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CHEMISTRY OF MIXED TRANSITION-METAL COMPLEXES

VII *. IRON- AND NICKEL-SUBSTITUTED CYCLOBUTADIENE COMPLEXES OF COBALT

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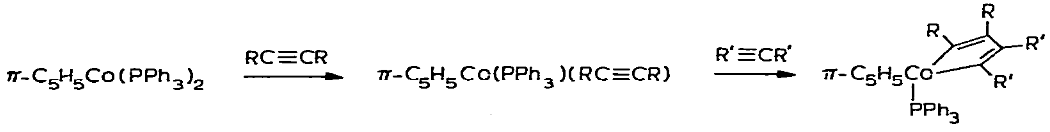
Summary

The preparation of π-cyclopentadienyl(substituted cyclobutadiene)cobalt complexes by the reaction of π-$C_5H_5Co(PPh_3)(RC{\equiv}CR')$ (R, R' = Ph, CO_2CH_3) with ethynyl complexes $R''C{\equiv}CM$ (R'' = Ph for M = π-$C_5H_5Fe(CO)(L)$; R'' = Ph, CO_2CH_3 for M = π-$C_5H_5Ni(PPh_3)$) is described.

π-Cyclopentadienyltriphenylphosphinecobaltacyclopentadiene complexes III have been shown to be very versatile intermediates in the preparation of substituted benzenes, cyclohexadienes, thiophenes, and pyrroles[2] and pyridines[3]. Such complexes can be formed in a stepwise process [3].



(1)

(I) (II) (III)

We report here the reaction of the monoacetylene complexes II with iron and nickel ethynyl complexes, IV and V, which gives iron- or nickel-substituted cyclobutadiene complexes of π-cyclopentadienylcobalt, VI and VII. These are the first preparations of cyclobutadiene complexes in which the second transition metal is attached directly to the cyclobutadiene ring. Cyclobutadiene complexes with silyl and stannyl substituents are known [4,5,6].

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* For part VI of this series, see ref. 1.

Results and discussion

Treatment of IVa with IIa in benzene at room temperature gave VIa as orange crystals in addition to the known cobaltacyclopentadiene complex III (R, R′ = Ph). The mass spectrum of VIa showed the molecular ion at *m/e* 580 (9%) followed by ions corresponding to successive loss of the carbonyls and a C_5H_4Fe fragment (*m/e* 404 (100%)). Peaks at *m/e* 302(29%) and 226(8%) corresponding to subsequent loss of PhC_2H or PhC_2Ph were also observed. The IR spectrum showed $\nu(C{\equiv}O)$ at 2005 and 1955 cm^{-1}, and the ^1H NMR spectrum spectrum showed the cyclopentadienyl proton signals at δ 4.70 and 4.62 ppm as two singlets. The elemental analysis and these data indicate structure VIa. The complexes VIb and VIc were also obtained by reaction 2 from IIb or IIc and IVa. The analysis and the ^1H NMR and IR spectral data are shown in Table 1.

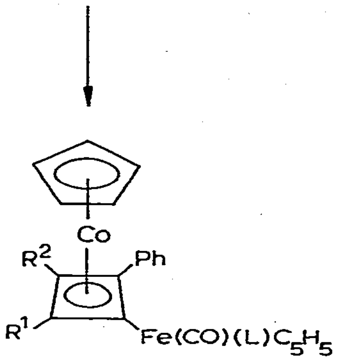
π-$C_5H_5Co(PPh_3)(R^1C{\equiv}CR^2)$ + π-$C_5H_5Fe(CO)(L)C{\equiv}CPh$

(II) (IV)

IIa; R^1, R^2 = Ph
IIb; R^1 = Ph, R^2 = CO_2CH_3
IIc; R^1, R^2 = CO_2CH_3

IVa; L = CO
IVb; L = PPh_3

(2)



VIa; R^1, R^2 = Ph, L = CO
VIb; R^1 = Ph, R^2 = CO_2CH_3, L = CO
VIc; R^1, R^2 = CO_2CH_3, L = CO
VId; R^1 = Ph, R^2 = CO_2CH_3, L = PPh_3

The triphenylphosphine derivative VId was obtained by using IVb in reaction 2 and could not be prepared from VIb and PPh_3 either thermally or photochemically. The downfield signal (δ 4.82 ppm) of the C_5H_5 protons of VId appeared as a doublet (*J*(PH) 1.2 Hz). This indicates that the downfield signals of the C_5H_5 rings in VIa—VIc (around δ 4.7 ppm) correspond to the ones attached to the Fe atoms and the upper field signals (around δ 4.6 ppm) to the ones attached to the Co atom.

