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ƐEPARATION AND SOME PROPERTIES OF ƳCLOPENTADIENYLCOBALT(I)-OLEFIN COMPLEXES

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ımmary

Cyclopentadienylcobalt(I) olefin complexes, $(\eta^5$-$C_5H_5)$Co(L)(olefin) [II (L = :phenylphosphine, III (L = CO), IV (L = 2,6-xylylisocyanide), and V (L = ;phenylphosphite)] were prepared by reactions of $(\eta^5$-$C_5H_5)$Co$(L)_2$ (I) with efins having electron-withdrawing groups. In the reaction of fumaronitrile .th Ia (L = PPh_3) the maleonitrile complex (IIe) was obtained together with e fumaronitrile complex (IId). The phosphine ligand of $(\eta^5$-$C_5H_5)$Co(PPh_3)-lefin) (II) was readily displaced by isocyanides to afford $(\eta^5$-$C_5H_5)$Co(CNR)-lefin) (IV).

In the cases of the *cis*-olefin complexes the presence of two conformational ›mers (A and B) was observed, and their structures were assigned by the ^{1}H ΛMR spectra. From the ratio of the isomers relative bulkiness of ligands around e cobalt atom was estimated. The bulkiness decreases in the order: triphenyl-ıosphine > η^5-cyclopentadienyl > isocyanide > carbon monoxide.

.troduction

Over the past few decades, a very large number of olefin complexes of ansition metals have been prepared and their chemical and structural studies ıve been extensively developed [1]. However, those of cobalt(I) synthesized › to date are relatively limited. Previously, one of the authors reported briefly .e synthesis of $(\eta^5$-$C_5H_5)$Co(PPh_3)(olefin) by displacement of the diphenyl-etylene ligand of $(\eta^5$-$C_5H_5)$Co$(PPh_3)(PhC_2Ph)$ with some olefins [2]. The esent paper provides a general procedure for the preparation of $(\eta^5$-$C_5H_5)$-›(L)(olefin) by reactions of $(\eta^5$-$C_5H_5)$Co$(L)_2$, where L = PPh_3, CO, CNC_6H_3-6-$(CH_3)_2$, and $P(OPh)_3$, with olefins having electron-withdrawing substituents ıd a description of the chemistry of the olefin complexes.

Results and discussion

Preparation of (η^5-C_5H_5)Co(L)(olefin)

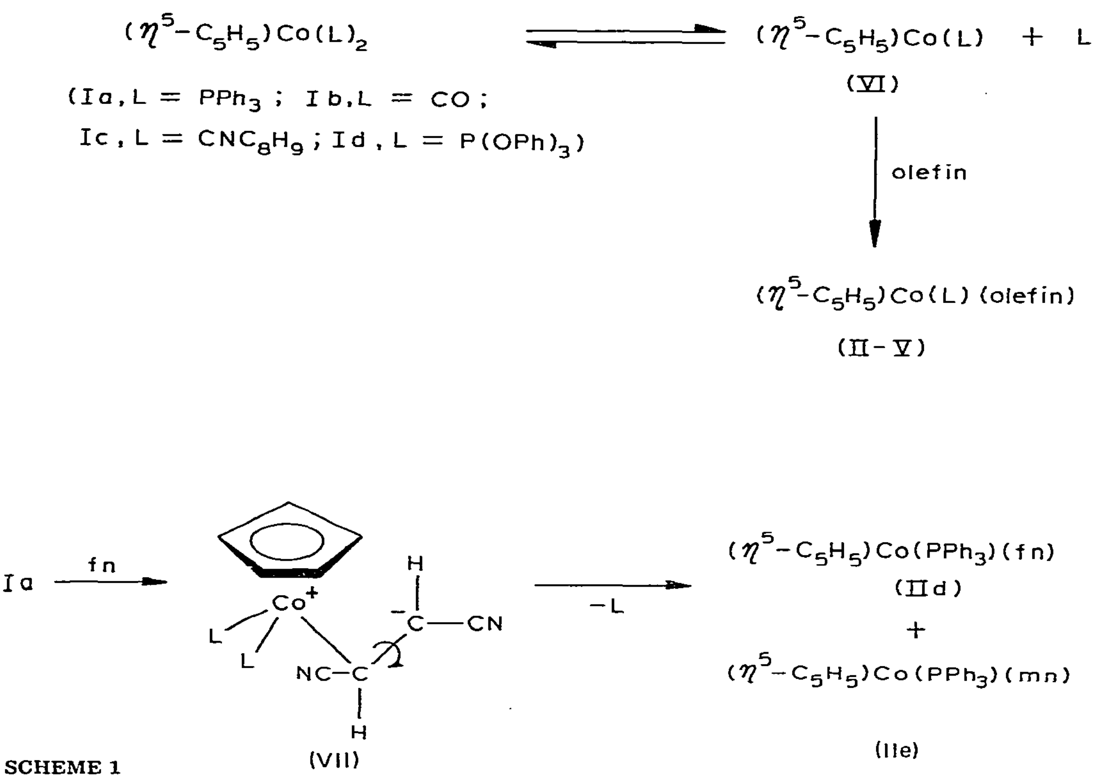
When a solution of (η^5-C_5H_5)Co(PPh_3)$_2$ (Ia) in benzene was treated with dimethyl fumarate (dmfu) at room temperature, the solution turned gradually from red to reddish brown. From the reaction mixture, (η^5-C_5H_5)Co(PPh_3)(dmfu) (IIa) [2] was obtained in an 89% yield. Similarly, dimethyl maleate (dmma) and maleic anhydride (mah) reacted with Ia to give the corresponding complexes IIb [2] and IIc in 78 and 66% yields, respectively.

