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PREPARATION AND X-RAY CRYSTAL STRUCTURE OF (BENZONITRILE)TRIS(TRIPHENYLPHOSPHORANE)NICKEL(0)

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Summary

Treatment of triphenylphosphine with bis(cycloocta-1,5-diene)nickel(0) in toluene followed by addition of benzonitrile gave two nickel(0) complexes. When the nickel/phosphine ratio was 1 : 3 the (benzonitrile)tris(triphenylphosphorane)-nickel(0) complex was obtained. With a nickel/phosphine ratio of 1 : 2, along with the first complex a quite different (unidentified) product was obtained.

The crystal and molecular structure of (benzonitrile)tris(triphenylphosphorane)nickel(0) was determined from X-ray diffractometer data. The structure was solved by Patterson and Fourier methods and refined by least-squares techniques to $R = 0.103$ for 3580 independent reflections. Crystals are monoclinic, space group $C2/c$, with $Z = 8$, in a unit cell of dimensions: $a = 42.035(29)$, $b = 10.677(9)$, $c = 25.095(10)$ Å; $\beta = 109.75(6)°$.

The coordination of the nickel atom is nearly tetrahedral. The benzonitrile residue is linked to the metal through its N atom (Ni—N distance = 1.889(11) Å). The overall shape of the molecule is determined by the juxtaposition around the metal of the phosphorous atoms, which have nearly tetrahedral coordinations. Three of the nine P—C(Phen) bonds take up nearly eclipsed conformations while the other six are in nearly staggered positions. The triphenylphosphorane groups assume a propeller-like shape.

Introduction

We have recently made some nickel(0) organometallic compounds containing R—C≡N ligands where R is an alkyl or an aryl radical. The structures of these compounds are of interest both for appreciation of the coordination around the metal and for understanding the way in which the nitrile ligand is linked to the metal.

The preparation of two of these compounds, and the X-ray crystal structure of one of them, viz. (benzonitrile)tris(triphenylphosphorane)nickel(0) (I), are now reported.

Preparation

The complex $[(C_6H_5)_3P]_3Ni(C_6H_5CN)$ (I), which has previously been observed in solution [1], can be prepared according to eq. 1:

$$\mathrm{Ni(COD)_2 + 3\,P(C_6H_5)_3 \xrightarrow[\text{in toluene}]{+C_6H_5CN} \underset{(I)}{[(C_6H_5)_3P]_3Ni(C_6H_5CN)} + 2\,COD} \qquad (1)$$

On addition of triphenylphosphine to a suspension of bis(cycloocta-1,5-diene)-nickel(0) in toluene (in the ratio 1 : 3), the solid dissolves and the solution turns deep red. On addition of benzonitrile the colour of the solution darkens and its IR spectrum shows a band at 2154 cm^{-1} due to complex I, in addition to the band of the free nitrile at 2230 cm^{-1}. Complex I is obtained as deep red crystals by diluting the toluene solution with n-hexane.

The IR spectrum of this complex shows a strong band at 2150 cm^{-1} due to $\nu(CN)$ which disappears on decomposition of the complex in air while the $\nu(CN)$ of the free nitrile appears. This substantial shift of $\nu(CN)$ to lower frequency $(\Delta\nu(CN) = -80\ cm^{-1})$ in the coordinated benzonitrile can be interpreted in terms of the unusually strong π-back-bonding ability of $[(C_6H_5)_3P]_3Ni$ moiety. The nitrile group is bound to the metal atom in a very labile way, however, and in many experiments with various substrates we have never observed any nitrile insertion but only reactions attributable to the $[(C_6H_5)_3P]_3Ni$ moiety.

Complex I can be obtained, together with a bright red solid II, in two ways. If the reaction 1 is carried out with a nickel/phosphine ratio of 1 : 2 instead of 1 : 3 the reaction proceeds as follows (eq. 2):

$$\mathrm{Ni(COD)_2 + 2\,P(C_6H_5)_3 \xrightarrow{\text{in toluene}} [(C_6H_5)_3P]_2Ni(COD) + COD} \qquad (2)$$

$$\downarrow \mathrm{C_6H_5CN}$$

$$\mathrm{\underset{(I)}{[(C_6H_5)_3P]_3Ni(C_6H_5CN)} + COD + \underset{(II)}{\text{Red solid}}}$$

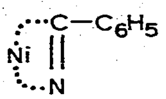
The same compounds can be obtained starting from the complex $[(C_6H_5)_3P]_2Ni(C_2H_4)$ (eq. 3).

$$\mathrm{[(C_6H_5)_3P]_2Ni(C_2H_4) + C_6H_5CN \xrightarrow[-C_2H_4]{\text{in toluene}} \underset{(I)}{[(C_6H_5)_3P]_3Ni(C_6H_5CN)} + \underset{(II)}{\text{Red solid}}} \qquad (3)$$

The red solid (II), which is extremely air sensitive, shows a IR strong band at 1750 cm^{-1} in the region normally assigned to C=N stretching frequencies [2]. This band disappears on decomposition of the compound in air while the $\nu(CN)$ of the free nitrile appears. This position of the band suggests that in compound II the nitrile must be π-complexed via its p_π—p_π bonds to the metal atom.

