

## Chlorobis(triphenylphosphine)-nickel(I) tetrahydrofuran solvate and an unsolvated trigonal phase of chlorotris(triphenylphosphine)-nickel(I)

Dianne D. Ellis\* and Anthony L. Spek

Bijvoet Center for Biomolecular Research, Department of Crystal and Structural Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands  
Correspondence e-mail: d.d.ellis@chem.uu.nl

Received 17 May 2000

Accepted 8 June 2000

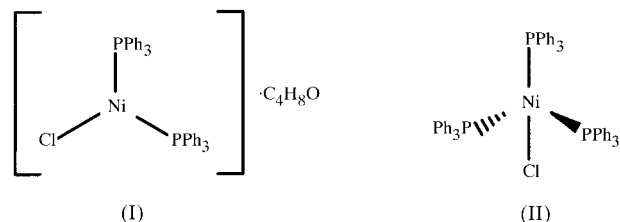
In  $[\text{NiCl}(\text{C}_{18}\text{H}_{15}\text{P})_2] \cdot \text{C}_4\text{H}_8\text{O}$ , the Ni atom is coordinated by three ligands in a distorted trigonal–planar configuration, with a P–Ni–P angle of  $111.52(2)^\circ$ . In  $[\text{NiCl}(\text{C}_{18}\text{H}_{15}\text{P})_3]$ , there are three independent molecules in the asymmetric unit, with each Ni–Cl bond on a crystallographic threefold rotation axis. Each Ni centre is tetrahedrally bound. The Ni atoms in both compounds have a  $d^9$  configuration and a formal oxidation state of  $\text{Ni}^{\text{I}}$ . A comparison is made between the form of  $[\text{NiCl}(\text{PPh}_3)_3]$  presented here and that of a known toluene solvate.

### Comment

Aryl halides may be cyanated using sodium cyanide in the presence of a catalyst such as tris(triphenylphosphine)nickel(0). An important step in the reaction mechanism is the oxidative addition of an aryl halide to the zero-valent nickel complex, to form chloro(aryl)bis(triphenylphosphine)-nickel. Nickel(0) complexes can be stabilized with sterically demanding phosphine ligands, even so, di- and trivalent monomeric nickel complexes are relatively uncommon compared with their palladium and platinum analogues, possibly due to difficulties in crystallization. Under fairly harsh reaction conditions, the two title nickel(I) complexes, (I) and (II), were formed as by-products in recrystallization processes (van Soolingen, 1995).

In  $[\text{NiCl}(\text{PPh}_3)_2] \cdot \text{THF}$  (THF is tetrahydrofuran), (I) (Fig. 1), the nickel ion is coordinated by two  $\text{PPh}_3$  groups with Ni–P distances of 2.2091 (6) and 2.2012 (6) Å, and a chloride ion with an Ni–Cl distance of 2.1481 (6) Å, and lies 0.051 (1) Å out of the P···P···Cl plane. Complex (I) shows a distorted trigonal geometry; the P–Ni–P angle of  $111.52(2)^\circ$  is significantly smaller than the corresponding Cl–Ni–P angles of  $126.98(2)^\circ$  and  $121.33(2)^\circ$ . These angular differences are thought to be caused by the space requirement of the lone

pairs on the chloride ligand, which brings it in closer proximity to the metal than the corresponding P atoms. A similar reasoning was proposed by Brammer & Stevens (1988) in