The reaction of fumaronitrile with Ia gave, unexpectedly, a mixture of the fumaronitrile and the maleonitrile complexes. Thus, when fumaronitrile was added to a solution of Ia, the solution immediately turned to green, suggesting the formation of a charge transfer complex, and then to reddish brown, from which two kinds of complexes (IId and IIe) having the same empirical formula, (η^5-C_5H_5)Co(PPh_3)($C_4H_2N_2$), were obtained in 44 and 43% yields, respectively. The complex (IId) obtained from the first eluate by alumina column chromatography was identified as the known fumaronitrile (fn) complex, (η^5-C_5H_5)Co(PPh_3)(fn) [2], from the IR and ^{1}H NMR spectra. The ^{1}H NMR spectrum of the other (IIe) revealed one singlet at δ 4.63 ppm due to five protons of the η^5-cyclopentadienyl ring and one doublet corresponding to two protons at δ 0.87 ppm (J(PH) = 8 Hz), attributable to equivalent olefinic protons. On the basis of these data, the complex IIe was assigned to the maleonitrile (mn) complex, (η^5-C_5H_5)Co(PPh_3)(mn). Neither IId nor IIe converted into each other under the reaction conditions. On heating IId at 140—145°C, however, the isomerization into IIe occurred to give a mixture of IId and IIe (1: 2.3), but no reverse reaction was observed. This suggests that the isomer IIe is thermodynamically more stable than IId.

On the other hand, the reactions of (η^5-C_5H_5)Co(CO)$_2$ (Ib), (η^5-C_5H_5)Co[CNC_6H_3-2,6-(CH_3)$_2$]$_2$ (Ic), and (η^5-C_5H_5)Co[P(OPh)$_3$]$_2$ (Id) with fumaronitrile did not occur at room temperature, but occurred at elevated temperatures to give the corresponding fumaronitrile complexes in good yields; Ib (at 110°C), Ic (80°C), and Id (140°C) gave (η^5-C_5H_5)Co(CO)(fn) (IIIa, 76%), (η^5-C_5H_5)Co(CNC_8H_9)(fn) (IVa, 60%), and (η^5-C_5H_5)Co[P(OPh)$_3$](fn) (Va, 64%), respectively. No maleonitrile complexes were obtained in these reactions.

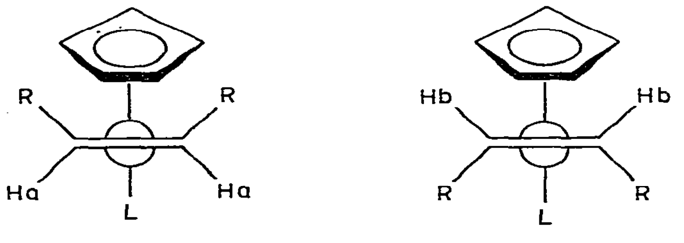
It is noteworthy that the reaction of fumaronitrile with Ia gives the product (IIe) arising from isomerization of the olefin, though the reactions of dimethyl fumarate and dimethyl maleate with Ia give the corresponding olefin complexes (IIa and IIb) and no maleonitrile complex is formed in the reactions of fumaronitrile with Ib—Id or (η^5-C_5H_5)Co(PPh_3)(PhC_2Ph) [2]. These should be attributed to the difference in π-acidities of olefins and in basicities of starting cobalt complexes (I). In general the reaction of I seems to proceed via coordinatively unsaturated species (η^5-C_5H_5)Co(L) (VI) formed by the dissociation of a ligand as shown in Scheme 1. However, more π-acidic fumaronitrile than the other olefin may directly interact with more basic phosphine complex Ia itself to form a charge transfer complex (VII), which permits the rotation about the C—C double bond to give the maleonitrile complex IIe.

