

Trimeric Nickel(II) Complexes with Bridging Triphosphine Ligand 1,1,1-tris-(diphenylphosphinoethyl)ethane (etp₃). X-Ray Structure of the Complex [Ni₃Cl₆(etp₃)₂] · 0.7CHCl₃

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The tripod-like triphosphine (PPh₂CH₂CH₂)₃-CCH₃, etp₃, forms with nickel(II) halides trinuclear complexes of formula [Ni₃X₆(etp₃)₂] (X = Cl, Br, I), where the etp₃ phosphine acts as trimetallic ligand, its three phosphorus atoms being linked to the three different nickel atoms. The chloroderivative has been studied by X-ray analysis, using diffractometer data. The crystals are monoclinic, space group P2₁/a, a = 26.27(1), b = 28.84(2), c = 11.91(1), β = 99.0(2)°, d_m = 1.36 g cm⁻³, d_c = 1.354 g cm⁻³ for Z = 4. The structure has been solved by three-dimensional Patterson and Fourier syntheses and refined by least-squares techniques to final R and R_w factors of 0.072 and 0.073 respectively. The complex molecule is trinuclear, with three four-coordinate nickel ions, bridging two etp₃ ligands.

Introduction

The polytertiary tripod-like ligand 1,1,1-tris(diphenylphosphinomethyl)ethane, triphos, forms several mononuclear or dinuclear metal complexes with coordination number ranging from four to six. Generally this triphosphine acts as monometallic ligand, the three phosphorus atoms being linked to the same metal atom [1].

In order to study the influence of the skeleton shape of the ligand on its coordination capacities, the ligand of formula (PPh₂CH₂CH₂)₃CCH₃, etp₃, which differs from triphos for having three ethylenic chains in the place of the three methylenic ones has been synthesized.

By reacting etp₃ with nickel(II) halides in ethanol solution, trinuclear complexes of formula [Ni₃X₆(etp₃)₂], X = Cl, Br, I are obtained, where the ligand etp₃ acts as a trimetallic ligand, its three phosphorus atoms being linked to the three different nickel atoms. These compounds were characterized by the

usual physical methods. An X-ray analysis of the [Ni₃Cl₆(etp₃)₂] · 0.7HCCl₃ complex has been carried out.

Experimental

Preparation of the CH₃-C(CH₂-CH₂-PPh₂)₃ (etp₃) Phosphine

All operations were carried out in a nitrogen atmosphere. 0.03 l mol of CH₃-C(CH₂-CH₂-Br)₃, 1,1,1-tris(bromoethyl)ethane [2], in dry tetrahydrofuran (50 ml) was added with continuous stirring to 0.10 mol of KPPH₂ · 2(dioxan) [3] dissolved in tetrahydrofuran (200 ml). The solution was heated under reflux for 5 h and then concentrated to a small volume on a steam bath. The residue was treated cautiously with diethyl ether and water; the organic phase was separated, and the solvent removed *in vacuo*. The residue was dissolved in methylene chloride, the resulting solution was filtered and concentrated. Ethanol was added and colorless crystals of the triphosphine separated (16 gr, yield 76%, mp 167-168 °C). *Anal.* Calcd. for C₄₄H₄₅P₃: C, 79.26; H, 6.80. Found: C, 79.21; H, 6.95. The ¹H nmr spectrum of the compound shows a thirty-proton multiplet centered at 7.32, a six-proton multiplet centered at 1.66, a six-proton multiplet at 1.36 and three-proton singlet at 0.85 which are assigned to the C₆H₅, P-CH₂, C-CH₂-C and CH₃ protons respectively.

Preparation of the [Ni₃Cl₆(etp₃)₂] · 0.7CHCl₃ Complex

1 mmol of NiCl₂ · 6H₂O in 10 ml of ethanol was added to 0.7 mmol of triphos in 20 ml of CHCl₃. After distillation of the solvent, red crystals precipitated, which were filtered off and washed with ethanol and petroleum ether before being dried. The compound is indefinitely stable in dry atmosphere. *Anal.* Calcd. for C_{88.7}H_{90.7}Cl_{8.1}Ni₃P₆: C, 58.99; H, 5.06; Ni, 9.75. Found: C, 59.10; H, 5.21; Ni, 9.58. *Anal.* Calcd. for C₈₉H₉₂Br₆Cl₂Ni₃P₆: C, 51.54; H, 4.47; Ni, 8.49. Found: C, 51.56; H, 5.54; Ni, 8.25.

