Journal of Organometallic Chemistry, 193 (1980) 117—126

π-POLYOLEFIN AND π-ACETYLENE COBALT(I) COMPLEXES WITH THE TRIS(TERTIARY PHOSPHINE) 1,1,1-TRIS(DIPHENYLPHOSPHINOMETHYL)ETHANE. X-RAY STRUCTURE OF $[(\text{triphos})\text{Co}(\eta^4\text{-C}_7\text{H}_8)]\text{ClO}_4 \cdot 0.5\ \text{CH}_2\text{Cl}_2$

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(Received January 2nd, 1980)

Summary

Cationic cobalt(I) complexes with the general formula [(triphos)Co(L)]Y (triphos = 1,1,1-tris(diphenylphosphinomethyl) ethane; L = 1,3-butadiene, isoprene, 1,3-cyclohexadiene, 1,3,5-cycloheptatriene, 1,3,5,7-cyclooctatetraene, phenylacetylene, diphenylacetylene) have been obtained by reaction of cobalt perchlorate with a variety of conjugated polyolefins or with acetylenes in the presence of the triphos ligand. The crystal structure of the complex $[(\text{triphos})\text{Co}(\text{C}_7\text{H}_8)]\text{ClO}_4 \cdot 0.5\ \text{CH}_2\text{Cl}_2$ has been determined by an X-ray analysis using diffractometric data. The crystals are monoclinic, space group $P2_1/c$ with cell dimensions a 10.514(3), b 15.041(5), c 54.795(12) Å, β 92.61(3)°, $Z = 8$. The structure was solved by direct methods and refined by least-squares techniques to a final conventional R factor of 0.091. The structure, which consists of $[(\text{triphos})\text{Co}(\text{C}_7\text{H}_8)]^+$ cations, perchlorate anions, and interposed CH_2Cl_2 solvent molecules, shows that the cycloheptatriene molecule acts as a *tetrahapto* ligand. The coordination polyhedron can be regarded either as a distorted square pyramid or as a distorted octahedron. The coordination geometries of all complexes have been assigned on the basis of this structure determination and of IR and NMR data.

Introduction

Few complexes of cobalt with phosphines and π-bonded conjugated olefins are known [1,2] and up to now only the structure of a butadiene derivative has been determined by direct X-ray analysis [3].

We have found that cobalt perchlorate reacts with a variety of conjugated straight-chain and cyclic polyolefins or with acetylenes in the presence of the tripod-like triphosphine 1,1,1-tris(diphenylphosphinomethyl)ethane, triphos, yielding π-olefin or π-acetylene cobalt(I) complexes. These compounds have the general formula [(triphos)Co(L)]Y (L = 1,3-butadiene, (1), isoprene (2), 1,3-cyclohexadiene (3), 1,3,5-cycloheptatriene (4), 1,3,5,7-cyclooctatetraene (5), phenylacetylene (6), or diphenylacetylene (7)). They have been characterized by means of conductivity, and ^{1}H NMR and other spectroscopic measurements. A complete X-ray structural analysis has been carried out on the compound [(triphos)Co(C_7H_8)]ClO_4 · 0.5 CH_2Cl_2 to elucidate the binding mode of the cycloheptatriene molecule. This is of particular interest because of the different bonding geometries of cycloheptatriene in related complexes as revealed by the two reported crystal structures [4,5].

Experimental

The materials and solvents were of reagent grade quality and were used without further purification. The 1,1,1-tris(diphenylphosphinomethyl)ethane was prepared as previously described [6]. All reactions were carried out using oxygen-free solvents in an inert atmosphere. The complexes were dried in a stream of dry nitrogen.

Preparation of [(triphos)Co(C_4H_6)]BPh_4 · 3 $(CH_3)_2CO$ (1), [(triphos)Co(C_5H_8)]ClO_4 (2), [(triphos)Co(C_6H_8)]ClO_4 · $(CH_3)_2CO$ (3)

A solution of Co(ClO_4) · 6 H_2O (1 mmol, 0.37 g) in butanol (80 ml) was concentrated by heating to ca. 5 ml. After addition of isopropanol (30 ml) and triphos (1 mmol, 0.63 g) in methylene chloride (20 ml), the mixture was treated with a large excess of diene until an orange solution was obtained (ca. 2 h). The orange product crystallized out on slow evaporation of the solvent, and was filtered off and washed with isopropanol and then with petroleum ether. All the complexes were recrystallized twice from acetone/isopropanol. Crystals of the butadiene derivative were obtained by addition of $NaBPh_4$ (1 mmol, 0.35 g) in isopropanol (10 ml).