In contrast with Ia, Ic reacted with maleic anhydride in refluxing benzene to give two isomers of (η^5-C_5H_5)Co(CNC_8H_9)(mah) [IVb-A and IVb-B (36:64)]



SCHEME 1

in a total yield of 39%. The ^1H NMR spectrum of IVb-A showed two singlets at δ 4.63 and 3.24 ppm due to cyclopentadienyl and olefinic protons, respectively, and that of IVb-B similarly showed two singlets at δ 4.56 and 3.99 ppm. The only one singlet absorption for the coordinated maleic anhydride in either IVb-A or IVb-B shows that the olefin is oriented perpendicular to the (η^5-C_5H_5)—Co—L plane in the molecule and that the compounds are conformational isomers as shown in Fig. 1. The reaction of Ib with maleic anhydride gave (η^5-C_5H_5)Co(CO)(mah) (IIIb, 73%). The ^1H NMR spectrum again showed the presence of two conformational isomers, IIIb-A and IIIb-B, in a 22:78 ratio. No attempt to separate two isomers was made. These olefin complexes are summarized in Table 1.



(A) (B)

Fig. 1. Conformational Isomers of (η^5-C_5H_5)Co(L)(*cis*-RCH=CHR)

TABLE 1

$(\eta^5\text{-}C_5H_5)Co(L)(olefin)$

	Olefin[a]	L	Color	M.p. (°C)	^{1}H NMR (δ, ppm)[c]	
					η^5-C_5H_5	Olefinic protons
IId	fn	PPh_3	brown-red	170—172	4.39	1.29[t, J(PH) = J(HH) = 10 Hz] 2.65[dd, J(HH) = 10 Hz, J(PH) = 3 Hz]
IIIa	fn	CO	orange	106—107	4.58	2.09(d, 10 Hz), 2.70 (d, 10 Hz)
IVa	fn	C_8H_9NC	red	202—204	4.68	2.00(d, 10 Hz), 2.70(d, 10 Hz)
IVe	fn	$C_6H_{11}NC$	red	115—116	4.62	1.85(d, 10 Hz), 2.65 (d, 10 Hz)
Va	fn	$P(OPh)_3$	red-brown	172—174	4.11	2.28[dd, J(HH) = 12 Hz, J(PH) = 10 Hz] 2.70[dd, J(HH) = 12 Hz, J(PH) = 4 Hz]
IVc	dmfu	$C_6H_{11}NC$	red	109—110	[e]	
IIc	mah	PPh_3	brown-red	235(dec.)	4.39	2.39[d, J(PH) = 8 Hz]
IIIb-A	mah	CO	red-brown	[b]	5.14 [d]	3.73(s)
IIIb-B	mah	CO	red-brown	[b]	5.48 [d]	4.48(s)
IVb-A	mah	C_8H_9NC	red	164	4.63	3.24(s)
IVb-B	mah	C_8H_9NC	red	176—177	4.56	3.99(s)
IVd-A	mah	$C_6H_{11}NC$	red	[b]	4.54	3.14(s)
IVd-B	mah	$C_6H_{11}NC$	red	152—154	4.50	3.95(s)
IVf-A	mah	C_6H_5NC	red	[b]	4.60	3.28(s)
IVf-B	mah	C_6H_5NC	red	[b]	4.54	4.01(s)
IIe	mn	PPh_3	brown-red	192—193	4.63	0.87[d, J(PH) = 8 Hz]
IVg-A	mn	$C_6H_{11}NC$	red	149—150	4.76	1.72(s)
IVg-B	mn	$C_6H_{11}NC$	red	159—160	4.50	2.46(s)

[a] fn = Fumaronitrile; dmfu = dimethyl fumarate; mah = maleic anhydride; mn = maleonitrile. [b] Not isolated. [c] In chlorobenzene. [d] In acetone-d_6. [e] A sufficient datum not obtained because of the instability.

