Cobalt Metallacycles. Part 15.[1] Regioselective Formation and Rearrangement of 4-Iminocobaltacyclobutene Complexes

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The reaction of $[Co(\eta^5\text{-}C_5H_5)(PPh_3)(R^1C{\equiv}CR^2)]$ (**1**) (R^1 = H, Me, or Ph; R^2 = Ph, CO_2Me, or CN) with isocyanides R^3NC (R^3 = Ph, $p\text{-}MeC_6H_4$, or $2,6\text{-}Me_2C_6H_3$) gives the 1-(η^5-cyclopentadienyl)-4-imino-1-(triphenylphosphine)cobaltacyclobutene complexes $[\overline{Co\{C(R^1){=}C(R^2)C}(=NR^3)\}(\eta^5\text{-}C_5H_5)(PPh_3)]$ (**3**). When (**1**) containing an unsymmetrical acetylene is used, the reaction is highly regioselective as only one of the two possible regioisomers has been detected. It has been concluded that the regioselectivity originates not from a steric effect but from an electronic requirement such that the acetylenic carbon with an electron-withdrawing substituent becomes the β carbon of the metallacycle. That this requirement leads to kinetically-controlled products has been demonstrated by thermal skeletal rearrangement of (**3bi**) (R^1 = Ph, R^2 = CO_2Me) and (**3ci**) (R^1 = Ph, R^2 = CN) to $[\overline{Co\{C(R^1){=}C(R^2)C}(=NC_6H_4Me\text{-}p)\}(\eta^5\text{-}C_5H_5)(PPh_3)]$ (**8a**) (R^1 = CO_2Me, R^2 = Ph) and (**8b**) (R^1 = CN, R^2 = Ph), respectively. These regioselectivity observations have been rationalized by *ab initio* molecular orbital calculations. The imino configuration in these complexes is *syn* with respect to the metal and the substituent on the nitrogen. Methyl iodide reacts with (**3bi**) to give a PF_6^- salt of $[\overline{Co\{C(Ph){=}C(CO_2Me)C}(NMeC_6H_4Me\text{-}p)\}(\eta^5\text{-}C_5H_5)(PPh_3)]^+$ (**9a**), where the methyl group is bonded to the nitrogen *anti* to the metal. In solution, (**9a**) isomerizes to (**9b**) at room temperature by rotation of the C=N bond. Reactions of (**3ai**) with PhC_2Ph, CO, CS_2, and MeNCS have been studied.

In earlier parts of this series we have described the facile formation of five-membered cobalt metallacycles by the reaction of acetylenes or olefins with $[Co(\eta^5\text{-}C_5H_5)(PPh_3)(R^1C{\equiv}CR^2)]$ (1) (R^1,R^2 = CO_2Me).[2,3] Isocyanide is another reactive reagent towards (1) and gives mainly a 1,4-di-iminobuta-1,3-dienecobalt complex and a 2,5-di-iminocobaltacyclopentene, together with a small amount of a 4-iminocobaltacyclobutene.[1] We are interested in the 4-iminocobaltacyclobutene complex, it being the first example of a four-membered metallacycle of a $Co(\eta^5\text{-}C_5H_5)$ group. The five-membered metallacycles containing a $Co(\eta^5\text{-}C_5H_5)$ unit display a rich chemistry and their formation, especially from two molecules of acetylene, has been investigated in detail.[4] It seemed important to extend our knowledge to the four-membered analogue by improving the preparation and to clarify the mechanism of the metallaring formation. Of particular interest is the effect of substituents on the metallaring formation: we believe it gives an important clue to understanding the fundamental nature of the reaction.

In connection with the mechanism for olefin and acetylene methathesis reactions, examples have been reported of four-membered metallacycles formed by the reaction of two unsaturated units on transition metals.[5–7] Substituent effects in such reactions, however, have not been well explored.