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TABLE I. Atomic^a Parameters ($\times 10^4$) with Estimated Standard Deviations.

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ni1	1051(1)	1151(1)	2348(2)	379(14)	408(14)	481(16)	3(13)	39(12)	5(12)
Ni2	2829(1)	3316(1)	3424(2)	484(15)	398(15)	433(16)	-2(13)	76(12)	-37(12)
Ni3	3771(1)	1119(1)	4742(2)	376(14)	518(15)	478(16)	-4(13)	25(12)	25(12)
P1	930(2)	1205(2)	4142(4)	295(28)	426(31)	477(32)	-35(27)	21(24)	-14(23)
P2	2560(2)	3387(1)	5109(4)	454(30)	393(30)	431(32)	-50(26)	74(25)	-54(24)
P3	3564(2)	1241(2)	6469(4)	361(30)	552(34)	488(35)	24(28)	34(26)	32(25)
P4	1349(2)	1069(2)	708(4)	377(29)	420(30)	503(34)	-53(27)	-22(26)	25(24)
P5	2979(2)	3227(2)	1643(4)	426(31)	416(31)	436(33)	21(26)	63(26)	-35(24)
P6	3950(2)	1034(2)	2971(4)	359(29)	448(32)	496(35)	31(27)	11(26)	15(24)
Cl1	788(2)	440(1)	2284(4)	546(31)	458(30)	669(35)	-52(27)	23(27)	-154(24)
Cl2	1062(2)	1898(1)	2204(4)	911(38)	435(30)	654(37)	30(27)	239(30)	117(26)
Cl3	3254(2)	2695(1)	4001(4)	485(29)	516(31)	504(32)	81(25)	37(24)	29(23)
Cl4	2572(2)	4014(1)	2972(4)	1114(41)	419(31)	636(36)	78(27)	261(32)	70(28)
Cl5	3019(2)	816(2)	4184(4)	532(32)	857(38)	618(36)	-109(30)	94(27)	-185(27)
Cl6	4567(2)	1252(2)	5407(4)	379(28)	906(39)	581(34)	-83(29)	-23(25)	18(25)

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

TABLE II. Atomic Parameters ($\times 10^4$) with Estimated Standard Deviations.

Atom	x/a	y/b	z/c	U
C1	2015(6)	2040(5)	6992(14)	459(48)
C2	2177(6)	1994(5)	5788(14)	446(48)
C3	1843(5)	1636(5)	5005(12)	370(43)
C4	1239(6)	1697(5)	4951(14)	534(50)
C5	2118(5)	2476(5)	5147(12)	365(44)
C6	2456(5)	2854(5)	5880(13)	415(45)
C7	2747(6)	1837(5)	5857(13)	388(45)
C8	2885(6)	1377(5)	6511(13)	405(45)
C9	2862(6)	1713(5)	-144(13)	436(46)
C10	2744(6)	1788(5)	1081(13)	398(45)
C11	2275(6)	1494(5)	1319(13)	443(47)
C12	1796(6)	1539(5)	398(13)	430(47)
C13	2615(5)	2316(5)	1278(13)	397(45)
C14	3098(5)	2636(5)	1185(13)	374(44)
C15	3221(5)	1655(5)	1998(13)	418(45)
C16	3403(5)	1139(5)	1813(13)	442(46)
*C17	472(13)	2980(12)	6919(31)	1294(33)
*Cl71	873(7)	3232(6)	6387(16)	1294(33)
*Cl72	642(19)	2885(18)	5800(46)	1294(33)
*Cl81	326(6)	3220(6)	8092(15)	1294(33)
*Cl82	620(9)	2766(8)	8338(21)	1294(33)
*Cl91	276(10)	2566(9)	5986(23)	1294(33)
*Cl92	560(11)	2430(11)	7089(28)	1294(33)

*Atomic positions belonging to solvent molecule.

Preparation of the $[Ni_3Br_6(etc)_3] \cdot CH_2Cl_2$ Complex

The compound was obtained as purple crystals with a method analogous to that described above.

Preparation of the $[Ni_3I_6(etc)_3] \cdot CH_2Cl_2$ Complex

The compound was obtained as green crystals with a method analogous to that above described. *Anal.*

Calcd. for $C_{89}H_{92}Cl_2I_6Ni_3P_6$: C, 45.37; H, 3.94; Ni, 7.48. Found: C, 46.58; H, 4.37; Ni, 6.99.

