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CHEMISTRY OF MIXED TRANSITION-METAL COMPLEXES

VIII *. PREPARATIONS OF π-CYCLOPENTADIENYL(FERROCENYLCYCLOBUTADIENE)COBALT COMPLEXES AND 1,1'-(o-PHENYLENE)FERROCENES

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Summary

Reactions of mono- and bis-(phenylethynyl)ferrocenes with π-$C_5H_5Co(PPh_3)$-($RC{\equiv}CR'$) (R, R' = Ph, CO_2CH_3) or π-$C_5H_5Co(PPh_3)_2$ at 80°C were examined and several ferrocenylcyclobutadienecobalt complexes were isolated. New ferrocenes bridged with *o*-phenylene groups were also obtained by the reaction of bis-(phenylethynyl)ferrocene.

In a previous paper [1], we reported the reaction of transition metal ethynyl complexes, $RC{\equiv}CM$ (M = π-$C_5H_5Fe(CO)_2$, π-$C_5H_5NiPPh_3$), with π-C_5H_5Co-(PPh_3)($RC{\equiv}CR'$). The reaction has been extended to phenylethynylferrocenes to prepare ferrocenyl-substituted cyclobutadienecobalt complexes. π-Cyclopentadienyltetraferrocenylcyclobutadienecobalt has been reported hitherto [2].

Results and discussion

Reaction of phenylethynylferrocene (I)

Reaction of I with π-cyclopentadienyl(triphenylphosphine)diphenylacetylenecobalt (IIa) in toluene at 85°C gave π-cyclopentadienyl(ferrocenyltriphenylcyclobutadiene)cobalt (IIIa) (50% yield) as orange crystals. The mass spectrum of IIIa showed the molecular ion M^+ at *m/e* 588 and the ^1H NMR spectrum showed the FeC_5H_5 protons at δ(ppm) 3.92 (5, singlet), the FeC_5H_4 protons at δ 4.13 and 4.28 (2,2, A_2B_2 spin type signals [3]), the CoC_5H_5 protons at δ 4.58 (5, singlet) and the phenyl protons at δ 7.0—7.5 and 7.7—7.9 (10, multiplets).

Similar treatment of I with IIb gave the isomeric methoxycarbonyl derivatives IIIb and IIIc in addition to a cobaltacyclopentadiene type product IVa. The

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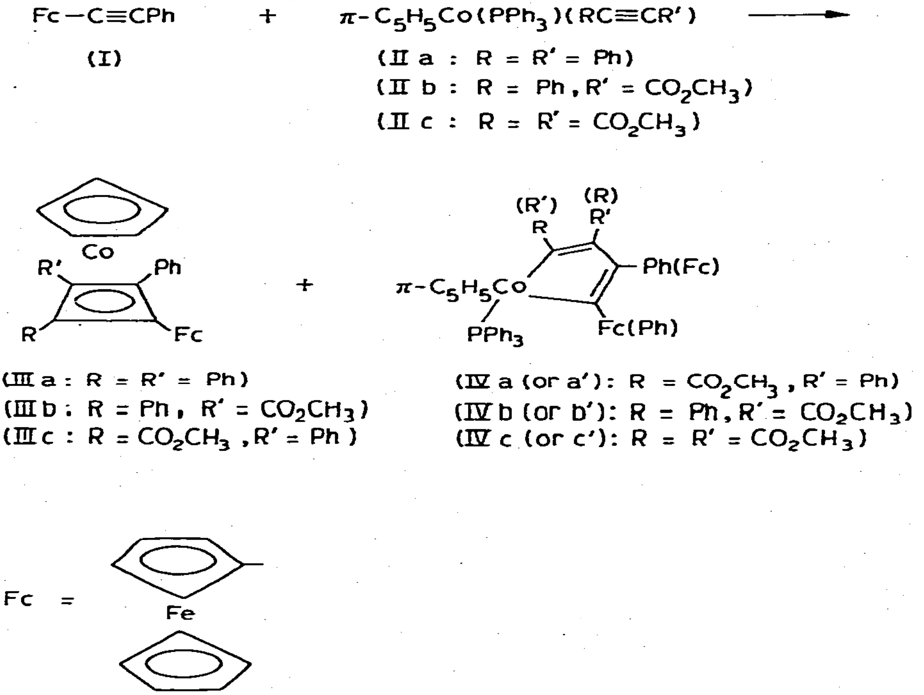
[*] Part VII of this series, see ref. 1.

