Synthesis, Properties, and *X*-Ray Structural Characterization of [Tris(2-diphenylphosphinoethyl)phosphine]nickel(I) Perchlorate and Triphenylphosphine[tris(2-diphenylarsinoethyl)amine]nickel(I) Perchlorate *

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The cationic nickel(I) complexes $[Ni\{P(CH_2CH_2PPh_2)_3\}]ClO_4$ (1) and $[Ni\{N(CH_2CH_2AsPh_2)_3\}(PPh_3)]ClO_4$ (2) have been synthesized by reaction of the nickel(0) derivative $[Ni(C_2H_4)(PPh_3)_2]$ with $[C_3Ph_3]ClO_4$ and the appropriate tripod-like ligand. The crystal structures of these two complexes have been determined from counter *X*-ray diffraction data. Crystal data: (1), space group *Cc*, $a = 16.599(9)$, $b = 12.810(7)$, $c = 18.650(9)$ Å, $\beta = 90.3(1)°$, and $Z = 4$; (2), space group $P2_1/a$, $a = 24.051(10)$, $b = 13.267(7)$, $c = 17.048(9)$ Å, $\beta = 92.7(1)°$, and $Z = 4$. Both structures were solved by the heavy-atom method and refined by full-matrix least-squares techniques to *R* of 0.060. Compound (1) exhibits the uncommon trigonal-pyramidal geometry, the nickel atom being surrounded by the four phosphorus atoms of the ligand. In compound (2) the nickel atom is five-co-ordinated by the four donor atoms of the arsine ligand and by the phosphorus atom of the triphenylphosphine in a distorted trigonal-bipyramidal geometry.

Although the number of nickel(I) complexes is steadily increasing, these species are still rather uncommon.[1]

Recent research performed in our Institute has shown that tripod-like polytertiary phosphines or closely related ones, such as 1,1,1-tris(diphenylphosphinomethyl)ethane, 1,1,1-tris(diphenylarsinomethyl)ethane, tris(2-diphenylphosphinoethyl)phosphine, tris(2-diphenylphosphinoethyl)amine, and tris(2-diphenylarsinoethyl)amine, are suitable ligands to form stable uncharged nickel(I) complexes of general formula NiLX (X = halide).[2] Such complexes, which have tetrahedral or trigonal-bipyramidal structure according to whether L is a tri- or quadri-dentate ligand, have generally been synthesized by reduction of the corresponding nickel(II) derivatives with sodium tetrahydroborate. Sometimes the reduction occurs without the use of a specific reducing agent.[2a,3]

We have now synthesized two ionic nickel(I) complexes of formulae $[Ni\{P(CH_2CH_2PPh_2)_3\}]ClO_4$ (1) and $[Ni\{N(CH_2CH_2AsPh_2)_3\}(PPh_3)]ClO_4$ (2) by oxidation of nickel(0) species. The complexes have been studied by physical methods and fully characterized by complete *X*-ray structural analyses.

Preliminary communications of this work have already appeared.[4]

Experimental

All operations were carried out under a nitrogen atmosphere. The solvents were purified by standard methods, distilled before use, and deoxygenated. Magnetic, spectrophotometric, and conductivity measurements were carried out using methods described elsewhere.[5] The ligand tris(2-diphenylarsinoethyl)amine,[6] and the compounds $[Ni(C_2H_4)(PPh_3)_2]$ [7] and $[C_3Ph_3]ClO_4$ [8] were prepared by previously reported methods. The ligand tris(2-diphenylphosphinoethyl)phosphine was purchased from Pressure Chemical Co., Pittsburgh, Pennsylvania.

Synthesis of the Complexes.—$[Ni\{P(CH_2CH_2PPh_2)_3\}]ClO_4$ (1). A solution of $[C_3Ph_3]ClO_4$ (0.5 mmol) in boiling methanol (40 cm^3) was added to a solution of $[Ni(C_2H_4)(PPh_3)_2]$ (0.5 mmol) in tetrahydrofuran (30 cm^3). The solid ligand $P(CH_2CH_2PPh_2)_3$ (0.5 mmol) was added and the resulting solution was heated at 50 °C until pale violet crystals precipitated. They were filtered off, washed with methanol and light petroleum, and dried under a stream of nitrogen, yield 30% (Found: C, 60.5; H, 5.5; Ni, 7.0; P, 15.6. Calc. for $C_{42}H_{42}ClNiO_4P_4$: C, 60.8; H, 5.1; Ni, 7.1; P, 14.9%). When sodium tetraphenylborate (0.5 mmol) in n-butanol (20 cm^3) was added to the filtrate the orange-yellow compound $[Ni(\eta^3\text{-}C_3Ph_3)\{P(CH_2CH_2PPh_2)_3\}]BPh_4$[9] suddenly precipitated, yield 45%.