Physical Measurements

Conductivity measurements, magnetic susceptibilities and electronic spectra were recorded by previously described methods [4]. The 1H nmr spectra were recorded on Varian CFT20 apparatus.

Collection and Reduction of X-Ray Data

A well-formed, prismatic shaped crystal having dimensions $0.35 \times 0.3 \times 0.15$ mm was set up on the goniometric head along its a-axis. The crystals are monoclinic, space group $P2_1/a$ with the following crystal data: $a = 26.27(1)$, $b = 28.84(2)$, $c = 11.91(1)$ Å, $\beta = 99.0(2)^\circ$, $U = 8911.48$ Å³, $d_m = 1.36$ g cm⁻³, $d_c = 1.354$ g cm⁻³ for $Z = 4$, $\mu(Mo-K\alpha) = 10.23$ cm⁻¹. The lattice constants were determined by the least-squares refinement of 20 reflections centered on a Philips PW 1100 automatic computer-controlled diffractometer. Intensity data were recorded on the same diffractometer using Mo-K α radiation monochromatized by a flat graphite crystal. The ω - 2θ scan technique was used with a scan rate of $0.07^\circ/s$ and a scan width calculated according to the formula $(A + B\theta)$, the values of A and B being 0.7 and 0.69° respectively. Backgrounds were measured at each end of the scan for a total time equal to one-half of the scan time. After correction for backgrounds, the standard deviation $\sigma(I)$ of the intensity I was calculated as described elsewhere [5], using for the instability factor k a value of 0.04. From a total of 9011 reflections measured out to a 2θ value of 40° , 4175 had significant intensity ($I \geq 3\sigma(I)$). The intensity data were corrected for Lorentz, polarization and absorption effects, the range of the trans-

TABLE III. Thermal and Derived Positional Parameters of Group Atoms ($\times 10^4$) with Estimated Standard Deviations.

Atom	x/a	y/b	z/c	U
C1,1	257(3)	1257(4)	4286(9)	457(47)
C2,1	54(3)	1693(4)	4468(9)	630(55)
C3,1	-468(3)	1739(4)	4545(9)	784(62)
C4,1	-787(3)	1350(4)	4441(9)	801(65)
C5,1	-584(3)	914(4)	4259(9)	812(64)
C6,1	-62(3)	868(4)	4182(9)	757(62)
C1,2	1182(4)	722(3)	5045(9)	492(49)
C2,2	1645(4)	524(3)	4851(9)	562(52)
C3,2	1879(4)	178(3)	5574(9)	567(52)
C4,2	1649(4)	30(3)	6492(9)	712(60)
C5,2	1186(4)	228(3)	6686(9)	816(65)
C6,2	953(4)	574(3)	5963(9)	598(53)
C1,3	3036(4)	3700(4)	6133(9)	443(47)
C2,3	3239(4)	3514(4)	7190(9)	592(53)
C3,3	3590(4)	3770(4)	7946(9)	669(57)
C4,3	3739(4)	4211(4)	7643(9)	561(52)
C5,3	3537(4)	4397(4)	6586(9)	646(56)
C6,3	3185(4)	4141(4)	5830(9)	578(53)
C1,4	1967(4)	3717(4)	5003(10)	470(48)
C2,4	1931(4)	4130(4)	5596(10)	683(57)
C3,4	1470(4)	4379(4)	5445(10)	960(73)
C4,4	1045(4)	4215(4)	4702(10)	1025(76)
C5,4	1081(4)	3802(4)	4109(10)	1084(78)
C6,4	1542(4)	3553(4)	4260(10)	750(61)
C1,5	3889(4)	1726(3)	7293(10)	509(49)
C2,5	3970(4)	1727(3)	8479(10)	638(55)
C3,5	4142(4)	2129(3)	9071(10)	788(63)
C4,5	4234(4)	2529(3)	8478(10)	933(71)
C5,5	4153(4)	2528(3)	7292(10)	856(66)
C6,5	3980(4)	2126(3)	6700(10)	588(53)
C1,6	3703(6)	725(4)	7313(10)	608(54)
C2,6	3331(6)	376(4)	7223(10)	859(66)
C3,6	3443(6)	-45(4)	7781(10)	1070(79)
C4,6	3926(6)	-118(4)	8430(10)	1125(82)
C5,6	4298(6)	231(4)	8521(10)	1060(79)
C6,6	4187(6)	653(4)	7962(10)	1030(76)
C1,7	1743(3)	556(3)	543(11)	412(45)
C2,7	1895(3)	468(3)	-508(11)	618(55)
C3,7	2262(3)	127(3)	-605(11)	760(61)
C4,7	2477(3)	-127(3)	349(11)	752(61)
C5,7	2325(3)	-40(3)	1400(11)	800(64)
C6,7	1959(3)	302(3)	1497(11)	641(56)
C1,8	836(4)	1047(4)	-517(8)	474(47)
C2,8	563(4)	635(4)	-756(8)	655(56)
C3,8	156(4)	614(4)	-1662(8)	803(63)
C4,8	23(4)	1006(4)	-2328(8)	816(64)
C5,8	295(4)	1419(4)	-2089(8)	955(72)
C6,8	702(4)	1439(4)	-1184(8)	861(67)
C1,9	3544(4)	3538(4)	1346(9)	493(49)
C2,9	3501(4)	4011(4)	1106(9)	529(50)
C3,9	3935(4)	4263(4)	929(9)	663(57)
C4,9	4411(4)	4042(4)	992(9)	670(57)
C5,9	4453(4)	3569(4)	1232(9)	890(68)
C6,9	4020(4)	3317(4)	1409(9)	646(55)
C1,10	2448(4)	3415(4)	562(10)	467(47)
C2,10	2537(4)	3523(4)	-532(10)	687(58)
C3,10	2125(4)	3634(4)	-1377(10)	933(71)

