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Reactivity of cobalt(0) and cobalt(I) complexes with diynes towards C=C, C≡N, and C≡C bonds. X-Ray structure of a cyclopentadienylcobaltacyclopentadiene complex *

Zhiming Zhou [a], Luigi Pietro Battaglia [b], Gian Paolo Chiusoli [a], Mirco Costa [a], Mario Nardelli [b], Corrado Pelizzi [b] and Giovanni Predieri [b]

[a] *Istituto di Chimica Organica, Università di Parma, Viale delle Scienze, 43100 Parma (Italy)*
[b] *Istituto di Chimica Generale, Università di Parma, Viale delle Scienze, 43100 Parma (Italy)*

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Abstract

The reactivities towards triple and double bonds of some new cobaltacyclopentadiene complexes, derived from cobalt(0) and cobalt(I) complexes, have been compared. Their different abilities to undergo dissociation of ligands and the different stabilities of the resulting complexes account for the lower reactivity of cobalt(I) towards activated olefins. The crystal structure of a cyclopentadienylcobaltacyclopentadiene(III) complex is described.

Introduction

Our previous work [1,2] has shown that the use of cobalt(0) and cobalt(I) catalysts in certain cycloaddition reactions leads to different chemoselectivities. In particular dialkynes I (X = CH_2 and homologues, O, NR; R = alkyl, aryl, acyl; R^I, R^{II} = H, alkyl; R^{III}, R^{IV} = alkyl, aryl) react with nitriles to give condensed pyridines in the presence of cobalt(I), but mainly result in incorporation of acetylenic triple bonds in the case of cobalt(0). The latter can act as a very efficient catalyst for nitrile incorporation, but if appropriate conformational and steric effects are exerted by geminal groups α to the triple bonds or by bulky R groups in X. In both cases the intermediacy of cobaltacyclopentadienes has been postulated (eq. 1).

We also recently observed [3] that cobalt(0) complexes, such as bis(acetonitrile) bis(diethyl fumarate)cobalt(0) [4], are able to catalyze cycloaddition reactions of diynes with activated olefins even at room temperature (eq. 2). Under our mild conditions such reactions do not take place with cobalt(I) complexes of the cyclopentadienyl type and occur with only low conversion and selectivity with cobalt(I) complexes containing a σ Co–alkyl bond, such as (5-methyl-2,6-

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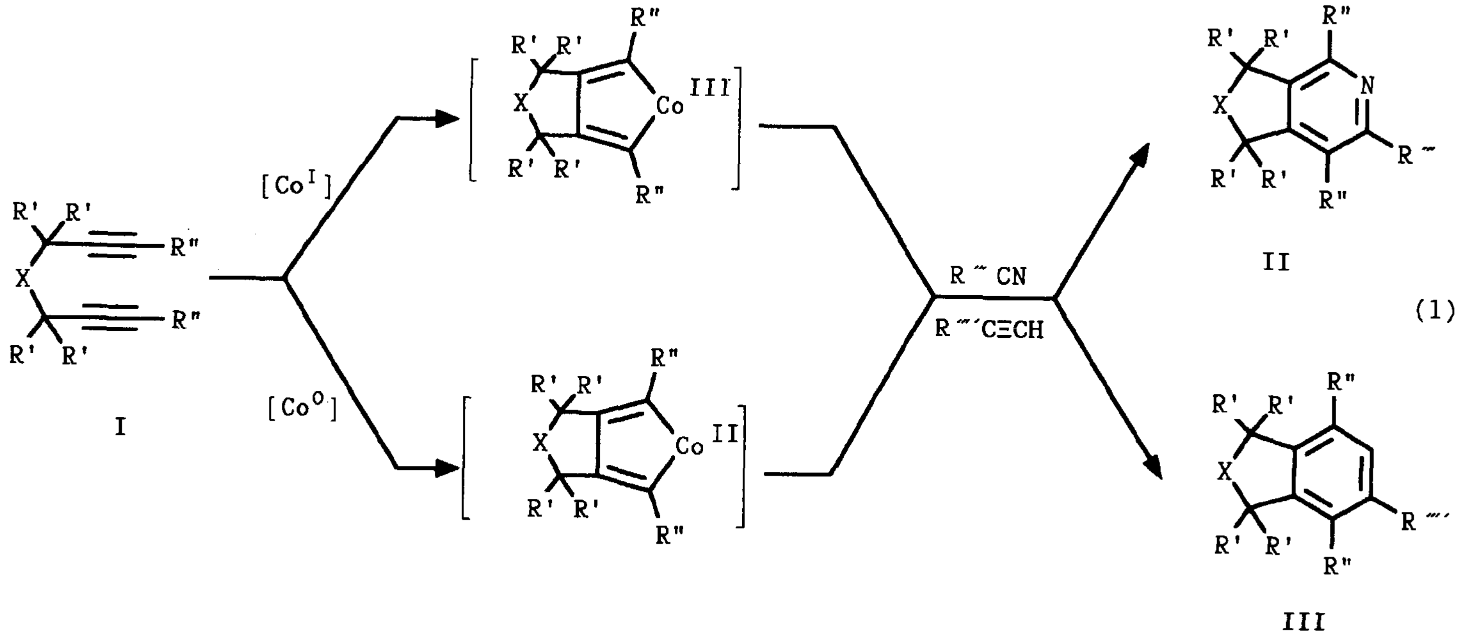
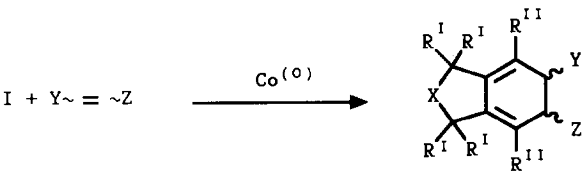
* Dedicated to the memory of Professor Piero Pino.



