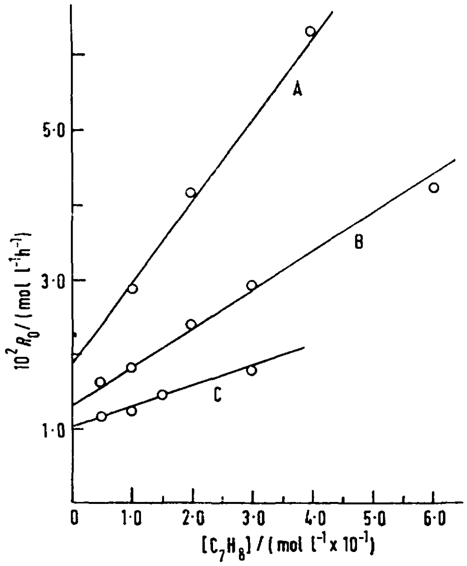
The complex $CoC_{15}H_{21}$ in solution absorbs two moles of carbon monoxide yielding a diamagnetic, dark red complex, m.p. 0—5°, of formula $Co(C_7H_9)(CO)_2$ whose structure was assigned on the basis of its i.r. spectrum which contained three carbonyl stretching bands in terminal carbonyl regions and its n.m.r. spectrum which contained olefinic proton signals (5H, δ 4·65 p.p.m.). G.l.c. analysis of volatile products showed the presence solely of cyclo-octa-1,5-diene. Similarly, substitution of $Co(C_8H_{13})(C_8H_{12})$ with carbon monoxide and phosphines (L) under mild conditions produces a stable enyltricarbonyl complex, $Co(C_8H_{13})(CO)_3$, and bis-phosphine complex, $Co(C_8H_{13})L_2$, respectively (Scheme 1). In both cases preferential substitution of the 1,5-diene takes place leaving the enyl ligand intact. Hence $C_{15}H_{21}Co$ was formulated as $Co(C_7H_9)(C_8H_{12})$. This receives further support from the ^1H n.m.r. spectrum.[7] The complex is a fluxional molecule as revealed by the temperature-dependent n.m.r. spectrum, its stable molecular configuration being deduced from the low-temperature data.[7]



SCHEME 1

Kinetics.—In n-hexane or similar solvents the reaction of π-cyclo-octenyl-π-cyclo-octa-1,5-diene with cycloheptatriene proceeds smoothly at 60 °C or above. For example a preparative run with a 0·4M-solution of the cobalt complex and an excess of the triene (1 : 3 in mole ratio in n-heptane went practically to completion within 3 h at 65 °C. The reaction can be carried out in benzene also with a comparable yield and rate.

The kinetic study was carried out at 65 °C in n-heptane, with 0·06—0·2M solutions of the cobalt complex and the mole ratio of $C_7H_8 : Co$ varying from 6 to 0·5. The overall rate of each run was obtained from the tangent to the plot of cycloheptatriene consumption against time. The Figure shows plots of the initial rates (R_0) thus obtained against initial concentrations of the triene (C_7H_8). The rate depends linearly on the triene concentration for the concentration range studied but apparently does not fall to nil upon extrapolation to zero triene concentration. Then the rate is related to the triene concentration by a relationship, $R_0 = C[C_7H_8] + C'$. The gradient (C) and the intercepts (C') on the y-axis obtained from the Figure revealed the dependences of C and C' upon the initial concentration of the cobalt complex [Co]. These values are summarised in Table 1. Thus the overall rate is expressed by the rate equation (1). The volatile products liberated from $Co(C_8H_{13})(C_8H_{12})$ were analysed at appropriate intervals for typical runs in n-heptane and benzene. Some of the results are shown in Table 2 which also includes the weights of the two terms in the rate equation.



Plots of initial rates R_0 against initial concentration of C_7H_8 at 65 °C in n-heptane. A, [Co] = 2·0 × 10^{-1}M; B, [Co] = 1·0 × 10^{-1}M; and C, [Co] = 0·60 × 10^{-1}M

$$R_0 = k[Co][C_7H_8] + k'[Co]^{\frac{1}{2}} \qquad (1)$$

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[7] S. Otsuka and T. Taketomi, following paper.