Reactions of $(\eta^5\text{-}C_5H_5)Co(PPh_3)(olefin)$ (II) with isocyanides

The phosphine ligand of $(\eta^5\text{-}C_5H_5)Co(PPh_3)(olefin)$ (II) was readily displaced by isocyanides to give $(\eta^5\text{-}C_5H_5)Co(CNR)(olefin)$ (IV) in good yields. For example, the reactions of IIa (olefin = dmfu), IIc (mah), and IId (fn) with a small excess of cyclohexyl isocyanide at room temperature for 18 h gave $(\eta^5\text{-}C_5H_5)Co(CNC_6H_{11})(olefin)$, IVc (olefin = dmfu), IVd (mah), and IVe (fn) in 89, 92, and 95% yields, respectively. If the reaction of IIc is restricted to the configuration A (vide infra), two conformational isomers IVd-A and IVd-B are formed in a 1:9 ratio. The results are listed in Table 2.

$$\underset{\text{(II)}}{(\eta^5\text{-}C_5H_5)Co(PPh_3)(olefin)} + CNR \rightarrow \underset{\text{(IV)}}{(\eta^5\text{-}C_5H_5)Co(CNR)(olefin)} + PPh_3$$

Table 2 shows that the displacement reactions have been affected by both the bulkiness of an entering isocyanide and π-acidity of the coordinated olefin. The conversion of IIc to $(\eta^5\text{-}C_5H_5)Co(CNR)(mah)$ decreased with RNC in the order: R = C_6H_{11} (100%) ≈ Ph (100%) > 2,6-$(CH_3)_2C_6H_3$ (50%). This is in the

3LE 2

ACTIONS OF II WITH ISOCYANIDES [a]

strate fin)	RNC	Solvent	Conversion (%)	Product (Yield, %) [b]	Isomer ratio A/B
(dmfu)	$C_6H_{11}NC$	C_6H_6	100	IVc (89)	—
(mah)	$C_6H_{11}NC$	C_6H_6	100	IVd (92)	10/90
(mah)	C_8H_9NC	CH_2Cl_2	50	IVb (80)	36/64
(mah)	C_6H_5NC	CH_2Cl_2	100	IVf (56)	34/66
(fn)	$C_6H_{11}NC$	C_6H_6	92	IVe (95)	—
(fn)	C_8H_9NC	CH_2Cl_2	50	IVa (76)	—
(mn)	$C_6H_{11}NC$	C_6H_6	69	IVg (94)	87/13

solution of II and isocyanides (molar ratio of 1:2) in the solvent was stirred at room temperature for ı. [b] Based on consumed II.

erse order to the mean value of the fan-shaped angle [3]: $C_6H_{11}NC$ (63°) *, NC (63°), and C_8H_9NC (80°), indicating the important role of steric factor. e reactivity of II to cyclohexyl isocyanide decreased with the coordinated fin in the order: dmfu ≈ mah > fn > mn, suggesting the importance of the cidity of the olefin, which has an effect upon dissociation of the phosphine. us a decrease in π-acidity of the olefin in II would cause the phosphine to be re labile.

nformational isomers of (η^5-C_5H_5)Co(L)(cis-olefin) and bulkiness of the ınd

As stated above, the presence of two conformational isomers (A and B) s observed for the carbonyl and isocyanide complexes of maleic anhydride Ib and IVb). This demonstrates the high energy barrier to olefin rotation in complexes, in contrast with the smooth ethylene rotation in (η^5-C_5H_5)Rh-)(CH_2=CH_2) [4,5,6]. Presumably a large π-component in the olefin—metal nd is responsible for the lack of rotation about the bond.

The structures of the isomers were assigned on the basis of the chemical shift ference of the olefinic protons (Ha and Hb) **; a resonance at a higher magnetic ld to Ha (the structure A) and the other one to Hb (the structure B) as served in (η^5-C_5H_5)Rh(L)(olefin) [4,5] and [(η^5-C_5H_5)Fe(CO)$_2$(olefin)]$^+$ [7,8]. the other hand, the phosphine complex (IIc), consisting of only one isomer, s assigned the structure A, since the coupling constant (J(PH) = 8 Hz) was large as that of Ha in (η^5-C_5H_5)Co(PPh_3)(fn) [Ha: δ 1.29 ppm (triplet, J(PH) = IH) = 10 Hz), Hb: δ 2.65 ppm (double doublet, J(PH) = 3 Hz, J(HH) = 10)] ***.

