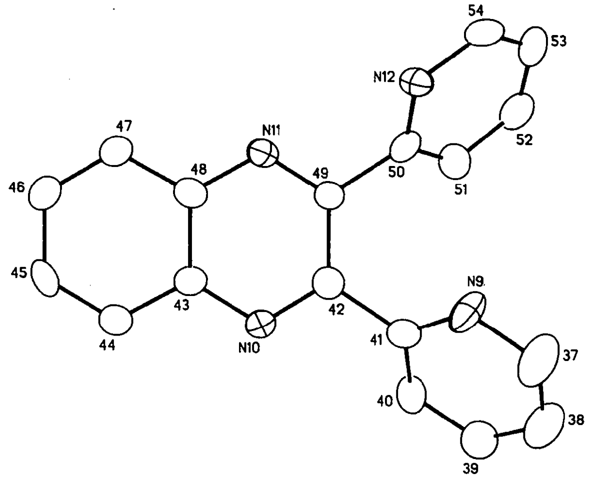

Fig. 2. Thermal ellipsoid plot (35% probability) and numbering scheme for the uncomplexed dpq molecule.

Related literature. The title compound represents the first example of copper coordinated to 2,3-di(2-pyridyl)quinoxaline. Related structures such as that of bis(2,2′-bipyridyl)monochlorocopper(II) perchlorate have been reported by Harrison, Kennedy, Power, Sheahan & Hathaway (1981, and references therein).

The Cu(1)—Br(1) distance is 2·446 (2) Å as compared to values of 2·394 (1) and 3·018 (1) Å observed for a system consisting of $CuBr_2$ units bridged by 2,2′-bipyrimidine (Julve, De Munno, Bruno & Verdaguer, 1988). In that compound, two short Cu–Br contacts lie *trans* to Cu—N bonds to the bridging ligand in a square-planar arrangement about the copper; two long Cu–Br contacts link the square-planar units into an extended array, and complete a distorted octahedral coordination about the Cu atom.

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Structure of 1,4-Diphenyl-2-tetrazenidobis(triethylphosphine)nickel

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Abstract. $[Ni(C_{12}H_{10}N_4)(C_6H_{15}P)_2]$, $M_r = 505{\cdot}33$, orthorhombic, $Pbc2_1$, $a = 8{\cdot}670\ (3)$, $b = 17{\cdot}169\ (6)$, $c = 17{\cdot}923\ (7)$ Å, $V = 2668\ (2)$ Å^3, $Z = 4$, $D_x = 1{\cdot}26$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 8{\cdot}62$ cm^{-1}, $T = 298$ K, $F(000) = 1080$. $R = 0{\cdot}065$ for 1564 reflections with $I > 3{\cdot}0\sigma(I)$ (2019 independent observations). The coordination sphere of Ni is a tetrahedron distorted toward a square plane with a dihedral angle of 56·9° between NiN_4 and NiP_2 planes. Short Ni—N bonds [1·883 (8), 1·883 (10) Å] and three similar N—N bonds[1·28 (2)–1·36 (2) Å] indicate a delocalization of π-electron density in the metallacycle.

Experimental. X-ray data were collected with a Nicolet *R3m/V* automated diffractometer equipped with a Mo X-ray tube and a graphite crystal monochromator. Crystals of $Ni(1,4\text{-}Ph_2N_4)(PEt_3)_2$ were unexpectedly obtained from the reaction between $NiCl_2(PEt_3)_2$ and $[Li(THF)_x]_2(PhN_3NHCH_2CH_2NHN_3Ph)$ in tetrahydrofuran (THF) solvent. Details on crystal data and intensity data are given in Table 1. The orientation matrix and unit-cell parameters were determined from 25 machine-centered reflections with $15 < 2\theta < 30°$. The intensities of three check reflections ($3\bar{2}1$, 222, 320) were monitored after every 100 reflections and showed statistical variations within 3%. Data were corrected for Lorentz and polarization effects. No absorption correction was applied. The systematic absences $0kl(k = 2n + 1)$, $h0l(l = 2n + 1)$, $0k0(k = 2n + 1)$, and $00l(l = 2n + 1)$ indicated two possible space groups: $Pbc2_1$ and $Pbcm$. A statistical analysis of intensities suggested a non-centrosymmetric space group and the structure

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Table 1. *X-ray data collection and structure refinement for* Ni(1,4-Ph_2N_4)(PEt_3)$_2$

