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Reactions of cobaltacyclopentadiene complexes with organic azides directed toward synthesis of highly substituted pyrroles

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Abstract

The reactions of the cobaltacyclopentadiene complexes $(\eta^5\text{-}C_5H_5)(PPh_3)\overline{Co(-CR^1{=}CR^2{-}CR^3{=}C}R^4)$ (I) with organic azides were investigated. The complex Ia ($R^1 = R^2 = R^3 = R^4 = Ph$) reacts with phenyl azide at 80 °C to give 1,2,3,4,5-pentaphenylpyrrole in 73% yield. Similarly, the reactions of Ia with benzoyl and t-butoxycarbonyl azides give 1-benzoyl- and 1-(t-butoxycarbonyl)-2,3,4,5-tetraphenylpyrroles in 41 and 64% yields, respectively, but reaction with *p*-toluenesulfonyl azide gives 2,3,4,5-tetraphenylpyrrole and 3,4,5,6-tetraphenylpyridazine in 35 and 45% yields, respectively, in place of the expected 1-(*p*-toluenesulfonyl)-2,3,4,5-tetraphenylpyrrole. The reaction of Ic ($R^1 = R^4 = Ph$, $R^2 = R^3 = CO_2CH_3$) with phenyl azide at 130 °C gives 1,2,5-triphenyl-3,4-bis(methoxycarbonyl)pyrrole (IIc) and 2,5-diphenyl-3,4-bis(methoxycarbonyl)pyrrole (Vb) in 22 and 15% yields, respectively. The reaction of Ic with benzenesulfonyl azide gives only Vb in 57% yield. In the reaction of Id ($R^1 = R^3 = Ph$, $R^2 = R^4 = CO_2CH_3$) with benzenesulfonyl azide, Vb was unexpectedly obtained in 26% yield, together with 2,4-diphenyl-3,5-bis(methoxycarbonyl)pyrrole (Vc, 30%), which suggests that a skeletal rearrangement of the metallacycle IXd to IXc occurs during the reaction. The reaction of Ic or Id with benzoyl azide at 130 °C gives the 2(1*H*)-pyridinone derivatives VIIIa (82%) and VIIIb (53%), which are the products of the reaction of the corresponding cobaltacyclpentadiene with phenyl isocyanate generated by the rearrangement of benzoyl nitrene, in place of the expected, corresponding pyrrole.

Introduction

Transition metal-mediated cyclization reactions have received much attention in organic synthesis [1]. Metallacyclopentadiene complexes are important intermediates in the catalytic cyclization involving alkynes as cycloaddends, and are useful starting materials for preparing five- or six-membered cyclic organic compounds. It has been reported that the cobaltacyclopentadiene complexes $(\eta^5\text{-}C_5H_5)$-

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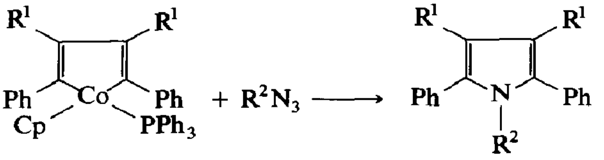
$(\mathrm{PPh_3})\overline{\mathrm{Co(-CR^1{=}CR^2{-}CR^3{=}C}}\mathrm{R^4})$ (I) are readily prepared by the reaction of an alkyne with (η^5-C_5H_5)Co(PPh_3)$_2$ or (η^5-C_5H_5)Co(PPh_3)(alkyne) [2a,b]. The products react with various unsaturated compounds to generate homo- or hetero-cyclic organic compounds [2c–2i]. Pyrroles such as 1,2,3,4,5-pentaphenylpyrrole (IIa) and 1,2,5-triphenyl-3,4-dimethylpyrrole (IIb) are obtained by the reactions of the complexes Ia ($R^1 = R^2 = R^3 = R^4 = Ph$) and Ib ($R^1 = R^4 = Ph$, $R^2 = R^3 = CH_3$) with nitrosobenzene [2d]. The reaction proceeds by the replacement of the cobalt atom in the metallacycle with phenyl nitrene generated from nitrosobenzene. In order to establish a more convenient method of synthesis of highly substituted pyrroles from the cobaltacyclopentadiene complexes (I) we examined the reaction in which an organic azide was used as a nitrene precursor. Pyrrole derivatives have been obtained from classical condensation reactions such as the Knorr and the Paal–Knorr syntheses [3]. We report here the transition metal-mediated cyclization of two alkynes and a nitrene to form a pyrrole product.