SCHEME 1



^{1}H NMR spectrum of IIIb showed the FeC_5H_4 protons at δ 4.16 and 4.30 (2,2) as simple A_2B_2 type signals indicating that it is the 2,4-diphenyl isomer. The ^{1}H NMR signals of IIIc appeared at δ 4.12 (2, multiplet), 4.24 (1, multiplet) and 5.03 (1, multiplet) indicating that it is the 2,3-diphenyl isomer. In the 1,2-structure, the FeC_5H_4 proton signals may not be a simple A_2B_2 spin type because of lack of symmetry in the ring. The fragmentation patterns of the mass spectra also support these assignments. Compound IVa, when heated in toluene (100°C, 8 h), gave only IIIc (55% yield). This fact suggests structure IVa (or IVa'). (Scheme 1).

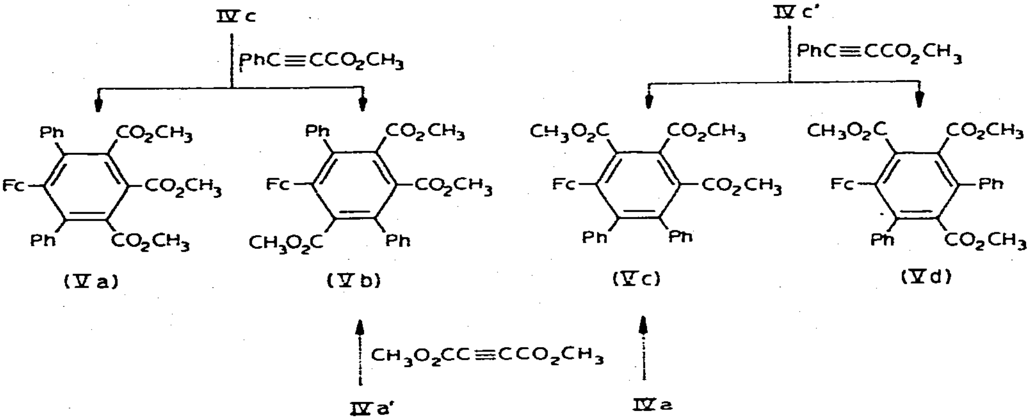
The other isomer IVb could be isolated (23.5% yield) together with IVa (25% yield) and IIIb (8% yield) when the reaction was carried out at room temperature. Compound IVb gave IIIb (75% yield) when heated (100°C, 1 h).

On the other hand, only a cobaltacyclopentadiene type product IVc was formed from I and IIc. This product could not be converted to the corresponding cyclobutadiene complex by heating in toluene. Structure IVc is proposed on the basis of the following evidence: Reaction of cobaltacyclopentadiene compounds with acetylenes to give substituted benzenes is known [4]. In this case, reaction of IVc with excess $PhC{\equiv}CCO_2CH_3$ at 100°C gave two isomeric ferrocenyltris(methoxycarbonyl)diphenylbenzenes (V) with m.p. 181.5–182.5°C and V' with m.p. 247–248°C.

If the starting structure were IVc, isomers Va and Vb would be produced. On the other hand, Vc and Vd must be formed from structure IVc' (Scheme 2).

The ^{1}H NMR spectrum of isomer V showed the OCH_3 protons as two singlets

SCHEME 2



in 1/2 ratio at δ 3.42 and 3.39, and the FeC_5H_4 protons as a singlet at δ 4.05(4). The spectrum of isomer V' showed the OCH_3 protons also as two singlets in 1/2 ratio at δ 3.79 and 3.41, and the FeC_5H_4 protons as an A_2B_2 spin type centered at δ 3.51(2) and 3.88(2). Whether the products were Va and Vb, or Vc and Vd could not be determined unequivocally by means of their OCH_3 proton signals because the observed signals for both isomers were two singlets instead of expected two singlets (1/2) and three singlets (1/1/1) for the Va and Vb pair, and three singlets (1/1/1) for each of Vc and Vd. However, the products are more likely to be Va and Vb since the probability of the OCH_3 protons of both Vc and Vd appearing as two singlets would be much less than that for Vb alone. In addition, the difference in the FeC_5H_4 proton signals can be attributed to the isomeric pair Va and Vb which differ in the substituents (Ph, Ph for Va and Ph, CO_2CH_3 for Vb) at the positions *ortho* to the Fc group, whereas those of Vc and Vd are the same. Thus the isomers formed in this reaction are presumed to be Va and Vb.