(1)

[Co^I], [Co^0] = complexes of Co(I) and Co(0), respectively;   X = CH_2, O, NR

R = Alkyl, aryl, acyl; R', R" = H, alkyl, R"' = H, alkyl, R"', R"" = allyl, aryl heptadienyl)(butadiene)cobalt(I) (V) [5] (eq. 2, Y, Z = H or electron-withdrawing groups) [3]:



(2)

IV

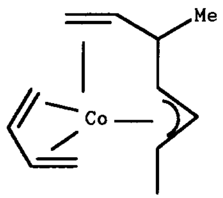
Understanding of the different behaviour of cobalt(I) and cobalt(0) complexes can be expected to come from a study of structure and reactivity of the proposed cobaltacyclopentadiene intermediates. Complex VI, formed in the reaction of $CpCo(PPh_3)_2$ with I (X = NMe, R^I, R^{II} = Me), has been recently prepared and its crystal structure is reported here. The structure of another complex (VII), formed in the reaction of dicobalt octacarbonyl with I (X = NMe, R^I = Me, R^{II} = H) was recently described [2]. Complex VII was suggested to be converted into a cobaltacyle dimeric complex VIII [6], which was actually isolated [7]. There was thus an opportunity to compare the only two metallacyclic complexes of dipropargylic amines known to date, obtained from the reaction of cobalt(I) and cobalt(0) complexes, respectively. The comparison of their reactivities towards triple and double bonds is reported below.

Results

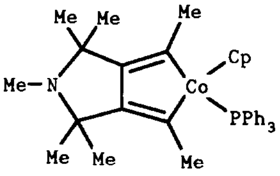
The complexes shown below were treated at temperatures ranging from −5 to 110 °C with an excess of diethyl fumarate, phenylacetylene, or benzonitrile, as representatives of activated olefins, alkynes and nitriles, respectively. Complex V [5] was treated with a stoichiometric amount of I (X = NH, R^I = Me, R^{II} = H) and an excess of the above-mentioned reagents. Results of a study of catalytic organic syntheses of diynes with various activated olefins will be published in due course.

The new complex VI was prepared starting from I (X = NMe; R^I, R^{II} = Me) and $CpCo(PPh_3)_2$. An X-ray diffraction study revealed the molecular structure, depicted in Fig. 1, which shows that the cobalt atom is surrounded by one η^5-bonded cyclopentadienyl group, one triphenylphosphine molecule, and the C(24) and C(28) atoms σ-bonded to the metal in a metallacyclopentadiene ring. The metal coordination can be described as a "three-legged piano stool" with C(24), C(28) and P as legs. The C(24), C(26), C(27) and C(28) atoms of the cobaltacyclic ring lie in a plane from which cobalt deviates by 0.371(1) Å. This plane and that of the cyclopentadienyl ring form a dihedral angle of 26.1(6)°, and the C(24)–Co–C(28) angle is 85.3(5)°.

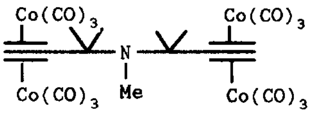
The Co–C(24) and Co–C(28) bonds show values consistent with the sp^2 character of these carbons and with the moderate hindrance of the methyl groups. Bond distances and angles in the heterocyclic ring have values in the usual range (Table 1). The nitrogen atom shows a small but significant pyramidality, being 0.32(1) Å away from the plane through C(30), C(33), C(34), and steric effects exerted by the five adjacent methyls probably have some influence on this geometry. The bond angles involving nitrogen are C(30)–N–C(33) 116(1)°, C(30)–N–C(34) 111(1)°,



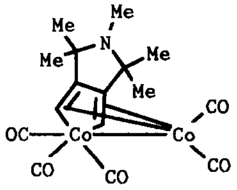
V



VI



VII



VIII

C(33)–N–C(34) 119(1)°. Table 2 presents a comparison of the relevant structure data for a number of cobaltacyclo-pentane, -pentene and -pentadiene complexes. The data for compound VI can be seen to be not very different from those for the other compounds listed (see for example [8]), indicating a similarly crowded ligand arrangement.