Two previous reactions of a specific acetylene complex with isocyanide have been reported. The first is the formation of a 4-iminoplatinacyclobutene from a cyclohexyne complex and Bu^tNC,[8] the second is the reaction of a diphenylacetylene complex of Fe^0 with Bu^tNC.[9] Closely related reactions, formation of metallacyclobutenones or metallacyclobutenethiones by bond formation between co-ordinated CO or CS with substituted acetylenes, have also been reported.[10–12]

A preliminary account of some aspects of the present work has been reported.[13]

Results and Discussion

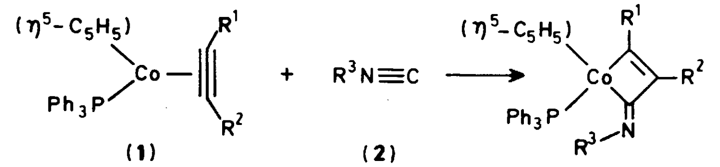
Preparation of 4-Iminocobaltacyclobutene Complexes.—1-(η^5-Cyclopentadienyl)-4-imino-1-(triphenylphosphine)-cobaltacyclobutene complexes, (**3ai**)—(**3ei**), are prepared by following equation (1) (see also Experimental section). Once formed complexes (3) do not react further with isocyanide under the reaction conditions. However, when the isocyanide is mixed directly with a solution of complex (1), complexes (4) and (5), where two isocyanide units are bonded to the acetylene unit, are formed in considerable quantity, giving a poor yield of the desired (3).[1]

This suggests that an intermediate in reaction (1) is most probably co-ordinatively unsaturated (7), which reacts readily with another molecule of isocyanide before being stabilized by co-ordination of PPh_3 to give (3). High yields of (3) are obtained by conducting the reaction in the presence of a large excess of PPh_3 and with very slow addition of highly diluted isocyanide. Yields, elemental analyses, and some physical properties of complexes (3) are listed in the Table.

By analogy with the known reactions of (1) with acetylenes or olefins, whose mechanism has been established by kinetic studies,[3,4] the key step in reaction (1) is postulated to be a (6) to (7) transformation.

Regioselectivity.—Although two regioisomers of (3) are possible from the reaction of acetylene complexes (**1b**)—(**1e**), only one of them is formed. The regioselectivity of reaction (1) is thus very strict.

The positions of the substituents in (**3bi**) and (**3ei**) have been determined by single-crystal *X*-ray analysis.[14] In both complexes the strongly electron-withdrawing substituent CO_2Me occupies the β position of the metallacycle, while the Ph (**3bi**) or Me (**3ei**) group goes to the α position. As the bulkiness

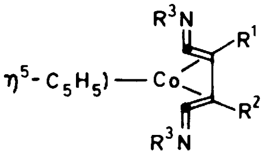


(1) (2) (3) (1)

a $R^1 = Ph, R^2 = Ph$
b $R^1 = Ph, R^2 = CO_2Me$
c $R^1 = Ph, R^2 = CN$
d $R^1 = H, R^2 = Ph$
e $R^1 = Me, R^2 = CO_2Me$

i $R^3 = p\text{-}MeC_6H_4$
ii $R^3 = 2,6\text{-}Me_2C_6H_3$
iii $R^3 = Ph$

ai $R^1 = R^2 = Ph, R^3 = p\text{-}MeC_6H_4$
aii $R^1 = R^2 = Ph, R^3 = 2,6\text{-}Me_2C_6H_3$
aiii $R^1 = R^2 = R^3 = Ph$
bi $R^1 = Ph, R^2 = CO_2Me, R^3 = p\text{-}MeC_6H_4$
bii $R^1 = Ph, R^2 = CO_2Me, R^3 = 2,6\text{-}Me_2C_6H_3$
ci $R^1 = Ph, R^2 = CN, R^3 = p\text{-}MeC_6H_4$
di $R^1 = H, R^2 = Ph, R^3 = p\text{-}MeC_6H_4$
ei $R^1 = Me, R^2 = CO_2Me, R^3 = p\text{-}MeC_6H_4$



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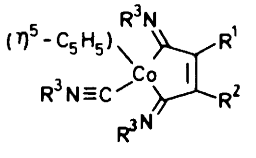

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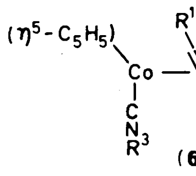