Results and discussion

When a solution of Ia (0.5 mmol) and phenyl azide (4.5 mmol) in benzene was refluxed for 1 h under nitrogen, a blue-green solution resulted. From the reaction mixture was isolated 1,2,3,4,5-pentaphenylpyrrole (IIa) in 73% yield, together with a small amount of the tetrazene complex (η^5-C_5H_5)Co(PhN=N–N=NPh) (6%) [4]. Similarly, the reaction of Ib afforded 1,2,5-triphenyl-3,4-dimethylpyrrole (IIb, 42%). The yields of IIa and IIb were higher than those obtained when nitrosobenzene was used as the phenyl nitrene precursor [2d].

The reaction of Ia with benzoyl azide at 80 °C gave 1-benzoyl-2,3,4,5-tetraphenylpyrrole (IIIa, 41%), together with the η^4-cyclobutadiene complex (η^5-C_5H_5)Co(η^4-C_4Ph_4) (20%) [5] and the iminophosphorane $Ph_3P{=}NCOPh$ (56%). Similarly, 1-benzoyl-2,5-diphenyl-3,4-dimethylpyrrole (IIIb, 46%) was obtained from Ib and benzoyl azide. The IR spectra of IIIa and IIIb show ν(CO) bands at 1700 and 1695 cm^{-1}, respectively, and the ^1H NMR spectrum of IIIb shows one singlet at δ 2.06, attributable to two equivalent methyl groups. These spectra are consistent with the *N*-benzoylpyrrole structure for IIIa and IIIb.

t-Butoxycarbonyl azide was also found to react with Ia at 80 °C to give 1-(t-butoxycarbonyl)-2,3,4,5-tetraphenylpyrrole (IVc, 64%) and the iminophosphorane $Ph_3P{=}NCO_2$-t-Bu (69%). Similarly, 1-(methoxycarbonyl)- and 1-(ethoxycarbonyl)-2,3,4,5-tetraphenylpyrroles (IVa and IVb) were obtained from the reactions with methoxycarbonyl and ethoxycarbonyl azides, respectively. The results are listed in Table 1.

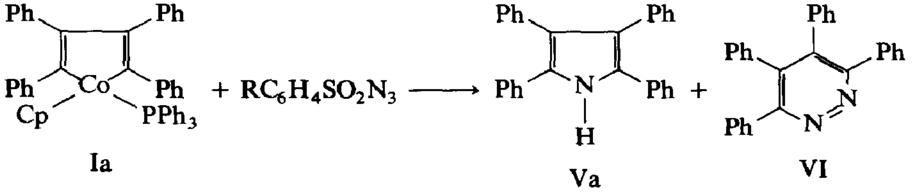


(1)

(Ia: $R^1 = Ph$;
Ib: $R^1 = Me$)

(II: $R^2 = Ph$;
III: $R^2 = PhCO$;
IV: $R^2 = R^3OCO$)

In contrast to the cases mentioned, the reaction of Ia with *p*-toluenesulfonyl azide gives 2,3,4,5-tetraphenylpyrrole (Va) and 3,4,5,6-tetraphenylpyridazine (VI) in place of the expected 1-(*p*-toluenesulfonyl)-2,3,4,5-tetraphenylpyrrole. Thus, when a solution of Ia (1 mmol) and *p*-toluenesulfonyl azide (ca. 4 mmol) was refluxed in benzene for 3 h, a red brown solution and a brick-red precipitate resulted. From the solution were isolated Va (35%) and VI (45%) together with the tetrazene complex (η^5-C_5H_5)Co($RSO_2N_4SO_2R$) (R = *p*-$CH_3C_6H_4$, 10%) and the iminophosphorane $Ph_3P{=}NSO_2C_6H_4CH_3$ (84%). These products were identifed from their IR, NMR, and mass spectra and by elemental analysis (see Table 2). The precipitate (VII, 200 mg) is poorly soluble in all organic solvents except for dichloromethane. Recrystallization of VII from dichloromethane gave brick-red crystals. The NMR spectrum showed broad peaks, which suggests that the compound is paramagnetic. Although its analysis approximates to $(C_5H_5)Co(C_7H_7SO_2)_2$, it is clearly more complex. It seems that the precipitate VII is closely related to the formation of Va and VI, which both contain nitrogen atoms but no sulfonyl groups. The formation of VI from Ia is of great interest, because the cobalt atom in the metallacycle is formally replaced by dinitrogen. It is known that organic azides react with transition metal complexes to give a variety of products, depending on the nature of azides—primarily determined by the solvent employed and by the character of the organic residue in the azides [6]. Notable among the products , in connection with the formation of VI in the present reaction, are the dinitrogen complex, *trans*-$Ir(PPh_3)_2(N_2)Cl$ [6d], and the diazene complexes, $Fe_2(CO)_6(PhN_2Ph)$ [6e] and $Rh_2(Ph_2PCH_2CH_2PPh_2)_4(RSO_2N_2SO_2R)$ (R = *p*-$CH_3C_6H_4$) [6f]. Either dinitrogen or the diazene ($RSO_2N_2SO_2R$) ligand are formed first, from the sulfonyl azide in the present reaction system, which then displaces the cobalt atom from the metallacycle. As shown in Scheme 1, displacement by a dinitrogen ligand generates the pyridazine VI directly (path a). Displacement by the diazene ligand provides bis(*p*-toluenesulfonyl)-pyridazine, which undergoes desulfonylation to form VI (path b). The formation of the precipitate VII tends to favor path b. The *N*-unsubstituted pyrrole Va is probably formed by the elimination of the sulfonyl group from *N*-sulfonylpyrrole. 2, sch 1