In Table 3 are given the isomer ratios in the complexes (η^5-C_5H_5)Co(L)(mah) tained by the reactions of I with maleic anhydride and by the displacement

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* The value is estimated from the chair-form having the NC group in an equatorial position, [width = 69°, thickness = 56°].

** The proton Ha is orientated away from the cyclopentadienyl ring and Hb is orientated towards it.

** The coupling constant between phosphine and hydrogen in the mutual *cis*-position is known to be larger than that in the mutual *trans*-position [9].

TABLE 3

CONFORMATIONAL ISOMER RATIOS OF (η^5-C_5H_5)Co(L)(mah) [a]

	L	Isomer ratio (A/B)	
		Reaction 1	Reaction 2
IIc	PPh_3	A only	—
IIIb	CO	22/78	—
IVd	$C_6H_{11}NC$	—	10/90
IVf	C_6H_5NC	—	36/64
IVb	C_8H_9NC	36/64	34/66

[a] Reaction 1: The reaction of I with olefin. Reaction 2: the reaction of II with isocyanides.

reactions of IIc with isocyanides. In IIc-A the olefinic protons are situated in the *cis*-position to the phosphine ligand to avoid the sterically repulsive interaction between PPh_3 and the $(CO)_2O$ moiety. In the complexes of CO and RNC, which are sterically smaller than PPh_3, the B form is more favorable than the A form. These results indicate that the bulkiness of the ligands around the cobalt atom decreases in the order: $PPh_3 > C_5H_5 > RNC > CO$.

In contrast to the reaction of IIc with cyclohexyl isocyanide, that of (η^5-C_5H_5)Co(PPh_3)(mn) (IIe) gave IVg-A and IVg-B in a 87:13 ratio. However, the isomer B was also more thermodynamically stable than A, since heating IVg-A at 110°C led to a mixture of IVg-A and IVg-B (1:4).

Experimental

All reactions were carried out under an atmosphere of nitrogen. Melting points were taken on a Mitamura capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on a Shimazu IR-27G spectrophotometer. ^1H NMR spectra were obtained on a Varian HA-100B spectrometer using tetramethylsilane as an internal reference. Mass spectra were measured on a Niphondenshi JPS-IS mass spectrometer with direct inlet system operating at 75 eV electron energy. The complexes (η^5-C_5H_5)Co(PPh_3)$_2$ [10] and (η^5-C_5H_5)Co[2,6-$(CH_3)_2C_6H_3NC$]$_2$ [11] were prepared according to published methods.

Preparation of (η^5-C_5H_5)Co(PPh_3)(dmfu) (IIa)

To a solution of (η^5-C_5H_5)Co(PPh_3)$_2$ (Ia) (1.5 g, 2 mmol) in benzene (50 ml) was added dimethyl fumarate (0.8 g, 5.6 mmol), and the mixture was stirred at room temperature for 1 h. The red solution was evaporated under reduced pressure, and the residue was subjected to column chromatography on alumina (Sumitomo Activated Alumina KCG-30, ϕ 2.5 cm × 20 cm). From a red fraction which was eluted with benzene/ethyl acetate (2/1), IIa (0.94 g, 89%) was obtained as brown-red crystals, which were recrystallized from benzene/hexane. The complex IIa was identified by comparison with the infrared spectrum of an authentic sample [2].

Preparation of (η^5-C_5H_5)Co(PPh_3)(mah) (IIc)

A mixture of Ia (1.5 g, 2 mmol), maleic anhydride (0.5 g, 5 mmol), and enzene (50 ml) was stirred at room temperature for 1 h to give a red-brown olution. After removal of the solvent under reduced pressure, the residue was eparated by column chromatography on silica (Wakogel C-200, ϕ 2.5 cm × 0 cm). From a red band eluted with dichloromethane/benzene (2/1), IIc 0.64 g, 66%) was obtained as brown-red crystals which were recrystallized rom dichloromethane/hexane. Found: C, 66.95; H, 4.60. Calcd. for $_{27}H_{22}O_3PCo$: C, 66.95; H, 4.58%.

eaction of Ia with fumaronitrile

When a solution of Ia (1.5 g, 2 mmol) and fumaronitrile (0.4 g, 5 mmol) n benzene (50 ml) was stirred at room temperature, the solution colour immeiately changed to green and then gradually to reddish brown. After stirring or 1 h, the solution was separated by column chromatography on alumina (ϕ .5 cm × 20 cm). Two reddish brown bands were observed. From the reddish rown fraction eluted with benzene/ethyl acetate (10/1), the fumaronitrile omplex IId (0.42 g, 44%) was obtained as brown-red crystals.

