Journal of Organometallic Chemistry, 139 (1977) 169—177

COBALT METALLOCYCLES

II *. DIELS—ALDER TYPE REACTION OF COBALTACYCLOPENTADIENES WITH OLEFINS

YASUO WAKATSUKI * and HIROSHI YAMAZAKI

The Institute of Physical and Chemical Research, Wako-shi, Saitama 351 (Japan)

(Received April 20th, 1977)

Summary

Several cobaltacyclopentadiene complexes, (π-C_5H_5)(PPh_3)($\overline{CoCR=CRCR=CR}$) (I), reacted with olefins (ethylene, propylene, styrene, methyl acrylate, dimethyl maleate) to give corresponding cyclohexadiene complexes. The first step of the reaction involves replacement of triphenylphosphine by olefin. Therefore the cycloaddition reaction takes place between two ligands bonded simultaneously to a transition metal. *Endo—exo* stereoselectivity was examined when dimethyl maleate was used as dienophile.

Introduction

Metallocyclopentadiene complexes are believed to be important intermediates in the transition metal-catalyzed cyclotrimerization of acetylenes. To date, several metallocyclopentadiene complexes have been prepared from acetylenes and some of these complexes i.e. cobalta-[1], rhodia-[2], iridia-[3], and palladia-[4]-cyclopentadienes have been treated with acetylenes to give substituted benzenes. However, reactions of olefins with transition metallocyclopentadienes have not been reported, although this type of reaction has been suggested in some catalyzed cyclotrimerizations of acetylenes with olefins [5,6,7]. It is of interest that Collman et al. [3], Chalk [5], and Müller [2] have earlier attempted unsuccessfully reactions of olefins with an iridia- or rhodia-cyclopentadiene complex. Recently, Itoh et al. have reported a palladiacyclopentadiene complex with a cyclic diolefin ligand, which can be regarded as an intermediate in the cyclotrimerization of acetylene with olefins [7].

We have reported that (π-cyclopentadienyl)bis(triphenylphosphine)cobalt reacts stepwise with two molecules of acetylenes to give cobaltacyclopentadiene

---

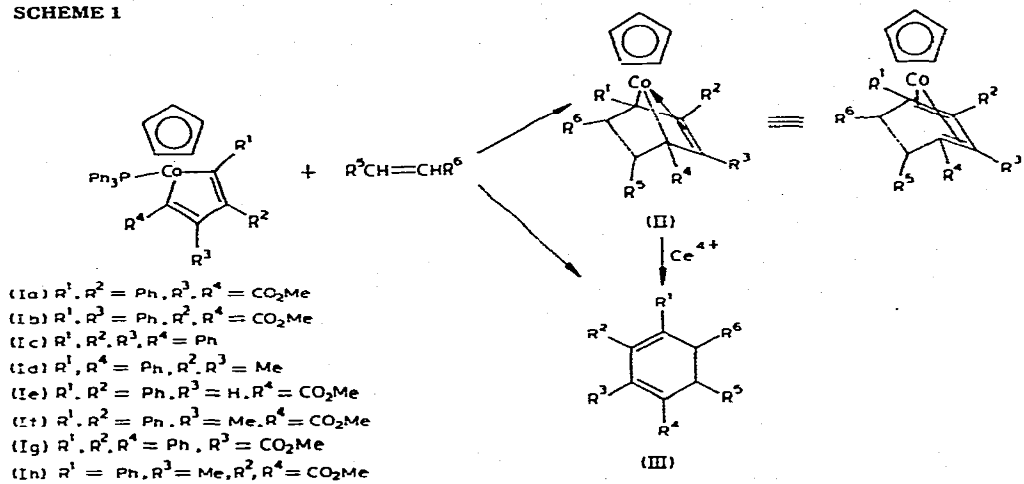
* For Part I see ref. 8.

complexes with various substituents and that these cobalt metallocycles react with acetylenes to give substituted benzenes [8,9]. We report here a detailed study on the reaction of these cobalt metallocycles with olefins.