Another isomer V" was obtained from the reaction of IVa with $CH_3O_2CC{\equiv}CCO_2CH_3$ (110°C, 4 h) along with IIIc. The isomer V" can be assigned to Vc on the basis of the above discussion since Vc and Vb are expected from structures IVa and IVa', respectively. The ^1H NMR spectrum of Vc showed the FeC_5H_4 proton signals as two sets of multiplets and three OCH_3 signals individually at δ 4.08(2)m, 3.93(3)s, 3.87(3)s + (2)m, and 3.44(3)s. The similarity of the FeC_5H_4 proton signals between V' and V" may assign V' to Vb and thus V to Va.

When I was treated with π-cyclopentadienylbis(triphenylphosphine)cobalt (VI) at 80°C (and also at room temperature), isomeric diferrocenylcyclobutadiene complexes IIId and IIIe were obtained (Scheme 3).

Separation of the isomers was performed by fractional recrystallization from a very dilute hexane solution. The less soluble isomer IIId showed the FeC_5H_4 proton signals as a simple A_2B_2 spin system centered at δ 4.10 and 4.16 indicating it to be the 1,3-diferrocenyl isomer *. Those of IIIe appeared at δ 4.23

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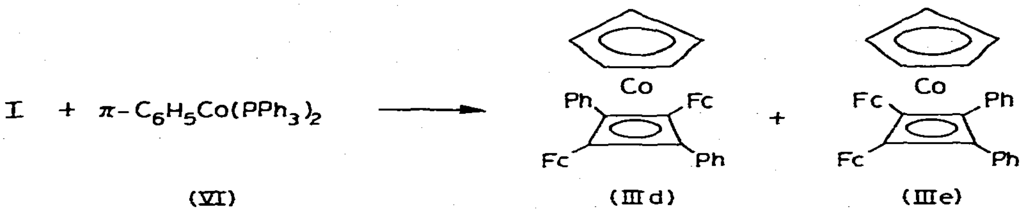
* Compounds IIId and IIIe have been prepared independently by Rausch and coworkers by the reaction of π-$C_5H_5Co(CO)_2$ with I and an X-ray structure determination of IIId has been carried out [5].

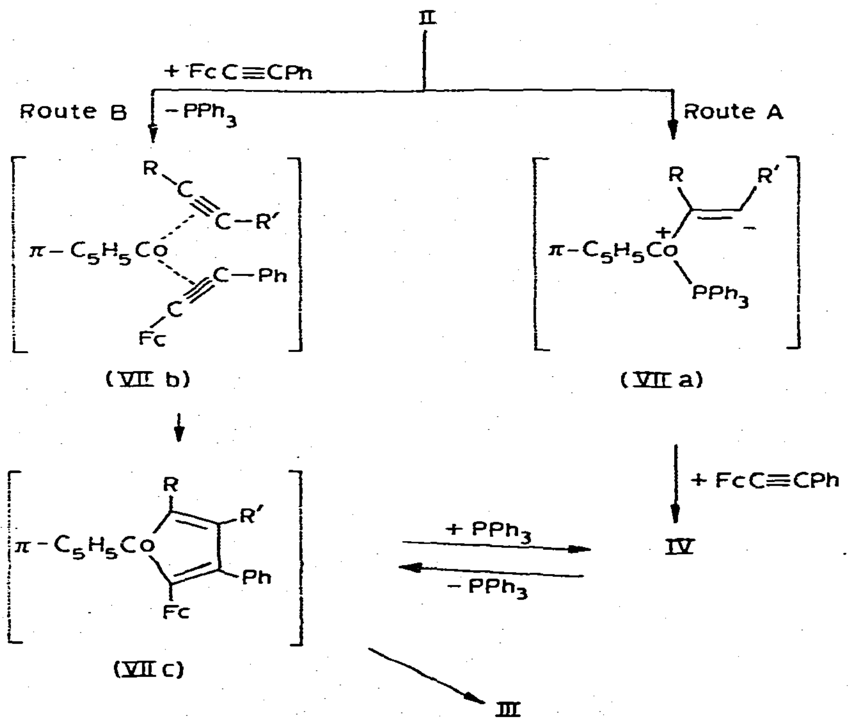
SCHEME 3



(4, multiplet), 4.39 (2, multiplet) and 4.59 (2, multiplet), thus indicating the 1,2-diferrocenyl structure.