Complex VI underwent no reaction with diethyl fumarate at temperatures below 80 °C. Only upon heating at 110 °C for 24 h did a reaction occur, leading to 50%

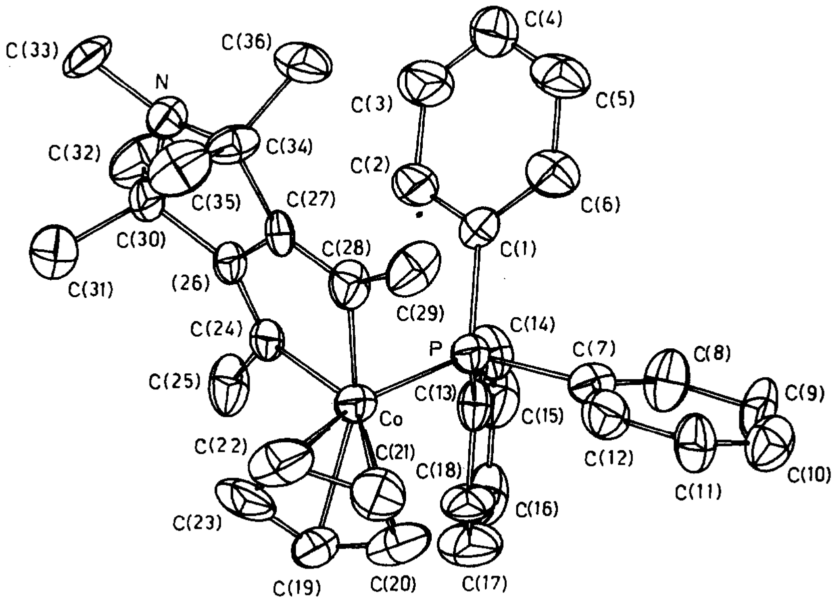
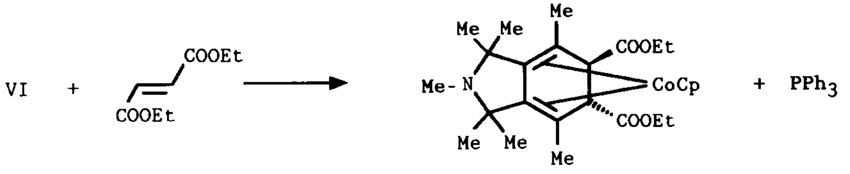


Fig. 1. A perspective view of the molecule VI.

yield of a stable complex IX (eq. 3), which was characterized by NMR spectroscopy. The latter did not contain a PPh_3 legend but only the cyclopentadienyl group and a new ligand resulting from the addition of the terminal carbon atoms of the cobaltacyclopentadiene ring to diethyl fumarate. The corresponding compound IV was liberated on addition of cerium ammonium nitrate.



IX

(3)

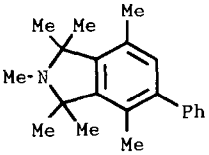
When treated with phenylacetylene at 110 °C for 24 h, complex VI gave a 74% yield of the expected aromatic product X. In addition phenylacetylene cyclic trimers were

Table 1

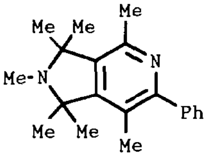
Selected bond distances (Å) and angles (°) with the e.s.d.'s in parentheses. Along the Table C* indicates the centroid of the Cp ring

Co–P	2.143(4)	Co–C(22)	2.086(16)
Co–C(19)	2.134(20)	Co–C(23)	2.083(23)
Co–C(20)	2.159(17)	Co–C(24)	1.975(9)
Co–C(21)	2.135(17)	Co–C(28)	1.987(16)
P–C(1)	1.82(2)	Co–C*	1.75(2)
P–C(13)	1.84(1)	P–C(7)	1.85(1)
C(24)–C(25)	1.50(2)	C(28)–C(29)	1.48(2)
C(24)–C(26)	1.38(2)	C(28)–C(27)	1.34(2)
C(26)–C(27)	1.46(2)		
C(26)–C(30)	1.50(2)	C(27)–C(34)	1.51(2)
C(30)–C(31)	1.52(2)	C(34)–C(35)	1.54(2)
C(30)–C(32)	1.54(2)	C(34)–C(36)	1.56(2)
N–C(30)	1.51(2)	N–C(34)	1.46(1)
N–C(33)	1.43(2)	C(21)–C(22)	1.40(2)
C(19)–C(20)	1.39(2)	C(22)–C(23)	1.42(3)
C(20)–C(21)	1.42(3)	C(23)–C(19)	1.40(3)
C*–Co–P	135.8(6)	P–Co–C(24)	88.8(4)
C*–Co–C(24)	120.4(8)	P–Co–C(28)	92.2(4)
C*–Co–C(28)	120.5(8)	C(24)–Co–C(28)	85.3(5)
Co–P–C(1)	117.8(4)	Co–P–C(7)	116.4(4)
Co–P–C(13)	98.8(6)	C(1)–P–C(7)	102.6(6)
C(1)–P–C(13)	104.6(6)	C(7)–P–C(13)	98.8(6)
Co–C(24)–C(25)	122.5(9)	Co–C(28)–C(29)	123(1)
Co–C(24)–C(26)	109.2(8)	Co–C(28)–C(27)	109(1)
C(25)–C(24)–C(26)	127(1)	C(29)–C(28)–C(27)	127(1)
C(24)–C(26)–C(27)	116(1)	C(28)–C(27)–C(26)	118(1)
C(24)–C(26)–C(30)	134(1)	C(28)–C(27)–C(34)	134(1)
C(26)–C(27)–C(34)	108(1)	C(27)–C(26)–C(30)	110(1)
C(26)–C(30)–C(31)	110(1)	C(27)–C(34)–C(35)	110(1)
C(26)–C(30)–C(32)	114(1)	C(27)–C(34)–C(36)	113(1)
C(26)–C(30)–N	101(1)	C(27)–C(34)–N	104(1)
C(30)–N–C(34)	111(1)	C(34)–N–C(33)	119(1)
C(30)–N–C(33)	116(1)		