TABLE III. (continued)

Atom	x/a	y/b	z/c	U
C4,10	1623(4)	3637(4)	-1128(10)	1078(79)
C5,10	1534(4)	3529(4)	-34(10)	1258(88)
C6,10	1946(4)	3418(4)	811(10)	951(71)
C1,11	4152(5)	451(3)	2738(11)	514(49)
C2,11	4577(5)	278(3)	3467(11)	671(57)
C3,11	4741(5)	-176(3)	3340(11)	878(67)
C4,11	4481(5)	-457(3)	2484(11)	822(64)
C5,11	4055(5)	-284(3)	1755(11)	927(69)
C6,11	3891(5)	170(3)	1882(11)	690(58)
C1,12	4453(4)	1395(4)	2535(10)	559(52)
C2,12	4748(4)	1240(4)	1732(10)	807(64)
C3,12	5106(4)	1536(4)	1355(10)	1057(78)
C4,12	5169(4)	1986(4)	1781(10)	936(71)
C5,12	4874(4)	2141(4)	2584(10)	900(69)
C6,12	4516(4)	1845(4)	2960(10)	655(56)

mission factors being 0.86–0.75. Atomic scattering factors and dispersion corrections, as well as absorption corrections, were taken from ref. 6.

Solution and Refinement of the Structure

The calculations were carried out using the SHELX76 crystallographic system on the CII 10070 computer [7]. A three dimensional Patterson synthesis showed the three nickel atoms of the asymmetric unit. Successive Fourier maps yielded the coordinates of all the non-hydrogen atoms. Least-squares refinements were carried out, the function minimized being $\sum w(|F_o| - |F_c|)^2$. w is the weight assigned to the F_o values, according to the expression $w = 1/\sigma^2(F_o)$. Since the number of the parameters to refined was very high, the structure refinement was performed by blocking the least-squares matrix and constraining the phenyl groups as rigid bodies of D_{6h} symmetry. Nickel, phosphorus and chlorine atoms were assigned anisotropic thermal vibrations. The detection of the chlorine atoms of the chloroform solvent molecule showed any difficulties. As a matter of fact in the difference fourier map there remained a rest of six peaks around the carbon atom of the chloroform at distances which ranged from 1.50 to 1.75 Å. Alternative refinement of the population parameters and overall thermal factor of such positions gave good results, the six peaks around the carbon atom being attributed to different orientations of the chlorine atoms of the solvent. From the final value of the occupancy factor of its carbon atom (0.73) the presence of 0.7 molecule of CHCl_3 in the complex was inferred (elemental analysis well agreeing with such value). The final conventional R and R_w factors were 0.072 and 0.073 respectively. The refined positional and thermal parameters are given in the Tables I–III.

TABLE IV. Maxima and Extinction Coefficients for the Electronic Spectra of the Complexes.