Results and discussion

Cobaltacyclopentadienes (I) reacted with olefins in benzene or toluene at 70–150°C to give cyclohexadienes (III) and/or intermediate cyclohexadiene complexes (II), depending on the reactants and reaction conditions (Scheme 1). The cyclohexadiene complexes liberate the free cyclohexadienes when de-

SCHEME 1



composed with Ce^{4+} in benzene/ethanol solution. The substituted cyclohexadienes thus obtained have been described in a previous communication [9].

Table 1 summarizes crystalline cyclohexadiene complexes which have been obtained. Dimethyl fumarate also reacted with I to give a complex which did not crystallize and which gave an unsatisfactory elemental analysis.

Table 2 shows that the addition of triphenylphosphine to the initial reaction mixture retarded the reaction Ie → IIe. The tendency shown in Table 2 can be explained by assuming that the primary step of the reaction is an equilibrium (eq. 1). The displacement of the triphenylphosphine by olefin (eq. 1) also is supported by the observation that (π-cyclopentadienyl)(methyldiphenylphosphine)tetraphenylcobaltacyclopentadiene, in which the phosphine ligand is bonded to the metal more strongly than that in the triphenylphosphine analog (Ic) *, did not react with dimethyl maleate under the same conditions as those under which Ic reacted readily.

The second step of the reaction (eq. 2) may formally be regarded as a

---

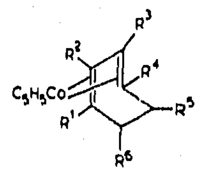
* The methyldiphenylphosphine analog of Ic was prepared by:

$$Co(C_5H_5)(PhC_2Ph)_2(PPh_3) + PPh_2Me \xrightarrow{70^\circ C} Co(C_5H_5)(PhC_2Ph)_2(PPh_2Me) + PPh_3$$

The reverse reaction did not occur, indicating that PPh_2Me is bonded to cobalt more strongly than PPh_3.

TABLE 1

CYCLOHEXADIENE COMPLEXES:



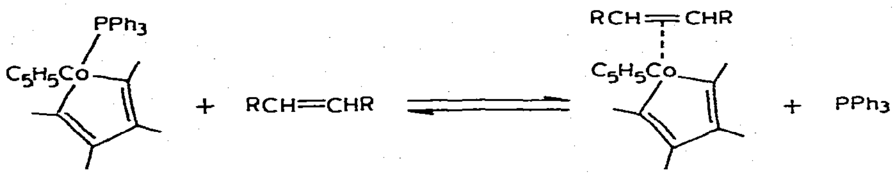
	R[1]	R[2]	R[3]	R[4]	R[5]	R[6]	Yield (%)	Analysis Found (calcd.) (%)	
								C	H
IIa	Ph	Ph	CO_2Me	CO_2Me	H	H	23	69.81(68.65)	5.51(5.33)
IIb-1	Ph	CO_2Me	Ph	CO_2Me	H	H	39	68.71(68.64)	5.25(5.35)
IIc-1	Ph	Ph	Ph	Ph	Me	H	36	82.35(82.74)	6.27(5.98)
IIc-2	Ph	Ph	Ph	Ph	Ph	H	9	83.68(84.23)	5.74(5.69)
IId	Ph	Me	Me	Ph	CO_2Me	H	50	73.60(73.30)	6.28(6.15)
IIc-3	Ph	Ph	Ph	Ph	CO_2Me	CO_2Me [a]	34	74.86(75.00)	5.40(5.34)
IIe	Ph	Ph	H	CO_2Me	CO_2Me	CO_2Me [a]	75	66.11(65.66)	5.14(5.13)
IIb-2	Ph	CO_2Me	Ph	CO_2Me	CO_2Me	CO_2Me [a]	46	66.74(66.67)	5.23(5.29)

[a] Dimethyl maleate.