(2)

The reactions of azides with cobaltacyclopentadienes having a methoxycarbonyl group as the substituent take place at rather high temperatures (> 130 °C) and not at 80 °C which somewhat limits their synthetic use. When the reaction of Ic ($R^1 = R^4 = Ph$, $R^2 = R^3 = CO_2CH_3$) with phenyl azide was carried out in chlorobenzene under reflux, 2,5-diphenyl-3,4-bis(methoxycarbonyl)pyrrole (Vb, 15%) was obtained together with the expected product 1,2,5-triphenyl-3,4-bis(methoxycarbonyl)pyrrole (IIc, 22%), showing that the N–Ph bond had been cleaved during the reaction. The reaction of Ic with ethoxycarbonyl azide or benzenesulfonyl azide gives the pyrrole Vb in 35 or 57% yield, respectively, without the corresponding *N*-substituted pyrrole. In the reaction with benzenesulfonyl azide, no corresponding

Table 1

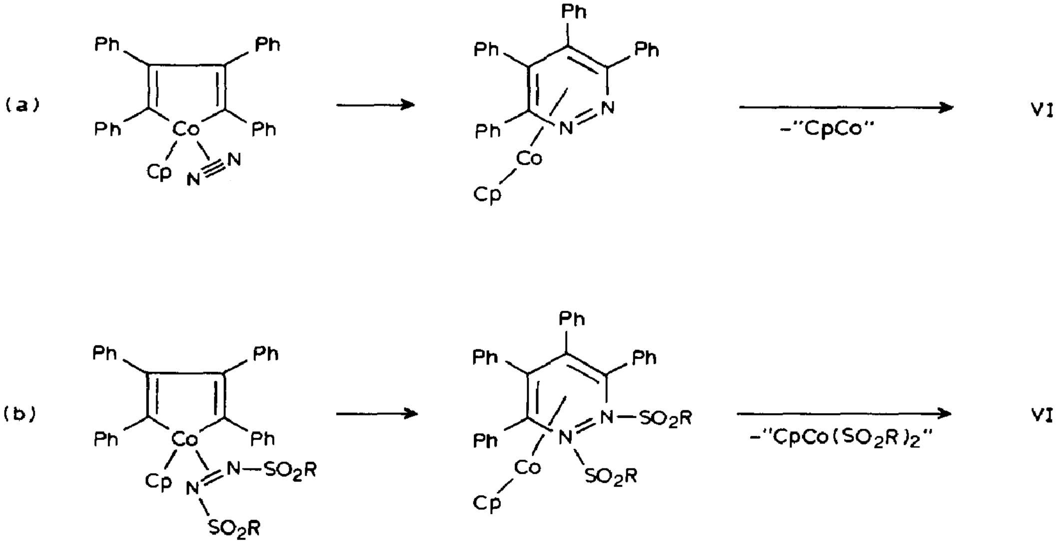
Reaction of organic azides with the cobaltacyclopentadiene complexes $(\eta^5\text{-}C_5H_5)(PPh_3)\overline{Co(-CR^1{=}CR^2-CR^3{=}C}R^4)$ (I)