Two routes, A and B, would be conceivable for the formation of III (Scheme 4). The route A involving a zwitterionic intermediate VIIa to the corresponding cobaltacyclopentadiene complex IV has been proposed [6]. The compounds IV could be converted to III via an intermediate state VIIc with thermal dissociation of the PPh_3 ligand. However, the formation of a considerable amount of IIIb in the reaction of IIb with I at room temperature cannot be explained by route A, since IVb, when it was isolated, could not give IIIb at all under the reaction conditions. This indicates that route B involving a bis(acetylene) intermediate VIIb to VIIc is very likely [1].

SCHEME 4



The coordinatively unsaturated cobaltacyclopentadiene intermediate VIIc competitively gives III or IV by recombination with the phosphine. Electronic and steric factors of the substituents may subtly exert an influence on the competition and also on the stability of IV. The formation of IIId and IIIe even at room temperature without isolation of the corresponding compound IV (Scheme 3) might be due to the bulkiness and electron-releasing character of the ferrocenyl group.

The elemental analyses and some physical properties of these products are shown in Table 1.

Reaction of 1,1'-bis(phenylethynyl)ferrocene (VIII)

Reaction of VIII with IIa at 80°C gave 1,2-(1,1'-ferrocenylene)-3,4,5,6-tetraphenylbenzene (Xa) in 24% yield. Similarly, 4-methoxycarbonyl and 4,5-dimethoxycarbonyl derivatives Xb and Xc could be obtained in 14 and 20% yields, respectively, by reactions of VIII with IIb and IIc.

The FeC_5H_4 proton signals of Xa and Xc appeared as simple A_2B_2 signals centered at δ 3.94, 4.81 and δ 3.94, 4.72, respectively. The OCH_3 protons of Xc appeared as singlet at δ 3.49. On the other hand, the FeC_5H_4 protons of Xb appeared as two broad multiplets centered at δ 3.95 and 4.78(4,4) and the OCH_3 protons as a singlet at δ 3.49. These indicate *o*-phenylene bridging of the benzene ring for X rather than the *m*- or *p*-phenylene type since only the *o*-phenylene bridging can give symmetry in the ferrocene ring of Xc.

In Scheme 5, a bis(acetylene) intermediate IXa undergoes coordination of the free acetylene moiety, in addition to coupling of the acetylenes to a type III complex or recombination with PPh_3 to a type IV complex. The first reaction, coordination of the free acetylene moiety in IXa to form the next intermediate IXb, would predominate in this case because of a favorable arrangement of the acetylene group and the entropy factor. Thus, *o*-phenylene bridging would be exclusively favored. A *m*- or *p*-phenylene type bridging can also be eliminated by steric considerations. The structure Xa has been confirmed by an X-ray diffraction study which will appear elsewhere [7].

Many bridged ferrocenes are now known, but those bridged with an aromatic ring have not yet been reported. In 1964, Little et al. tried the reaction of ferrocene with naphthalene-1,8-bis(diazonium tetrafluoroborate) which gave only 1,2-(1,8-naphthylene)ferrocene and not 1,1'-(1,8-naphthylene)ferrocene [8]. This is the first preparation of 1,1'-(*o*-phenylene)ferrocenes.

When VIII was similarly treated with VI, π-cyclopentadienyl-1,2-(1,1'-ferrocenylene)-3,4-diphenylcyclobutadienecobalt (XI) was obtained (10% yield). The mass spectrum of XI showed the molecular ion at *m/e* 510 (100%) followed by peaks corresponding to loss of the C_5H_5 fragment and Fe atom at *m/e* 445 (26%) and 389 (15%). The ^1H NMR spectrum showed the CoC_5H_5 protons at δ 4.95 (5, singlet) and the ferrocenyl protons as four distinct broad signals centered at δ 3.75, 3.96, 5.70 and 5.86 (ratio: 2/2/2/2). This shift and splitting of the ferrocenyl proton signals can be attributed to the dissimilarity caused by the CoC_5H_5 moiety in the α,α'- and β,β'-protons.

