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COBALT(II) AND NICKEL(II) COMPLEXES WITH 1,1-BIS(DIPHENYLPHOSPHINOMETHYL)-1-DIPHENYLPHOSPHINOETHYLETHANE, atriphos, AND 1,1,1-TRIS(DIETHYLPHOSPHINOMETHYL)ETHANE, etriphos. CRYSTAL STRUCTURES OF THE TRINUCLEAR COMPLEXES $[Co_3(atriphos)_2Cl_6]$ AND $[Ni_3(etriphos)_2Cl_6] \cdot 2\ CHCl_3$

C. BIANCHINI, A. MELI, A. ORLANDINI and L. SACCONI*

Istituto di Chimica Generale ed Inorganica dell'Università, Istituto CNR, 39 via J. Nardi, 50132 Florence (Italy)

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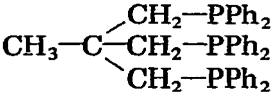
Summary

The coordination behaviour of the novel ligand 1,1-bis(diphenylphosphinomethyl)-1-diphenylphosphinoethylethane, $CH_3C(CH_2PPh_2)_2CH_2CH_2PPh_2$, atriphos, and of the ligand 1,1,1-tris(diethylphosphinomethyl)ethane, $CH_3C(CH_2PEt_2)_3$, etriphos, toward cobalt(II) and nickel(II) chlorides has been investigated. The crystal and molecular structures of the complexes $[Co_3(atriphos)_2Cl_6]$ (1) and $[Ni_3(etriphos)_2Cl_6] \cdot 2\ CHCl_3$ (4) have been determined by standard X-ray methods. Crystal data for 1: orthorombic space group $P2_12_12$, $a = 27.309(10)$, $b = 11.243(7)$, $c = 13.927(7)$ Å, $Z = 2$, $R = 0.055$. The structure consists of a non-linear trinuclear system of four-coordinate cobalt atoms each linked to two chlorine atoms and to two phosphorus atoms in a slightly distorted tetrahedral arrangement. Crystal data for 4: monoclinic, space group $P2_1/n$, $a = 13.460(8)$, $b = 23.359(10)$, $c = 9.439(7)$ Å, $\beta = 99.2(1)°$, $Z = 2$, $R = 0.074$. The structure consists of a linear trimeric array of nickel atoms, each square planar coordinated by two chlorine atoms and by two phosphorus atoms.

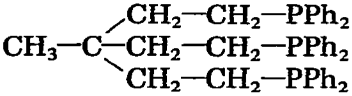
Introduction

In recent years the coordination chemistry of the tripodal triphosphines 1,1,1-tris(diphenylphosphinomethyl)ethane, triphos, (I), and 1,1,1-tris(diphenylphosphinoethyl)ethane, etp_3, (II), toward transition metals has been studied.



$$CH_3{-}C\begin{array}{l}\diagup CH_2{-}PPh_2\\ {-}CH_2{-}PPh_2\\ \diagdown CH_2{-}PPh_2\end{array}$$

(I)



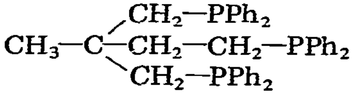
$$CH_3{-}C\begin{array}{l}\diagup CH_2{-}CH_2{-}PPh_2\\ {-}CH_2{-}CH_2{-}PPh_2\\ \diagdown CH_2{-}CH_2{-}PPh_2\end{array}$$

(II)

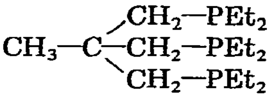
The triphos ligand, in combination with a variety of other donor groups, forms both mononuclear and dinuclear metal complexes having coordination numbers ranging from four to six [1].

The etp_3 ligand, which differs from triphos in having three ethylenic chains in place of three methylenic chains, reacts with nickel(II) halides to give stable trinuclear complexes in which the etp_3 ligand acts as a trimetallic ligand [2].

In order to obtain more information about the relative roles played by the shape of the skeleton and by the phosphorus substituents to determine both stoichiometry and structure of the resulting complexes, we have investigated the coordinating behaviour of the ligands 1,1-bis(diphenylphosphinomethyl)-1-diphenylphosphinoethylethane, atriphos, (III) and 1,1,1-tris(diethylphosphinomethyl)ethane, etriphos, (IV). These two ligands differ from triphos in having one ethylenic chain in place of one of the three methylenic chains and ethyl substituents in place of phenyl on the phosphorus atoms respectively.



(III)



(IV)

The synthesis of the ligand atriphos and the reactions of both atriphos and etriphos with cobalt(II) and nickel(II) chlorides are reported here. All the compounds have been characterized and their physical properties studied by the usual methods. Complete X-ray structural analyses have been carried out on the compounds $[Co_3(atriphos)_2Cl_6]$ and $[Ni_3(etriphos)_2Cl_6] \cdot 2\ CHCl_3$.