their analysis of  $[\text{NiCl}_2(\text{PPh}_3)_2]$ . Bulky ligands such as  $\text{PR}_3$  ( $R = \text{Ph}, \text{Cy}$ ) or  $\text{NR}'_2$  ( $R' = \text{Ph}, \text{SiMe}_3$ ) can be used for stabilizing low oxidation states and in many cases where the ligands are not identical, a distorted trigonal–planar geometry results. Thus, in the three-coordinate trigonal–planar nickel(I) species  $[\text{Ni}\{\text{N}(\text{SiMe}_3)_2\}(\text{PPh}_3)_2]$  (Bradley *et al.*, 1972) and the nickel(II) complex  $[\text{NiGe}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{PPh}_3)_2]$  (Litz *et al.*, 1997), the P–Ni–P bond angles are smaller than the Z–Ni–P angles ( $Z = \text{N}$  and  $\text{Ge}$ , respectively). By comparison, in the nickel(0) complex  $[\text{Ni}(\text{PPh}_3)_3]$  (Dick *et al.*, 1990) and the nickel(II) moiety  $[\text{Ni}(\text{NPh}_2)_3]^-$  (Hope *et al.*, 1985), all angles around the central nickel are close to  $120^\circ$ . The shortest contacts to the nickel centre in (I) occur between *ortho*-H atoms on the phenyl rings and nickel:  $\text{Ni1} \cdots \text{H12}$  2.84,  $\text{Ni} \cdots \text{H14}$  2.94 and  $\text{Ni1} \cdots \text{H26}$  3.07 Å. These are of a similar magnitude as those observed in  $[\text{Ni}(\text{PPh}_3)_3]$  (Dick *et al.*, 1990).

The crystal and molecular structure of  $[\text{NiCl}(\text{PPh}_3)_3]$ , (II), studied at 150 K is isomorphous with the bromide analogue,  $[\text{NiBr}(\text{PPh}_3)_3]$  (Mealli *et al.*, 1983), measured at 293 K. Compound (II) has slightly shorter cell dimensions [from the different van der Waals radii of bromide (1.85 Å) compared with chloride (1.75 Å) and temperature differences], and more accurate s.u. values on all geometric parameters. There are

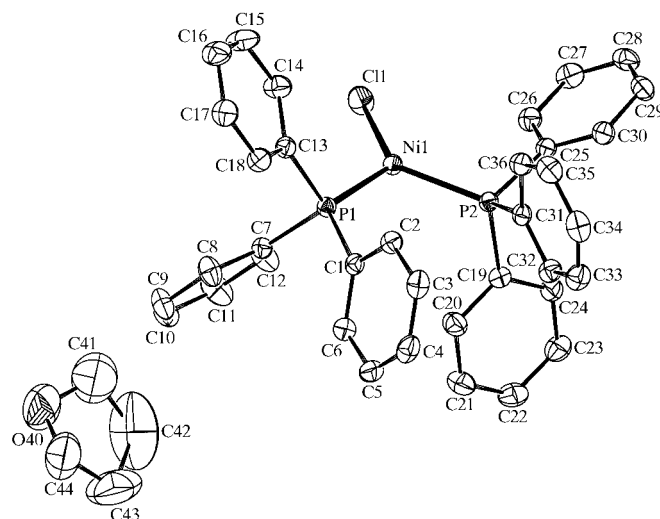
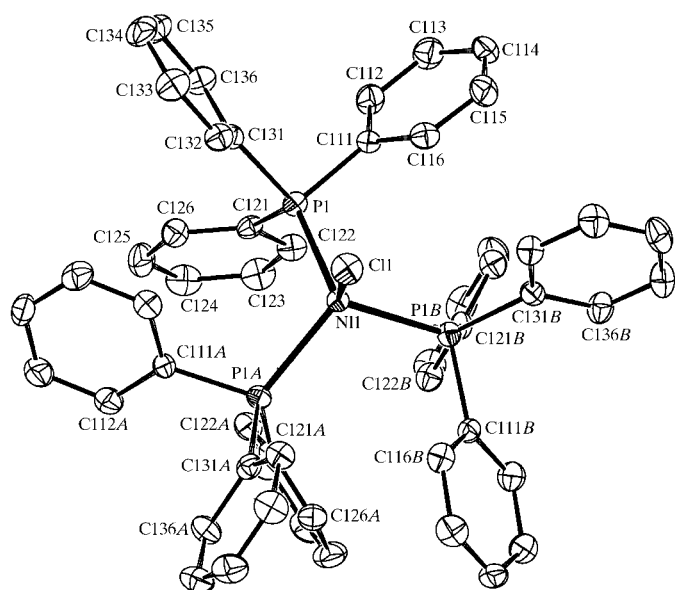


Figure 1

The displacement ellipsoid plot (*PLATON*; Spek, 2000) of (I) drawn at the 50% probability level. H atoms have been omitted for clarity.

