

The nickel(II) complex $[\text{NiBr}(\text{Ph})\{(\text{C}_6\text{H}_{11})_2\text{-P}(\text{CH}_2)_2\text{P}(\text{C}_6\text{H}_{11})_2\}]\cdot\text{PhCl}$

Alison J. Edwards, Mikael Retbøll and Eric Wenger*

Research School of Chemistry, Australian National University, ACT 0200, Australia

Correspondence e-mail: wenger@rsc.anu.edu.au

Key indicators

Single-crystal X-ray study
 $T = 200\text{ K}$
 Mean $\sigma(\text{C}-\text{C}) = 0.005\text{ \AA}$
 R factor = 0.030
 wR factor = 0.031
 Data-to-parameter ratio = 10.7

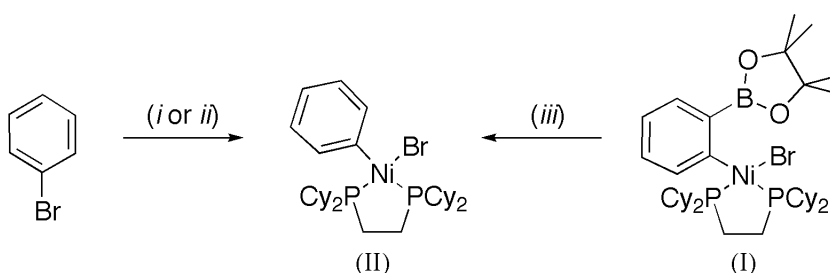
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The crystal and molecular structure of [bis(dicyclohexylphosphino)ethane- κ^2P,P']bromo(phenyl)nickel(II) chlorobenzene solvate, $[\text{NiBr}(\text{C}_6\text{H}_5)(\text{dcpe})]\cdot\text{C}_6\text{H}_5\text{Cl}$ [dcpe is bis(dicyclohexylphosphino)ethane, $(\text{C}_6\text{H}_{11})_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_{11})_2$ or $\text{C}_{26}\text{H}_{48}\text{P}_2$], is reported. The complex is square planar and the Ni—P bond *trans* to the phenyl group is longer than the bond *trans* to Br, reflecting the stronger *trans* influence of the aromatic ring.

Received 9 August 2002
 Accepted 20 August 2002
 Online 31 August 2002

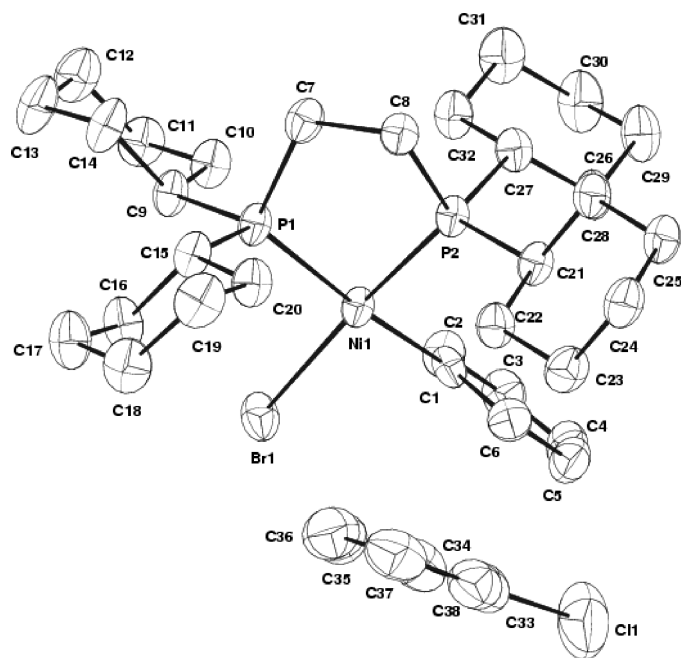
Comment

Arylnickel(II) complexes are usually prepared by oxidative addition of aryl halides to a nickel(0) centre. Compound (II) and related species have been obtained by reaction of bromobenzene with $[\text{Ni}(\eta^2\text{-C}_6\text{H}_4)(\text{dcpe})]$ (Bennett *et al.*, 1985) or with $[\text{NiBr}_2(\text{PPh}_3)_2]$ in the presence of activated zinc, followed by ligand exchange with dcpe (Bennett & Wenger, 1995). The present sample, however, was isolated after hydrolysis of the arylnickel(II) complex (I) bearing a boronic ester group in the *ortho* position. The latter complex, which has been studied as a precursor to the benzylenickel(0) complex $[\text{Ni}(\eta^2\text{-C}_6\text{H}_4)(\text{dcpe})]$ (Retbøll *et al.*, 2002), is highly reactive towards moisture, owing to the large steric interaction between the boronic ester substituent and the cyclohexyl groups on the diphosphine ligand. Cleavage of the C—B bond in (I) occurs readily and compound (II) was obtained from attempted crystallizations of (I).



