Dibromo{N-[2-(diphenylphosphino)-benzylidene]-2,6-diisopropylaniline-$\kappa^2 N,P$}nickel

Geraldo L. Crossetti,[a] Carlos A. L. Filgueiras,[a] R. Alan Howie,[b]* James L. Wardell[a] and Claudio M. Ziglio[a]

[a]Departamento de Química Inorgânica, Instituto de Química, Universidade Federal do Rio de Janeiro, 21945-970 Rio de Janeiro, RJ, Brazil, and [b]Department of Chemistry, University of Aberdeen, Meston Walk, Aberdeen AB24 3UE, Scotland
Correspondence e-mail: r.a.howie@abdn.ac.uk

In the title compound, $[NiBr_2(C_{31}H_{32}NP)]$, (I), the second reported example of a nickel–iminophosphine N,P-chelate in which the Ni atom has tetrahedral coordination, the Ni coordination is distorted as a consequence of the $N-Ni-P$ chelate bite angle of 91.07 (6)° compensated by the $Br-Ni-Br$ angle of 126.385 (18)°. In (I) and its analogue, *viz.* dichloro{[2-(4-isobutyloxazol-2-yl)phenyl]diphenylphosphine-N,P}nickel(II), the Ni—N and Ni—P distances are greater and the N—Ni—P ligand bite angles smaller than those observed in a series of related complexes with square-planar nickel.

Comment

Arising from the search for good catalysts, the Cambridge Structural Database (CSD; Allen & Kennard, 1993), accessible at the Chemical Database Service of the EPSRC (Fletcher *et al.*, 1996), was found to contain a number of entries for the structures of transition metal complexes (especially Ni and Pd) of α-diimines, $RN{=}CR'-CR'{=}NR''$, and bisphosphines, $R_2P-X-PR_2$ [*e.g.* $X = (CH_2)_n$ for $n = 1, 2, 3$ *etc.*]. Until recently, relatively few structural studies of mixed N,P-chelating ligands, such as the iminophosphines, $o\text{-}R_2P\text{-}C_6H_4\text{–CH}{=}NR$ (represented as N,P below), have been reported. The majority of these are for Pd complexes, typified by $[PdRX(N,P)]$, $[Pd(COR)X(N,P)]$, $[PdR(N,P)L_n][X]$ and $[Pd(N,P)L_n][X]_2$ (Bandoli *et al.*, 2000; Crociani *et al.*, 1999; Reddy *et al.*, 2001; Rülke *et al.*, 1996; Sanchez *et al.*, 1999; Sanchez, Momblona *et al.*, 2001; Sanchez, Serrano *et al.*, 2001; Watkins *et al.*, 2000). At the time of writing, there are, by comparison, relatively few structural reports of imino-phosphine complexes of nickel. Characterization of nickel–iminophosphine complexes by IR and NMR spectroscopic methods has, however, been reported, *e.g.* for $[Ni(C_6F_5)_2(o\text{-}Ph_2PC_6H_4CH{=}NR)]$ (R = Me, Et, Pr, ^iPr, ^tBu, Ph and NHMe) (Sanchez *et al.*, 1998).

Considering only those nickel–iminophosphine complexes for which coordinate data are currently available in the CSD, the structure of the title compound, (I) (Fig. 1), may thus be compared (Table 1) with that of dichloro[2-(4-isobutyloxazol-2-yl)phenyldiphenylphosphine-N,P]nickel(II) (PATQEG; Lloyd-Jones & Butts, 1998), (II), and further with the group comprising [2-(diphenylphosphino)benzaldehyde semithiocarbazonato]pyridinenickel(II) nitrate (RUTLEX; Leovac *et al.*, 1996), (III), chloro{3-hydroxy-3-phenyl-N-[2-(diphenylphosphino)benzylidene]-2-propylamine}nickel chloride ethanol solvate, (IV), and chloro{2-oxy-N-[(2-diphenylphosphino)-benzylidene]aniline}nickel, (V) (GONPAA and GONQAB, respectively; Bhattacharyya *et al.*, 1998), and chloro[2-(di-phenylphosphino)benzaldehyde benzoylhydrazone]nickel(II) (MALBEG; Bacchi *et al.*, 2000), (VI).
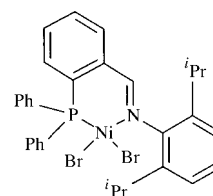
(I)