Preparation of [(triphos)Co(C_7H_8)]ClO_4 · 0.5 CH_2Cl_2 (4), [(triphos)Co(C_8H_8)]ClO_4 · 0.5 CH_2Cl_2 (5)

These complexes were prepared as described above except that the reaction mixture was warmed until crystals began to separate from the red brown solutions. The red orange cycloheptatriene and the red brown cyclooctatetraene derivatives were filtered off after ca. 2 h. Only 5 was recrystallized from methylene chloride/isopropyl alcohol, 4 being unstable in solution.

Preparation of [(triphos)Co(HC≡CPh)]ClO_4 · 0.5 CH_2Cl_2 (6) [(triphos)Co(PhC≡CPh)]ClO_4 (7)

These green crystalline products were prepared by a procedure analogous to that used for the diene derivatives except that the crystals obtained were washed first with 1 : 1 isopropanol/butyl ether and then with petroleum ether. They were recrystallized from methylene chloride/isopropanol.

Physical measurements

All physical measurements were performed as described elsewhere [7]. The

TABLE 1.

ANALYTICAL DATA AND PHYSICAL PROPERTIES

No.	Compound	Colour	Analysis found (calcd.)(%)				Λ_M [a] (ohm^{-1} cm^2 mol^{-1})
			C	H	Co	P	
1	$[(triphos)Co(C_4H_6)]BPh_4 \cdot 3(CH_3)_2CO$	orange	76.94 (76.09)	7.24 (6.79)	4.38 (4.78)		47
2	$[(triphos)Co(C_5H_8)]ClO_4$	orange	64.70 (64.90)	5.65 (5.56)	7.02 (6.92)		76
3	$[(triphos)Co(C_6H_8)]ClO_4 \cdot (CH_3)_2CO$	orange	65.69 (65.18)	6.31 (5.80)	5.96 (6.39)	10.30 (10.03)	76
4	$[(triphos)Co(C_7H_8)]ClO_4 \cdot 0.5\ CH_2Cl_2$	red-orange	64.12 (63.48)	5.47 (5.27)	6.25 (6.42)	10.20 (10.12)	— [b]
5	$[(triphos)Co(C_8H_8)]ClO_4 \cdot 0.5\ CH_2Cl_2$	red-brown	63.28 (63.95)	5.08 (5.20)	6.35 (6.34)		77
6	$[(triphos)Co(C_6H_8)]ClO_4 \cdot 0.5\ CH_2Cl_2$	green	64.29 (64.09)	5.01 (5.00)	6.02 (6.35)		80
7	$[(triphos)Co(C_{14}H_{10})]ClO_4$	green	67.74 (68.72)	5.30 (5.14)	5.86 (6.13)	9.74 (9.66)	84

[a] In nitroethane at 20°C for ca. 10^{-3} *M* solutions. [b] Decomposes in solution.

analytical and conductometric data are listed in Table 1.

The NMR spectra of the CD_2Cl_2 solutions were recorded on a Varian CFT 20 spectrometer equipped with a ^1H probe at 295 K. Chemical shifts (δ) are relative to tetramethylsilane.

Compound 1. 5.43 ppm, two central diene protons; the signals of the two CH_2 groups of butadiene overlap the signals of the triphos ligand.

Compound 2. 5.33 ppm, one diene proton; the signals of CH_3 and CH_2 groups of isoprene overlap other signals.

Compound 3. 6.03 ppm, two central diene protons; 3.28 ppm, terminal diene protons; 0.93 ppm, four protons of the two CH_2 groups of cyclohexadiene.

Compound 5. 5.51 ppm, eight protons of cyclooctatetraene.