Similarly, the nickel derivatives VII were prepared by the reaction 3 using the nickel ethynyl complexes V. In contrast to reaction 2, in reaction 3 the triphenylcyclobutadiene derivative VII (R^1, R^2, R^3 = Ph) could not be formed.

TABLE 1

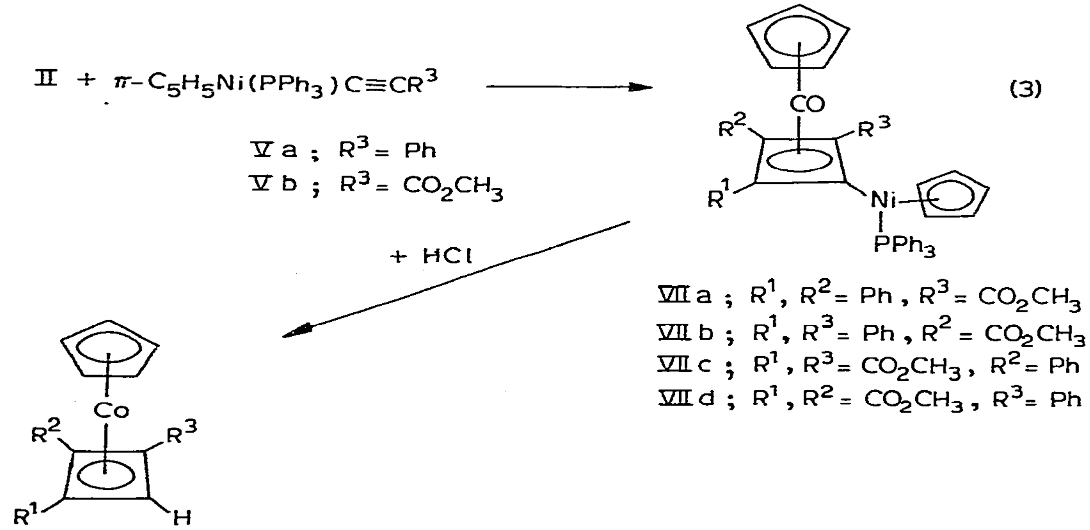
ANALYTICAL DATA AND SOME PHYSICAL CHARACTERISTICS OF THE PRODUCTS

Compound	Analysis found (calcd.) (%)				M.p. (°C)	M^+ (*m/e*)	^{1}H NMR δ (in CDCl$_3$)		ν(C≡O) (KBr) (cm^{-1})
	C	H	Co	Fe or Ni			C$_5$H$_5$	CH$_3$O and other signals	
VIa	69.69 (70.38)	4.34 (4.34)	8.9 (10.1)	9.2 (9.6)	180–182	580	4.70s 4.62s		2005 1955
VIb	63.88 (64.08)	4.14 (4.11)	9.6 (10.5)	9.7 (9.9)	194–195	562	4.79s 4.62s	3.59s	2005 1970 1958 ^{a}
VIc	58.36 (57.40)	4.01 (3.88)	—	9.8 (10.3)	oil	544	4.83s 4.72s	3.62s	2005 1970
VId	70.88 (70.87)	4.91 (4.81)	7.3 (7.4)	6.7 (7.0)	185–187		4.82d 4.64s (*J*(PH) 1.2 Hz)	3.79s 3.70s	1952
VIIa	73.17 (73.23)	5.21 (5.18)	—	7.7 (7.6)	186–187.5		5.38s 4.60s	3.68s	
VIIb	—	—	—	—	— ^{b}		5.37s 4.54s	3.66s	
VIIc	66.75 (66.96)	4.84 (4.82)	7.8 (7.8)	8.0 (7.8)	187–188		5.32s 4.62s	3.68s	
VIId	67.37 (66.96)	5.00 (4.82)	8.0 (7.8)	8.2 (7.8)	195–196		5.32s 4.61s	3.70s 3.68s	
Xa	67.22 (66.96)	4.86 (4.82)	8.4 (7.8)	8.2 (7.8)	149–152	752	5.10s 4.42s	3.72s 3.55s 1.54d (*J*(PH) 0.7 Hz)	
Xb	62.47	4.86	9.3	7.2	182–185	734	5.18s 4.50s	3.75s 3.70s 3.33s 1.51d (*J*(PH) 0.7 Hz)	