Electronic spectra of IIIa, IIId, IIIe, Xa, Xc and XI are shown in Table 2. The spectra of Xa and Xc showed absorption maxima at 330 nm (ϵ = 950 and 780) and 465 nm (ϵ = 470 and 430). It has been shown that the 440 nm band of ferrocene is particularly sensitive to ring-tilt distortion as seen in tetramethyl[2]-

TABLE 1

MELTING POINTS, ANALYSES, MOLECULAR IONS IN THE MASS SPECTRA AND PRINCIPAL ^{1}H NMR SIGNALS OF COMPOUNDS III—V, X AND XI

Compound	M.p. (°C)	Analyses Found (calcd.) (%)			M^+ (m/e)	^{1}H NMR [a] in $CDCl_3$ (δ, ppm)			
		C	H	Metal		CoC_5H_5	FeC_5H_5	FeC_5H_4	OCH_3
IIIa	133—134	75,68 (75,54)	5,05 (4,96)		588	4,58	3,92	4,13t(2), 4,28t(2)	
IIIb	197—198	68,60 (68,16)	4,85 (4,98)	Co 10,70 (10,33)	570	4,66	3,80	4,16t(2), 4,30t(2)	3,68s
IIIc	145—147	68,83 (68,16)	4,83 (4,98)	Co 10,71 (10,33)	570	4,63	3,96	4,12m(2), 4,24m(1), 5,03m(1)	3,88s
IIId	188—189	70,66 (70,73)	4,92 (4,78)	Fe 15,90 (16,03)	696	4,53	3,97	4,10t(4), 4,16t(4)	
IIIe	200—202	70,80 (70,73)	4,93 (4,78)	Fe 16,60 (16,03)	696	4,63	3,97	4,23m(4), 4,39q(2), 4,59m(2)	
IVa	174—176	74,59 (74,41)	5,32 (5,21) [b]			5,20	3,71	3,32m(1), 3,93m(2), 4,00m(1)	2,86s
IVb	168—169	74,66 (74,41)	5,39 (5,21) [b]			4,92	3,75	3,21m(1), 3,76m(1), 3,84m(2)	2,81s
IVc	197—198	70,33 (70,36)	5,19 (5,07) [b]	Co 7,45 (7,23)		5,12	3,59	3,14m(1), 4,00m(1), 4,12m(2)	3,19s, 3,21s
Va	181,5—182,5	69,02 (69,41)	4,80 (4,79)	Fe 11,3 (9,5)	588		3,97	4,05s(4)	3,39s(6), 3,42s(3)
Vb	247—248	69,64 (69,41)	4,88 (4,79)		588		3,71	3,51t(2), 3,88t(2)	3,41s(6), 3,79s(3)
Vc	214—215	69,43 (69,41)	4,85 (4,79)		588		3,99	3,87m(2), 4,08m(2)	3,44s(3), 3,87s(3), 3,93s(3)
Xa	365—367	85,21 (85,12)	5,04 (5,00)	Fe 11,3 (9,9)	564			3,94t(4), 4,81t(4)	
Xb	299—291	79,37 (79,14)	4,83 (4,80)		546			3,95m(4), 4,78m(4)	3,18s
Xc	307—309	72,31 (72,75)	4,64 (4,58)		528			3,94t(4), 4,72t(4)	3,49s
XI	230—240 [c]	73,25 (72,97)	4,70 (4,55)	Fe 11,1 (10,9) Co 12,0 (11,5)	510	4,94		3,75(br), 3,96(br), 5,70(br)	5,86(br)

[a] In addition, C_6H_5 protons appeared at δ 6,5—8,0 ppm for all those products. [b] Values for the compound containing 1/2 C_6H_6 as a crystallization solvent, which could be confirmed by means of ^{1}H NMR spectra after recrystallization from toluene/hexane. [c] Decomposition without melt.