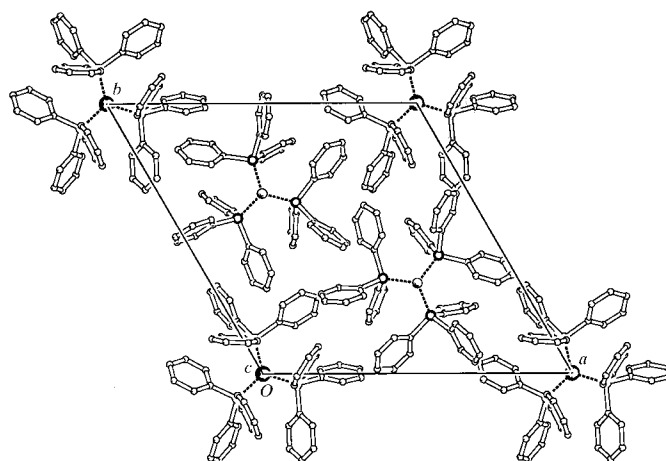


**Figure 2**  
The displacement ellipsoid plot (*PLATON*; Spek, 2000) of one molecule of (II) drawn at the 50% probability level. H atoms have been omitted for clarity. Symmetry operations used to generate equivalent positions: (A)  $-x + y, -x, z$ ; (B)  $-y, x - y, z$ .

three independent molecules in (II), with each Ni and Cl atom on a crystallographic threefold rotation axis; Fig. 2 shows a view of one molecule and Fig. 3 the packing diagram. Overall, each molecule is tetrahedrally coordinated at the Ni atoms and lies on the three (independent) crystallographic axes. The orientation of the molecules in the asymmetric unit is the same as in other  $[(\text{Ph}_3\text{P})_3\text{MX}]$  derivatives ( $M/X = \text{Co/Cl}, \text{Rh/NO}, \text{Ir/NO}, \text{Ni/Br}, \text{Cu/Cl}, \text{Cu/Br}$  and  $\text{Ag/Br}$ ), with two  $M-X$  vectors pointing in one direction, whilst the third has the opposite polarity.

The Ni–P and Ni–Cl bond dimensions in (II) are consistent within the three molecules, and are comparable to those found in the (toluene) solvated form of the same compound,  $[\text{NiCl}(\text{PPh}_3)_3] \cdot \text{C}_7\text{H}_8$  (Cassidy & Whitmire, 1991). The major differences involve the bond angles: in (II), the Cl–Ni–P value of  $110.71(3)^\circ$  is larger than in the solvated form [average Cl–Ni–P angle of  $104.3(40)^\circ$ ], and the P–Ni–P value of  $108.21(3)^\circ$  is significantly smaller than the value of  $114.2(55)^\circ$  found in  $[\text{NiCl}(\text{PPh}_3)_3] \cdot \text{C}_7\text{H}_8$ . Solvent, crystallization procedures and other effects may be causing differences in the molecular environment. In the case of (II), the symmetry of the molecule is coincident with the lattice symmetry element, as observed in other  $[(\text{Ph}_3\text{E})_3\text{MX}]$  ( $\text{E} = \text{P}, \text{As}, \text{Sb}$ ;  $X = \text{halide or pseudo-halides FBF}_3, \text{OCIO}_3$ ) moieties [see, for example, Bowmaker *et al.* (1997)].

Comparisons of the geometric parameters in (I) and (II) show some distinctions. The P–C bonds in (I) are shorter on average than those of (II) [mean values are  $1.824(7)$  versus  $1.838(2)$  Å], with a broader spread of values in (I). The C–P–C bond angles are more consistent in both complexes [ $103.7(9)$  versus  $102(3)^\circ$ ], except that in (II), there is a wider variation within each molecule. The average Ni–P–C angles