The coordination of the Ni atom in compounds (III)–(VI) is square planar, as is the case for Pd in all of the known four-coordinate palladium–iminophosphine chelates. In contrast, the Ni atom in (I) and (II) has a distorted tetrahedral environment, the distortion being brought about to a great extent by the ligand bite angles and compensated for by increased $X-Ni-X$ angles (X = Br or Cl). From this limited evidence, it is tempting to associate the tetrahedral coordination of Ni in (I) and (II) with the dihalide complexes. This holds true also for the α-diimine complex $[NiBr_2(^tBuN{=}CHCH{=}N^tBu)]$ (CESWEC; Jameson *et al.*, 1984). However, the square-planar coordination of nickel in the bisphosphine complexes $[NiBr_2(Ph_2PCH_2CH_2PPh_2)]$ (SAHYUC; Rahn *et al.*, 1989) and $[NiCl_2(Ph_2PCH_2CH_2PPh_2)]$ (forms A, B and C; Davison *et al.*, 2001, and references therein) tends to negate this argument, although the size of the chelate rings [six-membered in (I)–(VI) and five-membered in the remainder] may be of significance here. Of greater significance is the fact that the X atoms (Table 1) of compounds (III)–(VI) not only bind to the Ni atom *trans* to the iminophosphine P atom, but are also part of a substituent on the iminophosphine N atom. As a result, in addition to the six-membered iminophosphine N,P-chelate ring, a five-membered X,N-chelate ring is also formed and the ligands are now tridentate in nature. The nature of the C=N imine bond is expected to have a constraining effect upon the relative orientation of the chelate rings, and the angles between their least-squares planes, IP2 (Table 2), which range from 3.43 (13) to 28.76 (15)°, suggest that to some extent this is the case. The near planar arrangement of the chelate rings and the bite angles of the five- and six-membered chelates [$X-Ni-N$ = 89.03 (17)–91.98 (9)° and $N-Ni-P$ = 91.47 (10)–95.14 (12)°] all favour a square-planar coordination of nickel. The evidence presented above does, however,

suggest that the tetrahedral configuration is favoured when nickel forms a dihalo complex with a bidentate ligand containing an imine N atom as at least one of the donor atoms. According to Greenwood & Earnshaw (1997), four-coordinate nickel complexes are for the most part square planar and diamagnetic, but tetrahedral paramagnetic complexes also occur and there are no firm criteria for predicting which arrangement will occur in a given case.

In Table 1, it is clear that the Ni—N and Ni—P bond lengths for (I) and (II) are very similar but significantly longer than those found for (III)–(VI). As expected, the bite angles of the iminophosphine ligands or ligand fragments show comparatively little variation. It is noted, however, that the lowest values are associated with (I) and (II), and may therefore be associated with the comparatively long Ni—N and Ni—P bonds. As noted above, the bite angles are in any case much better suited to square-planar coordination of nickel than to tetrahedral coordination.

The six-membered chelate rings in (I)–(VI) are all puckered, but to varying degrees. The Cremer & Pople (1975) puckering parameters, along with selected interplanar angles, are presented in Table 2. In terms of the puckering amplitudes, the compounds fall into three categories, with (I) and (II) being the most puckered, (III)–(V) forming an intermediate group and (VI) the least puckered. This classification extends to the manner in which substituent atoms are disposed around the chelate rings. Thus, in (I) and (II), there are two axial groups, the halide Y in Table 1 (Br2 or Cl2) and one of the phenyl groups attached to P [$e.g.$ C26–C31 of (I)], and all other substituents are equatorial. In (III)–(V), the only axial substituent is one of the phenyl rings attached to the P atom. Here, again, (VI) constitutes a special case because the only substituents which might not be considered to be in equatorial sites are the two phenyl rings attached to P, but the comparatively planar nature of the chelate ring renders their equatorial or axial status indeterminate. The same classifica-
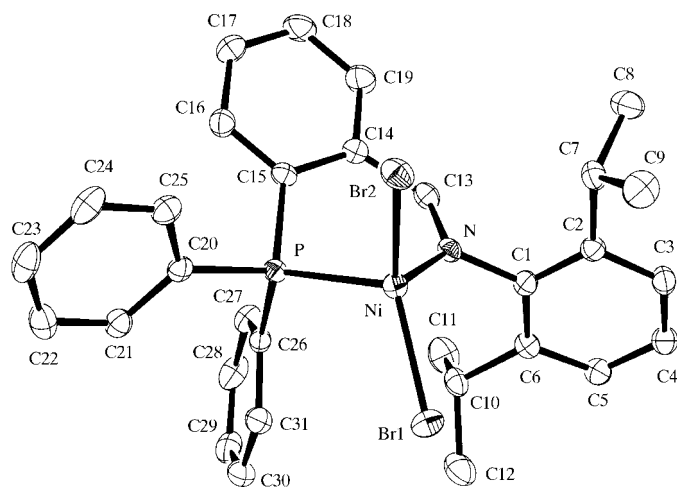
tion is also reflected in the variation of the angle, IP1 (Table 2), between the six-membered N,P-chelate ring and the benzene ring of the ligand.

