The tetrahedral tetrakis(phosphine) complex [bis(diphenylphosphino)butane-κP,P]nickel(0)–benzene (1/2.5)

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The nickel(0) complex $[\text{Ni(dppb)}_2]\cdot 2.5\text{C}_6\text{H}_6$ [dppb = $\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2$ or $\text{C}_{28}\text{H}_{28}\text{P}_2$] was obtained from reaction of the boronic ester nickel(II) complex $[\text{NiBr}\{\text{C}_6\text{H}_4\text{B}(\text{O}_2\text{C}_2\text{-Me}_4)\}(\text{dppb})]$ with KO^{t}Bu. The nickel metal centre is in a tetrahedral environment characteristic of NiP$_4$ species. Each asymmetric unit contains 2.5 disordered molecules of benzene and satisfactory refinement was achieved after removal of the solvent void contribution from the data. A mixed anisotropic/isotropic model was used for the non-H-atom sites.

Comment

Nickel(0) complexes of chelating phosphines have been extensively studied as precursors for oxidative additions and as catalysts (McAuliffe & Levason, 1979), and the effect of the diphosphine bite angle (P—M—P) has been shown to have a very important impact on the properties and reactivities of the complexes (Dierkes & van Leeuwen, 1999; van Leeuwen *et al.*, 2000). Complexes with chelate phosphines have also attracted attention for their ^{31}P NMR properties, because the chemical shifts of the phosphorus atoms vary dramatically with the size of the chelate ring (Garrou, 1981). For example, the P atom part of a four-membered metallacycle is always very shielded, whereas the five-membered analogues are the most deshielded of the series. Although the exact origin of this effect is not known, a relation with the M—P—C angle in the chelate ring has been observed (Lindner *et al.*, 1992; Bennett *et al.*, 2001). The structure of the title complex, (II), is particularly interesting in this context.
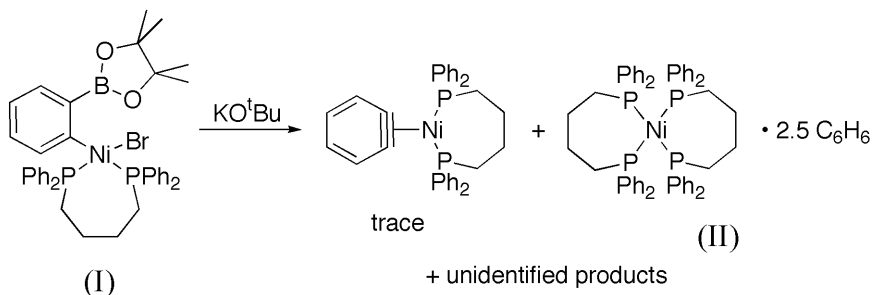
Complexes of the type Ni(0)P$_4$ are generally obtained by addition of the corresponding phosphine ligand to a nickel(0) precursor. We isolated complex (II) in the course of our study of the reaction of the boronic ester nickel(II) complex, (I), with KO^{t}Bu (see Scheme), while only traces of the expected nickel(0)–benzyne complex $[\text{Ni}(\eta^2\text{–C}_6\text{H}_4)(\text{dppb})]$ were observed (Retbøll *et al.*, 2002). The crystals obtained for compound (II) were very thin, the thickest one, used for the experiment, being only 20 μm thick. We note that for the
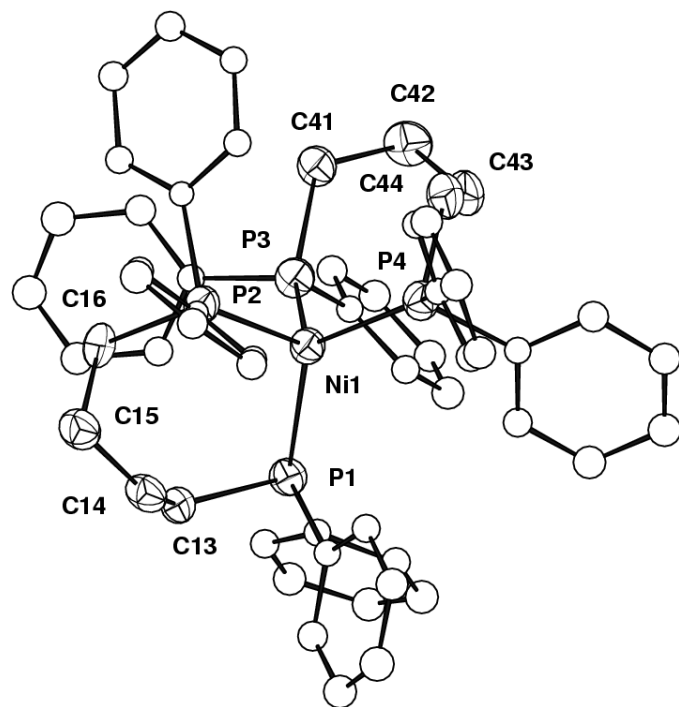
Figure 1
The molecular structure of (II), with selected atom labelling. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

specimen studied the thin dimension corresponded to the distance separating the (00±1) faces. This is also the location of the benzene layers separating adjacent unit cells.