Experimental

All materials and solvents were of reagent grade quality and were used without further purification. Tetrahydrofuran was purified by distillation over $LiAlH_4$. The ligand etriphos was prepared as previously described [3]. The complexes were dried in a stream of dry nitrogen. The physical measurements were executed by methods previously described [4]. The NMR spectra of the CD_2Cl_2 solutions were recorded at 295 K with a Varian CFT 20 spectrometer equipped with a ^1H probe. Chemical shifts (τ) are relative to tetramethylsilane. The analytical and magnetic data for the complexes are reported in Table 1. Table 2 lists the electronic spectral data.

Preparation of the $CH_3C(CH_2PPh_2)_2CH_2CH_2PPh_2$ (atriphos) phosphine

A solution of the trichloride $CH_3C(CH_2Cl)_2CH_2CH_2Cl$ (8.8 g, 0.046 mol), (prepared as outlined in Scheme 1) in dry tetrahydrofuran (50 ml) was added with continuous stirring to a solution of $KPPh_2 \cdot 2(dioxan)$ (62 g, 0.15 mol) in tetrahydrofuran (350 ml). The mixture was heated under reflux for 12 h and than concentrated to a small volume on a steam bath. The residue was treated cautiously with diethyl ether and water; the organic layer was separated, and the solvent removed in vacuo. The residue was dissolved in methylene chloride and the solution was filtered. Ethanol was added until a colourless oil separated, and this was washed with ethanol then dried in vacuo at 100°C for 4 h. The oil

TABLE 1

ANALYTICAL AND MAGNETIC DATA FOR THE COMPLEXES

Compound	Analysis Found (Calcd.) (%)				μ_{eff}, μ_B (293 K)
	C	H	M	P	
$[Co_3(atriphos)_2Cl_6$	60.12	4.85	10.12	11.56	4.35
	(60.52)	(4.96)	(10.61)	(11.15)	
$[Ni(atriphos)Cl_2]$	65.42	5.31	7.91	(12.69)	Diam
	(65.66)	(5.38)	(7.64)	(12.09)	
$[Co_2(etriphos)_2Cl_2](BPh_4)_2$	61.50	7.10	7.15		1.72
$\cdot$ 1.5 CH_2Cl_2	(61.62)	(7.49)	(7.24)		
$[Ni_3(etriphos)_2Cl_6] \cdot 2\,CHCl_3$	33.42	6.22	13.66		Diam
	(33.25)	(6.20)	(13.54)		

TABLE 2

ABSORPTION MAXIMA AND EXTINCTION COEFFICIENTS FOR THE ELECTRONIC SPECTRA OF THE COMPLEXES

Compound	Absorption max (cm^{-1}) (ϵ_M for soln)
[Co_3(atriphos)$_2$$Cl_6$]	[a] 6800 (sh), 8250, 11 750, 14 000, 16 500, 22 700, 25 000 (sh)
[Ni(atriphos)Cl_2]	[a] 22 000, 27 000 [b] 22 000(2400), 27 000(33 000)
[Co_2(etriphos)$_2$$Cl_2$](BPh$_4$)$_2$ · 1.5 CH_2Cl_2	[a] 11 000, 21 000
[Ni_3(etriphos)$_2$$Cl_6$] · 2 $CHCl_3$	[a] 22 000, 27 300

[a] Solid at room temperature. [b] Nitroethane solution.

solidified on cooling (16 g, yield 55%). Anal. Found: C, 78.76; H, 6.58; P, 14.62. Calcd. for $C_{42}H_{41}P_3$: C, 78.98; H, 6.47; P, 14.54%. The ^1H NMR spectrum of the compound shows a thirty-proton multiplet centered at 2.70 τ, a four-proton doublet at 7.73 τ, a four-proton multiplet centered at 8.27 τ and a three-proton singlet at 9.10 τ which are assigned to the C_6H_5, P—CH_2—C, P—CH_2—CH_2—C, CH_3 protons, respectively.

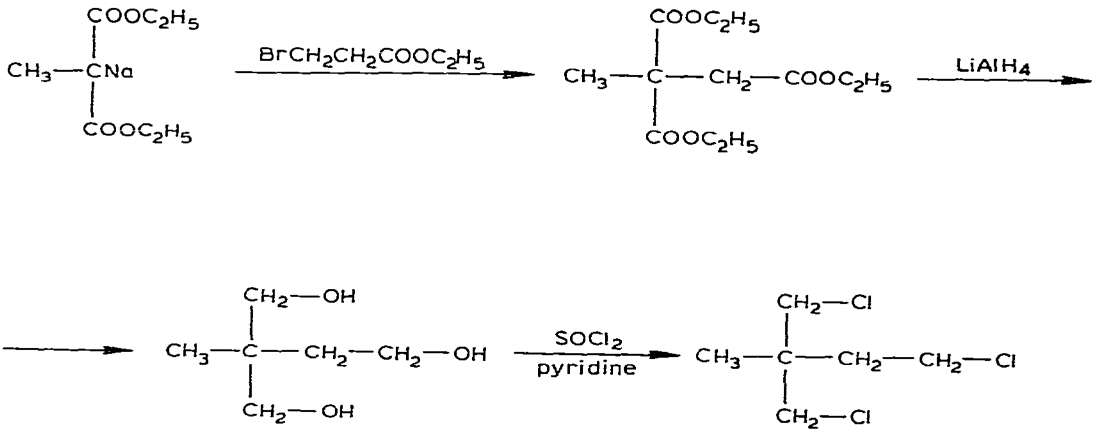
Preparation of the complexes

[Co$_3$(atriphos)$_2$Cl$_6$] (1). A solution of $CoCl_2 \cdot 6\ H_2O$ (1 mmol) in ethanol (20 ml) was added to atriphos (0.7 mmol) in acetone. On slow evaporation of the solvent turquoise crystals separated, and there were filtered off and washed with ethanol and petroleum ether.