At the moment we have not obtained a satisfactory complete analysis which could indicate the composition of compound II, but from the nickel analysis and decomposition of the complex with iodine we found a nickel/benzonitrile ratio of 1 : 1.

It can be concluded that the complex contains the grouping:



There is doubt about how many phosphine are bound to the metal atom, but the stoichiometry of the reaction (eq. 2 or 3) indicate the presence of only one phosphine per metal atom. In this complex too the nitrile is bound very loosely, and using many different substrates we have been unable to obtain any nitrile insertion. Work is in progress in order to clarify the nature of complex II.

Experimental

$Ni(COD)_2$ [3] and $[(C_6H_5)_3P]_2Ni(C_2H_4)$ [4] were prepared by published methods. All experiments were carried out under pure argon. Solvents were rendered water and oxygen free by distillation over sodium—potassium alloy. IR spectra were recorded on a Perkin—Elmer 225 spectrophotometer using Nujol mulls.

Preparation of [tris(triphenylphosphine)nickel]benzonitrile (I)

(a) From $Ni(COD)_2$ + 3 $(C_6H_5)_3P$. 1.83 g (7.0 mmol) of $(C_6H_5)_3P$ were added to a stirred suspension of 0.64 g (2.3 mmol) of $Ni(COD)_2$ in 15 ml of toluene. The mixture was stirred until a red solution was obtained, and 0.5 g (4.9 mmol) of C_6H_5CN were then added. Complex I was precipitated by dilution with n-hexane (15 ml) and collected as dark red crystals by filtration. After washing with n-hexane 1.75 g (1.85 mmol, 80%) of complex I were obtained (Found: C, 76.6; H, 5.7; N, 1.5; Ni, 6.2; P, 9.3. $C_{61}H_{50}NNiP_3$ calcd.: C, 77.2; H, 5.3; N, 1.5; Ni, 6.2; P, 9.8%.) In order to obtain good crystals for the structure determination it was necessary to add a smaller quantity of n-hexane (5 ml) and leave the solution for some days.

(b) From $Ni(COD)_2$ + 2 $(C_6H_5)_3P$. 1.50 g of $(C_6H_5)_3P$ (5.7 mmol) were added to a stirred suspension of 0.78 g (2.8 mmol) of $Ni(COD)_2$ in 15 ml of toluene. The mixture was stirred until a bright yellow precipitate was obtained, and then 0.5 g of C_6H_5CN (4.9 mmol) were added. A bright red precipitate (II) formed immediately. This was filtered off and washed with toluene and n-hexane (obtained 0.5 g). The solution was then treated as in *a* to give 1.06 g of complex I (1.1 mol).

(c) From $[(C_6H_5)_3P]_2Ni(C_2H_4)$. 1.00 g (9.7 mmol) of C_6H_5CN were added to a stirred suspension of 4.28 g (7.0 mmol) of $[(C_6H_5)_3P]_2Ni(C_2H_4)$ in 20 ml of toluene. A red precipitate (II) formed immediately. This was filtered off and washed with toluene and n-hexane (obtained 1.49 g). The solution was then treated as in *a* to give 2.66 g (2.8 mmol) of complex I.

Decomposition of red solid (II)

20 ml of n-hexane containing 0.30 g of I_2 were added to 0.48 g of the solid containing 0.9 mmol of Ni (Ni, 11%) and the solution was stirred for half an hour. The excess of iodine was destroyed with an aqueous solution of thiosulphate in the presence of starch-water. The benzonitrile in the hexane layer was determined by GC: found 0.9 mmol of C_6H_5CN.

X-Ray analysis

Experimental

The crystals of I were firmly mounted in Lindemann glass capillary tubes filled with dry nitrogen and flame sealed. Preliminary space group and unit cell dimensions were obtained from Weissenberg photographs.

A crystal, essentially a parallelepiped, having dimensions ca. 0.40 × 0.40 × 0.60 mm was mounted on a Picker FACS 1 four-circle computer controlled diffractometer equipped with a scintillation counter and a pulse-height analyser. The orientation matrix and cell dimensions were obtained from a least-squares fit of χ, ϕ, ω and 2θ values from 12 independent reflexions.

Crystal data

$C_{61}H_{50}NNiP_3$: Mol.wt. 948.71; monoclinic, $a = 42.035(29)$, $b = 10.677(9)$, $c = 25.095(10)$ Å; $\beta = 109.75(6)°$; $U = 10600.41$ Å^3; $D_o = 1.17$, $D_c = 1.189$ g cm^{-3}; $Z = 8$. Space group $C2/c$, from systematic absences (hkl) for $h + k$ odd, ($h0l$) for l odd, and from structure determination. Cu-K_α radiation, $\lambda = 1.54178$ Å, μ(Cu-K_α) = 16.19 cm^{-1}.