$[Ni\{N(CH_2CH_2AsPh_2)_3\}(PPh_3)]ClO_4$ (2). This complex was prepared as large yellow-green crystals by a method analogous to that used for the above phosphine derivative, yield 65% (Found: C, 59.7; H, 4.9; N, 1.1; Ni, 4.9. Calc. for $C_{60}H_{57}As_3ClNNiO_4P$: C, 59.7; H, 4.8; N, 1.2; Ni, 4.9%).

$[NiH_x\{N(CH_2CH_2PPh_2)_3\}]ClO_4$. These compounds were obtained when the above reaction was carried out by using the ligand $N(CH_2CH_2PPh_2)_3$, yield 70%. The samples obtained in different experiments were identified, on the basis of i.r. spectra and magnetic measurements as members of the known, non-stoicheiometric hydride series[3] with x in the range 0.04—0.10.

Collection and Reduction of X*-Ray Intensity Data.*—The crystals used for *X*-ray work were mounted on a glass fibre along the *c* crystallographic axis for compound (1) and in a random orientation for compound (2). Relevant crystal data and data collection parameters are given in Table 1 for both the complexes. Unit-cell parameters were determined at room temperature from least-square refinements of the angular settings of 20 (1) and 23 (2) reflections, carefully centred on a Philips PW 1100 automatic diffractometer. Space groups were chosen on the basis of systematic absences and chemical information. Indeed although the two space groups *Cc* and *C*2/*c* may be inferred from the systematic absences hkl for $h + k = 2n + 1$, $h0l$ for $l = 2n + 1$, and $0k0$ for $k = 2n + 1$, *Cc* was chosen on the basis of the chemical formula of compound (1), which allows neither a symmetry centre nor a binary axis. Compound (2) belongs to the monoclinic system, space group $P2_1/a$, the systematic absences being $h0l$ for $h = 2n + 1$ and $0k0$ for $k = 2n + 1$. The procedures followed in

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* *Supplementary data available* (No. SUP 23678, 36 pp.): thermal parameters, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Crystal data and data collection details

	$[Ni\{P(CH_2CH_2PPh_2)_3\}]ClO_4$ (1)	$[Ni\{N(CH_2CH_2AsPh_2)_3\}(PPh_3)]ClO_4$ (2)
Formula	$C_{42}H_{42}ClNiO_4P_4$	$C_{60}H_{57}As_3ClNNiO_4P$
M	828.86	1 206.03
a/Å	16.599(9)	24.051(10)
b/Å	12.810(7)	13.267(7)
c/Å	18.650(9)	17.048(9)
β/°	90.3(1)	92.7(1)
D_c/g cm^{-3}	1.388	1.474
U/Å^3	3 965.6	5 433.8
F(000)	1 723.9	2 459.7
Space group	Cc	$P2_1/a$
μ(Mo-K_α)/cm^{-1}	7.6	22.9
Colour	pale violet	yellow-green
Habit	parallelepiped	prism
Dimensions/mm	0.20 × 0.25 × 0.50	0.22 × 0.32 × 0.40
Max. deviation of standard (%)	±5	±2
Total data	2 017	5 485
Data with $I \geqslant 3\sigma(I)$	1 640	3 248
Variables	178	208

The following are common to both complexes: $Z = 4$; Philips PW 1100 diffractometer; λ(Mo-K_α) = 0.7107 Å; flat graphite crystal monochromator; ω—2θ scan; speed 0.07° s^{-1}, width 0.9 + 0.3 tan θ; background = half scan time; three check reflections every 120 min; $5 \leqslant 2\theta \leqslant 40°$.