Mechanism. The rate equation implies two concomitant pathways. The first term corresponds to an associative mechanism common to substitution reactions of square planar complexes. An approximately square planar alignment of the enyl (C_8H_{13}) and 1,5-diene ligands in $Co(C_8H_{13})(C_8H_{12})$ has been established.[8] For a limited S_N2 mechanism may be postulated an adduct $Co(C_7H_8)(C_8H_{13})(C_8H_{12})$ wherein the steric requirement as well as the inert gas formalism favours the *di-hapto* (monoene) co-ordination of the triene C_7H_8. The formation of the final product $Co(C_7H_9)(C_8H_{12})$ requires rapid hydrogen transfer from C_8H_{13} to C_7H_8. The hydrogen transfer may take place through a metal–hydride species but ^1H n.m.r. spectroscopy of the reaction failed to detect the presence of hydride complex whose lifetime may be too short for the time scale. Although preliminary *X*-ray analysis [8] indicated absence of abnormal metal–hydrogen distances in the solid state of $Co(C_8H_{13})(C_8H_{12})$, the n.m.r. spectrum in solution suggested that the axial hydrogen atoms attached to carbon atoms adjacent to the enyl group are under the influence of metal orbitals.[1] If the hydrogen atom of C_8H_{13} is to migrate, cyclo-octa-1,3-diene should be formed. Indeed the volatile products, as detected by g.l.c., contain the 1,3-diene as a major C_8 component together with a smaller amount of cyclo-octene, when the reaction is carried out with an excess of C_7H_8 to ensure that the reaction proceeds mainly through the first pathway. For example, in the reaction with a 0·2M solution for $Co(C_8H_{13})(C_8H_{13})$ and a 0·4M solution for C_7H_8, the first pathway occupies 70% of the overall reaction and the second pathway 30%, as estimated from the Figure. In this case the 1,3-diene and cyclo-octene found at an early stage of the reaction in amounts, respectively, of 0·17 and 0·11 mmole (Table 2, iii). A closely related observation is that an intermediate for isomerisation of cyclo-octadiene by $M(C_5Me_5)Cl_2$ (M = Rh or Ir) is a cyclo-octen-3-yl complex.[9]

A reaction mainly responsible for the cyclo-octene formation can be ascribed to the second pathway as discussed later. That cyclo-octa-1,5-diene occupies only a minor fraction (less than 4% of the total C_8 components) contrasts with the reaction of $Co(C_8H_{13})(C_8H_{12})$ with carbon monoxide or tertiary phosphine and excludes an alternative mechanism involving incipient substitution with the triene of the 1,5-diene followed by an intramolecular hydrogen transfer.

TABLE 1

Data derived from plot of the overall rate as a function of cycloheptatriene concentration for different concentration of $Co(C_8H_{13})(C_8H_{12})$; 65 °C, in n-heptane

[Co]/M	10^6C/s^{-1}	$10^6C'$/(mol l^{-1} s^{-1})	10^4C/[Co](l mol^{-1} s^{-1})	$10^6C'/[Co]^{0.5}$ (mol$^{0.5}$ l$^{-0.5}$ s^{-1})
0·1	14·4	3·67	1·44	11·6
0·2	29·7	5·22	1·49	11·7
0·06	7·5	2·86	1·25	11·7

TABLE 2

Distribution of volatile products (C_8) as functions of the kinetic pathways in n-heptane *

	(i) Data for [Co] = 0·1M and [C_7H_8] = 0·05M		(ii) Data for [Co] = 0·2M and [C_7H_8] = 0·1M		(iii) Data for [Co] = 0·2M and [C_7H_8] = 0·4M	
10^6 × Overall rate/(mol l^{-1} s^{-1})	4·40	(4·11)	8·05		17·40	
First term $k[Co][C_7H_8]$/(mol l^{-1} s^{-1})	0·72		2·82		12·17	
Second term k' $[Co]^{1/2}$/(mol l^{-1} s^{-1})	3·68		5·23		5·23	
Reaction time/min	60	120	40	80	30	60
Conversion (%)	16·0 (14·8)	31·5(29·5)	8·4	19·7	14·7	27·2
Cyclo-octa-1,3-diene/mmol	0·078(0·077)	0·174(0·159)	0·097	0·211	0·171	0·315
Cyclo-octene/mmol	0·154(0·146)	0·310(0·279)	0·141	0·297	0·115	0·207
Cyclo-octa-1,5-diene/mmol	0 (trace)	0(0·004)	0	0	0·011	0·025

* Except for the data in parentheses which were obtained in benzene as solvent.