Compound		Absorption max, cm^{-1} (ϵ for soln)
$[\text{Ni}_3\text{Cl}_6(\text{etp}_3)_2] \cdot 0.7\text{CHCl}_3$	a	11700 sh; 19200; 26500
	b	12000 (96); 19200 (2240); 26500 (37037)
$[\text{Ni}_3\text{Br}_6(\text{etp}_3)_2] \cdot \text{CH}_2\text{Cl}_2$	a	11500 sh; 18000; 24500
	b	11900 (168); 18000 (1917); 24500 (31833)
$[\text{Ni}_3\text{I}_6(\text{etp}_3)_2] \cdot \text{CH}_2\text{Cl}_2$	a	11200 sh; 16300; 24000
	c	11200 sh; 16200 (2409); 24000 sh

^aSolid at room temperature. ^bNitroethane solution. ^c1,2-dichloroethane solution.

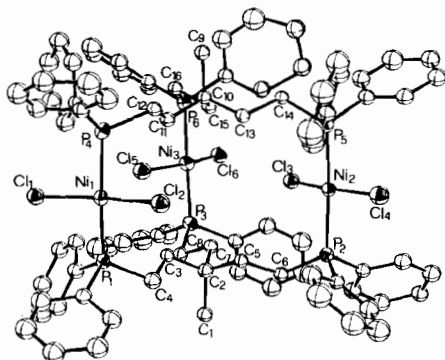


Fig. 1. Perspective view of the complex molecule $[\text{Ni}_3\text{Cl}_6(\text{etp}_3)_2]$. ORTEP drawing showing 30% probability ellipsoids.

Tables of structure factors are available from the Editor on request.

Results and Discussion

The $[\text{Ni}_3\text{X}_6(\text{etp}_3)_2]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) complexes are diamagnetic and soluble in polar organic solvents such as methylene chloride, 1,2-dichloroethane, nitroethane, where they behave as non-electrolytes.

The electronic spectra of the compounds are summarized in Table IV. The reflectance spectra are closely similar to the corresponding absorption spectra in 1,2-dichloroethane solution, the spectrochemical frequency order $\text{Cl} > \text{Br} > \text{I}$ being observed. Such spectra show two intense bands at frequencies higher than 15000 cm^{-1} which are typical of square-planar nickel(II) complexes [8]; the weak band at *ca.* 11000 cm^{-1} is to attribute to a spin forbidden transition.

The crystal structure, consisting of trinuclear molecules of $[\text{Ni}_3\text{Cl}_6(\text{etp}_3)_2]$ with non-stoichiometric disordered chloroform molecules interspersed in the lattice, resembles a prismatic cage, formed by two etp_3 ligands, held together by three bridging nickel atoms (see Fig. 1). The skeleton of the mole-

TABLE V. Selected Bond Lengths (Å) and Bond Angles ($^\circ$).