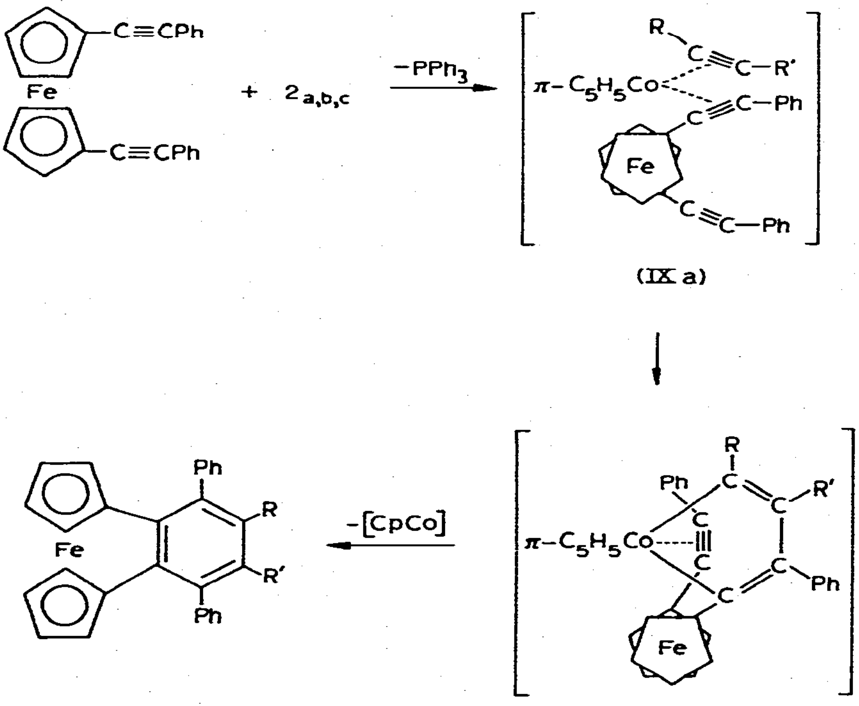
TABLE 2

ELECTRONIC ABSORPTIONS

Compound	λ_{max} (nm)/ϵ in $CHCl_3$		
IIIa	296/31000	450/2200	
IIId	298/33000	450/2700	
IIIe	298/30000	450/2400	
Xa	330/950	465/470	
Xc	330/780	466/430	
XI	304/22000	400/4000	450/2600 [a]

[a] Measured in C_6H_6 solution.

SCHEME 5



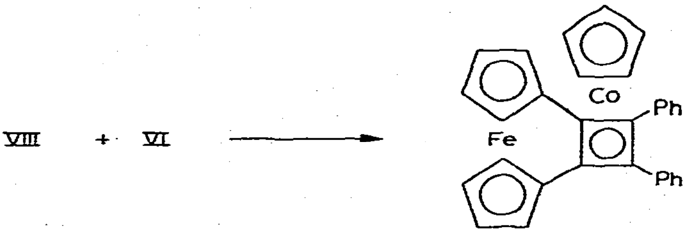
(IX a)

(IX b)

(X a : R = R' = Ph)
(X b : R = Ph, R' = CO_2CH_3)
(X c : R = R' = CO_2CH_3)

ferrocenophane [9]. The [2]ferrocenophane, which is ring-tilted as much as 23.2°, shows the corresponding absorptions at 326 nm (ϵ = 1070) and 466 nm (ϵ = 461) [10]. The intensities and shifts of the absorptions of X are comparable to those

SCHEME 6



(XI)

of the [2]ferrocenophane. The X-ray diffraction study has shown that the ring-tilt angle of Xa also corresponds well to that of the [2]ferrocenophane. 1,1'-Ferrocenylenecyclobutadiene complex XI showed much stronger absorptions in the same region which are attributable to the cyclobutadienecobalt moiety and which unfortunately obscure the ferrocenylene absorptions.

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. Metal analyses were carried out by the atomic absorption method. ^{1}H NMR spectra were obtained on JEOL L-60HL and Varian HA-100B spectrometers using tetramethylsilane as an internal reference. Mass spectra were measured on a Niphondenshi JPS-1S mass spectrophotometer with direct inlet system, at 75 eV electron energies. Electronic spectra were measured on a Cary-14 spectrophotometer. $Fe(C_5H_5)(C_5H_4C{\equiv}CPh)$ and $Fe(C_5H_4C{\equiv}CPh)_2$ [11], π-$C_5H_5Co(PPh_3)(RC{\equiv}CR')$ [1] and π-$C_5H_5Co(PPh_3)_2 \cdot C_6H_6$ [12] were prepared according to published methods.

Preparation of IIIa

A solution of I (0.182 g, 0.64 mmol) and IIa (0.375 g, 0.66 mmol) in toluene (10 ml) was heated for 6 h at 85°C with stirring. The reaction mixture was concentrated at water vacuum and chromatographed on alumina (1.5 × 10 cm). A minor pale yellow band which was eluted with 1/1 benzene/hexane was discarded, and a trailing orange band eluted with the same mixture was collected. Concentration of the eluate and addition of hexane gave orange crystals of IIIa (0.192 g, 50% yield based on the Co compound) which were recrystallized from hexane/methylene chloride.