Crystal data and data collection

The crystal used for data collection was a parallelepiped of dimensions 0.1 × 0.3 × 0.7 mm. The crystals are monoclinic and belong to the space group $P2_1/c$, with eight $[(triphos)Co(C_7H_8)]ClO_4 \cdot 0.5\ CH_2Cl_2$ formulae (two independent) in the unit cell which has the following dimensions: *a* 10.514(3), *b* 15.041(5), *c* 54.795(12) Å, β 92.61(3)°. Intensity data were collected on an automic computer-controlled diffractometer, Philips PW 1100, equipped with a graphite monochromator, using Cu-K_α radiation. All reflections with $6° \leqslant 2\theta \leqslant 100°$ were measured using the $\omega - 2\theta$ scan technique with a scan speed of 0.07° s^{-1} in a range of 0.9° across the peak. Three standard reflections were measured every 120 minutes during data collection, but no significant variation was noticed. The intensity data were corrected for Lorentz and polarization effects; the standard deviations $\sigma(I)$ were estimated as described elsewhere [8] with an instability factor equal to 0.03. A reflection was considered unobserved if the net intensity I was $<3\sigma(I)$. From the 9475 total reflections 3793 had intensity $\geqslant 3\sigma(I)$. An absorption correction, μ(Cu-K_α) 51.20 cm^{-1}, was applied by a

TABLE 2

POSITIONAL ($\times 10^4$) AND THERMAL ($\times 10^3$)[a] PARAMETERS FOR THE STRUCTURE OF [(triphos)-$Co(C_7H_8)$]$ClO_4 \cdot 0.5\ CH_2Cl_2$

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co(1)	1143(3)	4672(2)	3269(1)	34(3)	32(2)	48(3)	−1(2)	−8(2)	−7(2)
Co(2)	1803(4)	2664(2)	778(1)	42(3)	33(3)	58(3)	−3(2)	−12(2)	9(2)
P(1)	623(6)	4526(4)	2869(1)	45(5)	29(4)	53(6)	−2(4)	−16(4)	−1(4)
P(2)	−865(6)	4290(4)	3338(1)	38(5)	37(4)	69(6)	4(4)	−9(4)	−5(4)
P(3)	1786(6)	3258(4)	3323(1)	36(4)	33(4)	52(5)	−2(4)	−11(4)	0(4)
P(4)	3912(6)	2823(4)	777(1)	41(5)	39(4)	55(6)	−5(4)	−4(4)	4(4)
P(5)	1836(6)	2343(4)	376(1)	41(5)	31(4)	56(5)	−2(4)	−17(4)	6(4)
P(6)	1494(6)	4124(4)	691(1)	44(5)	27(4)	57(5)	−3(4)	−11(4)	4(4)
Cl(1)	7093(7)	3065(5)	2246(2)	61(6)	64(6)	101(8)	−6(5)	−20(6)	−14(6)
Cl(2)	4880(7)	2519(5)	4643(1)	43(5)	88(6)	68(6)	−3(5)	5(5)	3(5)

[a] The form of the thermal ellipsoid is $\exp(-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2\ U_{12}hka^*b^* + \ldots))$.

TABLE 3

POSITIONAL ($\times 10^4$) AND THERMAL ($\times 10^3$) PARAMETERS FOR THE STRUCTURE OF [(triphos)-$Co(C_7H_8)$]$ClO_4 \cdot 0.5\ CH_2Cl_2$