Intensity data were collected by use of nickel filtered Cu-K_α radiation with $2\theta \leqslant 90°$. The moving-crystal-moving counter technique was used with a 2θ scan rate of 1° min^{-1} and a scan range of 2.0—2.50°, in order to allow for the greater separation of the $K_{\alpha 1}$ and $K_{\alpha 2}$ peaks at increasing 2θ values. Background counts of 10 sec were measured at each end of every 2θ scan. Three standard reflections, measured after every 50 reflections, showed that the mounted crystal was slowly decomposing. The data collection was interrupted when the standard reflections were indicating a diminution of the intensity of about 10% (2000 reflections were already collected). A second crystal of approximately the same size as the former, was then mounted on the diffractometer and the data collection restarted. The scaling of intensity data was performed on the basis of the three standard reflections. During intensity data collection attenuator filters were automatically inserted in order to keep the counting rate below 10 000 counts per sec. 4264 independent reflections were measured of which 3580 were considered observed and had $I \geqslant 3\sigma$. An arbitrary intensity equal to 0.5 the observable limit was assigned to the non significant reflections. All intensities were corrected for Lorentz and polarization effects. No absorption correction was introduced due to the very low value of μR.

Determination and refinement of the structure

The structure of I, was solved by the heavy-atom method. A three-dimensional Patterson map was constructed and this gave the location of the Ni and P atoms. The interpretation of the vector set was complicated by the fact that Ni—P interatomic vectors had a weight similar to that of the Ni—Ni vectors. A Fourier map phased on the Ni and P atoms yielded a partial picture of the molecule and the coordinates of the atoms of the whole molecule were found by a step-wise introduction of the carbon atoms into the structure factor calculations. The coordinates of these atoms were derived from successive Fourier maps and on stereochemical grounds.

The positional and the isotropic thermal parameters of all the non-hydrogen atoms were defined by some cycles of block-diagonal least-squares by use of a program by Immirzi [5]. Atomic scattering factors were calculated from the expression in ref. [6] using values for the parameters given in [7]. A constant value of 3.1 e^- was subtracted from the scattering factor of the nickel atom to take into account the real part of anomalous scattering [8]. The weighting scheme of [9] was adopted $1/w = A + B\,|F_0| + C\,|F_0|^2$, where $A = 2\,F_0$ (min), $B = 1.00$, and $C = 2/F_0$ (max). At this point R was 0.142 for the 3580 non-zero reflections.

Four cycles of block-diagonal least-squares refinement were run, assuming anisotropic thermal parameters for the Ni, P, N and the C atoms of the central

TABLE 1

FINAL FRACTIONAL COORDINATES WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	*x/a*	*y/b*	*z/c*	*B* (Å²)
Ni	0.13266(4)	0.16255(17)	0.05545(7)	
P(1)	0.13931(8)	0.15480(29)	−0.02713(12)	
P(2)	0.10952(8)	0.33297(30)	0.07472(13)	
P(3)	0.17828(7)	0.11013(29)	0.12533(12)	
N	0.1033(2)	0.0323(10)	0.0601(4)	
C(1)	0.1636(3)	0.0202(11)	−0.0389(5)	
C(2)	0.1482(3)	−0.0858(12)	−0.0695(5)	3.71(27)
C(3)	0.1678(4)	−0.1848(13)	−0.0771(6)	4.41(30)
C(4)	0.2015(4)	−0.1819(14)	−0.0558(6)	5.05(33)
C(5)	0.2173(4)	−0.0787(14)	−0.0227(6)	5.05(32)
C(6)	0.1981(3)	0.0222(12)	−0.0133(5)	3.82(27)
C(7)	0.1617(3)	0.2773(11)	−0.0507(5)	
C(8)	0.1643(3)	0.3976(11)	−0.0246(5)	3.21(25)
C(9)	0.1802(3)	0.4944(13)	−0.0431(6)	4.51(30)
C(10)	0.1960(4)	0.4739(15)	−0.0836(6)	5.50(34)
C(11)	0.1938(4)	0.3578(14)	−0.1086(6)	5.00(32)
C(12)	0.1769(3)	0.2599(13)	−0.0925(5)	4.03(28)
C(13)	0.1005(3)	0.1379(12)	−0.0885(5)	
C(14)	0.0733(4)	0.0665(16)	−0.0808(7)	6.07(37)
C(15)	0.0430(5)	0.0510(19)	−0.1281(8)	8.48(46)
C(16)	0.0407(5)	0.1065(19)	−0.1806(9)	9.27(49)
C(17)	0.0662(5)	0.1735(19)	−0.1897(8)	8.78(47)
C(18)	0.0970(4)	0.1895(17)	−0.1418(7)	6.87(41)
C(19)	0.0697(3)	0.3064(12)	0.0876(5)	
C(20)	0.0692(4)	0.2084(14)	0.1246(6)	4.72(31)
C(21)	0.0389(4)	0.1821(16)	0.1360(7)	6.15(38)
C(22)	0.0116(4)	0.2529(17)	0.1107(7)	6.90(41)
C(23)	0.0116(5)	0.3496(19)	0.0757(9)	8.43(50)
C(24)	0.0417(4)	0.3776(14)	0.0642(6)	4.98(32)
C(25)	0.0961(3)	0.4549(12)	0.0205(5)	
C(26)	0.0793(3)	0.4170(13)	−0.0337(6)	4.20(29)
C(27)	0.0710(4)	0.5053(14)	−0.0792(6)	5.18(33)
C(28)	0.0796(4)	0.6282(15)	−0.0674(6)	5.45(35)
C(29)	0.0953(4)	0.6679(14)	−0.0112(6)	5.51(35)
C(30)	0.1039(3)	0.5811(13)	0.0313(5)	4.10(28)
C(31)	0.1324(3)	0.4292(11)	0.1365(5)	
C(32)	0.1195(4)	0.4581(15)	0.1781(6)	5.21(33)
C(33)	0.1372(4)	0.5300(16)	0.2279(7)	6.46(39)
C(34)	0.1710(4)	0.5665(15)	0.2312(7)	5.68(35)
C(35)	0.1836(4)	0.5389(14)	0.1880(6)	4.97(32)