Table 2. Positional parameters (× 10^4) for $[Ni\{P(CH_2CH_2PPh_2)_3\}]ClO_4$

Atom	x	y	z	Atom	x	y	z
Ni	−5 000	−4 661(1)	5 000	C(63)	−2 655(8)	−3 778(11)	6 170(6)
P(1)	−6 334(3)	−4 606(3)	5 017(2)	C(14)	−4 413(8)	−2 162(9)	5 652(5)
P(2)	−4 288(3)	−3 565(3)	5 678(2)	C(24)	−4 354(8)	−1 562(9)	6 274(5)
P(3)	−4 350(3)	−5 911(3)	4 422(2)	C(34)	−4 403(8)	−477(9)	6 234(5)
P(4)	−5 071(3)	−5 692(3)	5 911(2)	C(44)	−4 511(8)	9(9)	5 571(5)
C(1)	−6 653(10)	−5 759(14)	5 535(9)	C(54)	−4 571(8)	−591(9)	4 948(5)
C(2)	−6 112(10)	−5 864(14)	6 189(9)	C(64)	−4 521(8)	−1 677(9)	4 989(5)
C(3)	−4 515(11)	−3 960(14)	6 618(9)	C(15)	−4 929(6)	−6 736(9)	3 823(6)
C(4)	−4 507(10)	−5 145(12)	6 670(9)	C(25)	−4 710(6)	−7 770(9)	3 696(6)
C(5)	−3 976(10)	−6 779(12)	5 130(8)	C(35)	−5 148(6)	−8 371(9)	3 206(6)
C(6)	−4 643(10)	−6 943(13)	5 688(9)	C(45)	−5 804(6)	−7 936(9)	2 843(6)
C(11)	−6 729(7)	−3 500(7)	5 534(6)	C(55)	−6 023(6)	−6 902(9)	2 970(6)
C(21)	−7 281(7)	−3 571(7)	6 093(6)	C(65)	−5 585(6)	−6 301(9)	3 460(6)
C(31)	−7 524(7)	−2 672(7)	6 455(6)	C(16)	−3 462(7)	−5 652(8)	3 884(6)
C(41)	−7 215(7)	−1 702(7)	6 257(6)	C(26)	−2 769(7)	−6 268(8)	3 899(6)
C(51)	−6 662(7)	−1 631(7)	5 698(6)	C(36)	−2 116(7)	−6 015(8)	3 464(6)
C(61)	−6 420(7)	−2 530(7)	5 336(6)	C(46)	−2 157(7)	−5 146(8)	3 014(6)
C(12)	−6 948(7)	−4 605(8)	4 217(7)	C(56)	−2 850(7)	−4 530(8)	3 000(6)
C(22)	−6 754(7)	−3 904(8)	3 673(7)	C(66)	−3 502(7)	−4 783(8)	3 435(6)
C(32)	−7 205(7)	−3 890(8)	3 040(7)	Cl	101(3)	−3 003(4)	−2 291(3)
C(42)	−7 850(7)	−4 577(8)	2 951(7)	O(1)	−10(28)	−2 310(33)	−1 753(25)
C(52)	−8 043(7)	−5 279(8)	3 496(7)	O(2)	−538(18)	−2 883(26)	−2 747(17)
C(62)	−7 592(7)	−5 293(8)	4 129(7)	O(3)	868(19)	−2 726(29)	−2 552(19)
C(13)	−3 197(8)	−3 629(11)	5 605(6)	O(4)	10(23)	−4 006(27)	−2 101(20)
C(23)	−2 914(8)	−3 525(11)	4 905(6)	O(11)	747(46)	−2 369(56)	−2 048(46)
C(33)	−2 088(8)	−3 571(11)	4 771(6)	O(22)	−402(22)	−2 092(33)	−2 454(22)
C(43)	−1 546(8)	−3 720(11)	5 336(6)	O(33)	723(24)	−3 383(36)	−2 735(21)
C(53)	−1 830(8)	−3 824(11)	6 035(6)	O(44)	2(19)	−3 609(26)	−1 604(19)

data processing have been described elsewhere.[10] After correction for background, the intensities I were assigned a standard deviation $\sigma(I)$ calculated as previously,[11] by using a value of 0.04 for the instability factor k for both compounds. The raw intensity data were corrected for Lorentz-polarization effects, but not for absorption, the linear absorption coefficients being 7.57 and 22.91 cm^{-1} for compounds (1) and (2) respectively.

Determination and Refinement of the Structures.—All the calculations were carried out using the SHELX 76 crystallographic system of programs on a SEL 32/70 computer, installed in our Institute.[12] Neutral atom scattering factors and anomalous dispersion corrections for the non-hydrogen atoms were obtained from ref. 13, scattering factors for the hydrogen atoms from ref. 14. The refinements were based on F_o, the function minimized being $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1/[\sigma^2(F_o) + g(F_o)^2]$; g was set to 0 and 0.001 for complexes (1) and (2) respectively.