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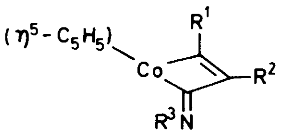
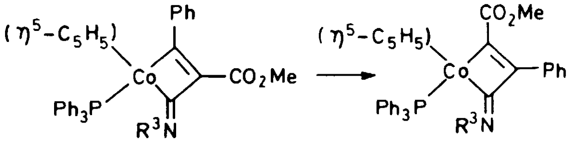


(7)

of these substituents decreases in the order Ph > CO_2Me > Me,[13] we conclude that the observed regioselectivity originates not from a steric effect but from an electronic effect of the substituents. Apparently, the acetylenic carbon bearing an electron-withdrawing group becomes the β carbon of the resulting metallacycle and the carbon with an electron-releasing or less electron-withdrawing substituent becomes an α carbon. This is in marked contrast to the previously reported bis(acetylene)cobalt to cobaltacyclopentadiene transformation, where the regioselectivity is controlled predominantly by the steric factor of the acetylenic substituents.[4]

Although we have no experimental proof for the geometries of (**3bii**), (**3ci**), or (**3di**), the positions of the substituents in these metallacycles have been postulated based on their electronic effect.

On heating a toluene solution of (**3ai**) at 160 °C, (η^5-cyclopentadienyl)(η^4-tetraphenylcyclobutadiene)cobalt is obtained in 11% yield. At 80 °C, the product obtained in 30% yield is (η^5-cyclopentadienyl)[η^4-tetraphenyl-5-(*p*-tolylimino)cyclopentadiene]cobalt, (**10**). These results suggest that fragmentation of the metallacycle framework into diphenylacetylene and isocyanide takes place. When (**3bi**) in benzene is heated at 95 °C, a new red, crystalline complex (**8a**) is isolated in 30% yield. A small amount of a fragmentation product, as two isomeric cobaltacyclopentadienes, $[\overline{Co\{C(CO_2Me)}{=}C(Ph)C(CO_2Me){=}\underline{C(Ph)\}}(\eta^5C_5H_5)(PPh_3)]$ and $[\overline{Co\{C(Ph)}{=}C(CO_2Me)C(CO_2Me){=}\underline{C(Ph)\}}(\eta^5C_5H_5)$-determined by a single-crystal *X*-ray analysis[14] to be the regioisomer of (**3bi**) [equation (2)]. Under the same conditions a similar isomerization has been observed for (**3ci**) but it is not as smooth as with (**3bi**), the yield of the rearranged product (**8b**) being only 7% and 63% of unreacted (**3ci**) is recovered.



(2)

(**3bi**) (**8a**)

In order to prevent the fragmentation and decomposition reactions, it is effective to carry out the reaction in the presence of an excess amount of triphenylphosphine, and under these conditions reaction (2) proceeds almost quantitatively. The effect of phosphine on this rearrangement reaction at 80 °C in C_6D_6 has been monitored by n.m.r. spectroscopy. The rate observed is first order with respect to the concentration of (**3bi**), and decreases with increasing amount of phosphine. For instance, when the initial concentrations of (**3bi**) and PPh_3 were 2.4×10^{-2} mol dm^{-3} and 3.6×10^{-2} mol dm^{-3} respectively, the rate of appearance of (**8a**) was 4.4×10^{-6} mol l^{-1} s^{-1} but the rate decreased to 1.8×10^{-6} mol l^{-1} s^{-1} when the concentration of PPh_3 was increased to 12.0×10^{-2} mol dm^{-3}. This result, together with the thermal fragmentation described above, strongly suggests that the rearrangement reaction takes place *via* a phosphine-free π-complex intermediate.

Taking into account the calculated geometries and relative energies of the reaction intermediates,[13] we propose an energy profile consistent with these substituent effects to be as shown in the Figure, where Z denotes an electron-withdrawing substituent. As an isocyanide carbon has a relatively large positive charge, it will favour the acetylenic carbon bearing Z as a partner to form a new C–C bond, since polarization of the