I	Azide	Azide/I	Temp. (°C)	Time (h)	Products
Ia ($R^1 = R^2 = R^3 = R^4 = Ph$)	PhN_3	9/1	80	1	1,2,3,4,5-pentaphenylpyrrole (IIa, 73%)
	$PhCON_3$	7/1	80	3	1-benzoyl-2,3,4,5-tetraphenylpyrrole (IIIa, 41%)
	$MeOCON_3$	10/1	80	2	1-(methoxycarbonyl)-2,3,4,5-tetraphenylpyrrole (IVa, 22%)
	$EtOCON_3$	9/1	80	2	1-(ethoxycarbonyl)-2,3,4,5-tetraphenylpyrrole (IVb, 30%)
	$t\text{-}BuOCON_3$	7/1	80	3	1-(t-butoxycarbonyl)-2,3,4,5-tetraphenylpyrrole (IVc, 64%)
	$p\text{-}MeC_6H_4SO_2N_3$	4/1	80	3	2,3,4,5-tetraphenylpyrrole (Va, 35%)/ 3,4,5,6-tetraphenylpyridazine (VI, 45%)
		3/1	110	1	Va (35%)/VI (29%)
	$PhSO_2N_3$	5/1	80	3	Va (34%)/VI (54%)
Ib ($R^1 = R^4 = Ph$, $R^2 = R^3 = Me$)	PhN_3	9/1	80	1	1,2,5-triphenyl-3,4-dimethylpyrrole (IIb, 42%)
	$PhCON_3$	10/1	80	3	1-benzoyl-2,5-diphenyl-3,4-dimethylpyrrole (IIIc, 46%)
Ic ($R^1 = R^4 = Ph$, $R^2 = R^3 = CO_2Me$)	PhN_3	9/1	130	2	1,2,5-triphenyl-3,4-bis(methoxycarbonyl)pyrrole (IIc, 22%)/ 2,5-diphenyl-3,4-bis(methoxycarbonyl)pyrrole (Vb, 15%)
	$EtOCON_3$	9/1	130	3	Vb (35%)
	$PhSO_2N_3$	5/1	130	2	Vb (57%)
	$PhCON_3$	13/1	130	3	1,3,6-triphenyl-4,5-bis(methoxycarbonyl)-2(1*H*)-pyridinone (VIIIa, 82%)
Id ($R^1 = R^3 = Ph$, $R^2 = R^4 = CO_2Me$)	PhN_3	9/1	130	2	1,2,4-triphenyl-3,5-bis(methoxycarbonyl)pyrrole (IId, 7%)/2,4-diphenyl-3,5-bis(methoxycarbonyl)pyrrole (Vc, 21%)/IIc (46%)
	$PhSO_2N_3$	5/1	130	2	Vc (30%)/Vb (20%)
	$PhCON_3$	13/1	130	3	1,4,6-triphenyl-3,5-bis(methoxycarbonyl)-2(1*H*)-pyridinone (VIIIb, 53%)

Table 2

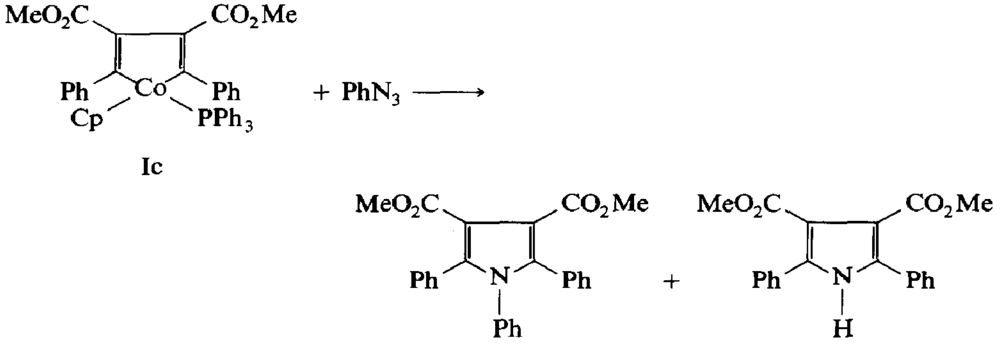
Analytical and physical data of the substituted pyrroles $\overline{NR^1-CR^2=CR^3-CR^4=CR^5}$