[Ni(atriphos)Cl$_2$] (2). A solution of $NiCl_2 \cdot 6\ H_2O$ (1 mmol) in ethanol (20 ml) was added to atriphos (1 mmol) in methylene chloride (10 ml). On slow evaporation of the solvent yellow orange crystals separated, and were washed as above. They were recrystallized from methylene chloride/ethanol.

[Co$_2$(etriphos)$_2$Cl$_2$](BPh$_4$)$_2$ · 1.5 CH$_2$Cl$_2$ (3). A solution of $CoCl_2 \cdot 6\ H_2O$ (1 mmol) in ethanol (20 ml) was added to etriphos (1 mmol) in methylene chloride (20 ml). On addition of $NaBPh_4$ (1 mmol) and slow evaporation of the sol-

SCHEME 1



vent red brown crystals were formed, and there were filtered off and washed as above. They were recrystallized from methylene chloride/ethanol.

[Ni_3(etriphos)$_2Cl_6$] · 2 $CHCl_3$ (4). A solution of $NiCl_2 \cdot 6\ H_2O$ (1 mmol) in ethanol (20 ml) was added to etriphos (0.7 mmol) in chloroform (20 ml). After concentration red orange crystals separated, and these were washed as above.

Collection and reduction of X-ray data

A turquoise parallelepiped crystal of dimensions 0.25 × 0.25 × 0.15 mm for compound 1 and a red orange, parallelepiped crystal of dimensions 0.2 × 0.15 × 0.15 mm for compound 4 were chosen for crystal data collection. The crystals of compound 1 belong to orthorombic system with extenctions (*h*00 with *h* odd and 0*k*0 with *k* odd) characteristic of the space group $P2_12_12$. The crystals of compound 4 belong to monoclinic system with extinctions (*h*0*l* with $h + l$ odd and 0*k*0 with *k* odd) characteristic of the space group $P2_1/n$. For both the compounds unit cell parameters were obtained from a least-squares fit of 20 reflections carefully centered in a Philips PW 1100 diffractometer. Crystal data and data collection details for the two compounds are given in Table 3. All data processing was carried out a previously described [5]. After correction for background the standard deviation $\sigma(I)$ of the intensity I was calculated using the value of 0.04 for the instability factor k for both the compounds. An absorption correction, based upon a numerical method, was applied to intensities of compound 4, the range of the transmission factors being 0.81—0.78. Atomic

TABLE 3

CRYSTAL DATA AND DATA COLLECTION DETAILS

	[Ni_3(etriphos)$_2Cl_6$] · 2 $CHCl_3$	[Co_3(atriphos)$_2Cl_6$]
Mol. formula	$C_{36}H_{80}Cl_{12}Ni_3P_6$	$C_{84}H_{82}Cl_6Co_3P_6$
Mol. wt.	1300.45	1666.95
a, *b*, *c* (Å)	13.460(8), 23.359(10), 9.439(7)	27.309(10), 11.243(7), 13.927(7)
β (deg)	99.2(1)	90.
d_{obs} (by flotation) (g cm^{-3})	1.46	1.30
d_{calcd} (g cm^{-3})	1.47	1.294
U ($Å^3$)	2929.6	4276.1
Z	2	2
Space group	$P2_1/n$	$P2_12_12$
Abs. coeff. (Mo-K_α) cm^{-1}	16.99	9.13
Color	red orange	turquoise
Habit	parallelepiped	parallelepiped
Dimensions (mm)	0.2 × 0.15 × 0.15	0.25 × 0.25 × 0.15
Diffractometer	Philips PW 1100	Philips PW 1100
λ(Mo-K_α) (Å)	0.7107	0.7107
Monochromator	flat graphite crystal	flat graphite crystal
Method	$\omega - 2\vartheta$	$\omega - 2\vartheta$
Scan speed	0.08	0.06
Scan range	A + Btgϑ, A = 1.1 B = 0.3	A + Btgϑ, A = 0.8 B = 0.3
background time	half scan time	half scan time
standards	3 every 2 h	3 every 2 h
2ϑ limits (deg)	5—40	5—40
No. of total data	3024	2307
No. of data with $I \geqslant 3\sigma(I)$	767	1190

scattering factors and dispersion corrections, as well as absorption corrections were taken from ref. 6.

Solution and refinement of the structures

The calculations were carried out using the SHELX76 crystallographic system [7] on a SEL 32/70 computer installed in our Institute. A three-dimensional Patterson synthesis coupled with successive Fourier maps showed the positions of all the non-hydrogen atoms for both the structures. Refinement was performed by using full-matrix least-squares techniques, the function minimized being $\Sigma w(|F_0| - |F_c|)^2$ in which w is the weight assigned to the F_0 according to the expression $w = 1/[\sigma^2(F_0) + g(F_0)^2]$ (g was set 0.08 and 0 for complexes 1 and 4, respectively). The hydrogen atoms were introduced in their geometrical calculated positions, but not refined.