Preparation of IIIb, IIIc and IVa

Similarly, a solution of I (0.181 g, 0.63 mmol) and IIb (0.357 g, 0.65 mmol) in toluene (10 ml) was heated for 8 h and the reaction mixture was chromatographed. After a pale yellow band eluted with benzene was discarded, a yellow-orange band was eluted with 3/1 to 1/1 benzene/methylene chloride. Evaporation of solvent at water vacuum gave a red-orange oil which was dissolved in a minimum volume of methylene chloride. Addition of a large amount of hexane to the solution gave red-orange crystals of IIIb (0.113 g), m.p. 197—198°C. Concentration of the mother liquor gave additional crystals (0.041 g), m.p. 176—179°C, whose ^{1}H NMR spectrum showed them to consist of more than 95% of IIIb. The second mother liquor, after concentration and storage in a refrigerator, gave orange crystals IIIc (0.053 g), m.p. 145—147°C. Further elution with methylene chloride gave brown needles of IVa (0.077 g).

The cobaltacyclopentadiene complex IVa (73.5 mg, 0.088 mmol) was dissolved in toluene (15 ml) and heated at 110°C for 8 h with stirring. The reaction mixture was concentrated and chromatographed on alumina. Elution with 5/1 benzene/methylene chloride gave an orange band. After evaporation of the solvent, the residue was dissolved in hexane and stored in a refrigerator overnight. Compound IIIc (22.7 mg, 45% yield) crystallized from the solution.

Preparation of IVb

A solution of IIb (0.501 g, 0.92 mmol) and I (0.294 g, 1.02 mmol) in benzene (30 ml) was stirred for 4 h at room temperature and the reaction mixture was chromatographed on alumina. Elution with benzene gave a yellow band from which 15 mg of I was recovered. Further elution with benzene gave a brownish band and an orange band. After concentration of the orange band, addition of hexane gave IIIb (0.042 g, 8% yield). Elution with 3/1 to 1/1 benzene/methylene chloride gave two brown bands. From the first portion, IVa (0.188 g, 25%) and from the second portion, IVb (0.180 g, 23.5%) were obtained. Compound IVb gave IIIb (75%) by heating (100°C, 1 h).

Preparation of IVc

A solution of IIc (0.402 g, 0.8 mmol) and I (0.204 g, 0.7 mmol) in toluene (12 ml) was treated at 85°C for 8 h and the reaction mixture was chromatographed. After a pale yellow band was eluted with benzene, elution with 5/1 benzene/ethyl acetate gave a brown band which gave IVc (0.339 g, 60% yield).

Reaction of IVc with $PhC{\equiv}CCO_2CH_3$

A toluene solution (5 ml) of IVc (0.255 g, 0.31 mmol) and excess $PhC{\equiv}CCO_2CH_3$ (0.4 ml) was heated at 110°C for 6 h. The resulting solution was concentrated and chromatographed on alumina (1.5 × 10 cm). After the column was eluted thoroughly with benzene, elution with 7/1 benzene/ethyl acetate gave an orange band which, after concentration and addition of hexane, gave 1,2,4-triphenyl-3,5,6-tris(carbomethoxy)benzene as yellow cubic crystals which were recrystallized from hexane/methylene chloride (18.4 mg, m.p. 206—208°C, lit. m.p. 204—206°C [13]) and orange needles of V (16.3 mg, m.p. 181.5—182.5 °C, 9% yield, recrystallized from hexane/methylene chloride), which were separated mechanically.

Elution with 2/1 benzene/ethyl acetate gave a mixture of light orange and darker orange bands. The mixture was rechromatographed on alumina. With 10/1 benzene/THF an orange band and a brown band were eluted separately. From the latter brown band unreacted IVc (14.1 mg) was recovered. The former orange band gave orange needles of V′ (31.2 mg, 14% yield). The needles were still contaminated with small amount of unknown by-product. For analytical purposes, V′ was purified by means of TLC (silica gel, 2/1 benzene/ether) to give material with m.p. 247—248°C.