Crystal size (mm)	0·3 × 0·4 × 0·5
Color	Purple
Scan type	ω–2θ
Scan width	0·6° below $K\alpha_1$, to 0·6° above $K\alpha_2$
Scan speed (° min^{-1})	3·01–15·00
2θ range (data collection) (°)	3–45
Range of *hkl*	$0 \le h \le 11, 0 \le k \le 21, 0 \le l \le 22$
No. of reflections measured	2019
No. of reflections with $I > 3\sigma(I)$	1564
No. of parameters refined	115
Weight = $[\sigma^2(F_o) + g(F_o)^2]^{-1}$, *g*	0·000290
Max. Δ/σ	0·082
Max., min. $\Delta\rho$ (e Å^{-3})	0·62, −0·22
R	0·065
wR	0·071
S	3·53

Table 2. *Atomic coordinates* (× 10^4) *and equivalent isotropic displacement parameters* (Å^2 × 10^3) *in* Ni(1,4-Ph_2N_4)(PEt_3)$_2$

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	*y*	*z*	U_{eq}
Ni	2374 (1)	8776 (1)	0	29 (1)
P(1)	851 (4)	8567 (2)	960 (2)	33 (1)
C(1)	1809 (18)	8983 (8)	1771 (9)	40 (4)
C(2)	2172 (18)	9847 (9)	1691 (12)	75 (5)
C(3)	365 (19)	7597 (9)	1323 (9)	48 (4)
C(4)	−647 (21)	7092 (9)	816 (11)	77 (5)
C(5)	−988 (18)	9063 (9)	961 (11)	54 (4)
C(6)	−1811 (20)	9113 (9)	1709 (11)	60 (5)
P(2)	856 (4)	8982 (2)	−951 (3)	34 (1)
C(7)	−1014 (17)	8427 (9)	−958 (10)	49 (4)
C(8)	−1923 (22)	8393 (9)	−1671 (11)	60 (5)
C(9)	294 (19)	9944 (9)	−1305 (9)	46 (4)
C(10)	−707 (18)	10412 (8)	−773 (10)	62 (4)
C(11)	1925 (21)	8598 (9)	−1766 (11)	55 (4)
C(12)	2313 (17)	7750 (9)	−1704 (11)	70 (5)
N(1)	4051 (11)	9434 (6)	−220 (6)	31 (3)
C(14)	3359 (10)	10784 (5)	−405 (5)	51 (4)
C(15)	3383	11469	−824	56 (4)
C(16)	4162	11490	−1505	62 (4)
C(17)	4917	10827	−1767	56 (6)
C(18)	4893	10142	−1349	49 (5)
C(13)	4114	10120	−668	35 (3)
N(2)	5477 (17)	9126 (7)	−143 (9)	55 (3)
N(3)	5486 (16)	8458 (7)	171 (8)	48 (3)
N(4)	4062 (12)	8131 (6)	234 (7)	42 (3)
C(20)	5004 (10)	7392 (5)	1325 (6)	47 (5)
C(21)	5071	6700	1732	76 (7)
C(22)	4281	6043	1480	63 (4)
C(23)	3425	6077	822	56 (4)
C(24)	3358	6769	416	51 (4)
C(19)	4148	7426	667	36 (3)

Table 3. *Bond lengths* (Å) *and angles* (°)