Pyrrole	R^1	R^2	R^3	R^4	R^5	Analysis (Found(calcd.))			m.p. (°C) [lit.]	^1H NMR
						C	H	N		
IIc	Ph	Ph	CO_2Me	CO_2Me	Ph				200–201 [196–197 [15]]	3.71(s, 2OMe), 6.7–7.3(m, 3Ph)
IId	Ph	Ph	CO_2Me	Ph	CO_2Me	75.77 (75.90	5.29 5.14	3.37 3.40)	142–143	3.35(s, OMe), 3.78(s, OMe), 7.1–7.4(m, 3Ph)
IIIa	COPh	Ph	Ph	Ph	Ph				240–241 [246–248 [13]]	
IIIb	COPh	Ph	Me	Me	Ph	85.27 (85.44	6.12 6.02	3.90 3.98)	177–179	2.06(s, 2Me), 7.0–7.6(m, 3Ph)
IVa	OCOMe	Ph	Ph	Ph	Ph	83.43 (83.89	5.44 5.40	3.29 3.26)	196(dec.)	3.46(s, Me), 6.8–7.3(m, 4Ph)
IVb	OCOEt	Ph	Ph	Ph	Ph	83.51 (83.95	5.78 5.68	3.15 3.16)	200(dec.)	0.76(t, Me), 3.95(q, OCH_2), 6.8–7.3(m, 4Ph)
IVc	$OCOCMe_3$	Ph	Ph	Ph	Ph	83.89 (84.05	6.19 6.20	2.91 2.97)	178(dec.)	1.12(s, CMe_3), 6.8–7.3(m, 4Ph)
Va	H	Ph	Ph	Ph	Ph				214–215 [215–216 [14]]	
Vb	H	Ph	CO_2Me	CO_2Me	Ph				147–149 [146–148 [16]]	3.66(2, 2OMe), 7.2–7.6(m, 2Ph), 9.09(bs, NH)
Vc	H	Ph	CO_2Me	Ph	CO_2Me	71.59 (71.63	5.10 5.11	4.04 4.18)	192–193	3.48(s, OMe), 3.59(s, OMe), 7.2–7.7(m, 2Ph), 9.66(bs, NH)



Scheme 1.

pyridazine formation was detected.

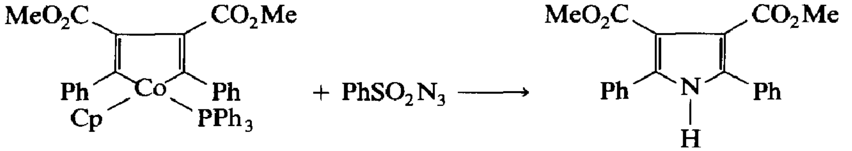


Ic

IIc

Vb

(3)



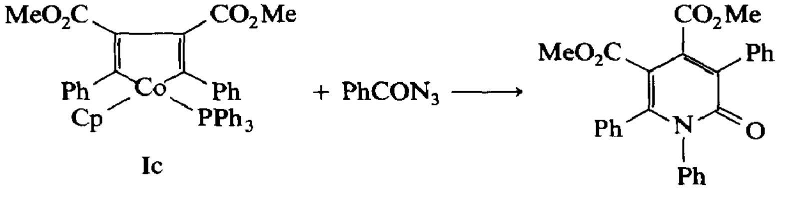
Ic

Vb

(4)

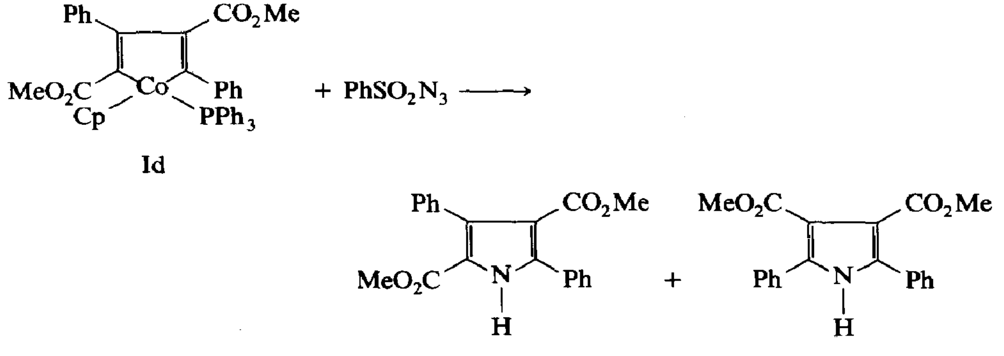
Treatment of Ic with benzoyl azide at 130 °C gave a colorless crystalline product (VIIIa, $C_{27}H_{21}NO_5$, 82%), whose molecular formula is consistent with that of the corresponding *N*-benzoylpyrrole. However, the ^1H NMR spectrum shows the presence of two kinds of methoxycarbonyl groups at δ 3.36 and 3.55, and the IR spectrum shows a strong band at 1665 cm^{-1}, suggestive of the conjugated six-membered ring lactam, along with two bands at 1745 and 1725 cm^{-1} for methoxycarbonyl grups. We assigned the structure 1,3,6-triphenyl-4,5-bis(methoxycarbonyl)-2(1*H*)-pyridinone to VIIIa, which can be obtained by the reaction of Ic with phenyl isocyanate [2e]. Similarly, the reaction of Id ($R^1 = R^3 = Ph$, $R^2 = R^4 = CO_2CH_3$) with benzoyl azide gives 1,4,6-triphenyl-3,5-bis(methoxycarbonyl)-2(1*H*)-pyridinone