**Figure 3**  
The unit cell of (II) projected down the  $c$  axis (*PLATON*; Spek, 2000).

are similar in both complexes, each having one Ni–P–C angle slightly wider than the other two. The orientation of the triphenylphosphine fragments can be described using the values associated with the Ni–P–C<sub>ipso</sub>–C<sub>ortho</sub> torsion angles (the smaller of the two values is chosen for this comparison). In complex (I), these are  $71.74(17)$ ,  $8.8(2)$  and  $27.07(18)^\circ$  for P1, and  $-47.71(18)$ ,  $-38.22(17)$  and  $-53.23(18)^\circ$  for P2. All the triphenylphosphine groups on P1 are orientated in the same direction; those on P2 also have the same sense but the signs are reversed (relative to P1) and the range of torsion angles is fairly compact (the values lie around  $45^\circ$ ). The phenyl rings on P2 adopt the low-energy (propeller-type) conformation (Dunitz, 1995). The P1–C1 bond adopts an eclipsed conformation with respect to the Ni–P2 bond [ $\text{P2–Ni1–P1–C1} = 0.80(8)^\circ$ ], whilst all the other P–C bonds in (I) are staggered. For complex (II), the Ni–P–C<sub>ipso</sub>–C<sub>ortho</sub> values are  $32.2(3)$ ,  $76.2(3)$  and  $-10.0(3)^\circ$  for P1 in molecule 1,  $37.6(3)$ ,  $-19.5(3)$  and  $80.5(3)^\circ$  for P2 in molecule 2, and  $-78.4(3)$ ,  $8.5(3)$  and  $-35.7(3)^\circ$  for P3 in molecule 3. The torsion angles around each P–C bond again show a wide distribution, varying from 8 to  $80^\circ$ . Although these values are comparable to those observed on P1 of complex (I), one of the phenyl rings has a different pitch, and all the P–C bonds in (II) have staggered conformations with respect to the Ni–X bonds ( $X = \text{Cl or P}$ ).

A search for  $X_2M(\text{PPh}_3)$  trigonal-planar moieties and  $X_3M(\text{PPh}_3)$  tetrahedral structures in the Cambridge Structural Database (CSD version 5.18, 207 507 entries; Allen & Kennard, 1993; where  $X$  is defined as any atom and  $M$  is any transition metal) revealed 38 and 95 examples, respectively. To our knowledge, only one other trigonal-planar nickel(I) species,  $[\text{Ni}\{\text{N}(\text{SiMe}_3)_2(\text{PPh}_3)_2\}]$  (Bradley *et al.*, 1972), has been structurally characterized. The small number of trigonal-planar fragments is consistent with the rarity of this coordination number: the only transition metals elements present were from groups 10 and 11. Tetrahedral fragments, on the other hand, occur more widely and encompass a more diverse range of metals (from groups 6 to 12) in the periodic table.

Experimental

Complex (I) was formed by decomposition of chloro(phenyl)bis(triphenylphosphine)nickel (van Soolingen, 1995) in a mixture of hexane and THF at 313 K. Complex (II) was formed by decomposition of chloro(2-thienyl)bis(triphenylphosphine)nickel (van Soolingen, 1995) in a mixture of hexane and toluene, with two equivalents of triphenylphosphine, at 333 K.

Compound (I)

Crystal data

[NiCl(C<sub>18</sub>H<sub>15</sub>P)<sub>2</sub>]<sub>2</sub>·C<sub>4</sub>H<sub>8</sub>O  
*M<sub>r</sub>* = 690.80  
 Monoclinic, *P*<sub>2</sub><sub>1</sub>/*c*  
*a* = 16.4393 (16) Å  
*b* = 11.2773 (12) Å  
*c* = 18.463 (2) Å  
 $\beta$  = 90.140 (9)°  
*V* = 3422.9 (6) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.341 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 Cell parameters from 25 reflections  
 $\theta$  = 11.56–12.23°  
 $\mu$  = 0.769 mm<sup>-1</sup>  
*T* = 150 (2) K  
 Plate, yellow  
 0.55 × 0.55 × 0.05 mm