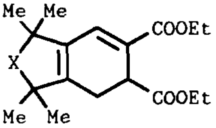
formed. Under the same conditions incorporation of benzonitrile gave the corresponding pyridine (XI) in 65% yield.



X



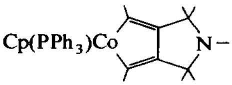
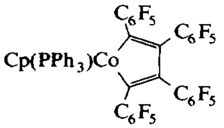
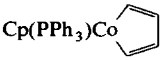
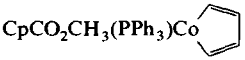
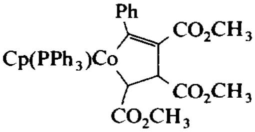
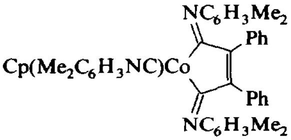
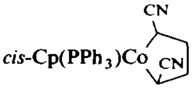
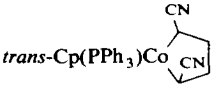
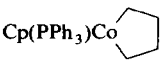
XI



XII

Table 2

Comparison of some relevant bond distances (Å) and angles (°) in selected five-terms cobaltacyclic structures containing Cp and PPh$_3$ ligands (except ref. 23)

		Co–P	Co–C(Cp) range	Co–C(ring)	C–Co–C(ring)
Present work		2.143(4)	2.083(23)– 2.159(17)	1.975(9)– 1.987(16)	85.3(5)
Ref. 21		2.234(3)	2.104(9)– 2.157(12)	1.993(11)– 1.995(11)	82.4(4)
Ref. 8		2.144(1)	2.085(6)– 2.136(6)	1.943(6)– 1.947(6)	83.2(3)
Ref. 8		2.148(2)	2.056(6)– 2.137(7)	1.928(6)– 1.933(7)	82.6(3)
Ref. 22		2.232(3)	2.119(14)– 2.140(14)	1.947(11)– 2.079(12)	82.0(4)
Ref. 23		–	2.120(5)– 2.169(5)	1.964(5)– 1.980(4)	83.9(2)
Ref. 24		2.199(2)	2.073(7)– 2.093(8)	2.024(6)– 2.029(6)	77.5(3)
Ref. 24		2.230(3)	2.084(11)– 2.112(10)	2.031(9)– 2.060(9)	81.7(4)
Ref. 25		2.146(1)	2.082(6)– 2.102(6)	2.027(5)– 2.021(5)	84.0(2)

As previously reported, complex V, known to be active in the synthesis of aromatics from alkynes and of pyridines from alkynes and nitriles [9,10], also reacted with I ($X = NH$, $R^I = Me$, $R^{II} = H$) and diethyl fumarate at 0 ° C, but it was less active and selective (52% yield of IV and its isomers) than the cobalt(0) complex bis(acetonitrile)bis(diethyl fumarate)cobalt (86% of IV under the same conditions) [3]. Compound IV readily isomerizes when placed on silica, and the main isomer isolated is XII.

Complex VII was also shown to react with diethyl fumarate (22% yield at 80 ° C for 4 h). Its reactions with benzonitrile (33% yield of the corresponding II) and alkynes were reported in a preceding paper [6].

Complex VIII was obtained as an additional product from the reaction that gave VII [7]. Its behaviour differs from that of VII in that it shows a higher reactivity towards diethyl fumarate (85% yield of the corresponding IV after 80 ° C for 4 h) and with phenylacetylene (95% of III) and gives no products arising from interaction of the metallacycle with benzonitrile; after prolonged treatment at 110 ° C an organic product was obtained, and shown to be the cyclic trimer of benzonitrile. Small amounts of a cyclopentenone, derived from CO insertion into the metallacycle [2], were also formed.