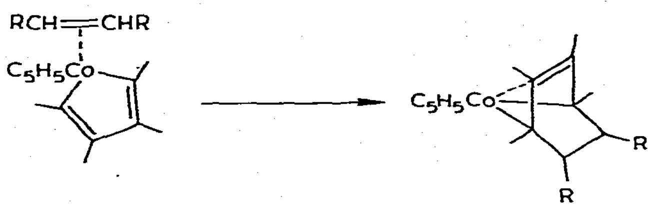
TABLE 2

EFFECT OF PPh_3 ADDED IN Ie → IIe; 90°C, 72 h

PPh_3/Ie	Ie recovered (%)	IIe formed (%)
0	24	37
0.5	43	17
1.0	53	7



(1)



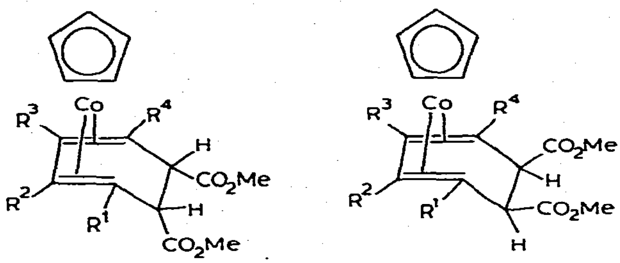
(2)

Diels—Alder reaction which takes place within the coordination sphere of a transition metal *. Since one of the well known features of the Diels—Alder reaction is the common preference for the *endo*-stereochemistry (the Alder rule), it was of interest to determine whether the reaction shown in eq. 2 shows this preference.

When dimethyl maleate was used, two isomeric cyclohexadiene complexes generally were formed, i.e., the *endo*- and *exo*-isomers (Fig. 1). Thus complex Ib reacted with dimethyl maleate at 120°C to give a 46% yield of a mixture of two isomers which were separated by chromatography on silica gel. The NMR spectrum of one of the isomers exhibited an AB type quartet signal centered at δ 3.88 ppm which is attributed to two protons of the dimethyl maleate moiety, whereas that of the other isomer was centered at δ 2.63 ppm. The structure of the isomer which showed the NMR signal at δ 3.88 ppm was determined by single-crystal X-ray analysis to have an *endo*-carbomethoxy configuration (Fig. 1A in which R^1, R^3 = Ph, R^2, R^4 = CO_2Me) [10]. On this basis, we have determined the stereochemistry of other cyclohexadiene complexes of the type shown in Fig. 1 from the chemical shift of the ring protons of the dimethyl maleate moiety.

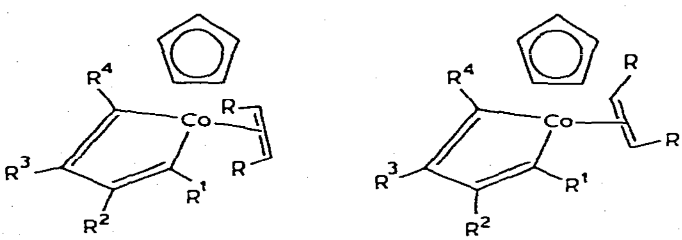
Table 3 shows the ratio of *endo* and *exo* isomers which were formed by the

* Another possibility, i.e., the insertion of the olefin into the cobalt—carbon bond, forming a seven-membered metallo ring, cannot be ruled out. Whether reaction 2 proceeds in a concerted [$2\pi + 4\pi$] manner or via a seven-membered metallocycle is a crucial question which remains to be answered. However, this point does not influence the subsequent discussions.



(A) (B)

Fig. 1. Cyclohexadiene complexes with (A) *endo*- and (B) *exo*-carbomethoxy groups. Here, *endo* and *exo* denote the direction in the cyclohexadiene ring and not the relative position to the cobalt.



(a) (b)

Fig. 2.

reaction of complexes I with dimethyl maleate. The *endo*-rule is obeyed when R^1, R^4 = Ph, but not in certain other cases.