[Co$_3$(atriphos)$_2$Cl$_6$]. Owing to the special position of one cobalt atom, which lies on a twofold axis, only one half of the trimeric molecule was determined. Refinement was carried out by some isotropic cycles on all atoms and then some mixed cycles where cobalt, phosphorus and chlorine atoms were assigned anisotropic thermal motions. During the refinement the phenyl rings were treated as rigid groups of D_{6h} symmetry with C—C = 1.395 Å. Owing to the acentric space group $P2_12_12$ the absolute configuration of the structure had to be to determined using the anomalous dispersion corrections (real and imaginary part). Final least-squares cycles gave R and R_w values of 0.055 and 0.065 for the x, y, z structure and values of 0.058 and 0.069 for the inverted $\bar{x}$, $\bar{y}$, $\bar{z}$. An analysis of the standard deviations of the parameters confirmed that the x, y, z structure was the correct one.

[Ni$_3$(etriphos)$_2$Cl$_6$] · 2 CHCl$_3$. Since the molecule contains a crystallographic inversion center, the structure solution required the determination of one half of the molecule. Refinement was undertaken by some isotropic cycles on all the non-hydrogen atoms, and then was performed with mixed cycles with aniso-

TABLE 4

POSITIONAL (X10^4) AND THERMAL ^{a} (X10^3) PARAMETERS WITH ESTIMATED STANDARD DEVIATIONS FOR [Co$_3$(atriphos)$_2$Cl$_6$]

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Co(1)	−2603(1)	285(3)	−2684(2)	56(2)	42(2)	41(2)	4(2)	0(1)	2(2)
Co(2)	−5000	0	547(3)	53(3)	75(4)	58(3)	0	0	−2(3)
P(1)	−2471(2)	−1274(5)	−1584(4)	55(4)	34(3)	37(3)	3(3)	4(3)	2(3)
P(2)	−3463(2)	292(6)	−2688(4)	60(4)	55(4)	36(3)	−2(4)	−3(3)	4(4)
P(3)	−4290(2)	−377(6)	1501(4)	52(4)	54(4)	52(3)	−7(4)	11(3)	0(4)
Cl(1)	−2450(2)	1873(5)	−1776(5)	72(5)	41(3)	86(5)	−10(3)	−10(4)	2(4)
Cl(2)	−2236(2)	165(7)	−4090(4)	93(4)	86(5)	55(3)	5(4)	17(3)	−13(4)
Cl(3)	−4795(3)	1566(8)	−312(6)	97(5)	136(7)	129(7)	69(6)	37(5)	23(6)
C(1)	−3624(8)	−2348(19)	−1545(16)	53(6)					
C(2)	−3492(7)	−1225(19)	−980(14)	42(5)					
C(3)	−2956(7)	−1205(20)	−693(14)	46(6)					
C(4)	−3668(7)	−48(20)	−1471(13)	49(6)					
C(5)	−3814(7)	−1318(18)	−19(13)	41(5)					
C(6)	−3753(7)	−347(21)	703(15)	57(6)					

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

TABLE 5

THERMAL ($\times 10^3$) AND DERIVED POSITIONAL PARAMETERS OF GROUP ATOMS ($\times 10^4$) WITH ESTIMATED STANDARD DEVIATIONS FOR [$Co_3(atriphos)_2Cl_6$]

Atom	*x/a*	*y/b*	*z/c*	*U*
C(1, 1)	−2452(6)	−2797(12)	−2040(10)	42(6)
C(2, 1)	−2339(6)	−2936(12)	−3010(10)	67(7)
C(3, 1)	−2317(6)	−4072(12)	−3411(10)	95(9)
C(4, 1)	−2409(6)	−5068(12)	−2842(10)	83(8)
C(5, 1)	−2523(6)	−4929(12)	−1872(10)	78(7)
C(6, 1)	−2544(6)	−3793(12)	−1470(10)	73(7)
C(1, 2)	−1922(5)	−1099(12)	−871(10)	38(5)
C(2, 2)	−1826(5)	−1796(12)	−64(10)	64(7)
C(3, 2)	−1393(5)	−1632(12)	452(10)	76(8)
C(4, 2)	−1057(5)	−771(12)	160(10)	79(8)
C(5, 2)	−1153(5)	−74(12)	−647(10)	68(7)
C(6, 2)	−1586(5)	−239(12)	−1162(10)	61(6)
C(1, 3)	−3707(6)	1756(14)	−2952(11)	67(7)
C(2, 3)	−4159(6)	2136(14)	−2603(11)	70(7)
C(3, 3)	−4330(6)	3273(14)	−2824(11)	78(8)
C(4, 3)	−4049(6)	4029(14)	−3395(11)	92(9)
C(5, 3)	−3596(6)	3648(14)	−3745(11)	95(9)
C(6, 3)	−3426(6)	2512(14)	−3523(11)	74(8)
C(1, 4)	−3809(6)	−699(15)	−3496(11)	56(7)
C(2, 4)	−4316(6)	−829(15)	−3431(11)	74(8)
C(3, 4)	−4558(6)	−1637(15)	−4025(11)	105(10)
C(4, 4)	−4293(6)	−2315(15)	−4683(11)	98(11)
C(5, 4)	−3787(6)	−2186(15)	−4748(11)	131(13)
C(6, 4)	−3544(6)	−1378(15)	−4154(11)	82(8)
C(1, 5)	−4258(4)	−1805(13)	2086(11)	41(6)
C(2, 5)	−3837(4)	−2285(13)	2502(11)	47(6)
C(3, 5)	−3864(4)	−3355(13)	3006(11)	81(9)
C(4, 5)	−4311(4)	−3946(13)	3093(11)	95(10)
C(5, 5)	−4731(4)	−3466(13)	2677(11)	106(10)
C(6, 5)	−4705(4)	−2395(13)	2174(11)	68(7)
C(1, 6)	−4161(5)	700(13)	2460(9)	57(7)
C(2, 6)	−3986(5)	1827(13)	2219(9)	51(6)
C(3, 6)	−3910(5)	2675(13)	2934(9)	80(8)
C(4, 6)	−4007(5)	2396(13)	3891(9)	83(9)
C(5, 6)	−4182(5)	1269(13)	4133(9)	106(10)
C(6, 6)	−4259(5)	421(13)	3417(9)	77(7)