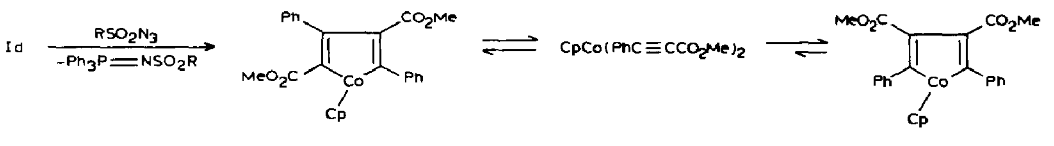
(VIIIb, 53%). The formation of VIIIa or VIIIb indicates the benzoyl nitrene generated during the early stages of the reaction rearranges to phenyl isocyanate under the reaction conditions, and so reacts with the metallacycle.


Ic + $PhCON_3$ ⟶ VIIIa (5)

$$PhCON_3 \longrightarrow [PhCO\ddot{N}:] \longrightarrow PhN{=}C{=}O \qquad (6)$$

The reaction of Id, an unsymmetrical isomer of Ic, with phenylazide was expected to give 1,2,4-triphenyl-3,5-bis(methoxycarbonyl)pyrrole (IId). However IId (7%) and 2,4-diphenyl-3,5-bis(methoxycarbonyl)pyrrole (Vc, 21%) were minor products, and a symmetrical pyrrole IIc (46%) was obtained as the major product. Similarly, the reaction of Id benzenesulfonyl azide gave a mixture of Vc (30%) and a symmetrical pyrrole Vb (20%). The formation of IIc and Vb from Id requires a skeletal rearrangement of the metallacycle. The first step for the rearrangement is probably the formation of the coordinatively unsaturated complex IXa, which is also the intermediate to the pyrrole. The azide interacts with Id as a phosphine acceptor to give IXa and $Ph_3PN_3SO_2Ph$ or Ph_3PNSO_2Ph. The metallacycle IXa can then isomerize into IXb via a bis(acetylene) intermediate (X) (Scheme 2). Such a rearrangement is unprecedented in the reactions of cobaltacyclopentadienes, but has been observed in the reactions of the iminocobaltacyclobutenes [17].


Id + $PhSO_2N_3$ ⟶ Vc + Vb (7)



Scheme 2.

Experimental

All reactions were carried out under nitrogen. Melting points were taken on a Mitamura capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on a Shimadzu IR-27G spectrophotometer. ^{1}H NMR spectra were recorded on a Varian HA-100B spectrometer with tetramethylsilane as internal reference. Mass spectra were measured on a JEOL JPS-IS mass spectrometer with a direct inlet system operating at 75 eV. The complexes $(\eta^5\text{-}C_5H_5)(PPh_3)\text{-}\overline{Co(CR_1{=}CR_2{-}CR_3{=}C}R_4)$ (I) [2b], PhN_3 [7], $PhCON_3$ [8]. EtO_2CN_3 [9], $p\text{-}CH_3C_6H_4SO_2N_3$ [10], and $PhSO_2N_3$ [11] were prepared by published procedures [2b].

Reaction of $(\eta^5\text{-}C_5H_5)(PPh_3)\overline{Co(-CPh{=}CPh{-}CPh{=}C}Ph)$ *(Ia) with phenyl azide*

A mixture of Ia (0.371 g, 0.5 mmol) and phenyl azide (0.5 ml) in benzene solution (20 ml) was refluxed for 1 h to give a blue-green solution. After removal of the solvent under reduced pressure, the residue was submitted to column chromatography on alumina (Sumitomo activated alumina KCG-30, 1.0 × 15 cm). Elution with hexane/benzene (2/1) gave 1,2,3,4,5-pentaphenylpyrrole (IIa, 0.164 g, 73%). From the brownish-red band that was eluted with dichloromethane/ethyl acetate (5/1) was obtained $(\eta^5\text{-}C_5H_5)Co(PhN{=}N{-}N{=}NPh)$ (0.010 g, 6%) [4] as brownish-red needles.