TABLE 1 (continued)

Atom	x/a	y/b	z/c	B (Å^2)
C(36)	0.1647(3)	0.4688(11)	0.1418(5)	2.99(24)
C(37)	0.2146(3)	0.2164(11)	0.1480(5)	
C(38)	0.2207(3)	0.2863(11)	0.1051(5)	2.68(23)
C(39)	0.2473(3)	0.3705(12)	0.1189(5)	3.89(28)
C(40)	0.2678(3)	0.3884(13)	0.1729(5)	4.06(29)
C(41)	0.2626(3)	0.3190(13)	0.2153(6)	4.53(31)
C(42)	0.2362(3)	0.2306(12)	0.2033(5)	3.43(26)
C(43)	0.1678(3)	0.0789(12)	0.1889(5)	
C(44)	0.1569(3)	−0.0381(12)	0.1998(5)	3.37(26)
C(45)	0.1438(4)	−0.0544(14)	0.2442(6)	4.78(31)
C(46)	0.1415(4)	0.0437(14)	0.2777(6)	5.05(33)
C(47)	0.1537(4)	0.1585(13)	0.2702(6)	4.62(31)
C(48)	0.1659(3)	0.1791(12)	0.2259(6)	4.08(29)
C(49)	0.1991(3)	−0.0399(11)	0.1199(4)	
C(50)	0.2331(3)	−0.0625(12)	0.1484(5)	3.92(28)
C(51)	0.2468(4)	−0.1808(14)	0.1431(6)	5.02(33)
C(52)	0.2270(4)	−0.2746(14)	0.1114(6)	5.14(33)
C(53)	0.1936(4)	−0.2505(14)	0.0834(6)	4.83(31)
C(54)	0.1792(3)	−0.1327(12)	0.0875(5)	3.70(27)
C(55)	0.0852(3)	−0.0401(12)	0.0677(5)	
C(56)	0.0620(3)	−0.1279(13)	0.0783(6)	
C(57)	0.0294(4)	−0.1298(21)	0.0432(8)	
C(58)	0.0064(5)	−0.2074(23)	0.0517(10)	
C(59)	0.0167(5)	−0.2824(22)	0.1009(12)	
C(60)	0.0490(6)	−0.2845(22)	0.1354(9)	
C(61)	0.0729(5)	−0.2079(19)	0.1251(8)	

TABLE 2

ANISOTROPIC THERMAL PARAMETERS

The temperature factor is in the form: Ti = exp —1/4 ($B_{11}a^{*2}h^2 + B_{22}b^{*2}k^2 + B_{33}c^{*2}l^2 + 2B_{12}a^*b^*hk + 2B_{13}a^*c^*hl + 2B_{23}b^*c^*kl$)

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ni	3.83(9)	4.26(10)	3.66(9)	−0.14(7)	1.04(7)	−0.15(7)
P(1)	2.68(15)	2.59(15)	1.86(14)	0.01(12)	0.39(12)	−0.15(12)
P(2)	2.33(15)	2.97(16)	2.64(15)	0.01(12)	0.87(12)	−0.34(13)
P(3)	2.31(15)	2.54(15)	1.83(14)	0.03(12)	0.59(11)	−0.02(12)
N	2.83(48)	4.12(55)	2.92(47)	−0.40(41)	0.77(39)	0.19(42)
C(1)	4.01(63)	2.54(59)	2.52(55)	0.20(49)	1.59(49)	0.18(47)
C(7)	3.99(63)	2.69(59)	2.34(54)	0.64(50)	1.21(49)	0.57(47)
C(13)	5.53(76)	4.07(69)	1.53(55)	0.18(58)	0.45(62)	−0.29(50)
C(19)	2.18(59)	4.47(70)	4.58(69)	0.17(53)	1.09(52)	−1.14(58)
C(25)	1.95(55)	3.65(64)	3.24(59)	0.78(48)	0.39(46)	−0.05(51)
C(31)	3.49(63)	2.92(61)	3.11(59)	−0.13(50)	1.41(50)	−0.85(49)
C(37)	1.69(53)	3.41(61)	2.85(56)	0.21(46)	0.59(45)	−0.60(49)
C(43)	1.89(53)	3.84(65)	2.51(55)	0.76(48)	−0.15(44)	−0.07(49)
C(49)	3.00(59)	3.06(61)	1.93(52)	0.24(48)	0.54(45)	0.35(46)
C(55)	4.38(67)	3.73(66)	2.67(59)	−0.37(54)	1.46(52)	−0.46(52)
C(56)	4.18(70)	3.91(70)	4.84(72)	−1.42(56)	2.00(59)	−0.33(58)
C(57)	3.86(84)	12.46(150)	8.77(118)	−3.34(92)	1.74(82)	1.00(108)
C(58)	6.03(103)	11.88(156)	11.10(146)	−4.09(107)	2.60(100)	−1.34(124)
C(59)	6.75(115)	10.56(150)	18.44(211)	−5.44(112)	6.36(131)	−0.78(146)
C(60)	10.84(143)	10.82(152)	9.99(135)	−3.42(122)	4.49(116)	4.01(120)
C(61)	7.23(107)	8.78(118)	8.37(111)	−4.26(94)	1.95(89)	1.59(95)