tropic thermal factors assigned to nickel, phosphorus and chlorine atoms. The solvent molecule of $CHCl_3$ was refined isotropically. A final difference Fourier map showed no residual electron density greater than 0.4 $e^-/Å^3$. This residue was near the terminal carbon atoms of the ethylenic chains as well as in the region of the solvent molecule. At convergence the final R and R_w factors were 0.074 and 0.067, respectively.

The refined positional and thermal parameters are given in Tables 4, 5 and 6. Tables of structure factors are available on request (from L.S.).

Results and discussion

Atriphos complexes

Atriphos reacts with cobalt(II) chloride in acetone/alcohol to give turquoise crystals of composition [$Co_3(atriphos)_2Cl_6$] (1). This compound is stable in air

TABLE 6

POSITIONAL ($\times10^4$) AND THERMAL[a] ($\times10^3$) PARAMETERS WITH ESTIMATED STANDARD DEVIATIONS FOR [Ni_3(etriphos)$_2Cl_6$] · 2 $CHCl_3$

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ni(1)	5000	5000	5000	42(5)	58(6)	42(5)	−1(5)	3(4)	−10(4)
Ni(2)	1390(4)	2919(2)	3909(6)	40(3)	73(5)	80(4)	6(4)	−6(3)	−9(3)
P(1)	5479(8)	4347(5)	6732(10)	46(7)	61(10)	34(7)	2(7)	1(6)	−3(7)
P(2)	1674(8)	3104(6)	6185(13)	50(8)	105(12)	81(9)	23(9)	3(7)	−20(8)
P(3)	2889(7)	3134(5)	3498(11)	49(7)	60(11)	61(8)	9(8)	−6(6)	7(7)
Cl(1)	4448(7)	5526(5)	6606(11)	49(8)	47(9)	49(8)	−15(7)	9(6)	9(7)
Cl(2)	−112(7)	2645(6)	4208(12)	66(8)	200(14)	114(10)	−22(10)	3(8)	−59(8)
Cl(3)	1021(8)	2759(5)	1579(11)	93(8)	118(12)	72(8)	−1(9)	−18(7)	−29(8)
C(1)	2893(22)	4240(14)	5564(33)	42(10)					
C(2)	3549(26)	3756(15)	6179(37)	44(10)					
C(3)	4494(26)	3919(16)	7280(39)	67(14)					
C(4)	2906(27)	3365(19)	6979(41)	83(14)					
C(5)	3872(22)	3398(16)	5015(34)	45(11)					
C(6)	6371(26)	3812(17)	6367(44)	74(14)					
C(7)	7412(26)	4077(18)	6290(43)	91(17)					
C(8)	5981(27)	4644(15)	8469(35)	72(13)					
C(9)	6279(26)	4278(16)	9754(37)	67(13)					
C(10)	1472(32)	2545(21)	7430(49)	128(19)					
C(11)	1969(33)	2025(23)	7286(54)	134(21)					
C(12)	769(30)	3678(17)	6641(44)	87(15)					
C(13)	948(35)	3906(20)	8134(52)	130(20)					
C(14)	2841(29)	3666(18)	2084(42)	84(15)					
C(15)	3665(32)	3617(18)	1139(47)	125(18)					
C(16)	3483(25)	2514(17)	2913(40)	77(14)					
C(17)	3481(28)	2009(18)	3989(43)	95(15)					
C(18)[b]	361(38)	5944(22)	7772(55)	141(20)					
Cl(4)[b]	847(13)	5570(8)	9450(20)	206(8)					
Cl(5)[b]	−564(14)	5388(8)	7011(22)	216(8)					
Cl(6)[b]	1408(14)	5659(9)	6849(21)	208(8)					

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

in the solid state and virtually insoluble in all common organic solvents except *N,N*-dimethylformamide. Conductivity measurements in the latter solvent indicate some dissociation in solution (the values fall in the range 71—79 cm^2 ohm^{-1} mol^{-1} for 10^{-3} molar solutions).