Complex (1). Because of the isomorphism, the structure of compound (1) was resolved with the help of the known atom positions of the non-stoicheiometric hydrido-complex.[3] The structure was refined by full-matrix least-squares techniques applying anisotropic thermal parameters for nickel and phosphorus. During the refinement the phenyl rings were treated as rigid bodies, pivoting on the carbon atom attached

Table 3. Positional parameters ($\times 10^4$) for $[Ni\{N(CH_2CH_2AsPh_2)_3\}(PPh_3)]ClO_4$

Atom	*x*	*y*	*z*
Ni	1 689(1)	2 362(1)	2 780(1)
As(1)	731(1)	2 809(1)	2 476(1)
As(2)	1 872(1)	591(1)	2 918(1)
As(3)	2 221(1)	3 484(1)	3 638(1)
P	2 096(2)	2 725(3)	1 589(2)
N	1 255(4)	1 992(8)	4 109(6)
C(1)	399(6)	2 804(11)	3 508(8)
C(2)	644(6)	1 961(11)	3 997(8)
C(3)	1 451(5)	184(10)	3 834(7)
C(4)	1 467(6)	1 027(11)	4 424(8)
C(5)	2 011(5)	3 081(10)	4 690(8)
C(6)	1 418(5)	2 790(11)	4 679(8)
C(11)	204(4)	1 925(6)	1 911(6)
C(21)	−244(4)	2 300(6)	1 451(6)
C(31)	−616(4)	1 637(6)	1 067(6)
C(41)	−539(4)	599(6)	1 144(6)
C(51)	−91(4)	224(6)	1 604(6)
C(61)	281(4)	887(6)	1 988(6)
C(12)	468(4)	4 088(7)	2 014(6)
C(22)	595(4)	4 273(7)	1 237(6)
C(32)	419(4)	5 164(7)	869(6)
C(42)	115(4)	5 870(7)	1 278(6)
C(52)	−12(4)	5 686(7)	2 055(6)
C(62)	164(4)	4 795(7)	2 423(6)
C(13)	2 604(4)	80(7)	3 255(5)
C(23)	2 815(4)	−828(7)	2 981(5)
C(33)	3 351(4)	−1 134(7)	3 219(5)
C(43)	3 677(4)	−533(7)	3 730(5)
C(53)	3 467(4)	375(7)	4 004(5)
C(63)	2 930(4)	681(7)	3 766(5)
C(14)	1 653(4)	−441(7)	2 143(5)
C(24)	1 225(4)	−1 125(7)	2 266(5)
C(34)	1 079(4)	−1 838(7)	1 691(5)
C(44)	1 360(4)	−1 868(7)	995(5)
C(54)	1 789(4)	−1 185(7)	873(5)
C(64)	1 935(4)	−471(7)	1 447(5)
C(15)	3 032(4)	3 564(8)	3 803(5)
C(25)	3 322(4)	4 050(8)	3 224(5)
C(35)	3 895(4)	4 201(8)	3 328(5)
C(45)	4 177(4)	3 864(8)	4 012(5)
C(55)	3 887(4)	3 378(8)	4 592(5)
C(65)	3 314(4)	3 227(8)	4 487(5)
C(16)	2 042(4)	4 914(7)	3 667(6)
C(26)	1 478(4)	5 154(7)	3 573(6)
C(36)	1 310(4)	6 161(7)	3 557(6)
C(46)	1 706(4)	6 927(7)	3 635(6)
C(56)	2 270(4)	6 686(7)	3 730(6)
C(66)	2 438(4)	5 679(7)	3 746(6)
C(17)	2 325(3)	4 036(7)	1 504(5)
C(27)	1 965(3)	4 781(7)	1 757(5)
C(37)	2 116(3)	5 794(7)	1 714(5)
C(47)	2 626(3)	6 062(7)	1 416(5)
C(57)	2 985(3)	5 317(7)	1 163(5)
C(67)	2 835(3)	4 304(7)	1 207(5)
C(18)	2 717(4)	2 003(6)	1 382(4)
C(28)	3 098(4)	1 817(6)	2 008(4)
C(38)	3 564(4)	1 219(6)	1 896(4)
C(48)	3 650(4)	807(6)	1 158(4)
C(58)	3 269(4)	993(6)	533(4)
C(68)	2 803(4)	1 591(6)	645(4)
C(19)	1 655(3)	2 568(6)	690(5)
C(29)	1 699(3)	3 175(6)	27(5)
C(39)	1 347(3)	3 012(6)	−635(5)
C(49)	952(3)	2 243(6)	−634(5)
C(59)	908(3)	1 636(6)	28(5)
C(69)	1 260(3)	1 799(6)	690(5)
Cl	5 189(2)	3 133(4)	6 493(3)
O(1)	4 922(10)	4 070(19)	6 315(14)
O(2)	5 342(10)	3 057(18)	7 310(15)
O(3)	5 717(10)	3 340(16)	6 217(13)
O(4)	5 033(10)	2 289(21)	6 049(15)