Experimental

The ligand 2,6-^{i}Pr$_2$C$_6$H$_3$N=CHC$_6$H$_4$-2-PPh$_2$, (VII), was prepared by the addition of 2,6-diisopropylaniline (0.9 ml, 4.3 mmol), formic acid (ca 0.2 ml of an 88% aqueous solution) and anhydrous sodium sulfate to a solution of 2-(diphenylphosphinyl)benzaldehyde (1.16 g, 4.0 mmol) in CH$_2$Cl$_2$ (30 ml). The reaction mixture was stirred for 24 h, the solvent removed and the crude product column chromatographed on silica gel using CHCl$_3$ as eluent, affording (VII) as a yellow solid (1.44 g, 80% yield). IR (CsI): ν(C=N) 1630 cm^{-1}; ^{1}H NMR (CDCl$_3$, 200 MHz, p.p.m.): δ 0.91 (d, 6H, J = 6.8 Hz, Me), 2.70 ($sept$, 1H, J = 6.8 Hz, CHMe$_2$), 6.7–8.2 (m, 5H, phenyl-H), 8.85 (d, 1H, $J_{\text{H-P}}$ = 5.5 Hz, N=CH); ^{31}P{^{1}H} NMR (CDCl$_3$, 122 MHz, p.p.m.): δ −15.0. A solution of (VII) (0.33 g, 0.74 mmol) in CH$_2$Cl$_2$ (10 ml) was added to a suspension of anhydrous nickel bromide (0.15 g, 0.71 mmol) in CH$_2$Cl$_2$/MeCN (3:1, v/v). The resulting dark-red solution was stirred for 3 h at room temperature, the solvent removed under reduced pressure and the solid product washed several times with dry hexane to afford (I) in 98% yield. Crystals suitable for X-ray analysis were obtained from CH$_2$Cl$_2$/hexane. IR (CsI): ν(C=N) 1611 cm^{-1}.

Crystal data

[NiBr$_2$(C$_{31}$H$_{32}$NP)]	D_x = 1.515 Mg m^{-3}
M_r = 668.08	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 13 744
a = 10.6639 (2) Å	reflections
b = 14.4016 (3) Å	θ = 2.9–27.5°
c = 19.7744 (4) Å	μ = 3.47 mm^{-1}
β = 105.2700 (13)°	T = 120 (2) K
V = 2929.68 (10) Å^3	Cube, dark red
Z = 4	0.18 × 0.18 × 0.17 mm

Data collection

Enraf–Nonius KappaCCD area-detector diffractometer	6683 independent reflections
	4970 reflections with $I > 2\sigma(I)$
φ and ω scans to fill the Ewald sphere	R_{int} = 0.057
	θ_{max} = 27.5°
Absorption correction: multi-scan ($SORTAV$; Blessing, 1995, 1997)	h = −13 → 13
	k = −17 → 18
T_{min} = 0.843, T_{max} = 0.947	l = −25 → 25
22 746 measured reflections	

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)]$ = 0.036	$w = 1/[\sigma^2(F_o^2) + (0.0359P)^2]$
$wR(F^2)$ = 0.083	where $P = (F_o^2 + 2F_c^2)/3$
S = 1.05	$(\Delta/\sigma)_{\text{max}}$ = 0.001
6683 reflections	$\Delta\rho_{\text{max}}$ = 0.48 e Å^{-3}
329 parameters	$\Delta\rho_{\text{min}}$ = −0.70 e Å^{-3}

Figure 1
The molecule of (I) showing the atom-labelling scheme. Non-H atoms are shown as 50% probability ellipsoids and H atoms have been omitted for clarity.

In the final stages of refinement, aryl, methyl and tertiary H atoms were introduced in calculated positions with C—H distances of 0.95, 0.98 and 1.00 Å, respectively, and refined as riding with U_{iso} = 1.2U_{eq}, 1.5U_{eq} and 1.2U_{eq}, respectively.