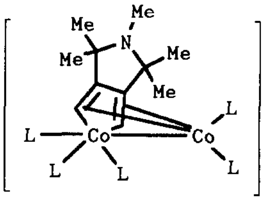
Discussion

The results can be interpreted in terms of different abilities to undergo coordination of unsaturated substrates. Incorporation of diethyl fumarate into a cobaltacyclopentadiene intermediate formed from cobalt(0) is favored in spite of the bulk of the fumarate. The cyclopentadienylcobalt(III) complex apparently undergoes coordination of fumarate less readily (no interaction between added fumarate and the cobalt complex was observed by NMR spectroscopy at room temperature), and no fumarate incorporation occurs under mild conditions. Structural data also point to the hindrance to the approach of fumarate and to the need for preliminary phosphine dissociation. In this connection it is noteworthy (Table 2) that complex VI is similar to other crowded cobaltacycle compounds. Moreover, the C–Co–C angle is the largest and the Co–P distance is one of the shortest among the known structures, indicating that there is some crowding of the ligands about metal and a relatively strong bonding of the phosphine. No other ligand can enter the metal coordination sphere unless the phosphine first dissociates, a process requiring a substantial increase in temperature. A stable complex, containing the additional product of one molecule of diethyl fumarate to the cobaltacycle and without PPh_3, was isolated after reaction at 110 ° C. This complex, which may also be written as a valence tautomer, with σ-bonding to cobalt, turns out to be similar to those reported by Wakatsuki and Yamazaki [11]. It may well be that a Diels–Alder addition to the cobaltacyclopentadiene takes place at 110 ° C, but there is no evidence of this at present. A direct Diels–Alder process, not involving phosphine dissociation, was also suggested some years ago [12] on the basis of kinetic evidence (see [13] for review). In contrast with the fumarate, phenylacetylene and benzonitrile react satisfactorily, although at 110 ° C, to give the desired compounds, which, in this case can readily leave the complex.

As to the way in which cobaltacycle complexes formed from $Co_2(CO)_8$ can react, our results suggest that stabilization occurs through formation of a dimeric complex,

$$2Co_2(CO)_8 + I(X = NMe, R^I = Me, R^{II} = H) \longrightarrow VII$$

$$VII + L \longrightarrow$$



(4)

XIII

$L = CO,\ Y\sim\!\equiv\!\sim Z,\ PhC{\equiv}CH,\ PhC{\equiv}N$

as we previously proposed [6] to account for the reactivity with unsaturated substrates of complex VII, derived from dicobalt octacarbonyl and containing the dipropargylamine substrate as a linear molecule (eq. 4).

This mechanism involves initial coordination of the incoming molecule to form a mixed ligand complex XIII. Cleavage of the Co–Co bond may also occur, followed by ring enlargement through insertion of unsaturated molecule and final ring closure. The dimeric cobalt complex would thus act as a source of a reactive monomeric species. The reason why triphenyltriazine was obtained from complex VIII and benzonitrile rather than the expected pyridine derivative is not clear, especially in view of the fact that complex VII gave 33% of the latter. Complexes VII and VIII however contain carbonyl groups which are not replaced by the nitrile in the same way, so the ligand arrangement in the resulting complex XIII (L = CO and PhCN) may not be the same.

In conclusion the different reactivities of cobalt(0) and cobalt(I) complexes appears to be related to differences in accessibility to the metal center and to the stability of the organometallic intermediates involved.

Experimental details

All the starting materials were pure commercial products (Fluka, Strem, Aldrich), except for tetramethyl-substituted dipropargylamines [14], $CoCl(PPh_3)_3$ [15], $CpCo(PPh_3)_2$ [11], (5-methyl-2,6-heptadienyl)(butadiene)cobalt(I) [5], and cobalt complexes VII [2] and VIII [7], which were prepared by published methods.

Products were isolated by conventional methods and identified by ^1H and ^{13}C NMR and by mass and IR spectra. The ^1H and ^{13}C NMR spectra were recorded on Bruker AC100 or CXP200 instruments using TMS as internal standard. The $^{31}P\text{-}\{^1H\}$ and ^{59}Co NMR spectra were recorded on a Bruker CXP200 instrument at 81.0 and 47.4 MHz, respectively with C_6D_6 as solvent, using deuterium lock. Chemical shifts are given relative to external 85% H_3PO_4 and $K_3Co(CN)_6$ (aq.), respectively. Mass spectra were obtained with a Finnigan Mat 1020 mass spectrometer at 70 eV and IR spectra with a Perkin–Elmer 283B model. Analytical GLC was carried out with a Dani 3900 chromatograph, fitted with a methylsilicone (OV101)-coated capillary column.