to phosphorus. Hydrogen atoms, introduced in their geometrical calculated positions, were not refined. The disordered perchlorate ion was refined isotropically taking into account two different orientations for the oxygen atoms around the same chlorine atom. The two models obtained, which were assigned refined population parameters of 0.6 and 1—0.6 respectively, gave reasonable bond distances and angles. The absolute configuration of the structure was determined by a double refinement of x,y,z and $\bar{x},y,\bar{z}$ parameters for all the atoms. The refinement of the x,y,z structure gave R and R' values of 0.060 and 0.062, while that of the inverted structure $\bar{x},y,\bar{z}$ gave R and R' of 0.063 and 0.064 respectively. That the x,y,z was the correct form was confirmed by analysis of the standard deviations.

Final non-hydrogen parameters together with their estimated standard deviations appear in Table 2.

Complex (2). A three-dimensional Patterson synthesis revealed the positions of the arsenic atoms. The positions of the remaining non-hydrogen atoms were obtained from subsequent difference-Fourier maps. A full-matrix least-squares refinement was carried out, by assigning anisotropic thermal parameters to arsenic, nickel, phosphorus, and nitrogen. The phenyl groups were treated as rigid bodies of D_{6h} symmetry. The hydrogen atoms, introduced in their calculated positions, were not refined. The final R and R' factors were 0.060 and 0.065 respectively. The final atomic parameters with their estimated standard deviations are given in Table 3.

Results and Discussion

As previously reported the co-ordinatively unsaturated nickel(0) complex $[Ni(C_3Ph_3)(PPh_3)_2]ClO_4$ (3) forms stable η^3-cyclopropenyl derivatives of formula $[Ni(C_3Ph_3)L]BPh_4$, where L is a terdentate ligand such as $CH_3C(CH_2PPh_2)_3$, $CH_3C(CH_2AsPh_2)_3$, *etc.*, by simple metathesis reactions.[15] When the complex (3) is allowed to react with the potentially quadridentate phosphine $P(CH_2CH_2PPh_2)_3$ again a η^3-cyclopropenyl derivative of formula $[Ni(C_3Ph_3)\{P(CH_2CH_2PPh_2)_3\}]BPh_4$, in which a terminal PPh_2 group is unco-ordinated, has been obtained, in high yield (70%).[9] Now we have found that, if in the latter reaction the complex (3) is prepared *in situ* by adding a methanolic solution of $[C_3Ph_3]ClO_4$ to a tetrahydrofuran solution of $[Ni(C_2H_4)(PPh_3)_2]$, with moderate heating (50 °C), upon addition of the ligand $P(CH_2CH_2PPh_2)_3$ the nickel(I) complex $[Ni\{P(CH_2CH_2PPh_2)_3\}]ClO_4$ is obtained (yield 30%) together with the above η^3-cyclopropenyl complex (yield 45%). All attempts to prepare complex (1) from the phosphine ligand and (3) were unsuccessful.

Because repeated experiments have shown that (*i*) the air-stable complex $[Ni(C_3Ph_3)\{P(CH_2CH_2PPh_2)_3\}]BPh_4$ is practically unaffected by continuous heating, the only result being the oxidation of the unco-ordinated PPh_2 group to $POPh_2$[9] and (*ii*) the reaction of $[Ni(C_2H_4)(PPh_3)_2]$ with $NBu^n{}_4ClO_4$ and $P(CH_2CH_2PPh_2)_3$ under similar conditions yields only a mixture of intractable products, it seems evident that complex (1) does not arise from the $[Ni(C_3Ph_3)\{P(CH_2CH_2PPh_2)_3\}]^+$

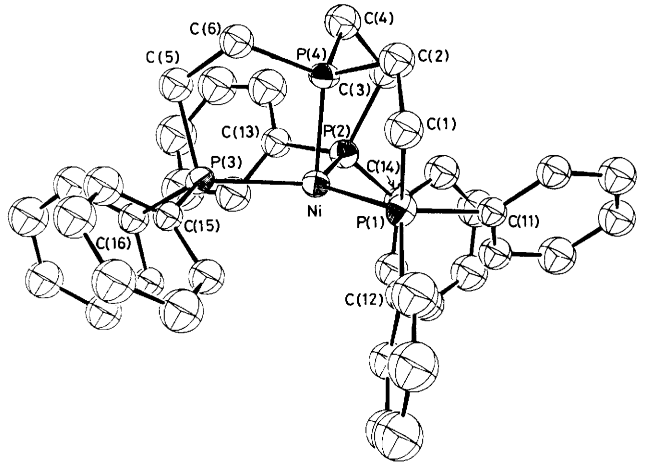

Figure 1. Perspective view of the complex cation $[Ni\{P(CH_2CH_2PPh_2)_3\}]^+$: ORTEP drawing with 30% probability ellipsoids