Table. Physical and analytical data of cobaltacyclobutenes

Complex	Yield (%)	M.p.[a]/ °C	Analysis[b] (%)	$\delta(^1H)$[c]/p.p.m. C_5H_5	$\delta(^1H)$[c]/p.p.m. Me
(**3ai**)	59	169—171	C 79.40 (79.30) H 5.45 (5.45) N 2.25 (2.05)	4.70	2.30 (s)
(**3aii**)	27	118—120	C 79.20 (79.40) H 5.60 (5.65) N 2.15 (2.00)	4.71 (*syn*)[d] 4.97 (*anti*)	1.77, 2.38 (s, *syn*) 1.79 (s, *anti*)
(**3aiii**)	39	165—168	C 79.60 (79.15) H 5.35 (5.30) N 2.15 (2.10)	4.75	
(**3bi**)	80	180—183	C 67.80 (67.40)[e] H 4.80 (5.00) N 1.80 (1.85)	4.78	2.35 (s) 3.50 (s, CO_2Me)
(**3bii**)	43	139—141	C 68.05 (67.75)[e] H 5.15 (5.15) N 1.85 (1.85)	4.82	1.71 (br, s) 2.32 (br, s) 2.70 (s, CO_2Me)
(**3ci**)	88	182—185	C 75.15 (76.20) H 5.10 (5.10) N 4.40 (4.45)	4.85	2.40 (s)
(**3di**)	35[f]	163—165	C 76.95 (77.35) H 5.50 (5.50) N 2.30 (2.30)	4.80[g]	2.36 (s)
(**3ei**)	40[f]	147—150	C 67.90 (68.05)[h] H 5.10 (5.30) N 2.15 (2.15)	4.52	2.20 (s) 2.34 [d, ring-Me, J(PH) = 3 Hz] 3.40 (s, CO_2Me)
(**8a**)	95	198—201	C 74.10 (74.20) H 5.25 (5.30) N 2.10 (2.10)	4.76	2.40 (s) 3.36 (s, CO_2Me)
(**8b**)	7	203	C 75.10 (76.20) H 5.10 (5.10) N 4.25 (4.45)	4.60	2.22 (s)

[a] With decomposition. [b] Calculated values in parentheses. [c] In $CDCl_3$. [d] Measured in C_6D_6. [e] Contains CH_2Cl_2 as solvent of crystallization. [f] Based on $[Co(\eta\text{-}C_5H_5)(PPh_3)_2]\cdot C_6H_6$. [g] Measured in CD_2Cl_2. [h] Contains $0.5CH_2Cl_2$ as solvent of crystallization.

acetylene π electrons must be $H-\overset{\delta+}{C}\equiv\overset{\delta-}{C}-Z$. A transition state (**6a**) will be thus at lower energy than (**6b**) and conformer (**6a**) will result in the metallacycle (**7a**) having Z at the β position. The final complex of this route, (**3**), is therefore a kinetically-controlled product. Under heating conditions phosphine dissociates from (**3**), (**7a**) goes back to (**6a**), and with rotation of the acetylene unit to give (**6b**) the metallacycle (**8**) forms *via* (**7b**). The metal–carbon bond in (**7b**) would be thermodynamically more stable than in (**7a**) because its α carbon atom has an electron-withdrawing substituent.[15]

We have performed *ab initio* molecular orbital (m.o.) calculations to check if these energy relationships between the α and β isomers of (**7**) are reasonable. As their models, we took the previously calculated geometries[13] for the π-complexed form (**6**) and the metallacycle form (**7**) where Z = H, and then substituted the α or β hydrogens with a CHO group. In the metallacycle form the dihedral angle between the η^5-C_5H_5 ring and the metallacycle plane has been calculated to be 74.5°[13] and this angle was also assumed for the angle between the η^5-C_5H_5 ring and the plane defined by the acetylene and isocyanide units in (**6a**) and (**6b**). Thus (**6a**) was calculated to be 6.3 kJ mol^{-1} more stable than (**6b**), and (**7a**) to be 45.4 kJ mol^{-1} more unstable than (**7b**). The relative positions of the acetylenic carbons and isocyanide units in (**6a**) and (**6b**), which have been used for the calculation, are derived just by rotating the acetylene units to a coplanar geometry from an upright orientation of the most stable π-complexed form (**1**). Such a geometry cannot be a transition state. We suppose that in the real transition state the energy difference between (**6a**) and (**6b**) is larger than the value calculated here.