Data collection

Enraf–Nonius CAD-4 diffractometer  
*w*/*2*θ scans  
 Absorption correction:  $\psi$  scan (North *et al.*, 1968)  
*T*<sub>min</sub> = 0.664, *T*<sub>max</sub> = 0.953  
 16 135 measured reflections  
 7820 independent reflections  
 6179 reflections with *I* > 2σ(*I*)  
*R*<sub>int</sub> = 0.036  
 $\theta$ <sub>max</sub> = 27.46°  
*h* = -21 → 21  
*k* = 0 → 14  
*l* = -23 → 23  
 3 standard reflections  
 frequency: 60 min  
 intensity decay: <1%

Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.036  
*wR*(*F*<sup>2</sup>) = 0.096  
*S* = 1.018  
 7820 reflections  
 406 parameters  
 H-atom parameters constrained  
*w* = 1/[σ<sup>2</sup>(*F<sub>o</sub>*<sup>2</sup>) + (0.0469*P*)<sup>2</sup> + 2.2443*P*]  
 where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3  
 (Δ/σ)<sub>max</sub> = 0.002  
 Δρ<sub>max</sub> = 0.76 e Å<sup>-3</sup>  
 Δρ<sub>min</sub> = -0.60 e Å<sup>-3</sup>

Compound (II)

Crystal data

[NiCl(C<sub>18</sub>H<sub>15</sub>P)<sub>3</sub>]  
*M<sub>r</sub>* = 880.97  
 Trigonal, *P*<sub>3</sub>  
*a* = 19.0125 (8) Å  
*b* = 19.0125 (8) Å  
*c* = 10.4507 (7) Å  
 $\alpha$  = 90.00°  
*V* = 3271.6 (3) Å<sup>3</sup>  
*Z* = 3  
*D<sub>x</sub>* = 1.341 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 Cell parameters from 25 reflections  
 $\theta$  = 11.71–13.88°  
 $\mu$  = 0.654 mm<sup>-1</sup>  
*T* = 150 (2) K  
 Block, yellow  
 0.50 × 0.25 × 0.25 mm

Table 1

Selected geometric parameters (Å, °) for (I).

Ni1—Cl1	2.1481 (6)	Ni1—P1	2.2091 (6)
Ni1—P2	2.2012 (6)		
Cl1—Ni1—P2	126.98 (2)	P2—Ni1—P1	111.52 (2)
Cl1—Ni1—P1	121.33 (2)		
P2—Ni1—P1—C1	0.80 (8)	Ni1—P1—Cl13—Cl14	27.07 (18)
Cl1—Ni1—P2—C31	143.72 (8)	Ni1—P1—Cl13—Cl18	-156.44 (16)
Cl1—Ni1—P2—C19	-91.84 (8)	Ni1—P2—Cl19—C24	132.25 (16)
Cl1—Ni1—P2—C25	24.01 (8)	Ni1—P2—Cl19—C20	-47.71 (18)
Ni1—P1—Cl—C2	71.74 (17)	Ni1—P2—C25—C30	138.92 (16)
Ni1—P1—Cl—C6	-103.30 (16)	Ni1—P2—C25—C26	-38.22 (17)
Ni1—P1—C7—C12	8.8 (2)	Ni1—P2—C31—C32	129.36 (15)
Ni1—P1—C7—C8	-171.54 (17)	Ni1—P2—C31—C36	-53.23 (18)

Data collection

Enraf–Nonius CAD-4 diffractometer  
*w*/*2*θ scans  
 10 742 measured reflections  
 5286 independent reflections  
 4500 reflections with *I* > 2σ(*I*)  
*R*<sub>int</sub> = 0.055  
 $\theta$ <sub>max</sub> = 27.49°  
*h* = -24 → 23  
*k* = -23 → 24  
*l* = -13 → 0  
 3 standard reflections  
 frequency: 60 min  
 intensity decay: <1%

Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.031  
*wR*(*F*<sup>2</sup>) = 0.066  
*S* = 1.016  
 5286 reflections  
 533 parameters  
 H-atom parameters constrained  
*w* = 1/[σ<sup>2</sup>(*F<sub>o</sub>*<sup>2</sup>) + (0.0260*P*)<sup>2</sup> + 0.0482*P*]  
 where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3  
 (Δ/σ)<sub>max</sub> = 0.001  
 Δρ<sub>max</sub> = 0.30 e Å<sup>-3</sup>  
 Δρ<sub>min</sub> = -0.52 e Å<sup>-3</sup>