Ni—P(1)	2·199 (4)	Ni—P(2)	2·182 (4)
Ni—N(1)	1·883 (9)	Ni—N(4)	1·883 (10)
P(1)—C(1)	1·820 (16)	P(1)—C(3)	1·836 (16)
P(1)—C(5)	1·807 (16)	C(1)—C(2)	1·523 (21)
C(3)—C(4)	1·533 (24)	C(5)—C(6)	1·521 (27)
P(2)—C(7)	1·882 (15)	P(2)—C(9)	1·835 (16)
P(2)—C(11)	1·851 (19)	C(7)—C(8)	1·502 (26)
C(9)—C(10)	1·519 (22)	C(11)—C(12)	1·499 (22)
N(1)—C(13)	1·426 (13)	N(1)—N(2)	1·351 (17)
N(2)—N(3)	1·278 (18)	N(3)—N(4)	1·360 (17)
N(4)—C(19)	1·439 (14)		
P(1)—Ni—P(2)	106·0 (2)	P(1)—Ni—N(1)	136·5 (3)
P(2)—Ni—N(1)	101·8 (3)	P(1)—Ni—N(4)	101·3 (4)
P(2)—Ni—N(4)	137·6 (4)	N(1)—Ni—N(4)	78·4 (4)
Ni—P(1)—C(1)	106·7 (5)	Ni—P(1)—C(3)	124·3 (5)
C(1)—P(1)—C(3)	100·3 (7)	Ni—P(1)—C(5)	116·9 (6)
C(1)—P(1)—C(5)	102·5 (8)	C(3)—P(1)—C(5)	103·0 (7)
P(1)—C(1)—C(2)	113·7 (12)	P(1)—C(3)—C(4)	115·8 (12)
P(1)—C(5)—C(6)	116·1 (13)	Ni—P(2)—C(7)	116·3 (6)
Ni—P(2)—C(9)	125·2 (5)	C(7)—P(2)—C(9)	103·0 (7)
Ni—P(2)—C(11)	104·9 (6)	C(7)—P(2)—C(11)	104·2 (8)
C(9)—P(2)—C(11)	100·4 (7)	P(2)—C(7)—C(8)	118·5 (12)
P(2)—C(9)—C(10)	114·3 (11)	P(2)—C(11)—C(12)	113·6 (13)
Ni—N(1)—C(13)	130·0 (7)	Ni—N(1)—N(2)	116·7 (8)
C(13)—N(1)—N(2)	110·2 (9)	N(1)—C(13)—C(14)	117·8 (5)
N(1)—C(13)—C(18)	122·2 (5)	N(1)—N(2)—N(3)	113·7 (13)
N(2)—N(3)—N(4)	113·6 (13)	Ni—N(4)—N(3)	116·4 (8)
Ni—N(4)—C(19)	130·9 (7)	N(3)—N(4)—C(19)	110·2 (9)
N(4)—C(19)—C(20)	121·2 (6)	N(4)—C(19)—C(24)	118·8 (6)

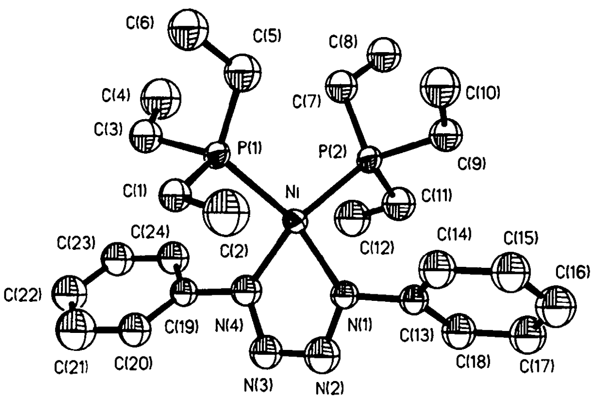

Fig. 1. *ORTEP* (Johnson, 1965) drawing of Ni(1,4-Ph_2N_4)(PEt_3)$_2$ showing the atomic labeling scheme and 50% probability thermal ellipsoids.

could be solved only in the space group $Pbc2_1$. The structure was solved by direct methods and refined by full-matrix least-squares calculations of *F*'s, initially with isotropic and finally with anisotropic temperature factors for Ni and P. The benzene rings were treated as isotropic rigid groups. All H atoms were generated in idealized positions for the structure factor calculations but were not refined independently. All calculations were carried out on a MicroVAXII computer with *SHELXTL-PLUS* (Sheldrick, 1988) with atomic scattering factors and anomalous dispersion corrections from *International Tables for X-ray Crystallography* (1974). Final atomic coordinates with bond distances and angles are given in Tables 2, 3.* The molecular structure and atomic numbering scheme are shown in Fig. 1.

Related literature. Structures of Pd and Pt analogues: Lee, Miller, Campana & Trogler (1988); preparation of a ligand [Li(THF)$_x$]$_2$[PhNN=NNPh]: Lee, Miller, Campana, Maciejewski & Trogler (1987); structure

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* Lists of structure factors, anisotropic thermal parameters, least-squares planes and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52520 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

of $Ni(1,4\text{-}Ph_2N_4)(PPh_2Me)_2$: Lee, Miller, Campana & Trogler (1988); structure of (η^5-C_5H_5)Ni[1,4-(4-$MeC_6H_4)_2N_4$]: Overbosch, van Koten, Speck, Roelofsen & Duisenberg (1982); structure of Ni[1,4-(3,5-$Me_2C_6H_3)_2N_4]_2$: Overbosch, van Koten & Overbeek (1980).