part of the molecule (see Table 2). The hydrogen atoms also were introduced into the calculations but not refined, their coordinates being assigned on stereochemical grounds. The assumed B value for the hydrogen atoms is 5.0 Å^2.

The refinement converged to $R = 0.103$. The final shifts of the atomic parameters were negligible, all being well below the corresponding σ. A final difference Fourier synthesis revealed no unusual features.

Table 1 reports the final fractional coordinates and the isotropic thermal parameters with the corresponding standard deviations of the non-hydrogen atoms of the I independent unit. Table 2 lists the anisotropic thermal parameters of the Ni, P, N and of the carbon atoms refined anisotropically. The calculated and observed structure amplitudes are listed in a table. A copy of this table can be obtained by application to the authors.

Results and discussion

Views of the molecule of I are shown in Fig. 1 and 2. Both figures have been obtained by the ORTEP computing and drawing programs [10]. The geometric parameters of the molecule with their estimated standard deviations are reported in Table.3. The nickel atom is bonded to four atoms; the three phosphorous atoms of the triphenylphosphorane residues and the nitrogen atom of the benzonitrile residue. The coordination polyhedron around the nickel atom corresponds to a distorted tetrahedron (the average value of the bond angles is 109.2°). The Ni—P distances are coincident within the limits of the standard deviations, and on the average are 2.190(5) Å. These Ni—P distances are in line with the values quoted for $C_{10}H_{16}NiP(cyclo\text{-}C_6H_{11})_3$, 4, [11] (2.19 Å); for bis[bis(tricyclohexylphosphine)nickel]dinitrogen [12] (2.19 Å); and for bis[bis(dicyclo-

(continued on p. 294)

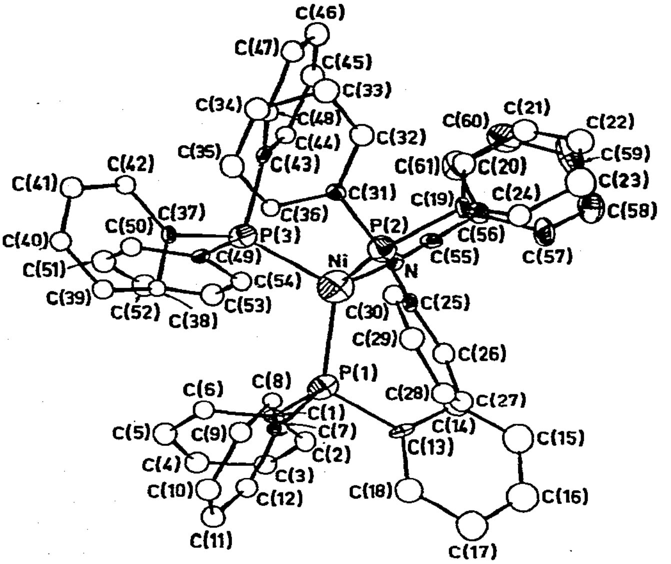


Fig. 1. View of the (benzonitrile)tris(triphenylphosphorane)nickel(0) indicating the atoms labelling scheme and the 30% probability thermal vibrations ellipsoids.