derivative and the compound $[C_3Ph_3]ClO_4$ does not participate in the reaction as a simple source of ClO_4^- anions. We suggest that the cyclopropenylium $[C_3Ph_3]^+$ can react with $[Ni(C_2H_4)(PPh_3)_2]$ by substituting C_2H_4 with formation of (3) or oxidation of nickel(0) to nickel(I), the latter process being favoured by heating. Thus in the presence of $P(CH_2CH_2PPh_2)_3$ both the complexes $[Ni\{P(CH_2CH_2PPh_2)_3\}]^+$ and $[Ni(C_3Ph_3)\{P(CH_2CH_2PPh_2)_3\}]^+$ are formed. The propensity of cyclopropenylium cations towards one-electron reduction to the corresponding radicals and then to the formation of bicyclopropenyl compounds is well established.[16] Unfortunately we were not able to isolate the bi(triphenylcyclopropenyl) from the reaction mixture.

When similar reactions are carried out by using the closely related ligands $N(CH_2CH_2AsPh_2)_3$ or $N(CH_2CH_2PPh_2)_3$, the complexes $[Ni\{N(CH_2CH_2AsPh_2)_3\}(PPh_3)]ClO_4$ (yield 65%) and $[Ni\{N(CH_2CH_2PPh_2)_3\}]ClO_4$ (yield 70%) are obtained. The latter species is accompanied by traces (i.r. spectra) of the isostructural hydride $[NiH\{N(CH_2CH_2PPh_2)_3\}]^+$: therefore the products of the $N(CH_2CH_2PPh_2)_3$ reactions are practically hydrogen-poor members of the previously reported non-stoicheiometric hydrides $[NiH_x\{N(CH_2CH_2PPh_2)_3\}]Y$.[3] The better yields of nickel(I) derivatives in these reactions are probably due to the instability of the hypothetical cyclopropenyl complexes which we were unable to isolate.

All the complexes decompose in air. Complex (1) is practically insoluble in the common organic solvents, (2) is slightly soluble in polar organic solvents such as methylene chloride, 1,2-dichloroethane, and nitroethane, where it behaves as a 1 : 1 electrolyte. The complexes are paramagnetic, with magnetic moments at room temperature of 2.10 and 2.01 μ_B (*ca.* 1.95×10^{-23} and 1.86×10^{-23} A m^2) for (1) and (2) respectively, as expected for a d^9 configuration.

The crystal structure of compound (1) consists of discrete complex cations $[Ni\{P(CH_2CH_2PPh_2)_3\}]^+$ and perchlorate anions. A perspective view of the cation is given in Figure 1. Selected bond distances and angles are in Table 4. The co-ordination sphere around the metal atom is a trigonal pyramid, whose vertices are occupied by the phosphorus atoms, the central one being at the apex of the pyramid. The nickel atom lies nearly in the plane of the remaining three phosphorus, its displacement from that plane being 0.08 Å. No contacts closer than 3.2 Å between nickel and phenyl hydrogen atoms are envisaged, excluding any nickel–phenyl interaction.

Table 4. Selected bond distances (Å) and angles (°)

(*a*) $[Ni\{P(CH_2CH_2PPh_2)_3\}]ClO_4$

Ni–P(1)	2.217(4)	P(1)–Ni–P(3)	121.3(2)
Ni–P(2)	2.226(4)	P(2)–Ni–P(3)	118.3(2)
Ni–P(3)	2.214(5)	P(4)–Ni–P(1)	87.1(2)
Ni–P(4)	2.155(4)	P(4)–Ni–P(2)	88.3(2)
P(1)–Ni–P(2)	120.0(2)	P(4)–Ni–P(3)	88.3(2)

(*b*) $[Ni\{N(CH_2CH_2AsPh_2)_3\}(PPh_3)]ClO_4$

Ni–As(1)	2.411(2)	P–Ni–As(1)	101.4(1)
Ni–As(2)	2.400(2)	P–Ni–As(2)	101.8(1)
Ni–As(3)	2.412(2)	P–Ni–As(3)	99.6(1)
Ni–P	2.346(4)	N–Ni–As(1)	79.3(2)
Ni–N	2.584(10)	N–Ni–As(2)	78.9(2)
As(1)–Ni–As(2)	115.5(1)	N–Ni–As(3)	79.1(2)
As(1)–Ni–As(3)	116.9(1)	N–Ni–P	178.7(3)
As(2)–Ni–As(3)	117.1(1)		