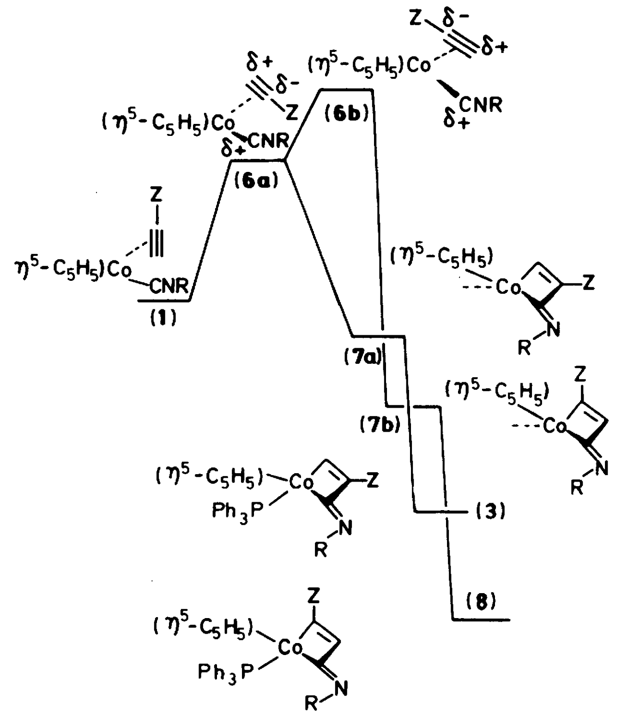
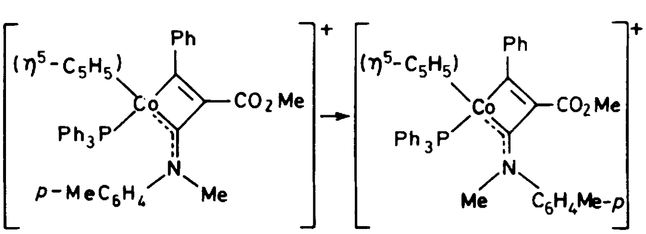


Figure. Schematic energy profile for reactions (1) and (2)

Finally, the Co–P bond in (**8**) should also be stronger than that in (**3**) because we know the presence of electron-withdrawing substituents makes the Co–P bond in cobaltacyclopentadiene complexes stronger.[16]

Stereoselectivity of the Imino Group.—Addition of an alkyl iodide to the iminocobaltacyclobutenes is expected to give formally cationic cobaltacyclobutadiene complexes. Thus complex (**3bi**) in benzene reacted smoothly with methyl iodide to give a red solution from which a red crystalline complex (**9a**) and a small amount of orange crystals of (**9b**) were isolated as PF_6^- salts. Complex (**9a**) in CD_2Cl_2 solution slowly isomerizes to the thermodynamically more stable (**9b**) at room temperature, which has been followed by n.m.r. The half-life of (**9a**) is *ca.* 16 h. Based on the X-ray analysis of (**9a**),[14] the structures of (**9a**) and (**9b**) are best represented as illustrated below.

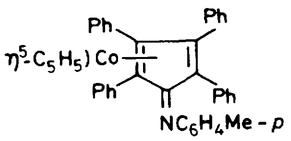


(**9a**) (**9b**)

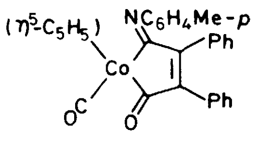
The imino N-substituent in the parent complex (**3bi**) takes a *syn* configuration with respect to Co, as evidenced by X-ray analysis.[14] This configuration must be retained in solution too because (**9a**) is the sole product in the initial step of the reaction with methyl iodide. This is consistent with the n.m.r. study listed in the Table. The ^1H n.m.r. spectrum of (**3bii**) shows two broad methyl absorptions due to the 2,6-dimethylphenyl group while resonances of the CO_2Me and C_5H_5 protons are sharp singlets. The two methyl resonances of the 2,6-dimethylphenyl group are attributable to hindered rotation as a result of the neighbouring bulky triphenylphosphine in the *syn* form. The *syn* form is expected to be sterically more crowded than the *anti* form and thermodynamically unstable. This is in accord with the observation that the cationic derivative (**9a**), with the bulky C_6H_4Me-*p* group in the *syn* position and the less bulky Me at the *anti*, isomerizes to (**9b**). Addition of methyl to the nitrogen atom of (**3bi**) reduces the C=N bond order making it possible to rotate the bond to a more stable isomeric form.