^{a} 2026, 1970 in CH$_2$Cl$_2$ solution. ^{b} Not isolated.

There is no clear evidence to account for the difference in reactivity of IIa—IVa and IIa—Va, but this may arise partly from the difference in size of the π-$C_5H_5Ni(PPh_3)$ and π-$C_5H_5Fe(CO)_2$ moieties, and partly from the difference in electronic character [7].

Treatment of IIa with Vb at room temperature for 20 h gave VIIa, whereas IIb with Va under the same conditions gave VIIa and VIIb as an inseparable mixture. The isomer ratio VIIa/VIIb was estimated to be 55 : 45 from the height of their NMR signals. When the reaction was carried out at 70°C, the ratio changed to 70 : 30, showing that the formation of the isomer VIIa is favoured at higher temperature. When IIb reacted with Vb at 70°C, only the symmetrical isomer VIIc was formed. The unsymmetrical isomer VIId was obtained from IIc and Va. The NMR spectrum of VIIc showed its carbomethoxy protons at δ 3.68 as a singlet and those of VIId appeared at δ 5.32 and 4.61 as two different signals. The cyclopentadienyl proton signals of the complexes VII appeared at δ 5.32—5.38 and δ 4.54—4.62 ppm as two singlets assignable to C_5H_5Ni and C_5H_5Co, respectively.



V a ; R^3 = Ph
V b ; R^3 = CO_2CH_3

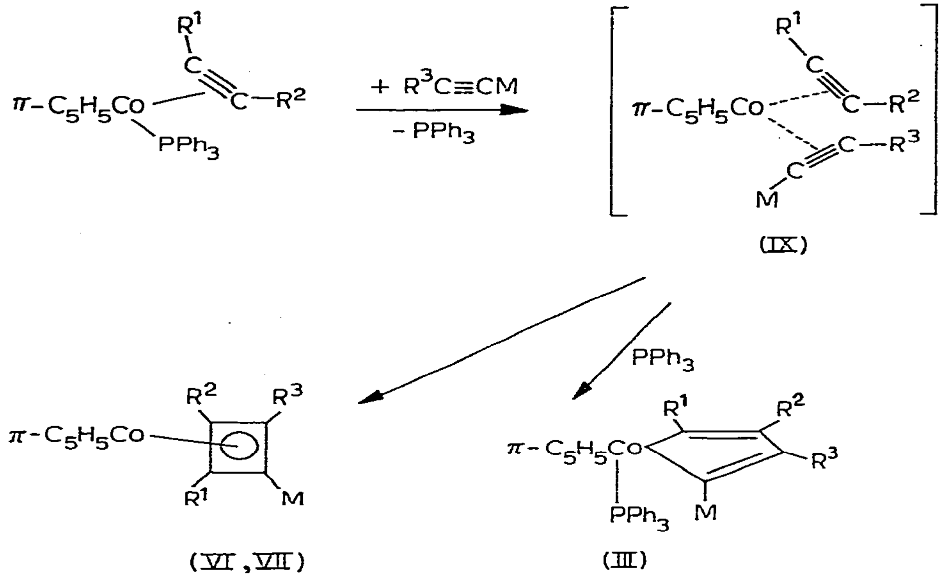
VII a ; R^1, R^2 = Ph , R^3 = CO_2CH_3
VII b ; R^1, R^3 = Ph , R^2 = CO_2CH_3
VII c ; R^1, R^3 = CO_2CH_3 , R^2 = Ph
VII d ; R^1, R^2 = CO_2CH_3 , R^3 = Ph