The second term independent of the triene concentration appears to imply rapid formation of a dinuclear intermediate containing C_7H_8. The product analysis indicates that when 84% of the overall reaction proceeds through the second path, cyclo-octene amounts to 65% of the total C_8 ligands liberated, but no cyclo-octa-1,5-diene is formed (Table 2, i). The parallel trend between the mole ratio of $1,3\text{-}C_8H_{12} : C_8H_{14}$ and $k[Co][C_7H_8]/k'[Co]^{\frac{1}{2}}$ may be taken to mean that the second path involving a dinuclear complex is primarily responsible for the formation of cyclo-octene. The hydrogen atom book-keeping (Table 2) requires hydrogen atoms to be supplied to $Co(C_8H_{13})(C_8H_{12})$ from either the solvent molecules or cycloheptatriene. The reaction in benzene showed a rate and volatile products comparable with those observed for the reaction in n-heptane (Table 2, i). When $Co(C_8H_{13})(C_8H_{12})$ was treated with cyclo-octatetraene under similar conditions the volatile products contained cyclo-octadiene (mainly 1,3- and a small amount of 1,5-isomer) but no cyclo-octene. Hence we conclude that the extra hydrogen atoms supplied to

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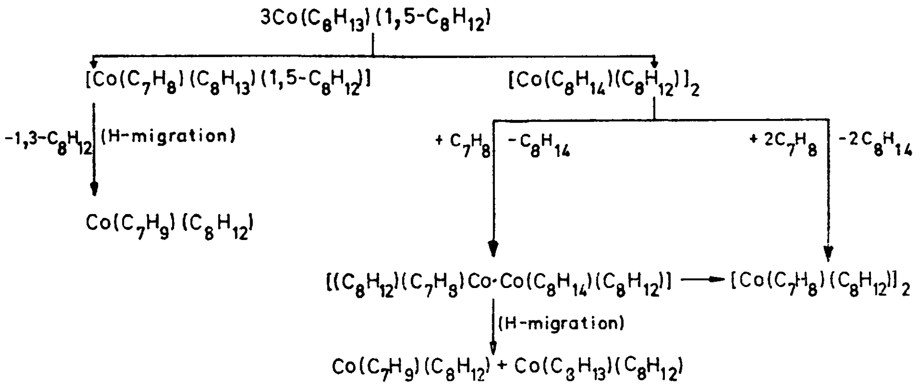
[8] S. Koda, A. Takenaka, and T. Watanabe, *Chem. Comm.*, 1969, 1293.

[9] G. Allegra, F. Lo Giudice, G. Natta, U. Giannini, G. Fagherazzi, and P. Pino, *Chem. Comm.*, 1967, 1263.

$Co(C_8H_{13})(C_8H_{12})$ to form the cyclo-octene ligand in the binuclear intermediate originated from C_7H_8.* Consistent with this is the formation of the triene dimer found in the reaction products.

If the formation of the dimer complex containing cyclo-octene is a rate-determining step, we should observe second-order dependency on [Co], which is not the case. Then the fast step involves an easy hydrogen abstraction by C_8H_{13} ligand. Easy hydrogen migration was also observed between an enyl and diene ligand of $CoC_{12}H_{19}$.[9,10] A dinuclear complex $[Co(C_7H_8)(C_8H_{12})]_2$ was isolated in small yield, although it may not be a true intermediate. Its formation would reasonably be accounted for by such an intervening species as $[Co(C_8H_{14})(C_8H_{12})]_2$ or $[(C_8H_{12})(C_7H_8)CoCo(C_8H_{14})(C_8H_{12})]$, since the cyclo-octene ligand is presumably a weak d_π acceptor susceptible to displacement with the conjugated triene, C_7H_8. In accord with the kinetics may be postulated slow hydrogen migration between the ligands, C_7H_8 and C_8H_{14}, within the dinuclear complex. Absence of a paramagnetic species during the entire course of reaction (as monitored by n.m.r. spectroscopy) suggests that achievement of the inert-gas configuration of a cobalt atom in the dinuclear intermediate facilitates simultaneous cleavage of the metal–metal bond releasing the final product. To summarise, the reaction scheme we deduced is illustrated in Scheme 2.



SCHEME 2

[0/1149 *Received, July 7th,* 1970]

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* *Added in proof.* Complexes of formula $Co(C_8H_9)(1,5\text{-}C_8H_{12})$ and $Co(C_8H_{11})(1,5\text{-}C_8H_{12})$ recently found as minor products of the reaction indicate that the cyclo-octenyl ligand in $Co(C_8H_{13})(C_8H_{12})$ is also a hydrogen source.

[10] G. Natta, U. Giannini, P. Pino, and A. Cassata, *Chimica e Industria*, 1965, **47**, 524.