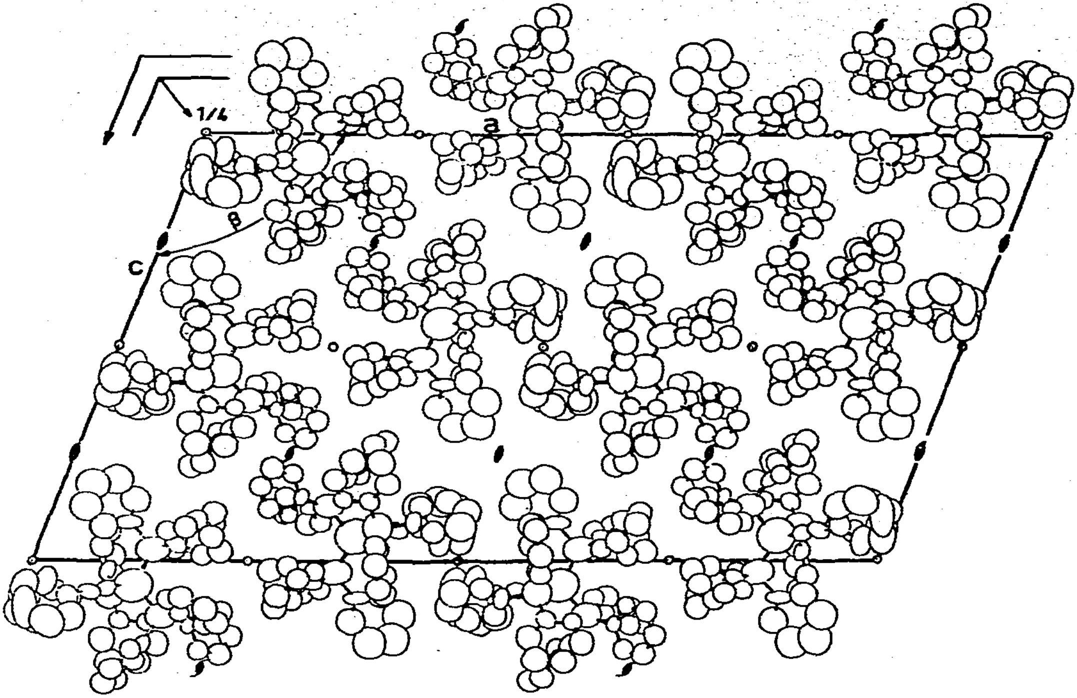


Fig. 2. Packing arrangement of (benzonitrile)tris(triphenylphosphorane)nickel(0) molecules as viewed down the *b* axis of the unit cell (The hydrogen atoms have been omitted for the sake of clarity).

TABLE 3

MOST SIGNIFICANT GEOMETRIC PARAMETERS OF THE MOLECULE I

Bond lengths (Å)					
Ni—P(1)	2.184(6)	C(7)—C(8)	1.43(1)	C(31)—C(32)	1.37(2)
Ni—P(2)	2.193(3)	C(7)—C(12)	1.41(2)	C(31)—C(36)	1.38(2)
Ni—P(3)	2.189(6)	C(8)—C(9)	1.40(3)	C(32)—C(33)	1.44(3)
Ni—N	1.889(11)	C(9)—C(10)	1.41(3)	C(33)—C(34)	1.45(2)
P(1)—C(1)	1.85(1)	C(10)—C(11)	1.38(1)	C(34)—C(35)	1.39(3)
P(1)—C(7)	1.83(2)	C(11)—C(12)	1.40(3)	C(35)—C(36)	1.38(2)
P(1)—C(13)	1.83(2)				
P(2)—C(19)	1.83(1)	C(13)—C(14)	1.44(2)	C(37)—C(38)	1.40(3)
P(2)—C(25)	1.83(2)	C(13)—C(18)	1.41(4)	C(37)—C(42)	1.39(3)
P(2)—C(31)	1.84(1)	C(14)—C(15)	1.43(4)	C(38)—C(39)	1.38(2)
P(3)—C(37)	1.83(1)	C(15)—C(16)	1.42(3)	C(39)—C(40)	1.35(3)
P(3)—C(43)	1.82(2)	C(16)—C(17)	1.37(3)	C(40)—C(41)	1.37(3)
P(3)—C(49)	1.85(1)	C(17)—C(18)	1.45(4)	C(41)—C(42)	1.40(2)
N—C(55)	1.15(2)	C(19)—C(20)	1.40(3)	C(43)—C(44)	1.39(2)
C(55)—C(56)	1.44(2)	C(19)—C(24)	1.36(3)	C(43)—C(48)	1.43(1)
C(56)—C(57)	1.36(4)	C(20)—C(21)	1.42(2)	C(44)—C(45)	1.41(3)
C(56)—C(61)	1.40(5)	C(21)—C(22)	1.34(4)	C(45)—C(46)	1.37(1)
C(57)—C(58)	1.35(3)	C(22)—C(23)	1.36(5)	C(46)—C(47)	1.37(2)
C(58)—C(59)	1.41(7)	C(23)—C(24)	1.42(3)	C(47)—C(48)	1.39(3)
C(59)—C(60)	1.34(5)				
C(60)—C(61)	1.39(4)	C(25)—C(26)	1.36(3)	C(49)—C(50)	1.39(3)
		C(25)—C(30)	1.39(1)	C(49)—C(54)	1.37(2)

(continued)

TABLE 3 (continued)