Atom	x	y	z	U (Å^2)
O(1)	8328(20)	2800(12)	2223(4)	111(7)
O(2)	6806(21)	3237(14)	2490(4)	127(9)
O(3)	6391(22)	2389(16)	2152(4)	148(10)
O(4)	6889(19)	3870(13)	2103(4)	101(8)
O(5)	5191(18)	1589(13)	4608(4)	110(7)
O(6)	5336(17)	2783(12)	4878(4)	92(6)
O(7)	3673(24)	2571(16)	4658(5)	146(10)
O(8)	5336(17)	3017(13)	4459(4)	95(7)
C(1)	2967(29)	5254(20)	3227(6)	55(11)
C(2)	1944(31)	5951(20)	3207(6)	34(11)
C(3)	1138(27)	5971(17)	3404(5)	44(10)
C(4)	1250(23)	5408(15)	3625(4)	58(8)
C(5)	2484(29)	5318(17)	3774(5)	61(10)
C(6)	3706(30)	5150(19)	3683(6)	55(11)
C(7)	3951(24)	5042(16)	3445(5)	55(9)
C(8)	1692(20)	2683(14)	1156(4)	38(7)
C(9)	1942(23)	1826(17)	1056(5)	55(9)
C(10)	1120(22)	1449(14)	875(4)	54(7)
C(11)	57(22)	1965(14)	810(4)	51(7)
C(12)	−892(26)	2294(17)	977(5)	74(10)
C(13)	−604(29)	2711(19)	1219(6)	76(11)
C(14)	570(22)	2935(14)	1283(4)	51(7)
C(15)	−197(22)	3436(15)	2799(5)	52(8)
C(16)	−1297(23)	3169(15)	3207(5)	54(8)
C(17)	773(24)	2466(17)	3123(5)	59(9)
C(18)	−440(23)	2825(16)	3014(5)	39(8)
C(19)	−1089(22)	1998(15)	2896(4)	45(8)
C(20)	4355(22)	3746(14)	560(4)	41(7)
C(21)	3094(19)	2940(13)	225(4)	37(7)
C(22)	2231(20)	4384(13)	393(4)	37(7)
C(23)	3363(23)	3882(15)	340(5)	46(8)
C(24)	4186(20)	4416(13)	151(4)	44(7)
Cl(3)[a]	666(23)	−84(17)	3349(5)	147(11)
Cl(4)	−991(28)	−573(18)	3093(5)	205(12)
Cl(5)	−1806(29)	−961(20)	3158(6)	154(11)
Cl(6)	−838(35)	−904(24)	3056(7)	181(14)
Cl(7)	1003(34)	−60(23)	3403(7)	107(14)

[a] This atom and the following atoms belong to the CH_2Cl_2 solvent molecules. Cl(3) and Cl(4) have population parameter of 0.5, whereas Cl(5), Cl(6), and Cl(7) have population parameter equal to 0.333.

numerical method: transmission factors varied between 0.21 and 0.77. Atomic scattering factors were taken from ref. 9. Corrections for anomalous dispersion effects were also applied [9].

Structure solution and refinement

The structure was solved by direct methods, using the SHELX program [10], which clearly showed the positions of cobalt, phosphorus, and chlorine atoms. The other non-hydrogen atoms were obtained from successive F_0 Fourier maps. The CH_2Cl_2 solvent molecules appear to be in disordered array, as shown by the several peaks of electron density found in the zone occupied by these molecules. In particular, five positions were considered to be occupied by the two chlorine atoms, two having a population parameter of 0.5, and three a population parameter of 0.333. The positions of the carbon atom of CH_2Cl_2 were localized, and were ignored in the subsequent calculations.

The structure was refined by least-squares techniques [10]. The minimized function is $\Sigma w(|F_0| - |F_c|)^2$, where w is the weight assigned to the F_0 values according to the expression $w = 1/\sigma^2(F_0)$. The carbon atoms belonging to the phenyl groups were refined using rigid-body models. The hydrogen atoms were not introduced. Anisotropic temperature factors were used for cobalt, phosphorus, and chlorine atoms of the perchlorate ions; isotropic temperature factors were used for the other atoms. The final refinement gave an R value of 0.091, whereas R_w, defined as $[\Sigma w(|F_0| - |F_c|)^2/\Sigma wF_0^2]^{1/2}$, was 0.082. A final ΔF Fourier did not show remarkable features. The final positional and thermal parameters are reported in Tables 2, 3 and 4.