The stereoselective *syn* imino configuration in (3) can be understood when the metallacycle forming step, (6)⟶(7) is considered. Triphenylphosphine does not participate in this reaction step and a *syn* geometry in (7) is apparently more favourable. Phosphine returns after the imino configuration is fixed. Although the *syn* form of the imino configuration is thus selectively formed, it is not perfectly strict. In the case of (**3aii**), *ca.* 20% of the *anti* form was detected (Table).

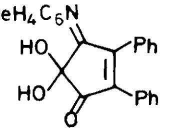
Reactions of Iminocobaltacyclobutenes.—(*i*) *With acetylene.* The smooth reaction of (**3ai**) with diphenylacetylene at 70 °C gives a 67% yield of the 5-iminocyclopenta-1,3-dienecobalt complex (**10**) which has been prepared previously by the reaction of tetraphenylcobaltacyclopentadiene with the isocyanide.[17]



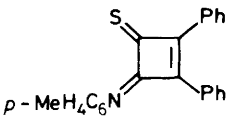
(**10**)



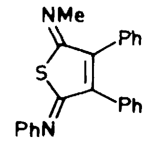
(**11**)



(**12**)



(**13**)



(**14**)

(*ii*) *With carbon monoxide.* A benzene solution of (**3ai**) reacts with CO (3 atm) at room temperature to give a 22% yield of an orange crystalline complex and a 29% yield of a yellow crystalline organic material. The complex has no triphenylphosphine but has a co-ordinated carbonyl (ν_{CO} 1 985 cm^{-1}). The presence of conjugated carbonyl (1 660 cm^{-1}) and imino groups (1 620 cm^{-1}), together with n.m.r. spectral and elemental analysis indicate structure (**11**). The analysis and spectral data of the organic compound is consistent with a hydrated cyclopentenetrione derivative (**12**). Easy hydration of the central carbonyl of cyclic triketones has been known.[18]

(*iii*) *With* CS_2 *or* MeNCS. Carbon disulphide reacts with (**3ai**) at room temperature to give a 17% yield of an organic material with composition (*p*-MeC_6H_4NC)(PhC_2Ph)(CS) (**13**). Similarly, methyl isothiocyanate reacts with (**3aiii**) at 80 °C to give a yellow crystalline compound with composition (PhNC)(PhC_2Ph)(MeNCS) (**14**) in 41% yield. We tentatively assign the structures of (**13**) and (**14**) as illustrated.

Experimental

All reactions and column chromatography were carried out under an atmosphere of argon.

Materials.—Complexes (**1a**) and (**1b**) were prepared according to the previously reported method.[2] Complex (**1c**) was prepared by the same method in 51% yield as dark green crystals, m.p. 156—157 °C (decomp.) (Found: C, 75.20; H, 5.05; N, 2.70. Calc. for $C_{32}H_{25}CoNP$: C, 74.85; H, 4.9; N, 2.75%); i.r.(KBr): 2 125 [ν(C≡N)], 1 785 [ν(C≡C)] cm^{-1}. Complexes (**1d**) and (**1e**) were prepared similarly but used *in situ* since they were too unstable to isolate. Alumina (Sumitomo KCG-30) used for chromatography of (**3**) and (**8**) was deactivated with 5 wt.% of water.

Preparation of Metallacyclobutenes (**3**).—To a stirred solution of (**1b**) (110 mg, 0.2 mmol) and triphenylphosphine (524 mg, 2 mmol) in benzene (10 cm^3) was added, during 12 h, a dilute solution of (**2i**) in benzene (65 cm^3 of a 0.04 mol dm^{-3} solution) through a mechanically controlled syringe. The resulting yellow-brown solution was concentrated under reduced pressure. If crystals deposited they were dissolved by adding the minimum volume of CH_2Cl_2. Chromatography of this concentrated solution on alumina gave an orange-yellow band which was eluted with CH_2Cl_2–thf (10:1) (thf = tetrahydrofuran). Removal of the solvent from the eluate and crystallization from CH_2Cl_2–hexane gave brown crystals of (**3bi**). Other complexes (**3ai**), (**3aii**), (**3aiii**), (**3bii**), and (**3ci**) were prepared by a similar procedure.