The molecular structure of 1 consists of a non-linear trinuclear system of cobalt atoms, each tetracoordinated by two chlorine atoms and by two phosphorus atoms in a slightly distorted tetrahedral arrangement. The central cobalt is coordinated by the phosphorus atoms of the ethylenic chain of two different atriphos ligands, while the other two cobalt atoms, which are crystallographically equivalent, are each coordinated by the remaining phosphorus atoms of each atriphos ligand. The three cobalt units, which are in a triangular array, are thus held together by two atriphos ligands. A perspective drawing of the complex molecule is shown in Fig. 1. Selected bond lengths and bond angles are given in Table 7. The values of the Co—P and Co—Cl bond distances agree well with those found for other tetrahedral cobalt(II) complexes [8].

The room temperature magnetic moment of 4.35 μ_B per metal center and the

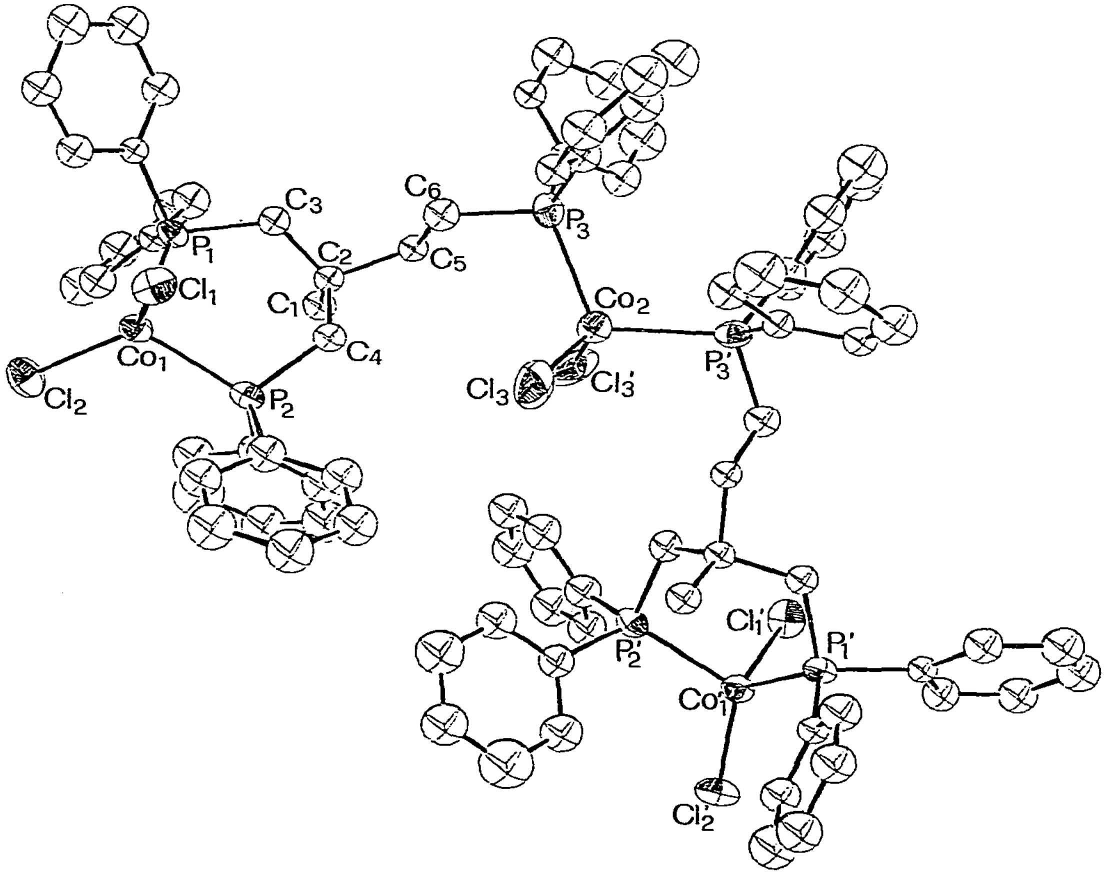


Fig. 1. Perspective view of the complex molecule $[Co_3(atriphos)_2Cl_6]$. ORTEP drawing with 50% probability ellipsoids.