Reaction of Ia with benzoyl azide

A mixture of Ia (371 mg, 0.5 mmol) ang benzoyl azide (547 mg, 3.7 mmol) in benzene solution (20 ml) was refluxed for 3 h. After removal of the solvent, the residue was chromatographed on alumina. From the yellow fraction, eluted with hexane/benzene (2/1), was obtained $(\eta^5\text{-}C_5H_5)Co(\eta^4\text{-}C_4Ph_4)$ (47 mg, 20%) as yellow crystals [5], and the light yellow fraction, eluted with hexane/benzene (1/2), yielded 1-benzoyl-2,3,4,5-tetraphenylpyrrole (IIIa, 98 mg, 41%) as pale yellow needles. Further elution with dichloromethane/ethyl acetate (10/3) gave $Ph_3P{=}NCOPh$ (105 mg, 56%) as colorless crystals.

Reaction of Ia with t-butoxycarbonyl azide

A mixture of Ia (371 mg, 0.5 mmol) and t-butoxycarbonyl azide (0.5 ml, 3.5 mmol) in benzene solution (20 ml) was refluxed for 3 h. After removal of the solvent, the residue was chromatographed on alumina. Elution with hexane/benzene (1/1) gave 1-(t-buthoxycarbonyl)-2,3,4,5-tetraphenylpyrrole (IVc, 150 mg, 64%) as colorless crystals. Further elution with dichloromethane/ethyl acetate gave $Ph_3P{=}NCO_2\text{-}t\text{-}Bu$ (130 mg, 69%).

Reaction of Ia with p*-toluenesulfonyl azide*

A mixture of Ia (742 mg, 1 mmol) and *p*-toluenesulfonyl azide (773 mg, 3.9 mmol) in benzene solution (40 ml) was refluxed for 3 h to give a reddish-brown solution and a brick-red precipitate. The precipitate was filtered off, washed with benzene, and dried; brick-red powder (220 mg), m.p. > 175 °C (decomp.). Found: C, 51.82; H, 4.32; S, 14.63. $C_{19}H_{19}CoO_4S_2$ calcd.: C, 52.53; H, 4.41; S, 14.76%.

The filtrate was evaporated in vacuo and chromatographed on alumina. Elution with hexane/benzene (1/1) and with benzene gave 3,4,5,6-tetraphenylpyridazine

(VI, 174 mg, 45%) and 2,3,4,5-tetraphenylpyrrole (Va, 130 mg, 35%), respectively. VI; colorless crystals, m.p. 192–193 °C [lit. 194 °C [12]], $M^+ = 384$. Found: C, 87.48; H, 5.32; N, 6.73. $C_{28}H_{20}N_2$ calcd.: C, 87.47; H, 5.24; N, 7.29%. Further elution with dichloromethane/ethyl acetate (4/1) gave $Ph_3P{=}NSO_2C_6H_4CH_3$ (360 mg, 84%). From the brown fraction, eluted with dichloromethane/ethyl acetate (2/1), was obtained $(\eta^5\text{-}C_5H_5)Co(RSO_2N_4SO_2R)$ ($R = p\text{-}CH_3C_6H_4$, 50 mg, 10%); brown crystals, m.p. 168 °C (decomp.). Found: C, 46.47; H, 3.90; N, 11.49. $C_{19}H_{19}CoN_4O_4S_2$ calcd.: C, 46.53; H, 3.90; N, 11.42%. NMR; δ 2.40 ($2CH_3$), 5.94 (s, C_5H_5), 7.30 (d, C_6H_4), 7.99 (d, C_6H_4).

Reaction of Ic ($R^1 = R^4 = Ph$, $R^2 = R^3 = CO_2CH_3$) with benzoyl azide

A mixture of Ic (353 mg, 0.5 mmol) and benzoyl azide (1 g) in chlorobenzene solution (20 ml) was refluxed for 4 h. After removal of the solvent from the resulting brown solution, the residue was chromatographed on alumina. Elution with benzene/ethyl acetate (20/1–10/1) gave 1,3,6-triphenyl-4,5-bis(methoxycarbonyl)-2(1*H*)-pyridinone (VIIIa, 180 mg, 82%); colorless crystals, m.p. 224–225 °C [lit. 224–225 °C [2e]].

Reaction of Ic with benzenesulfonyl azide

A mixture of Ic (306 mg, 0.4 mmol) and benzenesulfonyl azide (500 mg) in chlorobenzene solution (20 ml) was refluxed for 2 h. After removal of the solvent from the resulting brown solution under reduced pressure, the residue was chromatographed on alumina. Elution with benzene/ethyl acetate (25/1) gave 2,5-diphenyl-3,4-bis(methoxycarbonyl)pyrrole as colorless crystals (Vb, 77 mg, 57%).