Bond lenghts (Å)					
C(1)—C(2)	1.40(1)	C(26)—C(27)	1.43(4)	C(50)—C(51)	1.41(2)
C(1)—C(6)	1.37(2)	C(27)—C(28)	1.37(2)	C(51)—C(52)	1.37(2)
C(2)—C(3)	1.39(2)	C(28)—C(29)	1.41(3)	C(52)—C(53)	1.37(3)
C(3)—C(4)	1.34(3)	C(29)—C(30)	1.38(4)	C(53)—C(54)	1.41(2)
C(4)—C(5)	1.40(2)				
C(5)—C(6)	1.41(2)				
Bond angles (°)					
N—Ni—P(1)	109.1(3)	C(19)—P(2)—C(31)	100.8(9)	P(2)—C(19)—C(20)	116.8(9)
N—Ni—P(2)	104.5(2)	C(25)—P(2)—C(31)	99.9(5)	P(2)—C(19)—C(24)	123.2(10)
N—Ni—P(3)	100.1(2)			P(2)—C(25)—C(26)	117.1(12)
P(1)—Ni—P(2)	116.7(1)	Ni—P(3)—C(37)	120.2(4)	P(2)—C(25)—C(30)	123.4(10)
P(1)—Ni—P(3)	113.1(1)	Ni—P(3)—C(43)	110.1(6)	P(2)—C(31)—C(32)	122.7(9)
P(2)—Ni—P(3)	117.7(1)	Ni—P(3)—C(49)	118.0(5)	P(2)—C(31)—C(36)	118.1(7)
		C(37)—P(3)—C(43)	105.3(4)		
Ni—P(1)—C(1)	115.9(3)	C(37)—P(3)—C(49)	101.1(2)	P(3)—C(37)—C(38)	116.2(7)
Ni—P(1)—C(7)	121.8(6)	C(43)—P(3)—C(49)	99.6(4)	P(3)—C(37)—C(42)	124.9(9)
Ni—P(1)—C(13)—	116.0(6)	Ni—N—C(55)	173(7)	P(3)—C(43)—C(44)	122.0(9)
C(1)—P(1)—C(7)	97.5(3)	N—C(55)—C(56)	178(15)	P(3)—C(43)—C(48)	120.8(8)
C(1)—P(1)—C(13)	99.9(4)			P(3)—C(49)—C(50)	122.9(8)
C(7)—P(1)—C(13)	102.0(4)	P(1)—C(1)—C(2)	122.6(5)	P(3)—C(49)—C(54)	117.4(5)
		P(1)—C(1)—C(6)	117.8(7)		
Ni—P(2)—C(19)	114.2(3)	P(1)—C(7)—C(8)	117.5(6)	The average value of the C()—C()—C() angles of the ten benzene rings is 120.0(10) (maximum value = 124° minimum value = 116°)	
Ni—P(2)—C(25)	118.4(6)	P(1)—C(7)—C(12)	124.1(9)		
Ni—P(2)—C(31)	120.3(3)	P(1)—C(13)—C(14)	117.4(9)		
C(19)—P(2)—C(25)	99.8(5)	P(1)—C(13)—C(18)	122.5(16)		
Torsion angles (°)					
N—Ni—P(1)—C(1)	—70	N—Ni—P(3)—C(43)	—49	Ni—P(2)—C(25)—C(26)	44
N—Ni—P(1)—C(7)	172	N—Ni—P(3)—C(49)	64	Ni—P(2)—C(31)—C(36)	53
N—Ni—P(1)—C(13)	47			Ni—P(3)—C(37)—C(38)	—35
N—Ni—P(2)—C(19)	—2	Ni—P(1)—C(1)—C(6)	—76	Ni—P(3)—C(43)—C(48)	—85
N—Ni—P(2)—C(25)	241	Ni—P(1)—C(7)—C(8)	—22	Ni—P(3)—C(49)—C(54)	—27
N—Ni—P(2)—C(31)	119	Ni—P(1)—C(13)—C(14)	—35	N—C(55)—C(56)—C(57)	—87
N—Ni—P(3)—C(37)	188	Ni—P(2)—C(19)—C(20)	47	N—C(55)—C(56)—C(61)	—89
Most relevant intramolecular distances between atoms four or more bonds apart (Distances lower than 3.7 Å)					
C(1)···C(54)	3.43	C(13)···(C26)	3.52	C(42)···C(48)	3.24
C(2)···C(14)	3.40	C(14)···N	3.35	C(42)···C(50)	3.40
C(5)···C(53)	3.64	C(24)···C(26)	3.37	C(44)···C(54)	3.41
C(5)···C(54)	3.68	C(24)···C(30)	3.70	C(44)···C(55)	3.65
C(6)···C(12)	3.20	C(24)···C(32)	3.64	C(44)···N	3.55
C(6)···C(54)	3.34	C(30)···C(36)	3.30	C(54)···N	3.50
C(8)···C(25)	3.47	C(31)···C(48)	3.47	C(20)···C(32)	3.39
C(8)···C(26)	3.51	C(32)···C(48)	3.54	C(20)···C(55)	3.19
C(8)···C(38)	3.52	C(36)···C(37)	3.39	C(20)···N	3.13
C(12)···C(18)	3.25	C(36)···C(38)	3.41		

hexylphosphino)methane]nickel [13], (2.210(3) Å). The Ni—N distance of 1.889(11) Å agrees well with the value of 1.888(4) Å we have found in bis(ethylfumarate)(acetonitrile)nickel(0) [14], and noteworthy that the Ni—N azo distance found in bis(t-butylisocyanide)(azobenzene)nickel(0) is 1.898(4) Å [15]. If Ni and N covalent radii of 1.35 and 0.70 Å [16], respectively, are accepted, then the observed Ni—N distance is somewhat shorter than the single-bond distance predicted by summing the covalent radii. Similar observations of short metal—