The molecular geometry of (II) is shown in Fig. 1 and the geometric parameters are given in Table 1. The Ni atom in the complex is in a tetrahedral environment, with the four Ni—P distances equal [average value 2.206 (3) Å]. As expected, the P—Ni—P and Ni—P—C angles in the chelate ring of (II) are larger than those of related complexes having shorter bridges between the P atoms, *e.g.* [Ni(dcpm)$_2$] (dcpm = Cy$_2$PCH$_2$PCy$_2$) (Krüger & Tsay, 1972) and [Ni(dppe)$_2$] (dppe = Ph$_2$P(CH$_2$)$_2$PPh$_2$) (Hartung *et al.*, 1989). The average angle values for these complexes are given in Table 2, together with the ^{31}P NMR chemical shifts of the corresponding diphenylphosphine species (Fisher & Alyea, 1989). This comparison shows that the more shielded complex [Ni(dppm)$_2$] also possesses the largest Ni—P—C deviation from an ideal tetrahedral geometry at phosphorus, as indicated by the structure of the cyclohexyl analogue [Ni(dcpm)$_2$].

Table 1
Selected geometric parameters (Å, °).

Ni1—P1	2.208 (3)	P2—C17	1.87 (1)
Ni1—P2	2.208 (3)	P2—C23	1.85 (1)
Ni1—P3	2.207 (3)	P3—C41	1.88 (1)
Ni1—P4	2.201 (4)	P3—C29	1.865 (11)
P1—C13	1.868 (9)	P3—C35	1.845 (11)
P1—C1	1.873 (11)	P4—C44	1.845 (11)
P1—C7	1.864 (11)	P4—C45	1.841 (11)
P2—C16	1.86 (1)	P4—C51	1.865 (11)
P1—Ni1—P2	105.31 (13)	P1—Ni1—P4	121.2 (1)
P1—Ni1—P3	110.90 (14)	P2—Ni1—P4	110.48 (14)
P2—Ni1—P3	102.76 (9)	P3—Ni1—P4	104.79 (13)

Table 2
P—Ni—P(chelate) and Ni—P—C(metallacycle) angles (°) for selected NiP$_4$ complexes, with corresponding ^{31}P NMR chemical shifts.

Complex	P—Ni—P(chelate)	Ni—P—C(met)	$\delta(^{31}$P)
[Ni(dppm)$_2$]			5.6
[Ni(dcpm)$_2$]	77.5 (2)	93.3 (2)	
[Ni(dppe)$_2$]	90.8 (1)	105.6 (3)	44.7
[Ni(dppb)$_2$]	105.0 (2)	115.7 (4)	17.7

Experimental

Ni complex (I) (*ca* 150 mg) was mixed with solid KO^{t}Bu (2–3 equivalents) and THF (2 ml) was added. The mixture was stirred at room temperature and monitored by ^{31}P NMR spectroscopy. The very slow reaction yielded (II) as the major product. The data are similar to those previously reported (Fisher & Alyea, 1989).

A large solvent void (1590 Å^3 per 5920 Å^3 cell) is present. Three sites for benzene molecules (two full molecules and one molecule about a centre of inversion) could be discerned per molecule of complex; these were highly disordered and the contribution of the solvent void has been removed from the data by means of the *SQUEEZE* routine of *PLATON* (Spek, 1990). The data set obtained from these crystals proved to be sparse and this led to the use of a mixed anisotropic/isotropic model for the non-H-atom sites. Aniso-

tropic displacement parameters were employed for the metal and P atoms, together with the C atoms of the butyl chains, whilst the C atoms of the phenyl rings were refined isotropically. H atoms were included in geometrically calculated positions with their positions riding on the attached C atom at a distance of 1.00 Å.

Data collection: *COLLECT* (Nonius, 2001); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *CRYSTALS* (Watkin *et al.*, 2001); molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *CRYSTALS* and *maXus* (Mackay *et al.*, 1999).

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