(i) a) $\text{NiBr}_2(\text{PPh}_3)_2 / \text{Zn}$, b) dcpe; (ii) $[\text{Ni}(\eta^2\text{-C}_6\text{H}_4)(\text{dcpe})]$; (iii) H_2O

Complex (II) crystallized as a chlorobenzene solvate. The nickel centre of (II) is in a square-planar environment, with C1—Ni—P1 and Br1—Ni—P2 angles of $170.47(8)$ and $173.61(3)^\circ$, respectively. The Ni—P distances are not equivalent, the bond *trans* to atom C1 being longer than the bond *trans* to Br, as expected from the larger *trans* influence of the phenyl group. Similarly, the Ni—C1 distance [$1.981(3)\text{ \AA}$] is longer than that in complexes having *trans* phosphines and a halide *trans* to Ni—C; see for example $[\text{NiCl}(\text{o-}$


Figure 1

The molecular structure of the title compound, with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

$C_6H_4Me)(PPh_3)_2]$ (1.900 Å; Spek *et al.*, 2000) and $[NiCl(o-C_6H_4CF_3)(PPh_3)_2]$ (1.890 Å; Lutz *et al.*, 1998). The other geometric data of complex (II) are unexceptional.

Experimental

A solution of the boronic ester complex (I) (50 mg) was prepared with chlorobenzene (3 ml) and pentane was diffused into it at room temperature. Crystallization was very slow, but after 72 h, orange crystals of the title compound formed. Attempted recrystallizations of the title compound from CH_2Cl_2 /hexane or THF/hexane had similar outcomes. The NMR data are analogous to those of the iodo analogue $[Ni(Ph)(dcpe)]$ (Bennett *et al.*, 1985). 1H NMR (300 MHz, CD_2Cl_2 , p.p.m.): δ 1.15–1.95 (*m*, 42H, *dcpe*), 2.04–2.18 (*m*, 4H, *dcpe*), 2.34–2.46 (*m*, 2H, *dcpe*), 6.77 (*t*, 1H, $J = 7.2$ Hz, *p*-Ph), 6.95 (*t*, 2H, $J = 7.2$ Hz, *m*-Ph), 7.45 (*br t*, 2H, $J = 6.0$ Hz, *o*-Ph); ^{13}C NMR (75.4 MHz, CD_2Cl_2 , p.p.m.): δ 19.24 (*dd*, $J = 19.9$, 11.7 Hz, PCH_2), 24.90 (*t*, $J = 23.1$ Hz, PCH_2), 26.17–30.68 (*m*, CH_2), 34.50 (*d*, $J = 18.7$ Hz, PCH), 34.75 (*br d*, $J = 25.3$ Hz, PCH), 121.88 (*s*, *p*-CH), 126.04 (*d*, $J = 6.0$ Hz, *o*-CH), 137.68 (*s*, *m*-CH), 159.10 (*dd*, $J = 85.7$, 37.5, Ni–C); $^{31}P\{^1H\}$ NMR (80.96 MHz, CD_2Cl_2 , p.p.m.): δ 63.3 (*d*), 67.6 (*d*, $J_{PP} = 19.5$ Hz)

Crystal data

$[NiBr(C_6H_5)(C_{26}H_{48}P_2)] \cdot C_6H_5Cl$
 $M_r = 750.89$
 Monoclinic, $P2_1/n$
 $a = 11.8308$ (1) Å
 $b = 22.7790$ (3) Å
 $c = 14.5238$ (2) Å
 $\beta = 107.4072$ (5)°
 $V = 3734.82$ (8) Å³
 $Z = 4$

$D_x = 1.280$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 89742 reflections
 $\theta = 2.9$ – 27.5 °
 $\mu = 1.77$ mm⁻¹
 $T = 200$ K
 Prism, yellow
 0.20 × 0.16 × 0.15 mm

Data collection

Nonius KappaCCD diffractometer
 φ and ω scans
 Absorption correction: by integration (Coppens, 1970)
 $T_{min} = 0.662$, $T_{max} = 0.808$
 94198 measured reflections
 8553 independent reflections