Reaction of Id with benzenesulfonyl azide

A mixture of Id (353 mg, 0.5 mmol) and benzenesulfonyl azide (570 mg, 3.1 mmol) in chlorobenzene solution (20 ml) was refluxed for 2 h. After removal of the solvent, the residue was chlomatographed on alumina. Elution with benzene/ethyl acetate (50/1) gave 2,4-diphenyl-3,5-bis(methoxycarbonyl)pyrrole (Vc, 50 mg, 30%) as colorless crystals. Further elution with benzene/ethyl acetate (25/1) gave Vb (33 mg, 20%).

References

1 (a) K.P.C. Vollhardt, Acc. Chem. Res., 10 (1977) 1. (b) K.P.C. Vollhardt, Angew. Chem., Int. Ed. Engl., 23 (1984) 539. (c) E. Mueller, Synthesis, (1974) 761. (d) P.M. Maitlis, Acc. Chem. Res., 9 (1976) 93.

2 (a) H. Yamazaki and N. Hagihara, J. Organomet. Chem., 21 (1970) 431. (b) H. Yamazaki and Y. Wakatsuki, J. Organomet. Chem., 139 (1977) 157. (c) Y. Wakatsuki and H. Yamazaki, J. Chem. Soc., Chem. Commun., (1973) 280. (d) Y. Wakatsuki, T. Kuramitsu, and H. Yamazaki, Tetrahedron Lett., (1974) 4549. (e) P. Hong and H. Yamazaki, Synthesis, (1977) 50. (f) Y. Wakatsuki and H. Yamazaki, J. Organomet. Chem., 139 (1977) 169. (g) Y. Wakatsuki and H. Yamazaki, J. Chem. Soc., Dalton Trans., (1978) 1278. (h) H. Yamazaki and Y. Wakatsuki, Bull. Chem. Soc. Jpn., 52 (1979) 1239. (i) K. Yasufuku, A. Hamada, K. Aoki and H. Yamazaki, J. Amer. Chem. Soc., 102 (1980) 4363.

3 (a) R.J. Sunderg, Comprehensive Heterocyclic Chemistry, Pergamon Press, Oxford, Vol. 4, 1984, p. 313. (b) R.M. Acheson, An Introduction to the Chemistry of Heterocyclic Compounds, Wiley, New York, 1976, p. 113.

4 S. Otsuka and A. Nakamura, Inorg. Chem., 7 (1968) 2542.

5 H. Yamazaki and N. Hagihara, J. Organomet. Chem., 7 (1967) p22.

6 (a) S. Cenini, M. Piezzotti, F. Porta and G. LaMonica, J. Organomet. Chem., 88 (1975) 237 and ref. therein. (b) K. Burgess, B.F.G. Johnson, J. Lewis, and P.R. Raithby, J. Organomet. Chem., 224 (1982) C40. (c) M.D. Curtis, J.J. D'Errico, and W.M. Butler, Organometallics, 6 (1987) 2151. (d) J.P. Collman, M. Kubota, F.D. Vastine, J.Y. Sun, and J.W. Kang, J. Amer. Chem. Soc., 90 (1968) 5430. (e) M. Dekker and G.R. Knox, Chem. Commun., (1967) 1243. (f) W. Beck, W. Rieder, S. Cenini, F. Porca, and G. LaMonica, J. Chem. Soc., Dalton Trans., (1974) 298.

7 R.O. Lindsay and C.F.H. Allan, Organic Syntheses, Wiley, New York, 1955, Coll. Vol. 3, p. 710.

8 E.W. Barrett and C.W. Porter, J. Am. Chem. Soc., 63 (1941) 3434.

9 M.O. Forster and H.E. Fierz, J. Chem. Soc., 93 (1908) 72.

10 M. Regitz, J. Hocker, and A. Liedhegener, Organic Syntheses, Wiley, New York, 1973, Voll. Vol. 5, p. 179.

11 J.E. Leffler and Y. Tsuno, J. Org. Chem., 28 (1963) 190.

12 A.M. Comrie, J. Chem. Soc., (C), (1971) 2807.

13 A. Ranjen, Bull. Chem. Soc. Fr., (1971) 2063.

14 C.D. Hurd and C.M. Buess, J. Am. Chem. Soc., 78 (1956) 5667.

15 H.W. Heine and R. Peavy, Tetrahedron Lett., (1965) 3123.

16 A. Padwa, M. Dharan, J. Smolanoff, and S.I. Wetmore Jr., J. Am. Chem. Soc., 95 (1973) 1945.

17 Y. Wakatsuki, S. Miya, H. Yamazaki, and S. Ikuta, J. Chem. Soc., Dalton Trans., (1986) 1201.