TABLE 4

THERMAL (X10^3) AND DERIVED POSITIONAL PARAMETERS (X10^4) OF GROUP ATOMS

Atom	x	y	z	U (Å^2)
C(1,1)	1839(11)	4587(12)	2652(2)	44(7)
C(2,1)	2310(11)	5422(12)	2591(2)	57(8)
C(3,1)	3381(11)	5489(12)	2451(2)	78(9)
C(4,1)	3981(11)	4721(12)	2371(2)	94(10)
C(5,1)	3510(11)	3887(12)	2432(2)	104(12)
C(6,1)	2439(11)	3819(12)	2572(2)	56(8)
C(1,2)	−459(11)	5345(9)	2706(3)	49(7)
C(2,2)	−705(11)	6179(9)	2805(3)	52(7)
C(3,2)	−1561(11)	6754(9)	2684(3)	64(7)
C(4,2)	−2170(11)	6496(9)	2463(3)	61(8)
C(5,2)	−1924(11)	5661(9)	2365(3)	59(7)
C(6,2)	−1068(11)	5086(9)	2486(3)	58(7)
C(1,3)	−1390(15)	4102(8)	3656(2)	47(6)
C(2,3)	−2691(15)	3976(8)	3683(2)	60(7)
C(3,3)	−3150(15)	3816(8)	3914(2)	76(8)
C(4,3)	−2308(15)	3782(8)	4118(2)	71(8)
C(5,3)	−1007(15)	3909(8)	4091(2)	73(8)
C(6,3)	−548(15)	4069(8)	3860(2)	62(8)
C(1,4)	−2087(11)	5111(8)	3230(3)	50(7)
C(2,4)	−2182(11)	5902(8)	3360(3)	67(8)
C(3,4)	−3087(11)	6538(8)	3287(3)	71(7)
C(4,4)	−3896(11)	6383(8)	3082(3)	70(8)
C(5,4)	−3800(11)	5592(8)	2951(3)	64(7)
C(6,4)	−2896(11)	4956(8)	3025(3)	51(7)
C(1,5)	3347(11)	2752(10)	3242(3)	48(7)

TABLE 4 (continued)

Atom	x	y	z	U (Å^2)
C(2,5)	3614(11)	1889(10)	3322(3)	59(8)
C(3,5)	4640(11)	1426(10)	3231(3)	79(10)
C(4,5)	5400(11)	1825(10)	3060(3)	72(9)
C(5,5)	5134(11)	2688(10)	2980(3)	72(8)
C(6,5)	4107(11)	3152(10)	3071(3)	58(7)
C(1,6)	1692(15)	2784(9)	3624(2)	44(6)
C(2,6)	2636(15)	3069(9)	3793(2)	61(8)
C(3,6)	2611(15)	2792(9)	4036(2)	91(9)
C(4,6)	1643(15)	2231(9)	4109(2)	75(9)
C(5,6)	699(15)	1947(9)	3940(2)	93(9)
C(6,6)	724(15)	2223(9)	3697(2)	66(8)
C(1,7)	4798(12)	3096(11)	1066(2)	43(6)
C(2,7)	5254(12)	2402(11)	1214(2)	65(7)
C(3,7)	5845(12)	2586(11)	1442(2)	69(8)
C(4,7)	5979(12)	3464(11)	1521(2)	84(8)
C(5,7)	5523(12)	4158(11)	1372(2)	86(9)
C(6,7)	4933(12)	3974(11)	1145(2)	70(8)
C(1,8)	4858(13)	1837(8)	680(2)	56(7)
C(2,8)	4394(13)	980(8)	714(2)	55(7)
C(3,8)	5099(13)	245(8)	644(2)	55(7)
C(4,8)	6269(13)	369(8)	538(2)	63(7)
C(5,8)	6733(13)	1226(8)	503(2)	71(8)
C(6,8)	6027(13)	1960(8)	574(2)	61(7)
C(1,9)	387(11)	2629(8)	166(3)	58(7)
C(2,9)	—741(11)	2953(8)	257(3)	47(7)
C(3,9)	—1759(11)	3179(8)	97(3)	59(7)
C(4,9)	—1651(11)	3081(8)	—154(3)	53(6)
C(5,9)	—523(11)	2757(8)	—245(3)	59(7)
C(6,9)	495(11)	2531(8)	—85(3)	65(7)
C(1,10)	1999(14)	1169(6)	286(2)	41(6)
C(2,10)	984(14)	594(6)	322(2)	55(7)
C(3,10)	1063(14)	—296(6)	253(2)	59(7)
C(4,10)	2157(14)	—611(6)	147(2)	71(8)
C(5,10)	3173(14)	—36(6)	110(2)	73(8)
C(6,10)	3094(14)	854(6)	180(2)	50(7)
C(1,11)	2185(13)	4975(8)	906(3)	45(7)
C(2,11)	2904(13)	5677(8)	819(3)	55(7)
C(3,11)	3314(13)	6358(8)	977(3)	66(8)
C(4,11)	3004(13)	6337(8)	1222(3)	67(7)
C(5,11)	2285(13)	5636(8)	1309(3)	61(7)
C(6,11)	1875(13)	4955(8)	1151(3)	60(8)
C(1,12)	—100(10)	4620(9)	646(3)	54(7)
C(2,12)	—458(10)	5112(9)	438(3)	67(8)
C(3,12)	—1692(10)	5449(9)	409(3)	69(8)
C(4,12)	—2568(10)	5295(9)	588(3)	64(7)
C(5,12)	—2210(10)	4803(9)	796(3)	94(9)
C(6,12)	—976(10)	4466(9)	825(3)	67(7)

Results and discussion

All the [(triphos)CoL]Y complexes are diamagnetic crystalline solids. They behave as 1 : 1 electrolytes in nitroethane and are quite air stable in the solid state but rather unstable in solution; 4 undergoes rapid decomposition in solution even in an inert atmosphere.