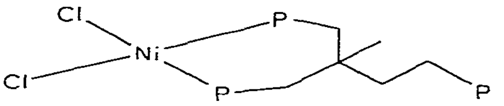
TABLE 7

SELECTED BOND LENGTHS (Å) AND BOND ANGLES (°) FOR $[Co_3(atriphos)_2Cl_6]$

Co(1)—P(1)	2.356(6)	P(2)—C(1, 3)	1.81(2)
Co(1)—P(2)	2.350(6)	P(2)—C(1, 4)	1.84(2)
Co(1)—Cl(1)	2.227(6)	P(3)—C(6)	1.84(2)
Co(1)—Cl(2)	2.204(6)	P(3)—C(1, 5)	1.80(2)
Co(2)—P(3)	2.388(6)	P(3)—C(1, 6)	1.84(2)
Co(2)—Cl(3)	2.201(8)	C(1)—C(2)	1.53(3)
P(1)—C(3)	1.82(2)	C(2)—C(3)	1.52(3)
P(1)—C(1, 1)	1.83(2)	C(2)—C(4)	1.57(3)
P(1)—C(1, 2)	1.81(2)	C(2)—C(5)	1.60(3)
P(2)—C(4)	1.83(2)	C(5)—C(6)	1.49(3)
P(1)—Co(1)—P(2)	99.0(2)	Cl(1)—Co(1)—Cl(2)	117.9(3)
P(1)—Co(1)—Cl(1)	101.4(2)	P(3)—Co(2)—Cl(3)	103.8(3)
P(1)—Co(1)—Cl(2)	117.6(3)	P(3)—Co(2)—Cl(3')	111.5(3)
P(2)—Co(1)—Cl(1)	100.7(2)	P(3)—Co(2)—P(3')	112.4(3)
P(2)—Co(1)—Cl(2)	116.9(2)	Cl(3)—Co(2)—Cl(3')	114.1(3)

reflectance spectrum (Table 2) are consistent with those reported for other pseudo-tetrahedral cobalt(II) complexes [9,10].

When atriphos reacts with nickel(II) chloride in methylene chloride/alcohol the solution turns red orange. Concentration of the solution precipitates yellow orange crystals of empirical formula $[Ni(atriphos)Cl_2]$ (2). Compound 2 is diamagnetic and stable in air both in the solid state and in solution. It is soluble in common organic solvents and the solutions do not conduct electricity. The electronic spectrum, with no absorption below 20000 cm^{-1}, is typical of square-planar nickel(II) complexes [11]. On the basis of analytical, spectroscopic, magnetic and conductivity measurements the nickel atom of this complex may be assumed to be square planar, coordinated by two chlorine atoms and by two phosphorus atoms belonging to the two shorter chains of the tripodal ligand, which thus displays an uncoordinated phosphorus atom (V).



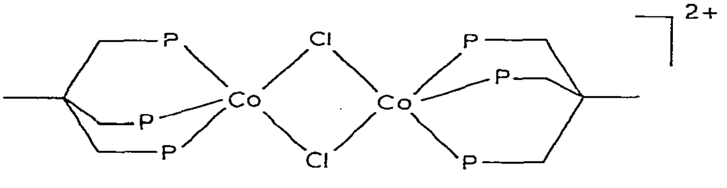
(V)

Such a structure is favoured because it involves a six-membered chelate ring rather than a less favourable seven-membered ring.

Etriphos complexes

When etriphos and cobalt(II) chloride react in methylene chloride/alcohol an intense dark brown solution is obtained. Upon addition of $NaBPh_4$ red brown crystals of composition $[Co_2(etriphos)_2Cl_2](BPh_4)_2 \cdot 1.5\ CH_2Cl_2$ (3) are precipitated. The complex is sparingly soluble in chlorinated hydrocarbons and decomposes rapidly in solvents such as nitroethane and nitromethane, as shown by absorption spectra. For this reason this compound has not been studied in solution. Compound 3 shows antiferromagnetic behaviour. The magnetic moment decreases with temperature from 1.72 μ_B at 295 K to 1.07 μ_B at 86 K.

The reflectance spectrum with bands at 11000 and 21000 cm^{-1} is fully comparable to that of the analogous complex $[Co_2(triphos)_2Cl_2](BPh_4)_2 \cdot 4\ CH_2Cl_2$ which has been assigned a double bridged structure with two chloride bridges between a pair of cobalt atoms [12]. Such a structure can also be assigned to compound 3, where each cobalt atom is five-coordinated by three phosphorus atoms of the etriphos ligand and by two bridging chlorine atoms (VI).



(VI)

The reaction of etriphos with nickel(II) chloride in chloroform/alcohol produces a red-orange solution, from which red-orange crystals of the composition $[Ni_3(etriphos)_2Cl_6] \cdot 2\ CHCl_3$ (4) are precipitated. Compound 4 is stable in air in the solid state and insoluble in common organic solvents. It is diamagnetic and has a reflectance spectrum, with two intense bands at frequencies higher that 20 000 cm^{-1}, clearly diagnostic of a four-coordinate planar environment [11].