Data collection: $DENZO$ (Otwinowski & Minor, 1997) and $COLLECT$ (Hooft, 1998); cell refinement: $DENZO$ and $COLLECT$; data reduction: $DENZO$ and $COLLECT$; program(s) used to solve structure: $SHELXS$97 (Sheldrick, 1990); program(s) used to refine

Table 1
Bond lengths and angles involving nickel (Å, °) for compounds (I)–(VI).

	(I)	(II)	(III)	(IV)	(V)	(VI)-1	(VI)-2
Ni—X	2.3365 (4)	2.203 (2)	2.167 (2)	1.975 (3)	1.875 (6)	1.877 (3)	1.881 (3)
Ni—Y	2.3597 (4)	2.211 (2)	1.895 (6)	2.144 (2)	2.148 (3)	2.1702 (13)	2.1540 (14)
Ni—P	2.2719 (7)	2.274 (3)	2.173 (2)	2.1378 (9)	2.142 (2)	2.1480 (13)	2.1374 (14)
Ni—N	2.006 (2)	2.000 (3)	1.891 (6)	1.875 (3)	1.900 (7)	1.860 (3)	1.848 (3)
X—Ni—Y	126.385 (18)	128.15 (6)	89.03 (17)	91.98 (9)	90.4 (2)	91.58 (9)	91.69 (9)
X—Ni—P	112.95 (2)	118.89 (7)	163.11 (9)	176.18 (11)	168.3 (2)	173.65 (9)	175.23 (9)
X—Ni—N	109.57 (6)	113.22 (15)	87.94 (17)	84.72 (12)	86.3 (3)	83.67 (14)	83.94 (12)
Y—Ni—P	102.63 (2)	98.00 (12)	90.57 (17)	91.77 (8)	92.26 (11)	89.90 (5)	89.21 (5)
Y—Ni—N	108.42 (6)	103.35 (9)	176.5 (2)	171.78 (4)	175.1 (2)	174.40 (11)	174.87 (11)
P—Ni—N	91.07 (6)	86.71 (9)	92.84 (17)	91.47 (10)	91.7 (2)	95.14 (12)	94.91 (10)

Notes: for (I) and (II), $X = Y$ = Br or Cl, and X = Br1 or Cl1, respectively, such that Ni—$X <$ Ni—Y. For (III)–(VI), with square-planar nickel, X represents the atom *trans* to the iminophosphine P atom [S for (III) and O for (IV)–(VI)]. Likewise, Y now represents the atom *trans* to the iminophosphine N atom [N for (III) and Cl for the rest]. The suffixes 1 and 2 distinguish between the two molecules in the asymmetric unit of (VI). The values for (II)–(VI) were calculated using *PLATON* (Spek, 1990) from CIF data extracted from the CSD; see text for CSD codes and full references.

Table 2
Puckering parameters and selected angles between planes for (I)–(VI).

Puckering amplitudes (Amp) are given in Å, and the θ and φ angles, and also the interplanar angles IP1 and IP2, are given in °.

	(I)	(II)	(III)	(IV)	(V)	(VI)-1	(VI)-2
Amp	0.724 (2)	0.832 (2)	0.425 (4)	0.509 (2)	0.446 (5)	0.163 (3)	0.236 (2)
θ	61.9 (2)	62.8 (1)	58.5 (8)	59.5 (3)	57.6 (9)	53.6 (14)	57.9 (10)
φ	26.3 (2)	24.76 (19)	24.6 (9)	30.8 (4)	11.9 (12)	49.0 (15)	45.1 (10)
IP1	24.52 (12)	25.50 (11)	10.1 (3)	14.69 (17)	10.9 (4)	4.33 (19)	6.14 (19)
IP2			14.3 (2)	28.76 (15)	19.7 (3)	3.43 (13)	7.19 (14)

Notes: compound designations are as for Table 1. For (V), the absolute configuration of the ring has been inverted and θ and φ adjusted accordingly for conformity with the other entries. IP1 is the acute angle between the least-squares planes of the six-membered chelate ring and the benzene ring of the iminophosphine ligand [*e.g.* C14–C19 for (I)] attached to it. IP2 is likewise the acute angle between the least-squares planes of the five-membered X,N- and six-membered N,P-chelate rings of (III)–(VI). In all cases, the values were obtained using *PLATON* (Spek, 1990).

structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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