Fig. 2 illustrates intermediate olefin complexes (a) and (b) which lead to *endo* (Fig. 1A) and *exo* (Fig. 1B) isomers. In conformation (a), steric interactions between R and R^1 or R^4 and in conformation (b), the interactions between R and the cyclopentadienyl protons must be considered. As had been expected, introduction of a methyl group into the cyclopentadienyl ring suppressed conformation (b). Thus, the methylcyclopentadienyl analog of Ib reacted with dimethyl maleate at 120°C to give the cyclohexadiene complex with the *endo* to *exo* isomer ratio equal to 73 : 27, i.e., the *exo* isomer decreased by ca. 10%. In contrast, the results listed in Table 3 indicate that conformation (a) is preferable when R^1, R^4 = Ph than when R^1 = Ph, R^4 = CO_2Me, although phenyl is much bulkier than the carbomethoxy group. This observation can be attributed either to an attractive diene system—dienophile substituent (CO_2Me) interaction when R^1, R^4 = Ph, or possibly dipole—dipole repulsion between the carbomethoxy groups on the diene and on the dienophile when R^1 = Ph, R^4 = CO_2Me. This type of electrostatic interaction also may play an important role in the *endo*—*exo* stereoselectivity of common Diels—Alder reactions.

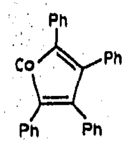
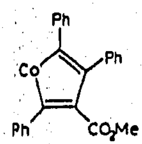
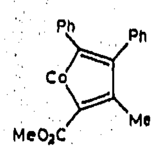
Experimental

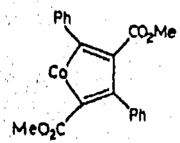
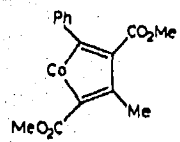
All reactions were carried out under nitrogen atmosphere. Melting points were uncorrected and determined on a Mitamura micro-melting point apparatus.

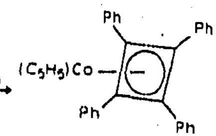
(continued on p. 176)

TABLE 3

THE RATIO OF *endo* TO *exo* ISOMERS FORMED IN THE REACTION OF I WITH DIMETHYL MALEATE

Cobaltacyclopentadiene used		Reaction temp. (°C)	II Yield (%)	II Isomer	II Ratio	NMR ($CDCl_3$) δ (ppm) Me	NMR CO$_2$Me	NMR C_5H_5	NMR Ring protons of cyclohexadiene
	(Ic)	70	40 [a]	A [b]	90		3.36(s)	4.60(s)	4.12(s)
				B [b]	10		3.72(s)	5.16(s)	2.74(s)
	(Ig)	70	67	A	70		3.30(s), 3.44(s), 3.46(s)	4.50(s)	4.05 (AB type q, J_{AB} 12 Hz, $\delta_A - \delta_B$ 0.20 ppm)
				B	30		3.27(s), 3.30(s), 3.40(s)	5.10(s)	2.78 (AB type q, J_{AB} 9 Hz, $\delta_A - \delta_B$ 0.22 ppm)
	(If)	120	95	A	40 (36) [c]	2.35 (s)	3.37(s), 3.49 (s), 3.72(s)	4.56(s)	3.95 (broad s) [d]
				B	60 (64) [c]	2.02(s)	3.22(s), 3.61(s), 3.68(s)	5.12(s)	2.56 (s) [d], 2.60(s) [d]

	(Ib)	120	80	A	64 (63) [c]		3.32(s) 3.41(s) 3.47(s) 3.54(s)	4.79(s)	3.88 { AB type q. J_{AB} 12 Hz $\delta_A - \delta_B$ 0.13 ppm
				B	36 (37) [c]		3.24(s) 2.26(s) 3.33(s) 3.63(s)	5.24(s)	2.63 { AB type q. J_{AB} 9.5 Hz $\delta_A - \delta_B$ 0.27 ppm
	(In)	120	95	A	40	2.58(s)	3.28(s) 3.42(s) 3.66(s) 3.73(s)	4.51(s)	3.78(s) [d]
				B	60	2.20(s)	3.19(s) 3.46(s) 3.54(s) 2.62(s)	5.02(s)	2.44(s) [d] 2.48(s) [d]

[a] Low yield is due to a side reaction: $Co(C_5H_5)(PPh_3)(PhC_2Ph)_2 \xrightarrow{-PPh_3}$  [b] A isomer with *endo*-carbomethoxy groups, B isomer with *exo*-carbomethoxy groups, see Fig. 1. [c] Reaction carried out at 95°C. [d] Only central peak(s) of AB type quartets are observed due to very small $|\delta_A - \delta_B|$.