The trigonal-pyramidal geometry still seems to be rare. As far as we know, only the complexes $[Ni\{N(CH_2CH_2PPh_2)_3\}]$ [2d] and $[Co\{N(CH_2CH_2PPh_2)_3\}]BF_4$[3] show such geometry. In the non-stoicheiometric hydrido-complex $[NiH_x\{N(CH_2CH_2PPh_2)_3\}]BF_4$ ($x \leqslant 1$) a trigonal-pyramidal geometry has been found for the $[Ni\{N(CH_2CH_2PPh_2)_3\}]^+$ ions which exist in the compound in some proportion.[3]

The nickel–phosphorus bond distances are well in the range reported for four-co-ordinated nickel(I) and nickel(II) phosphine complexes.[2c,d,3,17] The axial Ni–P(4) [2.155(4) Å] is significantly shorter than the three equatorial and nearly equivalent Ni–P distances [mean 2.219(4) Å].

The crystal structure of compound (2) consists of discrete complex cations $[Ni\{N(CH_2CH_2AsPh_2)_3\}(PPh_3)]^+$ and perchlorate anions. A perspective view of the cation is shown in Figure 2. Selected bond distances and angles are in Table 4. The nickel atom is five-co-ordinated by the four donor atoms of the amine ligand and by the phosphorus atom of the triphenylphosphine in a distorted trigonal-bipyramidal geometry. The nickel atom lies 0.45 Å below the equatorial plane of the three arsenic atoms, the average value of the N–Ni–As bond angles being 79.1(2)°. An interesting feature of this structure is the lengthening of the Ni–N and Ni–P axial bonds with respect to the three equatorial and nearly equivalent Ni–As distances. While the Ni–As bonds, ranging from 2.400(2) to 2.412(2) Å, are only somewhat longer than the sum of the covalent radii (2.35 Å), the axial distances Ni–N [2.584(10) Å] and Ni–P [2.346(4) Å] are significantly different from the corresponding sums of covalent radii, 1.90 and 2.21 Å respectively.[18] This axial weakening can be justified on the basis of the stereochemical activity of the *d* electrons of the nickel atom. As already noted for the monomeric $[NiI\{N(CH_2CH_2AsPh_2)_3\}]$ [2f] and dimeric $[Ni_2I\{N(CH_2CH_2AsPh_2)_3\}_2]BPh_4$[2e] complexes, the presence of only one electron in the d_{z^2} orbital can be determining for the increase in the axial distances in nickel(I) trigonal-bipyramidal complexes with respect to Ni^{II}. On the other hand, the steric requirements, which could be considered owing to the presence of the bulky triphenylphosphine ligand, seem to be not so important at least for the apical lengthening. Support for this point of view can be obtained from the $[Ni\{N(CH_2CH_2PPh_2)_3\}(SnPh_3)]BPh_4$ complex, where the Ni–N and Ni–Sn bonds appear normal, despite the presence of the bulky triphenyltin moiety.[19] Steric requirements could probably be invoked to explain the small increase in the Ni–As equatorial bonds with respect to literature values: in the $[NiI\{N(CH_2CH_2AsPh_2)_3\}]$ [2f] and $[Ni_2I\{N(CH_2CH_2AsPh_2)_3\}_2]BPh_4$[2e] complexes, where one iodine atom has replaced the triphenylphosphine group, the Ni–As distances are normal.

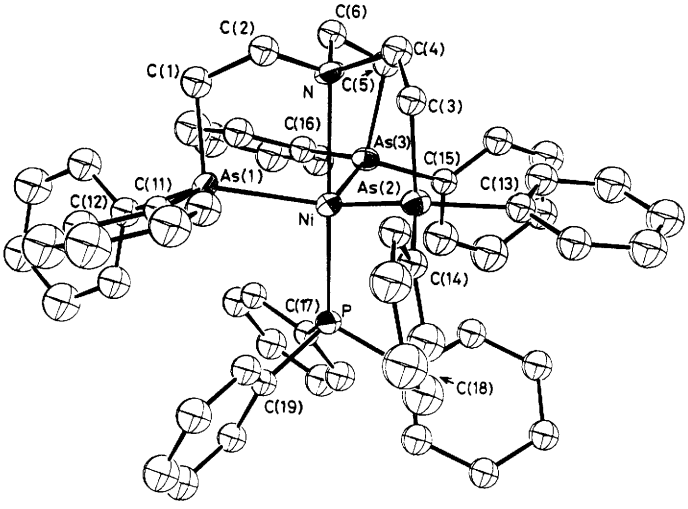

Figure 2. Perspective view of the complex cation $[Ni\{N(CH_2CH_2AsPh_2)_3\}(PPh_3)]^+$: ORTEP drawing with 30% probability ellipsoids