Compound I ($X = NMe$, $R^I = R^{II} = Me$). Compound I ($X = NMe$, $R^I = Me$, $R^{II} = H$), 0.58 g (3.56 mmol) was dissolved in 15 ml of dry tetrahydrofuran (THF) under N_2. The solution was cooled to ca. $-70\,°C$ and 7 ml of a hexane solution of butyllithium (1.6 *N*) was added dropwise with vigorous stirring. The mixture was allowed to reach -35, $-40\,°C$ and stirred for 90 min, then cooled again to $-70\,°C$, and a solution of MeI (30 mmol) in 5 ml THF was slowly added. The mixture was then stirred for 2 h at room temperature, hydrolysed, and extracted in the usual way. Oily product. MS, *m/e*: M^+ 191, 176 (100), 161, 160, 146, 79, 56; ^1H NMR ($CDCl_3$) δ (ppm); 1.53 (s, 12H, $4CH_3$); 1.78 (s, 6H, $2CH_3$); 2.37 (s, 3H, NCH_3).

Preparation of complex VI

An excess of I ($X = NMe$; R^I, $R^{II} = Me$), 0.450 g (2.29 mmol) was added to a solution of $CpCo(PPh_3)_2$, 1.00 g (1.500 mmol) in dry benzene (30 ml) at ca. $0\,°C$ under nitrogen. The mixture was stirred overnight at room temperature, then a little hexane was added. The solution was kept at $-20\,°C$ for one day; complex VI was filtered off as a brown-yellow, air-sensitive solid (0.39 g, 0.675 mmol, 45% yield). MW 577.16 Elemental analysis: Found: Co, 10.18; C, 74.86; H, 7.05; N, 2.41; $CoC_{36}H_{41}NP$ calc: Co, 10.21; C, 74.88; H, 7.10; N, 2.43%. IR (Nujol) (cm^{-1}): 3030, 1190, 1130, 1100, 815, 765, 730, 705. ^1H NMR (C_6D_6) δ (ppm): 0.77, 1.13, 1.23, 1.95, 2.05 (br s, 21H, $7CH_3$), 4.66 (br s, 5H, 5CH), 7.27–7.63 (aromatic H). ^{31}P NMR (C_6D_6) δ (ppm): 65.6. The ^{59}Co NMR spectrum (C_6D_6) shows a broad resonance ($w_{1/2} = 2.5 \times 10^4$ Hz) centered at -2160 ppm. Under the same conditions $CpCo(CO)_2$ resonates at -2760 ppm ($w_{1/2} = 1.4 \times 10^4$ Hz).

Preparation of complex IX

To complex VI, 0.230 g (0.4 mmol) under N_2 was added diethyl fumarate (8 ml). The mixture was stirred in a sealed tube at $110\,°C$ for 24 h. After distillation of the excess of diethyl fumarate under vacuum at $70\,°C$, the residue was separated by TLC on silica, with CH_2Cl_2/Et_2O 95/5 as eluent. Complex IX was obtained as a yellow, air stable oil (0.098 g, ca. 50% yield). MW 487.12. Elemental analysis: Found: Co, 12.00; C, 64.01; H, 7.28; N, 2.79; $CoC_{26}H_{38}NO_4$ calc: Co, 12.10; C, 64.07; H, 7.80; N, 2.86%. IR (liquid film) (cm^{-1}): 2995, 2990, 1735, 1480, 1460, 1380, 1265, 1160, 1040, 895, 810. ^1H NMR (C_6D_6) δ (ppm): 0.57 (t, 3H, CH_3, *J* 6.9 Hz); 0.71 (t, 3H, CH_3, *J* 6.9 Hz); 0.97, 1.02, 1.07, 1.14 (4s, 12H, $4CH_3$), 1.15 (s, 6H, $2CH_3$), 1.97 (s, 3H, NCH_3); 2.05 (d, 1H, CH, *J* 4.9 Hz), 3.06 (d, 1H, CH, *J* 4.9 Hz); 3.45, 3.54 (2dq, 2H, OCH_2, *J* 10.7, *J* 6.9 Hz); 3.69, 3.77 (2dq, 2H, OCH_2, *J* 10.7, *J* 6.9 Hz); 4.36 (d, 5H, 5CH, *J* 0.6 Hz). ^{13}C NMR (C_6D_6) δ (ppm): 14.14, 14.25 ($2CH_3$), 21.12, 22.46, 22.78, 22.84 ($4CH_3$), 25.68 (NCH_3), 29.68, 29.97 ($2CH_3$), 54.27, 56.60 (2CH), 59.96, 60.13 ($2CH_2$), 62.27, 62.85 (2 quaternary C), 82.74 (5C, CH), 171.81, 174.27 (2CO). The signals of the four quaternary C of the cyclohexadiene were not clear enough to be assigned.