Proton NMR spectra were obtained using JEOL-60 spectrometer. IR spectra were obtained using a Shimazu IR-27G spectrometer.

For column chromatography, Sumitomo Activated Alumina KCG-30 was used.

Preparation of complexes I has been described previously [8]. The methylcyclopentadienyl analog of Ib was prepared by a similar method, i.e., the reaction of $NaC_5H_4CH_3$ with $CoCl(PPh_3)_3$, followed by addition of methyl phenylpropiolate and isolation by chromatography, m.p. 206°C (dec.). Found: C, 73.36; H, 5.64. $C_{44}H_{38}O_4PCo$ calcd.: C, 73.33; H, 5.32%. NMR ($CDCl_3$) δ ppm: 1.80 (d, *J* 1.8 Hz, 3H, C—CH_3), 2.84 (s, 3H, CO_2CH_3), 3.04 (s, 3H, CO_2CH_3), 4.06, 4.7 and 5.0 (m, 4H, C_5H_4).

Reaction of Ia and Ib with ethylene

A benzene solution (10 ml) of Ia (100 mg, 0.14 mmol) and ethylene (50 kg cm^{-2} at 25°C) were heated in an autoclave (200 ml) at 150°C. After 4 h, the reaction mixture was chromatographed on Al_2O_3. A red band was eluted with dichloromethane; most of the solvent was removed from the eluate under reduced pressure. Addition of hexane to the residue gave brown-red crystals of IIa, m.p. 170—171°C. NMR ($CDCl_3$) δ ppm: 0.7—1.6 and 2.1—2.3 (m, 4H, ethylene moiety), 3.62 (s, 3H, CO_2CH_3), 3.77 (s, 3H, CO_2CH_3), 4.3 (s, 5H, C_5H_5).

Complex Ib reacted with ethylene in a similar fashion to give bronw-red crystals of IIb-1, m.p. 123—125°C. NMR ($CDCl_3$) δ ppm: 0.8—1.5 and 2.0—2.4 (m, 4H, ethylene moiety), 3.38 (s, 3H, CO_2CH_3), 3.41 (s, 3H, CO_2CH_3), 4.76 (s, 5H, C_5H_5).

Reaction of Ic with propylene

A benzene solution (10 ml) of Ic (400 mg) was placed in an autoclave (100 ml) and propylene (ca. 5 g) was introduced by cooling the bottom of the autoclave with a Dry Ice/methanol bath. The reaction was carried out at 150°C for 5 h. The reaction mixture was chromatographed on Al_2O_3. The red zone was eluted with benzene. After concentration of the eluate, hexane was added to give dark-red crystals of IIc-1, m.p. 204—206°C. NMR (C_6D_6) δ ppm: 0.9—1.0 and 2.6—2.85 (m, 6H, propylene moiety), 4.50 (s, 5H, C_5H_5).

Reaction of Ic with styrene

To a solution of Ic (900 mg) in benzene (20 ml) was added styrene (1 ml) and the mixture was heated at 120°C for 5 h. The reaction mixture was treated as described above to give brown-red crystals of IIc-2, m.p. 209—216°C. NMR ($CDCl_3$) δ ppm: 1.8—2.0 and 3.0—3.8 (m, 3H, styrene moiety); 4.74 (s, 5H, C_5H_5).