nitrogen distances in iron—azo complexes have been discussed by Doedens [17]. The N≡C distance found in I (1.15(2) Å) agrees well with the interatomic separation we have found in bis(ethylfumarate)(acetonitrile)nickel(0) [14] (1.129-(6) Å), and with the results of other recent studies [18,19]. The observed N≡C distance implies a triple bond character for this bond. The main features of the benzonitrile residue are coherent with that found for free benzonitrile and for acetonitrile [18,19]. The Ni—$\hat{\text{C}}$≡N angle may be considered as 180° as the N≡C-(55)—C(56) angle.

With regard to the four-fold coordinated phosphorous atoms there is a reduction of the local symmetry from tetrahedral to trigonal; in fact, while the Ni—$\hat{\text{P}}$—C(Phen) angles are considerably larger than the tetrahedral ones (average value 116.1(4)°) the C(Phen)—$\hat{\text{P}}$—C(Phen) angles are significantly less than 109.28° (average value 100.6(4)°). Similar distortions have been noted for many similar compounds [20], and, as we shall see, the triphenylphosphorane groups assume a propellerlike shape. The P—C(Phen) distances found in I (average value 1.834 Å) are in agreement with the values reported for the refined structure of bis(triphenylphosphine)(ethylene)nickel [21] (av. 1.841(9) Å). The P—C(Phen) average value of 1.834 Å is also in close agreement with the calue computed by Shomaker and Stevenson [22] for the P—C single bond (1.83 Å) and with the average values reported by Dunitz and Ibers [20] for this type of bond (1.83 Å).

The overall shape and conformation of the ten benzene rings contained in molecule I are quite acceptable. The bond lengths and the bond angles, within the limits of the estimated standard deviations, assume the usual values. The r.m.s. distances of the carbons atoms from their least-squares planes are as follows: C(1)···C(6) 0.028 Å, C(7)···C(12) 0.019 Å, C(13)···C(18) 0.006 Å, C(19)···C(24) 0.011 Å, C(25)···C(30) 0.021 Å, C(31)···C(36) 0.015 Å, C(37)···C(42) 0.014 Å, C(43)···C(48) 0.023 Å, C(49)···C(54) 0.006 Å, and C(56)···C(61) 0.027 Å.

The conformation assumed by the molecule of I is determined by the juxtaposition of the three tetrahedral polyhedra of the P atoms in respect of the tetrahedron surrounding the nickel central atom. By considering the values assumed by the N—Ni—P—C(Phen) torsion angles, three P—C(Phen) bonds results in a nearly eclipsed conformation: P(2)—C(19) in respect of the N—Ni bond, P(2)—C(25) in respect of the P(1)—Ni bond and P(2)—C(31) in respect of the P(3)—Ni bond. The N—Ni—P(2)—C(19) torsion angle is −2°, while the N—Ni—P(2)—C(25) and N—Ni—P(2)—C(31) torsion angles are 241° and 119° respectively. The other six P—C(Phen) bonds are nearly in a staggered comformation in respect of the N—Ni bond. The distances between the terminal atoms of the groups in eclipsed conformation are quite acceptable; N···C(19) being 3.42 Å while P(3)···C(31) and P(1)···C(25) are about 4.0 Å. The N···C(19) separation of 3.42 Å is the shortest intramolecular distance between atoms three bonds apart present in the skeleton of I. This conformation of the molecule may be the reason for the wide opening of the Ni—P—C(Phen) angles (116.1° on the average). The disposition of the benzene rings of the triphenylphosphorane groups on the skeleton of the molecule I is evident when the Ni—P—C(Phen)—C(Phen) torsion angles are considered. The smallest Ni—P—C(Phen)—C(Phen) torsion angles are: −22°, −35° and −76° when P(1) is involved, −27°, −35° and −85° when P(3) is involved, and 44°, 47° and 53° when P(2) is involved. Similar values are reported for many triphenylphosphorane groups [20,23]. The values of the Ni—P(2)—C(Phen)—C(Phen) torsion angles are different from the corresponding values found for P(1) and for P(3). This may be the consequence of the eclipsed conformations assumed by the P(2)—C(Phen) bonds, while, as we have seen before, the P(1)—C(Phen) and P(3)—C(Phen) bonds are in a nearly staggered conformation. As a result, in I, the triphenylphosphorane groups assume the well known propeller like shape [20], and the C(Phen)···C(Phen) separations between atoms three bonds apart, are all greater than 2.97 Å (C(24)···C-(25)).

The intramolecular distances observed in I have acceptable values, no C···C and C···N separation, between atoms four or more bonds apart, being less than 3.20 and 3.13 Å respectively. The molecular packing of I consists of an arrangement of up and down molecules around each inversion centre of the unit cell. No C···C intermolecular distance is shorter than 3.39 Å.

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