Reaction of IVa with $CH_3O_2CC{\equiv}CCO_2CH_3$

After heating a toluene solution (5 ml) of IVa (0.187 g, 0.22 mmol) with $CH_3O_2CC{\equiv}CCO_2CH_3$ (0.3 ml) at 110°C for 4 h, the reaction mixture was chromatographed. An orange band eluted with benzene gave IIIc (63.2 mg, 50% yield). From a brown band eluted with 3/1 benzene/methylene chloride, 23.5 mg of IVa was recovered. Elution with 1/1 of the same mixture gave an orange band, from which pale orange needles of Vc (17.5 mg, 13.5% yield) were obtained.

Preparation of IIId and IIIe

A solution of I (0.207 g, 0.72 mmol) and VI (0.3 g, 0.4 mmol) in toluene (20 ml) was heated at 80°C for 10 h. The mixture was concentrated and chromatographed on alumina. From a yellow band eluted with 2/1 hexane/methylene chloride unreacted I (ca. 0.01 g) was recovered. Further elution with 1/1 hexane/methylene chloride gave a yellow-orange band which gave red spherical crystals (m.p. 170—175°C) and orange columnar crystals (m.p. 199—200°C). Their ^{1}H NMR spectra showed that both crystals consisted of different fractions of two isomers. The isomers were separated by fractional crystallization from a dilute hexane solution. The crystals combined were dissolved in the minimal volume of methylene chloride. Hexane (ca. 40 ml) was added to the solution and solvent was distilled off to ca. 30 ml at water vacuum, from which orange crystals IIId (30 mg, m.p. 187—188°C) were obtained. Two recrystallizations from benzene/hexane gave material of m.p. 188—189°C. The analysis and ^{1}H NMR spectrum showed that the crystals of IIId contained 1/2 hexane as solvent of crystallization, which could be eliminated by drying in vacuum at 170°C. Concentration of the mother liquor to ca. 20 ml gave a second crop (35 mg, m.p. 179—181°C). The ^{1}H NMR spectrum showed that the second crop consisted of 90% of IIId (the combined yield of IIId, 23%). Concentration of the second mother liquor to ca. 10 ml gave red-orange crystals IIIe (82 mg, m.p. 200—202°C).

Preparation of Xa

A solution of VIII (0.14 g, 0.36 mmol) and IIa (0.45 g, 0.62 mmol) in benzene (10 ml) was heated at 70°C for 3 h. After concentration of the dark red reaction mixture, the residue was dissolved in the minimal volume of methylene chloride and chromatographed on alumina (1 × 10 cm). A yellow-orange band was eluted with 1/1 hexane/benzene. Concentration and addition of hexane gave brown crystals of π-cyclopentadienyltriphenylphosphinetetraphenylcobaltacyclopentadiene (0.17 g) and orange crystals of Xa (50 mg, 24% yield from VIII), which could be mechanically separated. For analytical purposes, Xa was redissolved in methylene chloride and chromatographed. Elution with 2/1 hexane/methylene chloride gave 35 mg of Xa.

Methoxycarbonyl derivatives Xb and Xc were prepared similarly in 14 and 20% yields, respectively, by reactions with IIb and IIc.

Preparation of XI

A solution of VIII (0.6 g, 1.6 mmol) and VI (1.01 g, 1.4 mmol) in benzene (20 ml) was heated at 80°C for 8 h. After evaporation of the solvent, the residue was extracted with methylene chloride and the extract was chromatographed on alumina (1.5 × 10 cm). Elution with 3/1 hexane/benzene gave an orange band which gave orange crystals of XI (90 mg). The product XI was rechromatographed (80 mg, 10% yield). Further elution with 1/1 hexane/benzene removed a small red-orange band which gave an orange residue after removal of solvent. The residue was extracted with methylene chloride and rechromatographed with methylene chloride to give XII, (11 mg, 1.7% yield), m.p. > 400°C. Found: C, 71.78; H, 4.63; Co, 11.5; Fe, 12.5. $C_{62}H_{46}Fe_2Co_2$ calcd.: C, 72.97; H, 4.55; Co, 11.5; Fe, 10.9%.

The mass spectrum of XII showed the molecular ion around at *m/e* ca. 1020. The value could not be read accurately even on a high resolution spectrum because the peaks of perfluorokerosene internally added were not strong enough to show their *m/e* values in the region. However, the high resolution spectrum showed dicharged peaks corresponding to $[M]^{2+}$ at *m/e* 510.052 (calcd. 510.048) and $[M + 1]^{2+}$ at *m/e* 510.564. The dicharged peaks have the same peak pattern to that of base peaks which indicated no contamination with any appreciable monocharged peak.

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