Reaction of Id with methyl acrylate

Complex Id (200 mg) in benzene (10 ml) was treated with methyl acrylate (1 ml) at 70°C in a sealed tube. After 40 h the reaction mixture was chromatographed on Al_2O_3. The red band was eluted with benzene/dichloromethane. The solvent was removed from the eluate and the residue was dissolved in hexane (5 ml). When the solution was cooled in a freezer for a few days, red-brown crystals of IId formed, m.p. 110—114°C. NMR spectrum (C_6D_6) showed the presence of two isomers with the ratio of isomer 1 to isomer 2 equal to 5 : 3. Isomer 1 δ ppm: 1.98 (s, 3H, C—CH_3), 2.11 (s, 3H, C—CH_3), 3.14 (s, 3H, CO_2CH_3), 4.62 (s, 5H, C_5H_5). Isomer 2 δ ppm: 2.19 (s, 3H, C—CH_3), 2.43 (s, 3H, C—CH_3), 3.14 (s, 3H, CO_2CH_3), 4.24 (s, 5H, C_5H_5).

Reaction of Ib with dimethyl maleate

Dimethyl maleate (1 ml) was added to a solution of Ib (200 mg) in benzene (20 ml) and the mixture was heated at 120°C in a sealed tube for 72 h. The reaction mixture then was chromatographed on Al_2O_3. The red band was eluted with dichloromethane. After the solvent has been removed from the eluate under high vacuum, the residue was dissolved in $CDCl_3$ (0.2 ml) and examined by NMR (Table 3). The reactions of Ie, Ih, and If with dimethyl maleate were carried out similarly, but a lower reaction temperature (70°C) was sufficient in the case of Ic or Ig. The reaction products II listed in Table 3 are very stable. They did not decompose under the reaction conditions. The NMR spectrum of IIe, formed by the reaction of Ie with dimethyl maleate, was not obtained owing, to the presence of a trace amount of paramagnetic impurity.

Decomposition of IIe with Ce^{4+}

To a solution of IIe (135 mg) in benzene (5 ml) was added an ethanol solution of cerium ammonium nitrate (150 mg/5 ml). After 10 min, the solvent was evaporated and the residue was treated with benzene (10 ml) to extract the organic materials. After concentration, the benzene solution was chromatographed on Al_2O_3. The eluate with dichloromethane was collected and concentrated to almost dryness. Addition of hexane and cooling to —20°C gave a 70% yield of colorless crystals of 1,5,6-trimethoxycarbonyl-3,4-diphenyl-1,3-cyclohexadiene, m.p. 117—119°C. Found: C, 70.58; H, 5.25; mol. wt. 406 (mass spectrum). $C_{24}H_{22}O_6$ calcd.: C, 70.93; H, 5.46%; mol. wt. 406.44. NMR ($CDCl_3$) δ ppm: 3.54 (s, 3H, CO_2CH_3), 3.65 (s, 3H, CO_2CH_3), 3.74 (s, 3H, CO_2CH_3), 4.40 (AB type q., J_{AB} 1.8 Hz, $\delta_A - \delta_B$ 0.06 ppm, 2H, dimethyl maleate moiety).

Other oxidation reactions of II with Ce^{4+} were carried out similarly.

References

1 H. Yamazaki and N. Hagihara, J. Organometal. Chem., 7 (1967) P22.
2 E. Müller, Synthesis, (1974) 761.
3 J.P. Collman, J.W. Kang, W.F. Little and M.F. Sullivan, Inorg. Chem., 7 (1968) 1298.
4 K. Mosely and P.M. Maitlis, J. Chem. Soc. Dalton, (1974) 169.
5 A.J. Chalk, J. Amer. Chem. Soc., 94 (1972) 5928.
6 D.M. Singleton, Tetrahedron Lett., (1973) 1245.
7 H. Suzuki, K. Itoh, Y. Ishii, K. Simon and J.A. Ibers, J. Amer. Chem. Soc., 98 (1976) 8494.
8 H. Yamazaki and Y. Wakatsuki, J. Organometal. Chem., 139 (1977) 157.
9 Y. Wakatsuki, T. Kuramitsu and H. Yamazaki, Tetrahedron Lett., (1974) 4549.
10 Y. Wakatsuki, K. Aoki and H. Yamazaki, unpublished results.