VIII a ; R^1 , R^2 = Ph , R^3 = CO_2CH_3
VIII b ; R^1 , R^3 = Ph , R^2 = CO_2CH_3
VIII c ; R^1 , R^3 = CO_2CH_3, R^2 = Ph
VIII d ; R^1 , R^2 = CO_2CH_3 , R^3 = Ph

The nickel—carbon bonds in VII were readily cleaved by HCl to give cyclobutadiene complexes VIII. Among them only VIIIc was obtained in crystalline form. The mass spectrum of VIIIc showed the molecular ion at *m/e* 368(100%, calcd. 368), ions of $(M - HC{\equiv}CCO_2CH_3)^+$ and $(M - PhC{\equiv}CCO_2CH_3)^+$ at *m/e* 284(5%) and 203(7%), and no ion corresponding to the loss of a PhC≡CH fragment. These data support structure VIIIc. The compounds VIIIa, VIIIb and VIIId were identified by means of their IR, NMR and mass spectra.

The iron—carbon bonds in VI are difficult to cleave with HCl. For example, the cleavage of VIc was incomplete after 24 h at 50°C. Nevertheless, VIb and VId could be converted to VIIIb and VIIId, respectively. Thus structure VIb could be assigned to the symmetrical one.

It may well be considered that the formation of VI and VII in these reactions proceeds via cobaltacyclopentadiene type intermediates III. However, attempts to isolate such complexes from the reactions failed, although III may not be so unstable as to preclude its isolation if it is formed. Known cobaltacyclopentadiene complexes generally require thermolysis above 200°C for conversion to the corresponding cyclobutadiene complexes [8].



(4)

On the other hand, the possibility of direct formation of the cyclobutadiene complexes from IX cannot be eliminated. A similar intermediate, [π-C_5H_5Co-(tolan)(isocyanide)], has been proposed for the reaction of IIa with RNC [9]. Interestingly, Stone et al. isolated a bis(acetylene) complex, π-$C_5H_5MoCl(CF_3$-$C_2CF_3)_2$, as a precursor for a molybdenacyclopentadiene complex, π-C_5H_5MoCl-$(PPh_3)(RC_2R)_2$ [10]. We propose that the first step of these reactions is the substitution of the PPh_3 ligand in II by the ethynyl complex to give IX. The latter might be competitively converted to III by combination with the phosphine or, to the cyclobutadiene complex by coupling of the acetylenes.

In the case of the reaction of IIc with Va, VIId was a minor product besides unknown Xa (31% yield), and the reaction of IIc with Vb gave unknown Xb (40%), rather than the expected VII (R^1, R^2, R^3 = CO_2CH_3). The mass spectra and the analyses indicate that the compositions of Xa and Xb are the same as those of VIId and VII (R^1, R^2, R^3 = CO_2CH_3), respectively. Xa and Xb, by treatment with HCl, produced no isolable products. X-ray diffraction studies will be carried out on these.

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 done by the atomic absorption method. Infrared spectra were recorded on a Shimazu IR-27G spectrophotometer. ^{1}H NMR spectra were obtained on JEOL L-60HL or Varian HA-100B spectrometers using tetramethylsilane as an internal reference. Mass spectra were measured on a Niphondenshi JPS-IS mass spectrometer with direct inlet system at 75 eV electron energies. The ethynyl complexes, π-$C_5H_5Ni(PPh_3)C{\equiv}CR$ (R = Ph, CO_2CH_3) [11] and π-$C_5H_5FeCO(L)C{\equiv}CPh$ (L = CO, PPh_3) [12], and π-$C_5H_5Co(PPh_3)_2 \cdot C_6H_6$ [13] were prepared according to published methods.