Ni1-P1	2.215(5)	P4-C1,7	1.83(1)
Ni1-P4	2.227(5)	P4-C1,8	1.83(1)
Ni1-Cl1	2.163(5)	P5-C14	1.83(1)
Ni1-Cl2	2.162(5)	P5-C1,9	1.82(1)
Ni2-P2	2.239(5)	P5-C1,10	1.82(1)
Ni2-P5	2.232(5)	P6-C16	1.85(1)
Ni2-Cl3	2.164(4)	P6-C1,11	1.80(1)
Ni2-Cl4	2.165(5)	P6-C1,12	1.82(1)
Ni3-P3	2.236(5)	C1-C2	1.56(2)
Ni3-P6	2.246(5)	C2-C3	1.56(2)
Ni3-Cl5	2.167(5)	C2-C5	1.58(2)
Ni3-Cl6	2.151(4)	C2-C7	1.55(2)
P1-C4	1.83(2)	C3-C4	1.59(2)
P1-C1,1	1.81(1)	C5-C6	1.58(2)
P1-C1,2	1.82(1)	C7-C8	1.55(2)
P2-C6	1.83(2)	C9-C10	1.55(2)
P2-C1,3	1.84(1)	C10-C11	1.56(2)
P2-C1,4	1.81(1)	C10-C13	1.58(2)
P3-C8	1.83(1)	C10-C15	1.58(2)
P3-C1,5	1.84(1)	C11-C12	1.54(2)
P3-C1,6	1.80(1)	C13-C14	1.59(2)
P4-C12	1.87(2)	C15-C16	1.59(2)
P1-Ni1-P4	167.7(2)	C6-P2-C1,3	102.7(6)
P1-Ni1-Cl1	90.3(2)	C6-P2-C1,4	106.3(6)
P4-Ni1-Cl1	91.2(2)	C1,3-P2-C1,4	106.0(5)
P1-Ni1-Cl2	90.8(2)	Ni3-P3-C8	115.9(5)
P4-Ni1-Cl2	91.5(2)	Ni3-P3-C1,5	116.8(4)
Cl1-Ni1-Cl2	161.9(2)	Ni3-P3-C1,6	109.0(5)
P2-Ni2-P5	171.8(2)	C8-P3-C1,5	101.2(6)
P2-Ni2-Cl3	90.6(2)	C8-P3-C1,6	106.0(7)
P5-Ni2-Cl3	92.7(2)	C1,5-P3-C1,6	107.0(5)
P2-Ni2-Cl4	90.5(2)	Ni1-P4-C12	114.4(5)
P5-Ni2-Cl4	88.0(2)	Ni1-P4-C1,7	117.5(4)
Cl3-Ni2-Cl4	166.9(2)	Ni1-P4-C1,8	112.9(4)
P3-Ni3-P6	176.5(2)	C12-P4-C1,7	100.4(6)
P3-Ni3-Cl5	90.2(2)	C12-P4-C1,8	105.9(6)
P6-Ni3-Cl5	89.1(2)	C1,7-P4-C1,8	104.2(6)
P3-Ni3-Cl6	89.8(2)	Ni2-P5-C14	117.0(5)
P6-Ni3-Cl6	91.7(2)	Ni2-P5-C1,9	113.6(4)
Cl5-Ni3-Cl6	166.4(2)	Ni2-P5-C1,10	114.1(5)
Ni1-P1-C4	116.2(6)	C14-P5-C1,9	102.6(6)
Ni1-P1-Cl1,1	112.8(4)	C14-P5-C1,10	102.4(6)
Ni1-P1-Cl1,2	115.0(4)	C1,9-P5-C1,10	105.9(5)

(continued on facing page)

TABLE V. (continued)

C4-P1-C1,1	104.2(7)	Ni3-P6-C16	115.4(5)
C4-P1-C1,2	101.1(6)	Ni3-P6-C,1,11	110.9(5)
C1,1-P1-C1,2	106.2(6)	Ni3-P6-C1,12	118.3(4)
Ni2-P2-C6	117.7(5)	C16-P6-C1,11	104.5(6)
Ni2-P2-C1,3	111.2(4)	C16-P6-C1,12	101.9(6)
Ni2-P2-C1,4	112.0(4)	C1,11-P6-C1,12	104.3(6)

cule can be best described as a distorted trigonal prism, whose six vertices are occupied by the six phosphorus atoms of two etp_3 ligands. The three nickel atoms, forming a triangle with non-bonded $\text{Ni}\cdots\text{Ni}$ separations (6.9, 7.1 and 7.8 Å) are half-way longitudinal edges, each coordinated in *trans* square planar geometry by two phosphorus atoms of two different etp_3 ligands and by two chlorine atoms. The environment around the nickel atoms, which have Ni-P and Ni-Cl bond lengths in the ranges previously found for a variety of square planar Ni(II) complexes [9], is very close to a planar coordination, the displacements of metal atoms from the least-squares planes being 0.05, -0.04 and 0.1 Å respectively. There are no unusual intra and intermolecular contacts. In Table V are reported selected bond lengths and bond angles of the structure.

The influence of the length of the tripodal ligand chains on the binding capabilities of the phosphorus donor atoms is clearly evidenced in the present structure. Indeed, the triphos ligand is known to coordinate to one metal atom in a bi- or tri-dentate fashion forming stable six-membered chelate rings. A similar binding mode by the etp_3 ligand should be energetically unfavourable, since it would result in the

formation of unstable eight-membered chelate rings. Thus the coordination of the three phosphine units of this ligand to three different metal ions is strongly favoured. From this point of view the triphosphine etp_3 behaves as three individual monodentate diphenyl-alkyl-phosphines, each bonding to a different nickel ion. The strain imposed by the fact that the three $-\text{CH}_2-\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$ moieties are linked through the apical C-CH₃ unit determines a square planar coordination around the nickel ion, while both square planar and tetrahedral coordination is observed in the $[\text{NiX}_2(\text{PPh}_2\text{R})_2]$ (X = Cl, Br, I; R = alkyl) complexes [9].

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