[$Co(\eta^5\text{-}C_5H_5)(PPh_3)_2$]·$C_6H_6$ (2.18 g, 3 mmol) and PPh_3 (15.7 g, 60 mmol) were dissolved in benzene (50 cm^3) and MeC_2CO_2Me (0.32 g, 3.3 mmol) was added. The solution was stirred for 2 h and then *p*-MeC_6H_4NC (3.4 mmol) in benzene (50 cm^3) was added during 12 h through a mechanically controlled syringe. The concentrated solution was chromatographed on alumina. A brown band and an orange band separated. The brown band was eluted with benzene–ethyl acetate (2:1), from which a 3:1 mixture of 1-(η^5-cyclopentadienyl)-2,4-bis(methoxycarbonyl)-3,5-dimethyl-1-(triphenylphosphine)cobaltacyclopentadiene and its 2,5-bis-(methoxycarbonyl)-3,4-dimethyl isomer was obtained in 38% yield. The orange band was eluted with CH_2Cl_2–thf (5:1). Removal of the solvent under reduced pressure and crystallization of the residue from CH_2Cl_2–hexane gave (**3ei**). Complex (**3di**) was prepared similarly.

Isomerization of (**3bi**) *and* (**3ci**) *to* (**8a**) *and* (**8b**).—A benzene solution of (**3bi**) (150 mg, 0.226 mmol) and triphenylphosphine (240 mg, 0.916 mmol) was heated at 80 °C for 12 h. Work-up on an alumina column, elution of the brown-yellow band with benzene, and crystallization from dichloromethane–hexane gave orange-red crystals of (**8a**). Isomerization of (**3ci**) to (**8b**) was performed similarly.

Reaction of (**3bi**) *with Methyl Iodide.*—To a benzene solution (30 cm^3) of (**3bi**) (100 mg, 0.15 mmol) was added methyl iodide (1 cm^3). The mixture was stirred for 1 h at room temperature, during which time an orange powder precipitated. The precipitate was collected by filtration and dissolved in methanol (30 cm^3). Addition of a calculated amount of NH_4PF_6 gave a precipitate of the hexafluorophosphate salt. Crystallization from CH_2Cl_2–hexane gave red crystals of the PF_6^- salt of (**9a**), m.p. 178—181 °C (Found: C, 60.50; H, 4.60; N, 1.70. Calc. for $C_{42}H_{38}CoF_6NO_2P_2$: C, 61.25; H, 4.65; N, 1.70%). ^1H N.m.r.

(CD_2Cl_2): δ 4.84 (s, C_5H_5), 3.63 (s, CO_2CH_3), 3.50 (s, N–CH_3), 2.50 (s, aryl CH_3). When (**9a**) was crystallized slowly (over 1 d), orange crystals of (**9b**) were also formed, m.p. 180—182 °C [Found (solvated with CH_2Cl_2): C, 57.10; H, 4.40; N, 1.55. Calc. for $C_{43}H_{40}Cl_2CoF_6NO_2P_2$: C, 56.85; H, 4.45; N, 1.55%). ^1H N.m.r. ($CDCl_3$): δ 5.30 (s, C_5H_5 + CH_2Cl_2), 3.89 (s, CO_2CH_3), 2.83 (s, N–CH_3), 2.31 (s, aryl CH_3); ^1H n.m.r. (CD_2Cl_2): δ 5.28 (s, C_5H_5 + CH_2Cl_2), 3.76 (s, CO_2CH_3), 2.82 (s, N–CH_3), 2.32 (s, aryl CH_3).

Thermal Decomposition of (**3ai**).—Complex (**3ai**) (127 mg, 0.19 mmol) in toluene (15 cm^3) was heated in a sealed tube at 160 °C for 20 h. Work-up by alumina chromatography gave a yellow band which was eluted with benzene–hexane (1:4). Removal of the solvent and crystallization from hexane gave yellow crystals of (η^5-cyclopentadienyl)(η^4-tetraphenylcyclobutadiene)cobalt[19] in 11% yield.