Decomposition of a solution of complex IX (0.1 g) in toluene was carried out by adding a solution of cerium ammonium nitrate, 0.2 g, in ethanol. The corresponding organic compound IV ($X = NMe$, R^I, $R^{II} = Me$; Y, Z = *E*-COOEt) was separated by preparative TLC on silica, using hexane/acetone (7/3) as the eluent. Oily product. MS *m/e*: 363 (M^+) absent, 362, 348 (100), 318, 274, 202, 172, 56. ^1H NMR ($CDCl_3$) δ (ppm): 1.14 (s, 6H, $2CH_3$), 1.18 (t, 6H, $2CH_3$, *J* 7.1 Hz), 1.27 (s, 6H,

$2CH_3$), 1.97 (s, 6H, $2CH_3$), 2.23 (s, 3H, NCH_3), 3.30 (s, 2H, 2CH), 4.08, 4.09 (2q, 4H, $2CH_2$, J 7.1 Hz).

Reactivity of complexes V–VIII

To complex V, 0.111 g (0.5 mmol) under N_2 at $-5\,°C$ were added I (X = NH, R^I = Me, R^{II} = H), 0.075 g (0.5 mmol) and diethyl fumarate (10 ml) and the solution was stirred at $-5\,°C$ for 1/2 h. After treatment with aqueous NH_4Cl at $0\,°C$, the organic products were extracted with Et_2O. The excess of the fumarate was distilled off under vacuum and compound XII was separated from its isomers by flash chromatography on silica, with hexane/acetone (7/3) as eluent. Oily product, 0.056 g, 35% yield. MS, m/e: 321 (M^+), 306 (100), 276, 248, 232, 203, 188, 166, 140, 84, 56. ^1H NMR ($CDCl_3$) δ (ppm): 1.07 (t, 3H, CH_3, J 7.1 Hz), 1.08, 1.09, 1.13, 1.14 (4s, 12H, $4CH_3$), 1.19 (t, 3H, CH_3, J 7.0 Hz), 1.77 (br s, 1H, NH), 2.32, (dd, 1H,

Table 3

Experimental data for the crystallographic analysis

Formula	$C_{33}H_{44}CoNP$
M	544.62
Space group	$P2_1$
a, Å	8.690(2)
b, Å	19.232(4)
c, Å	9.762(3)
β, °	113.05(5)
U, $Å^3$	1501.2(9)
Z	2
D_c	1.205
D_m	1.22
Number of reflections	24
Lattice parameters, θ range	9.3–14.3
$F(000)$	582
Temperature, K	294
Diffractometer	Philips PW 1100
Crystal size, mm	$0.13 \times 0.58 \times 0.65$
μ, cm^{-1}	6.42
Scan speed, ° min^{-1}	4.0–12.0
Scan width, °	$1.4 + 0.35$ tg θ
θ range, °	3.0–23.0
h, range	± 9
k, range	0, 20
l, range	0, 9
Standard reflection	-3 0 4
Max. intensity variation, %	0.044
Scan mode	$\omega - 2\theta$
No. of measured reflections	2136
No. of reflections used in the refinement	1446
No. of refined parameters	413
Absorption correction (min.–max.)	1.00–1.10
$R = \Sigma\lvert\Delta F\rvert / \Sigma\lvert F_o\rvert$	0.0397
$R' = [\Sigma w(\Delta F^2/\Sigma w F^2_o]^{1/2}$	0.0405
w, g in $w = k/[\sigma^2(F_o) + gF_o^2]$	1.0, 3.75×10^{-3}
Max., min. height in final ΔF map, e $Å^{-3}$	-0.10, 0.19

CH, *J* 17.6, *J* 7.5 Hz), 2.70 (dd, 1H, CH, *J* 7.5, *J* 3.5 Hz), 3.99, 4.14 (2q, 4H, 2CH$_2$, *J* 7.0, *J* 7.1), 6.98 (s, 1H, =CH).

To complex VI, 0.115 g (0.20 mmol) VII, 0.147 g (0.20 mmol) or VIII, 0.126 g (0.30 mmol) at room temperature under N$_2$ was added diethyl fumarate (4 or 6 ml to give an 0.05 molar concentration of the complex), followed by a few drops of toluene to help dissolution. The mixture was stirred at 80 °C for 4 h. In the cases of complexes VII and VIII a weak flow of N$_2$ was used to remove the evolved CO. Work-up was carried out as for the decomposition of complex XI. The expected compound IV was not obtained from the reaction of VI, but it was from those of