From the second reddish brown fraction eluted with benzene/ethyl acetate 4/1), the maleonitrile complex IIe (0.40 g, 43%) was obtained as brown-red rystals which were recrystallized from benzene/hexane. Found: C, 69.92; H, .82; N, 6.16. Calcd. for $C_{27}H_{22}N_2PCo$: C, 69.83; H, 4.78; N, 6.03%.

somerization of IId

A mixture of IId (100 mg) and toluene (10 ml) in an ampoule was heated t 140—145°C for 6 h. After removal of the solvent, the brown residue was eparated by chromatography on alumina to give IId (19 mg) and IIe (43 mg).

reparation of (η^5-C_5H_5)Co(CO)(fn) (IIIa)

A mixture of (η^5-C_5H_5)Co$(CO)_2$ (Ib, 0.4 g, 2.2 mmol) and fumaronitrile 0.25 g, 3.2 mmol) was heated at 110°C for 1.5 h. After cooling, the mixture vas chromatographed on silica. After the unreacted Ib and fumaronitrile vere washed out with benzene, an orange-red zone eluted with benzene/ethyl cetate (3/1) was collected. After removal of the solvent under reduced presure, the residue was crystallized from hexane/benzene (2/1) to give orange rystals (IIIa, 0.39 g, 76%). Found: C, 52.22; H, 3.07; N, 12.39. Calcd. for $_{10}H_7N_2OCo$: C, 52.20; H, 3.07; N, 12.17%.

reparation of (η^5-C_5H_5)Co(CO)(mah) (IIIb)

A mixture of Ib (0.6 g, 3.4 mmol), maleic anhydride (1.2 g, 12.2 mmol), nd xylene (20 ml) was heated at 140°C for 3 h to precipitate brown solids. he precipitate (0.83 g) separated by filtration was extracted with acetone (30 nl). The extract was concentrated under reduced pressure to afford IIIb as a ed-brown solid (0.61 g, 73%), which was recrystallized from acetone/hexane. ound: C, 47.72; H, 2.88. Calcd. for $C_{10}H_7O_4Co$: C, 48.03; H, 2.82%. M^+ 250 MW 250).

The ^1H NMR spectrum of the solid dissolved in $(CD_3)_2CO$ showed it to be mixture of the isomers A and B in a ratio of 22:78.

reparation of (η^5-C_5H_5)Co(CNC_8H_9)(fn) (IVa)

A solution of (η^5-C_5H_5)Co$(CNC_8H_9)_2$ (Ic, 0.26 g, 0.67 mmol) and fumaronitrile

(0.1 g, 1.28 mmol) in toluene (10 ml) was heated at 120°C. After 2.5 h, the solvent was removed under reduced pressure, and the residue was purified by chromatography on alumina. Elution with dichloromethane gave a yellow brown solution. Removal of the solvent and recrystallization of the residue from dichloromethane/hexane gave IVa (0.135 g, 60%). Found: C, 64.79; H, 4.80; N, 12.73. Calcd. for $C_{18}H_{16}N_3Co$: C, 64.87; H, 4.84; N, 12.61%.

Preparation of (η^5-C_5H_5)Co(CNC_8H_9)(mah) (IVb)

When a solution of Ic (0.20 g, 0.5 mmol) and maleic anhydride (0.20 g, 2 mmol) in benzene (20 ml) was refluxed for 2 h, a brownish red solution was obtained. After removal of the solvent, the residue was separated by chromatography on silica. Two red bands eluted with dichloromethane/ethyl acetate (4/1) were collected. The solution was concentrated under reduced pressure to give IVb as red crystals (0.07 g, 39%). The crystals were proved to be a mixture of the isomers A and B in a ratio of 1:2 by the ^{1}H NMR spectrum. The isomers could be separated by careful rechromatography of the mixture. IVb-A; Found: C, 61.05; H, 4.62; N, 4.09. Calcd. for $C_{18}H_{16}NO_3Co$: C, 61.20; H, 4.57; N, 3.96%. IVb-B; Found: C, 61.07; H, 4.62; N, 4.02. Calcd. for $C_{18}H_{16}NO_3Co$: C, 61.20; H, 4.57; N, 3.96%.