The crystal structure of 4 consists of [(triphos)Co(C_7H_8)]$^+$ cations, per-

TABLE 5

SELECTED BOND DISTANCES AND ANGLES

Bond distances (Å)			
Co(1)—P(1)	2.241(8)	Co(2)—P(4)	2.231(8)
Co(1)—P(2)	2.237(7)	Co(2)—P(5)	2.260(8)
Co(1)—P(3)	2.248(7)	Co(2)—P(6)	2.269(7)
Co(1)—C(1)	2.13(3)	Co(2)—C(8)	2.08(2)
Co(1)—C(2)	2.13(3)	Co(2)—C(9)	1.97(3)
Co(1)—C(3)	2.09(3)	Co(2)—C(10)	2.04(2)
Co(1)—C(4)	2.24(2)	Co(2)—C(11)	2.13(2)
C(1)—C(2)	1.50(4)	C(8)—C(9)	1.43(3)
C(1)—C(7)	1.58(4)	C(8)—C(14)	1.44(3)
C(2)—C(3)	1.40(4)	C(9)—C(10)	1.40(3)
C(3)—C(4)	1.48(4)	C(10)—C(11)	1.39(3)
C(4)—C(5)	1.51(4)	C(11)—C(12)	1.47(4)
C(5)—C(6)	1.42(4)	C(12)—C(13)	1.48(4)
C(6)—C(7)	1.35(4)	C(13)—C(14)	1.31(4)
Cl(1)—O(1)	1.37(2)	Cl(2)—O(5)	1.45(2)
Cl(1)—O(2)	1.41(2)	Cl(2)—O(6)	1.41(2)
Cl(1)—O(3)	1.34(2)	Cl(2)—O(7)	1.28(3)
Cl(1)—O(4)	1.45(2)	Cl(2)—O(8)	1.38(2)

Bond Angles (deg)			
P(1)—Co(1)—P(2)	87.2(3)	P(4)—Co(2)—P(5)	87.7(3)
P(1)—Co(1)—P(3)	95.5(3)	P(4)—Co(2)—P(6)	91.6(3)
P(2)—Co(1)—P(3)	90.8(3)	P(5)—Co(2)—P(6)	90.5(3)
P(1)—Co(1)—C(1)	96.7(9)	P(4)—Co(2)—C(8)	95.9(6)
P(1)—Co(1)—C(2)	90.9(9)	P(4)—Co(2)—C(9)	91.9(7)
P(1)—Co(1)—C(3)	115.7(8)	P(4)—Co(2)—C(10)	117.3(7)
P(1)—Co(1)—C(4)	153.9(6)	P(4)—Co(2)—C(11)	156.1(6)
P(2)—Co(1)—C(1)	170.1(8)	P(5)—Co(2)—C(8)	168.3(6)
P(2)—Co(1)—C(2)	129.9(9)	P(5)—Co(2)—C(9)	127.7(8)
P(2)—Co(1)—C(3)	99.3(8)	P(5)—Co(2)—C(10)	94.8(7)
P(2)—Co(1)—C(4)	89.3(7)	P(5)—Co(2)—C(11)	91.4(7)
P(3)—Co(1)—C(1)	97.9(7)	P(6)—Co(2)—C(8)	100.5(6)
P(3)—Co(1)—C(2)	139.2(9)	P(6)—Co(2)—C(9)	141.8(8)
P(3)—Co(1)—C(3)	147.4(8)	P(6)—Co(2)—C(10)	150.8(7)
P(3)—Co(1)—C(4)	110.3(6)	P(6)—Co(2)—C(11)	112.3(6)
C(1)—Co(1)—C(2)	41.3(12)	C(8)—Co(2)—C(9)	41.3(9)
C(1)—Co(1)—C(3)	70.8(11)	C(8)—Co(2)—C(10)	73.6(9)
C(1)—Co(1)—C(4)	83.2(10)	C(8)—Co(2)—C(11)	80.8(9)
C(2)—Co(1)—C(3)	38.8(12)	C(9)—Co(2)—C(10)	40.9(10)
C(2)—Co(1)—C(4)	71.8(10)	C(9)—Co(2)—C(11)	70.0(9)
C(3)—Co(1)—C(4)	39.7(10)	C(10)—Co(2)—C(11)	39.0(9)
C(7)—C(1)—C(2)	129.7(25)	C(14)—C(8)—C(9)	126.1(20)
C(1)—C(2)—C(3)	114.6(26)	C(8)—C(9)—C(10)	121.1(21)
C(2)—C(3)—C(4)	126.2(25)	C(9)—C(10)—C(11)	114.7(20)
C(3)—C(4)—C(5)	122.0(22)	C(10)—C(11)—C(12)	125.7(22)
C(4)—C(5)—C(6)	126.4(25)	C(11)—C(12)—C(13)	125.6(24)
C(5)—C(6)—C(7)	125.1(28)	C(12)—C(13)—C(14)	119.9(27)
C(7)—C(7)—C(6)	124.0(25)	C(8)—C(10)—C(12)	125.6(23)