The X-ray analysis of compound 4 has shown that it contains trinuclear complex molecules $[Ni_3(etriphos)_2Cl_6]$ with some chloroform interspersed in the

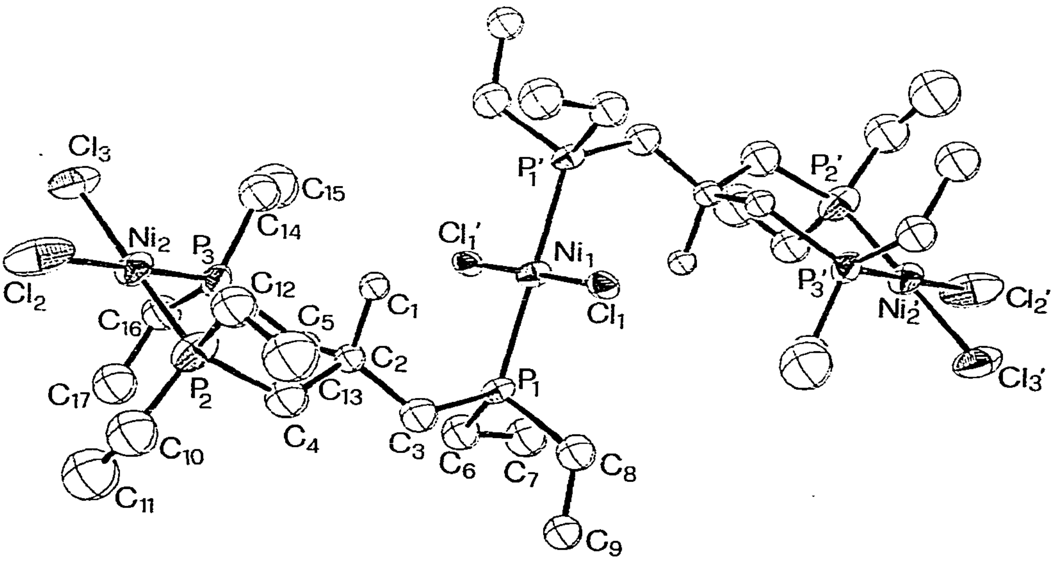


Fig. 2. Perspective view of the complex molecule $[Ni_3(etriphos)_2Cl_6]$. ORTEP drawing with 50% probability ellipsoids.

TABLE 8

SELECTED BOND LENGTHS (Å) AND BOND ANGLES (°) FOR $[Ni_3(etriphos)_2Cl_6] \cdot 2\ CHCl_3$

Ni(1)—P(1)	2.254(9)	P(3)—C(5)	1.89(3)
Ni(1)—Cl(1)	2.172(9)	P(3)—C(14)	1.82(4)
Ni(2)—P(2)	2.164(12)	P(3)—C(16)	1.78(4)
Ni(2)—P(3)	2.174(11)	C(1)—C(2)	1.50(4)
Ni(2)—Cl(2)	2.181(10)	C(2)—C(3)	1.56(4)
Ni(2)—Cl(3)	2.208(11)	C(2)—C(4)	1.54(4)
P(1)—C(3)	1.80(3)	C(2)—C(5)	1.50(4)
P(1)—C(6)	1.80(3)	C(6)—C(7)	1.54(4)
P(1)—C(8)	1.81(3)	C(8)—C(9)	1.49(4)
P(2)—C(4)	1.81(3)	C(10—C(11)	1.40(5)
P(2)—C(10)	1.81(4)	C(12)—C(13)	1.49(5)
P(2)—C(12)	1.91(4)	C(14)—C(15)	1.53(5)
		C(16)—C(17)	1.56(4)
P(1)—Ni(1)—Cl(1)	88.1(3)	P(3)—Ni(2)—Cl(2)	175.4(5)
P(2)—Ni(2)—P(3)	96.3(4)	P(3)—Ni(2)—Cl(3)	85.9(4)
P(2)—Ni(2)—Cl(2)	87.2(4)	Cl(2)—Ni(2)—Cl(3)	90.8(4)
P(2)—Ni(2)—Cl(3)	176.8(5)		

lattice. A perspective view of the complex molecule is shown in Fig. 2. Selected bond lengths and bond angles are reported in Table 8. The molecular structure of 4 consists of a centrosymmetric, and thus linear, array of three nickel atoms with two bridging etriphos ligands. Each nickel center is square planar coordinated. While the outer nickel atoms are each four coordinated by two chlorine atoms and by two phosphorus atoms of the same etriphos ligand in a *cis* arrangement, the central nickel is coordinated by two chlorine atoms and by two phosphorus atoms of two different etriphos ligands in a *trans* arrangement.

It is interesting to note that the distortion from an ideal square planar coordination is more evident in the terminal units than in the central unit, probably due to the steric requirements of the etriphos ligand when acting as a bidentate ligand toward a metal. Although the values found for the Ni—P and Ni—Cl bond distances are well with the ranges found for square-planar nickel(II) complexes [2,13], the Ni—P bonds are larger in the central unit (2.254(9) Å) than in the terminal uhit (2.169(12)Å) as already noted in the complex $[Ni_3(Etnp_3)_2Cl_4](BPh_4)_2$ [14].

Conclusions

The atriphos ligand coordinates to metal atoms in the following two different ways: biligate monometallic and triligate bimetallic. The coordination behaviour of atriphos seems to depend strongly on the length of its ethylenic chain and thus on the higher stability of the six- than of seven-membered chelate rings.

The etriphos ligand, which resembles triphos in its bonding in the cobalt derivative, shows a more specific behaviour in favouring the formation of a tricentric nickel complex. Steric hindrance of the phosphorus substituents seems to have a strong influence on the formation of such a complex. The effect of such an influence also on the coordination properties of variously substituted tetradentate ligands, namely np_3, $Menp_3$ and $Etnp_3$, has already been extensively investigated [14].

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