Reaction of (**3ai**) *with Diphenylacetylene.*—Complex (**3ai**) (150 mg, 0.23 mmol) and PhC_2Ph (280 mg, 1.65 mmol) were dissolved in benzene and heated at 70 °C in a sealed tube. After 9 h the solution was concentrated almost to dryness and hexane (3 cm^3) was added to give dark brown crystals of (**10**)[17] in 67% yield.

Reaction of (**3ai**) *with Carbon Monoxide.*—A benzene solution (40 cm^3) of (**3ai**) (160 mg, 0.24 mmol) was placed in an autoclave and carbon monoxide (3 atm, *ca.* 3×10^5 Pa) was introduced. After 9 d at room temperature, the solution was concentrated and chromatographed on silica gel. A yellow-orange band and a yellow-green band separated. The yellow-orange band was eluted with benzene. Crystallization of the concentrated eluate by adding hexane gave crystals of (**11**) in 22% yield, m.p. 185—187 °C (Found: C, 73.05; H, 5.00; N, 2.75. Calc. for $C_{29}H_{22}CoNO_2$: C, 73.25; H, 4.95; N, 2.95%). ^1H N.m.r. ($CDCl_3$): δ 4.84 (s, C_5H_5), 2.36 (s, CH_3). From the yellow-green band, which was eluted with CH_2Cl_2–thf (2:1), crystals of (**12**) were obtained in 29% yield, m.p. 117—120 °C (Found: C, 78.55; H, 5.55; N, 3.55. Calc. for $C_{24}H_{19}NO_3$: C, 78.05; H, 5.20; N, 3.80%); I.r. (KBr): 3 450s [ν(OH)], 1 735vs [ν(CO)], 1 520 [ν(C=N)] cm^{-1}.

Reaction of (**3ai**) *with Carbon Disulphide.*—Carbon disulphide (5 cm^3) and (**3ai**) (200 mg, 0.29 mmol) in benzene (20 cm^3) were stirred at room temperature for 5 d. Work-up by alumina chromatography gave a yellow band which was eluted with benzene. Crystallization from hexane gave yellow (**13**) in 17% yield, m.p. 248—250 °C (Found: C, 80.70; H, 5.30; N, 4.05; S, 9.14. Calc. for $C_{23}H_{17}NS$: C, 81.40; H, 5.05; N, 4.10; S, 9.45%). From the second dark yellow band, which was eluted with benzene–CH_2Cl_2 (1:1), unidentified black crystals (22 mg) were obtained, m.p. 215—216 °C (decomp.).

Reaction of (**3aiii**) *with Methyl Isothiocyanate.*—A mixture of (**3aiii**) (55 mg, 0.083 mmol), MeNCS (1 cm^3), and benzene (15 cm^3) was heated at 80 °C for 1 h. Work-up of the resulting brown solution by alumina chromatography and crystallization from hexane gave yellow crystals of (**14**) in 41% yield, m.p. 181 °C [Found: C, 77.85; H, 5.15; N, 7.85%; *M* (mass spectrum), 354. Calc. for $C_{23}H_{18}N_2S$: C, 77.95; H, 5.10; N, 7.90%; *M*, 354.5].

Molecular Orbital Calculations.—*Ab initio* calculations were performed using the program package PSHONDO.[20] In Hartree–Fock calculations the [Ar] core of Co was replaced by the effective core potential from Barthelat *et al.*[21] 4*s* and 4*p* orbitals of Co were three-term Gaussian-type orbitals evaluated by Topiol *et al.*[22] To represent 3*d*-valence orbitals, five-term Gaussian-type orbitals of Hay[23] were contracted to [2*d*]. The standard STO-3G set was used for the other atoms. Throughout the calculations the C_5H_5–Co distance was 1.8 Å with C–C and C–H distances of 1.43 and 0.95 Å respectively. The geometrical parameters for the (acetylene)(isocyanide)cobalt fragment or the metallacycle fragment were taken from the optimized geometry as given previously.[13] The CHO group was placed so that its plane was perpendicular to the plane defined by the (acetylene)(isocyanide)cobalt or the metallacycle framework with C–C, C=O, and C–H distances of 1.40, 1.15, and 1.0 Å, respectively.

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