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Structure of a Novel Iridium-Containing Hydrogenation Catalyst

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Abstract. (η^4-1,5-Cyclooctadiene)(pyridine)[tris(2-methoxyphenyl)phosphine]iridium(I) hexafluorophosphate, [$Ir(C_8H_{12})(C_5H_5N)\{P(C_7H_7O)_3\}][PF_6]$, $M_r = 876{\cdot}8$, triclinic, space group $P\bar{1}$, $a = 10{\cdot}501\ (5)$, $b = 12{\cdot}166\ (7)$, $c = 14{\cdot}073\ (7)$ Å, $\alpha = 99{\cdot}04\ (4)$, $\beta = 94{\cdot}35\ (4)$, $\gamma = 103{\cdot}38\ (4)°$, $V = 1715{\cdot}6$ Å^3, $Z = 2$, $D_x = 1{\cdot}70$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 40{\cdot}3$ cm^{-1}, $F(000) = 868$, $T = 295$ K, $R = 0{\cdot}085$, $wR = 0{\cdot}144$ for 3475 reflections with $|F^2| > 3\sigma(F^2)$. The geometry at iridium is approximately square planar, with the expected distortions due to the size of the phosphine ligand: Ir—P1 2·345 (7), Ir—N 2·04 (2) Å, P1—Ir—N 93·0 (6), *M*1—Ir—P1 92·6, *M*1—Ir—*M*2 87·6, *M*2—Ir—N 86·8° (*M*1 and *M*2 are the midpoints of the C27—C34 and C30—C31 bonds). The structure is severely crowded, which is reflected in very hindered rotation of the pyridine ligand noted in solution.

Experimental. The complex was prepared by the addition of tris(2-methoxyphenyl)phosphine to [$Ir(cod)(py)_2][PF_6]$ (Crabtree & Moorehouse, 1986) (cod = 1,5-cyclooctadiene) and well formed crystals obtained by diffusion of ether into a solution in dichloromethane. Data collected using a crystal *ca* 0·4 × 0·4 × 0·3 mm, coated in epoxy glue, on an Enraf–Nonius CAD-4 diffractometer, monochromated Mo $K\alpha$ radiation in the θ–2θ mode, with $\Delta\theta = (0{\cdot}8 + 0{\cdot}35\tan\theta)°$ and a maximum scan time of 1 min. Cell dimensions from setting angles for 25 reflections with $8 < \theta < 10°$. A total of 4176 unique reflections were measured for $2 < \theta < 22°$ and $h\ 0\rightarrow 11$, $k\ -12\rightarrow 12$, $l\ -14\rightarrow 14$, and 3475 reflections with $|F^2| > 3\sigma(F^2)$, where $\sigma(F^2) = [\sigma^2(I) + (0{\cdot}04I)^2]^{1/2}/\text{Lp}$, were used in the refinement. Two standard reflections measured every 60 min showed no significant variation. An absorption correction was applied using *DIFABS* (Walker & Stuart, 1983), after isotropic refinement, and gave maximum and minimum corrections of 1·27 and 0·61. The structure was solved by routine heavy-atom methods and refined on *F* by full-matrix least squares with the Ir, P and F atoms anisotropic. Attempts at refinement with the other non-H atoms anisotropic resulted in non-positive definite thermal parameters, perhaps indicative of slight disorder for the cyclooctadiene ligand and the pyridine group. As a consequence of this problem the final *R* factor is relatively high. H atoms were held fixed at calculated positions with $U_{\text{iso}} = 1{\cdot}3\ U_{\text{eq}}$ for the atoms to which they are bonded. With a weighting scheme of $w = 1/\sigma^2(F)$ and 234 variables, the final residuals were $R = 0{\cdot}085$ and $wR = 0{\cdot}144$, $S = 4{\cdot}3$, $(\Delta/\sigma)_{\text{max}} = 0{\cdot}28$, $\Delta\rho_{\text{max}} = 4{\cdot}2$, $\Delta\rho_{\text{min}} = -3{\cdot}1$ e Å^{-3}. Programs from the Enraf–Nonius (1982) *SDP-Plus* package were run on a MicroVAX computer. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

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