Preparation of (η^5-C_5H_5)Co[P(OPh)$_3$](fn) (Va)

A mixture of (η^5-C_5H_5)Co[P(OPh)$_3$]$_2$ (Id, 1.0 g), fumaronitrile (0.25 g), and toluene (15 ml) in an ampoule was heated at 140°C for 4 h. After removal of the solvent, the residue was separated by chromatography on alumina. From the reddish brown fraction eluted with benzene/ethyl acetate (10/1), Va (0.45 g, 65%) was obtained as red-brown crystals, which were recrystallized from benzene/hexane. Found: C, 63.23; H, 4.23; N, 5.16. Calcd. for $C_{27}H_{22}N_2O_3PCo$: C, 63.29; H, 4.33; N, 5.47%.

Reaction of IIa with cyclohexyl isocyanide

To a mixture of IIa (0.53 g, 1 mmol) and benzene (20 ml) was added a solution (1 *M*, 2 ml) of cyclohexyl isocyanide in benzene, and the mixture was stirred at room temperature for 18 h. After removal of the solvent, the residue was submitted to chromatography on alumina. Elution with benzene/ethyl acetate (3/1) and removal of the solvent gave red crystals of IVc (0.334 g, 89%). Found: C, 57.44; H, 6.42; N, 3.70. Calcd. for $C_{18}H_{24}NO_4Co$: C, 57.30; H, 6.41; N, 3.71%. M^+ 377 (MW 377).

Reaction of IId with cyclohexyl isocyanide

A mixture of IId (232 mg, 0.5 mmol), cyclohexyl isocyanide (1 mmol), and benzene (10 ml) was stirred at room temperature for 18 h. The solvent was removed under reduced pressure, and the residue was separated by chromatography on alumina. From a red band eluted with benzene/ethyl acetate (20/1), IVe (136 mg, 92%) was obtained as red crystals. Found: C, 61.76; H, 5.83; N, 13.67. Calcd. for $C_{16}H_{18}N_3Co$: C, 61.74; H, 5.83; N, 13.67%. Further elution with benzene/ethyl acetate (10/1) gave unreacted IId (19 mg, 8%).

Reaction of IIc with cyclohexyl isocyanide

A mixture of IIc (250 mg, 0.52 mmol), cyclohexyl isocyanide (1 mmol), and benzene (20 ml) was stirred at room temperature for 18 h. After removal of the solvent, the residue was purified by chromatography on silica. Elution with dichloromethane/ethyl acetate (10/1) gave a red solution. Removal of the solvent gave IVe (152 mg, 92%), which was shown to be a mixture of the isomers A and B in a ratio of 1:9 by the ^{1}H NMR spectrum. The isomer IVe-B was isolated by recrystallization of the mixture from benzene/hexane. Found: C, 58.00; H, 5.45; N, 4.34; Calcd. for $C_{16}H_{18}NO_3Co$: C, 58.01; H, 5.48; N, 4.23%.

Preparation of IVg-A from IIe and cyclohexyl isocyanide

A mixture of IIe (200 mg, 0.43 mmol), cyclohexyl isocyanide (1.5 mmol), and benzene (10 ml) was stirred at room temperature for 24 h. After removal of the solvent, the residue was separated by chromatography on silica. From a red band eluted with benzene/ethyl acetate (20/1), red crystals of IVg-B (16 mg, 12%) were obtained. Further elution with benzene/ethyl acetate (4/1) gave red crystals of IVg-A (108 mg, 81%). Found: C, 61.61; H, 5.83; N, 13.65. Calcd. for $C_{16}H_{18}N_3Co$: C, 61.74; H, 5.83; N, 13.50%.

Preparation of IVg-B by the isomerization of IVg-A

A solution of IVg-A (100 mg) in benzene (10 ml) in an ampoule was heated at 110°C for 6 h. After removal of the solvent, the residue was separated by chromatography on silica to give IVg-B (60 mg) and IVg-A (15 mg). IVg-B; Found: C, 61.72; H, 5.84; N, 13.69. Calcd. for $C_{16}H_{18}N_3Co$: C, 61.74; H, 5.83; N, 13.50%.

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