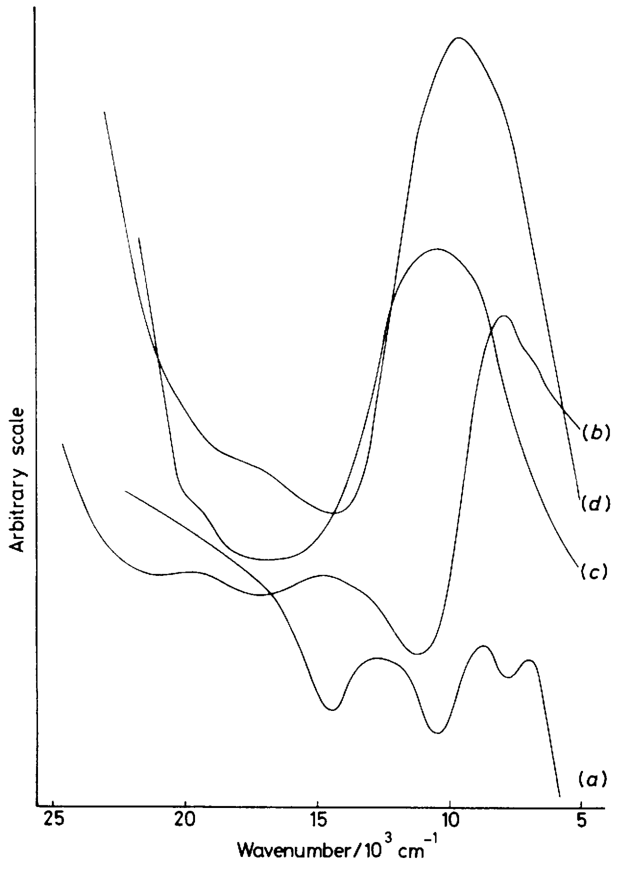

Figure 3. Reflectance spectra of $[Ni\{P(CH_2CH_2PPh_2)_3\}]ClO_4$ (*a*), $[Ni\{N(CH_2CH_2PPh_2)_3\}]ClO_4$ (*b*), $[Ni\{N(CH_2CH_2AsPh_2)_3\}(PPh_3)]ClO_4$ (*c*), and $[NiI\{N(CH_2CH_2AsPh_2)_3\}]$ (*d*)

The reflectance spectra* of compounds (1) and (2) are compared in Figure 3 with those of the related $[Ni\{N(CH_2CH_2PPh_2)_3\}]ClO_4$[3,†] and $[NiI\{N(CH_2CH_2AsPh_2)_3\}]$.[2e,f] The spectrum of complex (2) shows a broad band at 1 050 cm^{-1} and a shoulder at *ca.* 1 950 cm^{-1}. The first band, which is fully comparable both in shape and position to that of the isostructural $[NiI\{N(CH_2CH_2AsPh_2)_3\}]$ derivative, is typical of d^9 ions in a trigonal-bipyramidal ligand field,[2d–f] the shoulder at higher frequences being attributable to a charge-transfer transition. However, a similar behaviour, *i.e.* an intense broad absorption in the range 8 000—11 000 cm^{-1}, has been found also in the spectra of tetrahedral, $[Ni(PMe_3)_4]^+$,[17] or pseudo-tetrahedral, $[NiI\{CH_3C(CH_2PPh_2)_3\}]$,[2a,c] nickel(I) complexes. In contrast, the spectrum of $[Ni\{P(CH_2CH_2PPh_2)_3\}]^+$ which shows three bands at 7 000, 8 700, and 12 600 cm^{-1} and a shoulder at *ca.* 17 500 cm^{-1} may be compared only with that of the isostructural $[Ni\{N(CH_2CH_2PPh_2)_3\}]^+$ derivative (Figure 3). We think that a correct rationalization of these spectra, which is beyond the purposes of this work, can be achieved by use of polarized spectra of the single crystals.

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* The spectrum of complex (2) in 1,2-dichloroethane solution is similar.

† This complex can be prepared free from the isostructural diamagnetic hydride $[NiH\{N(CH_2CH_2PPh_2)_3\}]ClO_4$ by the reaction of $[Ni(H_2O)_6][ClO_4]_2$ with the amine ligand in boiling acetone under nitrogen.[20]

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