chlorate anions, and interposed CH_2Cl_2 solvent molecules. The two independent complex cations in the asymmetric unit are chemically equivalent. In Figure 1 a perspective view of the skeleton of one of the two complex cations is shown. Selected distances and angles are listed in Table 5.

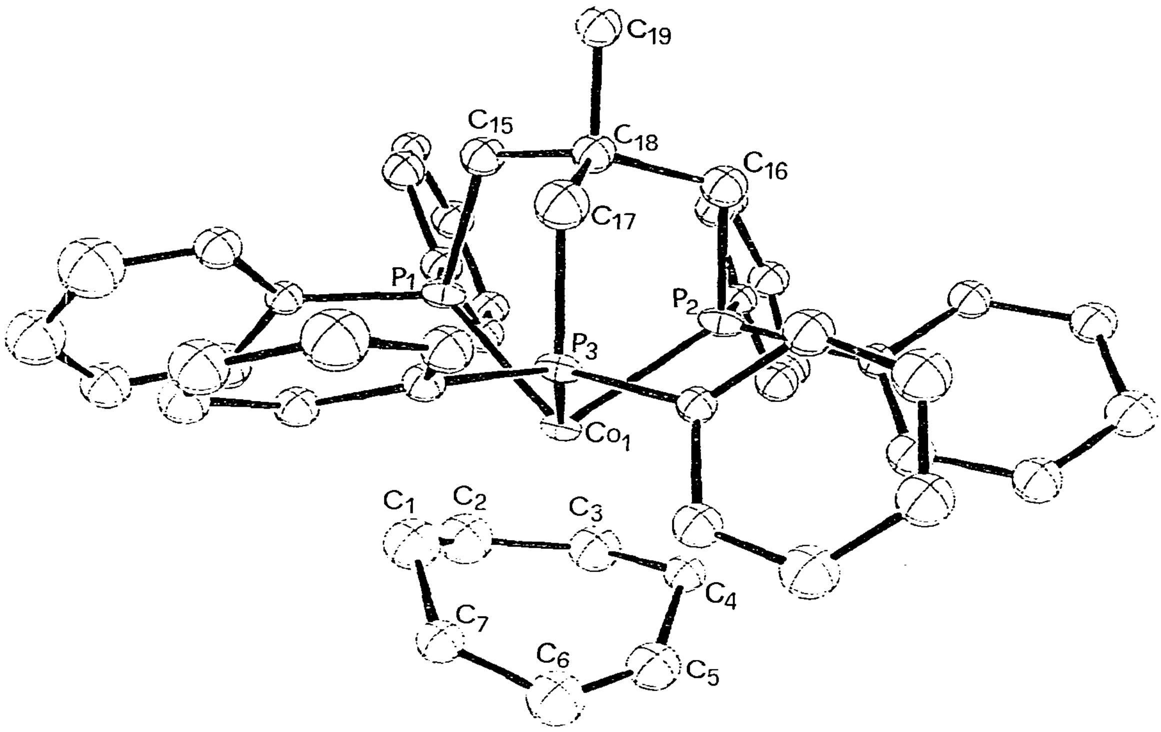
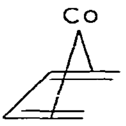


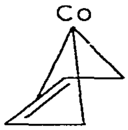
Fig. 1. Perspective view of one of the two complex cations $[(\text{triphos})Co(C_7H_8)]^+$.