Preparation of π-$C_5H_5Co(PPh_3)(CH_3O_2CC{\equiv}CCO_2CH_3)$

To a solution of π-$C_5H_5Co(PPh_3)_2 \cdot C_6H_6$ (2.35 g, 3.2 mmol) in benzene (50 ml) was added dropwise a solution of $CH_3O_2CC{\equiv}CCO_2CH_3$ (1 g, 7 mmol) in benzene (20 ml) at room temperature with stirring. After standing overnight at room temperature, the reaction mixture was chromatographed on alumina (2.5 cm × 15 cm). After the column had been thoroughly eluted with benzene, a chocolate brown solution was eluted with 5 : 1 benzene/ethyl acetate. Concentration of the solution and addition of hexane gave chocolate-brown crystals (0.93 g, 55% yield based on Co). M.p. 147—148°C. Found: C, 65.73; H, 4.78. $C_{29}H_{26}O_4PCo$ calcd.: C, 65.91; H, 4.96%. Mol. wt. 522 (calcd. 528) by vapor pressure osmometry in benzene. IR (in nujol) $\nu(C{\equiv}C)$ 1822 cm^{-1}, and ^{1}H NMR (in C_6D_6) δ 4.70 (C_5H_5) and 3.40 (OCH_3).

IIb and IIc were prepared similarly [2].

Preparation of VIa

The compounds IIa (0.43 g, 0.76 mmol) and IVa (0.26 g, 0.9 mmol) were dissolved in benzene (40 ml) and stirred for two days at room temperature. The color of the reaction mixture changed from red to brown. After evaporation of the solvent, the reaction mixture was chromatographed on a Florisil column. From a yellow band eluted with 1 : 1 hexane/benzene orange crystals of VIa (32 mg, 10% yield from IIa) were obtained, and from a trailing brown band III (R, R′ = Ph) (40 mg) was obtained as brown crystals. From an orange band eluted with benzene a small amount of IVb was obtained.

Preparation of VIIc

The compounds IIb (0.21 g, 0.38 mmol) and Vb (0.18 g, 0.38 mmol) were heated in benzene (13 ml) at 60°C for 10 h with stirring. After evaporation of the solvent, the residue was chromatographed on an alumina column (1.5 cm × 10 cm). A yellow-brown solution was eluted with 6 : 1 benzene/ether. After concentration, addition of hexane gave dark brown needles of VIIc (97.3 mg, 34% yield).

All cyclobutadiene complexes in Table 1 except VIa and VIIa were prepared similarly. VIIa was obtained by a similar procedure at room temperature.

Reaction of IIc with Va

The compounds IIc (0.212 g, 0.40 mmol) and Va (0.344 g, 0.71 mmol) were heated in benzene (12 ml) at 70°C for 8 h. The reaction mixture was concentrated to ca. 5 ml under water vacuum and chromatographed on alumina. After the column was washed with benzene, the dark brown band was eluted with 7 : 1 benzene/ethyl acetate. Dark brown crystals of Xa (93.3 mg) were obtained.

From a yellow-brown band eluted with the same mixture (2 : 1), light yellow-brown crystals of VIId (20 mg, 7% yield from IIc) were obtained.

Cleavage of VIIc with HCl

To a methylene chloride solution (6 ml) of VIIc (87 mg, 0.12 mmol), methanol (1 ml) and acetyl chloride (0.5 ml) were added at room temperature. The brown solution immediately turned pale yellow. After stirring for 15 min the reaction mixture was evaporated under water vacuum and the residual yellow-to-orange crystals were dissolved in the minimum volume of methylene chloride and chromatographed on an alumina column. A yellow band which was eluted with 1 : 1 benzene/methylene chloride was collected. Evaporation of the solvent gave yellow-orange crystals (13.5 mg, 25% yield). M.p. 158–159°C. Found: C, 61.66; H, 4.64. $C_{19}H_{17}O_4Co$ calcd.: C, 61.98; H, 4.64%. $M^+ m/e$ 368 (calcd.: 368) and ^1H NMR spectrum: δ 4.90(H), 4.73(C_5H_5), 3.66(2CH_3O).

VIIIa, M^+ m/e 286, ^1H NMR spectrum: δ 4.85(H), 4.73(C_5H_5), 3.66 (CH_3O). VIIIb, M^+ m/e 386, ^1H NMR: δ 4.90 (H), 4.64 (C_5H_5), 3.86 (CH_3O). VIIId, M^+ m/e 368, ^1H NMR: δ 4.92 (H), 4.82 (C_5H_5), 3.84 and 3.73 (2CH_3O).

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