Table 4

Fractional atomic coordinates with e.s.d.'s in parentheses

Atom	*x*	*y*	*z*
Co	−0.0018(2)	0.0000(0)	0.5670(2)
P	−0.0530(4)	−0.1047(2)	0.6112(4)
N	0.0762(13)	0.1001(6)	1.0470(11)
C1	−0.0989(16)	−0.1205(6)	0.7755(13)
C2	0.0267(21)	−0.1156(7)	0.9153(17)
C3	−0.0020(27)	−0.1318(9)	1.0449(20)
C4	−0.1629(22)	−0.1468(8)	1.0280(20)
C5	−0.2904(22)	−0.1514(8)	0.8925(20)
C6	−0.2595(18)	−0.1383(8)	0.7650(18)
C7	−0.2286(15)	−0.1488(7)	0.4625(14)
C8	−0.2452(20)	−0.2199(7)	0.4566(18)
C9	−0.3748(22)	−0.2529(9)	0.3392(22)
C10	−0.4822(19)	−0.2119(9)	0.2268(18)
C11	−0.4724(20)	−0.1429(8)	0.2330(18)
C12	−0.3453(17)	−0.1108(9)	0.3507(16)
C13	0.1148(14)	−0.1670(6)	0.6279(15)
C14	0.1728(16)	−0.2172(8)	0.7379(17)
C15	0.2967(19)	−0.2644(9)	0.7450(22)
C16	0.3600(19)	−0.2622(9)	0.6326(22)
C17	0.2993(21)	−0.2124(10)	0.5229(19)
C18	0.1776(18)	−0.1671(8)	0.5185(17)
C19	0.1386(21)	0.0086(10)	0.4310(16)
C20	−0.0269(22)	−0.0058(12)	0.3384(16)
C21	−0.1283(24)	0.0486(10)	0.3558(19)
C22	−0.0267(25)	0.0961(8)	0.4613(17)
C23	0.1400(24)	0.0711(11)	0.5052(20)
C24	0.1793(12)	0.0033(10)	0.7676(12)
C25	0.3535(16)	−0.0218(7)	0.7984(20)
C26	0.1297(14)	0.0442(6)	0.8585(14)
C27	−0.0479(14)	0.0618(6)	0.8006(14)
C28	−0.1452(15)	0.0388(7)	0.6647(16)
C29	−0.3282(16)	0.0481(9)	0.5856(16)
C30	0.2203(15)	0.0786(8)	1.0057(16)
C31	0.3207(22)	0.1397(10)	0.9871(20)
C32	0.3335(21)	0.0294(10)	1.1284(17)
C33	0.1144(19)	0.1519(9)	1.1613(16)
C34	−0.0800(16)	0.1052(8)	0.9154(14)
C35	−0.1253(23)	0.1800(9)	0.8583(20)
C36	−0.2205(19)	0.0742(10)	0.9593(19)

VII (22% GLC yield) and VIII (85% yield). It readily isomerized on silica to give a compound identical with *N*-methylated XII.

In a similar procedure complex VII was treated, in the same molar ratio, with phenylacetylene or benzonitrile at 110 °C for 24 h. Compound X was shown by GLC to be present in 74% yield in a mixture with phenylacetylene trimers. MS m/e: 293 (M^+), 292, 278 (100), 263, 262, 248, 232, 139, 132, 131, 124, 122, 115, 56. Compound XI (65% yield) was isolated by flash chromatography on silica, followed by preparative TLC on silica with hexane/acetone (8/2) as the eluent. Oily product. MS m/e: 294 (M^+), 279 (100), 264, 263, 247, 131, 77, 56. ^{1}H NMR ($CDCl_3$) δ (ppm): 1.43, 1.44 (2s, 12H, $4CH_3$), 2.28 (s, 3H, NCH_3), 2.43 (s, 3H, CH_3), 2.63 (s, 3H, CH_3), 7.38–7.48 (m, 5 aromatic H).

The same procedure with complex VIII did not give the expected compound II, but instead yielded triphenyltriazine (320% with respect to Co) and a cyclopentenone (34% yield) resulting from CO incorporation in to the metallacycle [2]. Use of phenylacetylene in place of the nitrile gave III (X = NMe, R^I = Me, R^{II} = H, 95% yield) and phenylacetylene trimers. Compound III was purified by TLC on silica with hexane/acetone (8/2) as eluent. Oily product. MS m/e: 365 (M^+), 251, 250 (100), 235, 234, 178, 118, 117, 77, 56. ^{1}H NMR ($CDCl_3$) δ (ppm): 1.51 (s, 12H, $4CH_3$), 2.23 (s, 3H, NCH_3), 6.9–7.5 (m, 8H, aromatic H).

Crystal data, X-ray intensity measurements, solution of the structure and refinements

A crystal of compound VI was mounted on a Philips PW 1100 automated diffractometer in a random orientation: The crystal data and the details of the data collection and refinement are summarized in Table 3. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares by use of the SHELX76 system of programs [16]. The hydrogen atoms, placed at the calculated positions, were introduced in the last refinement cycle but not refined; the atomic scattering factors and the anomalous scattering coefficients were taken from ref. 17; final atomic coordinates are given in Table 4. All the calculations were carried out on the Gould 32/77 Computer of the Centro di Studio per la Strutturistica Diffrattometrica del CNR (Parma); in addition to the quoted programs LQPARM [18] for lattice parameter refinement and PARST [19] for geometrical analysis, ORTEP [20] were used. A complete list of bond lengths and angles and lists of thermal parameters and structure factors are available from the authors.

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