The cobalt atom is coordinated by the three phosphorus atoms of the triphos ligand, and through π-bonding, by the butadiene fragment of cycloheptatriene. The carbon atoms of the seven-membered ring form two planar systems, that of the four C(1) to C(4) atoms of the butadiene fragment and that of the five C(4) to C(1) atoms which contains the uncomplexed double bond. The deviation of the carbon atoms from the two planes is less than 0.08 Å. The dihedral angles between these two planes are 40.3 and 45.6° for the two independent cations.

The C—C bond lengths within the butadienoid moiety of the ligand (see Table 5) are indicative of an internal bonding intermediate between the ground state and the first excited state, implying linkage to the cobalt atom either as in I or II.



(I)



(II)

Thus the coordination geometry around the metal may be regarded either as a square pyramid with the P(3) phosphorus atom in the apical position or as an octahedron formed by the three phosphorus atoms of the triphos ligand, by the

C(1) and C(4) atoms, and by the centre of the C(2)—C(3) bond. Analogous considerations can be extended to the other independent cation. The latter geometry is supported by the positions of the P(1), P(2), and P(3) atoms which are approximately opposite to the C(4) and C(5) atoms, and to the centre of the C(2)—C(3) linkage. The octahedral scheme (II) seems to be favoured also by the high donor capacity of the phosphorus atoms, which would increase the flow of metal electron density into the antibonding "butadiene" orbitals and consequently enhance the protomotion to its first excited state.

Concerning the length of the Co—C(butadiene fragment) bonds, the inner ones are shorter than the outer, as found in the complex $[(CO)_3Fe(C_7H_7Ph)]$ [11]. The values of the Co—P distances are close to each other and unexceptional.

As the d^8 metal in the complex cations requires only ten electrons to complete its shell, i.e. six from the three phosphorus atoms and four from cycloheptatriene, the cycloheptatriene molecule still possesses one free double bond. The perusal of distances within the two independent cycloheptatriene molecules suggests that this double bond is located between C(6)—C(7) and C(13)—C(14) respectively. This uncoordinated double bond, however, can not be detected by IR spectroscopy as in the case of the complex $[(CO)_3Fe(C_7H_8)]$ [12]. This may be ascribed to an interaction of the ring π-electrons as already suggested by Lipscomb for the compound $[(CO)_3Fe(C_8H_8)]$ [13].

On the basis of the above reported structural investigation and IR and NMR data, the coordination geometry around the cobalt atom in all the complexes of the series [(triphos)Co(polyolefin)]Y, can be assumed to be essentially the same as that of 4.

The complex cation $[(\text{triphos})Co(C_8H_8)]^+$ is of particular interest. Its ^1H resonance spectrum shows the equivalence of the eight protons of the cyclooctatetraene molecule while the infrared spectrum does not indicate any uncoordinated double bond. According to these data the complex cation can be assigned a similar structure to that of $[(CO)_3Fe(C_8H_8)]$ with the (triphos)Co group linked to only one of the two butadiene fragments of the ring [13]. It is noteworthy that the isoelectronic complex $[C_5H_5Co(C_8H_8)]$ has been reported to have the eight-membered ring in the tub from coordinated to the cobalt atom by two non-conjugated double bonds [14].

The pronounced affinity of the (triphos)Co moiety for unsaturated systems is confirmed by the preparation of the two π-acetylene derivatives $[(\text{triphos})Co(HC{\equiv}CPh)]ClO_4 \cdot 0.5\ CH_2Cl_2$ and $[(\text{triphos})Co(PhC{\equiv}CPh)]ClO_4$. The lack of characteristic IR absorption in the region of alkynes or alkenes suggests a significant perturbation of the triple bonds by their bonding to the metal. This fact is consistent with the acetylene molecules acting as formal four-electron donors [15].

Acknowledgements

Thanks are due to Messrs. F. Nuzzi and G. Vignozzi for microanalyses and to Mr. P. Innocenti for NMR measurements.

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