4771 reflections with $I > 3\sigma(I)$
 $R_{int} = 0.044$
 $\theta_{max} = 27.5$ °
 $h = -15 \rightarrow 15$
 $k = -29 \rightarrow 29$
 $l = -18 \rightarrow 18$

Refinement

Refinement on F
 $R = 0.030$
 $wR = 0.031$
 $S = 1.05$
 4771 reflections
 446 parameters
 Only H-atom U 's refined

Weighting scheme: Chebyshev polynomial with four parameters
 0.522, -0.637 , 0.215, -0.339
 (Carruthers & Watkin, 1979)
 $(\Delta/\sigma)_{max} = 0.001$
 $\Delta\rho_{max} = 0.56$ e Å⁻³
 $\Delta\rho_{min} = -0.51$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Ni1–Br1	2.3390 (5)	P2–C27	1.848 (3)
Ni1–P1	2.2223 (7)	C1–C2	1.400 (4)
Ni1–P2	2.1387 (8)	C1–C6	1.338 (4)
Ni1–C1	1.981 (3)	C2–C3	1.391 (4)
P1–C7	1.838 (3)	C3–C4	1.372 (5)
P1–C9	1.848 (3)	C4–C5	1.381 (5)
P1–C15	1.850 (3)	C5–C6	1.399 (4)
P2–C8	1.851 (3)	C7–C8	1.538 (4)
P2–C21	1.844 (3)		
Br1–Ni1–P1	92.87 (2)	Ni1–P1–C15	123.3 (1)
Br1–Ni1–P2	173.61 (3)	Ni1–P2–C8	109.45 (9)
P1–Ni1–P2	89.19 (3)	Ni1–P2–C21	113.97 (9)
Br1–Ni1–C1	89.78 (7)	Ni1–P2–C27	120.48 (9)
P1–Ni1–C1	170.47 (8)	Ni1–C1–C2	114.0 (2)
P2–Ni1–C1	89.16 (7)	Ni1–C1–C6	125.9 (2)
Ni1–P1–C7	107.89 (9)	P1–C7–C8	110.43 (19)
Ni1–P1–C9	113.02 (9)	P2–C8–C7	111.46 (18)

H atoms were included at calculated positions riding on the attached C atom and individual isotropic displacement parameters were refined.

Data collection: *COLLECT* (Nonius, 1997); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1999); program(s) used to refine structure: *CRYSTALS* (Watkin *et al.*, 2001) and *maxUs* (Mackay *et al.*, 1999); molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *CRYSTALS* and *maxUs*.

EW is grateful to the Australian Research Council for the award of a QEII Research Fellowship.

References

- Altomare, A., Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
 Bennett, M. A., Hambley, T. W., Roberts, N. K. & Robertson, G. B. (1985). *Organometallics*, **4**, 1992–2000.
 Bennett, M. A. & Wenger, E. (1995). *Organometallics*, **14**, 1267–1277.
 Carruthers, J. R. & Watkin, D. J. (1979). *Acta Cryst.* **A35**, 698–699.
 Coppens, P. (1970). In *Crystallographic Computing*, edited by F. R. Ahmed, S. R. Hall and C. P. Huber, pp. 255–270. Copenhagen: Munksgaard.

- Lutz, M., Spek, A. L., Brandsma, L. & Peters, T. A. (1998). Private communication to the Cambridge Crystallographic Data Centre, refcode NAVSOS.
- Mackay, S., Gilmore, C. J., Edwards, C., Stewart, N. & Shankland, K. (1999). *maXus*. Bruker–Nonius, Delft, The Netherlands, MacScience, Japan, and The University of Glasgow, Scotland.
- Nonius (1997). *COLLECT*. Nonius BV, Delft, The Netherlands.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr and R. M. Sweet, pp. 307–326. New York: Academic Press.
- Retbøll, M., Edwards, A. J., Rae, A. D., Willis, A. C. & Wenger, E. (2002). *J. Am. Chem. Soc.* **124**, 8348–8360.
- Spek, A. L., Kooijman, H. & Smeets, W. J. J. (2000). Private communication to the Cambridge Crystallographic Data Centre, refcode VEWRUK.
- Watkin, D. J., Prout, C. K., Carruthers, J. R., Betteridge, P. W. & Cooper R. I. (2001). *CRYSTALS*. Issue 11. Chemical Crystallography Laboratory, Oxford, England.
- Watkin, D. J., Prout, C. K. & Pearce, L. J. (1996). *CAMERON*. Chemical Crystallography Laboratory, Oxford, England.