X-ray data were collected using Zr β-filtered Mo *K*α radiation. The THF molecule in complex (I) is rotationally disordered, but refinement of the atom positions corresponding to a second orientation proved to be unstable. The unit cell of (I) is close to orthorhombic [ $\beta$  = 90.140 (9)°], but successive twinning matrices did not provide a stable refinement. Flack (1983) parameter refinement included 272 Friedel pairs but was inconclusive and refinement of the *TWIN/BASF* parameter gave a value of 0.19 (2) Å. Three solvent voids of 35.5 Å<sup>3</sup> were found in complex (II) using *PLATON* (Spek, 2000). The closest contacts to the main molecules are to H atoms on the phenyl groups. The voids could not be assigned to any material used in the preparation of the crystal. All H atoms were constrained and allowed to ride on their C atoms with *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C).

For both compounds, data collection: locally modified *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *SET4* (de Boer & Duisenberg, 1984); data reduction: *HELENA* (Spek, 1997); program(s) used to solve structure: *DIRDIF* (Beurskens *et al.*, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2000); software used to prepare material for publication: *PLATON*.

Crystals were kindly provided by Dr J. van Soolingen, Dr T. H. A. Peters and Professor Dr L. Brandsma, Utrecht University, The Netherlands. The authors would also like to thank Professor K. Whitmire for providing additional infor-

Table 2

Selected geometric parameters (Å, °) for (II).

Ni1—Cl1	2.2933 (17)	Ni2—P2	2.2887 (9)
Ni1—P1	2.3082 (9)	Ni3—P3	2.2966 (9)
Ni2—Cl2	2.2858 (16)	Ni3—Cl3	2.2982 (16)
Cl1—Ni1—P1	110.71 (3)	P2 <sup>ii</sup> —Ni2—P2	107.06 (3)
P1—Ni1—P1 <sup>i</sup>	108.21 (3)	P3 <sup>iii</sup> —Ni3—P3	108.03 (3)
Cl2—Ni2—P2	111.79 (3)	P3—Ni3—Cl3	110.88 (3)
Ni1—P1—Cl11—Cl116	32.2 (3)	Ni2—P2—C221—C226	166.1 (2)
Ni1—P1—Cl11—Cl112	-149.7 (3)	Ni2—P2—C231—C232	-91.5 (3)
Ni1—P1—Cl121—Cl126	-96.1 (3)	Ni2—P2—C231—C236	80.5 (3)
Ni1—P1—Cl121—Cl122	76.2 (3)	Ni3—P3—C321—C322	8.5 (3)
Ni1—P1—Cl131—Cl132	-10.0 (3)	Ni3—P3—C321—C326	-175.0 (3)
Ni2—P2—C211—C212	37.6 (3)	Ni3—P3—C331—C336	-35.7 (3)
Ni2—P2—C211—C216	-145.5 (3)	Ni3—P3—C331—C332	146.8 (3)
Ni2—P2—C221—C222	-19.5 (3)		

Symmetry codes: (i) -*y*, *x* - *y*, *z*; (ii) 1 - *y*, 1 + *x* - *y*, *z*; (iii) 1 - *y*, *x* - *y*, *z*.

mation pertaining to  $[\text{NiCl}(\text{PPh}_3)_3]\cdot\text{C}_7\text{H}_8$ . The investigations were supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization of Scientific Research (NWO).

---

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1605). Figures for molecules 2 and 3 of compound (II) are also available. Services for accessing these data are described at the back of the journal.

---

## References

- Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 31–37.
- Beurskens, P. T., Admiraal, G., Beurskens, G., Bosman, W. P., García-Granda, S., Gould, R. O., Smits, J. M. M. & Smykalla, C. (1997). *The DIRDIF97 Program System*, Technical Report. Crystallography Laboratory, University of Nijmegen, The Netherlands.
- Boer, J. L. de & Duisenberg, A. J. M. (1984). *Acta Cryst.* **A40**, C-410.
- Bowmaker, G. A., Hart, R. D., De Silva, E. N., Skelton, B. W. & White, A. H. (1997). *Aust. J. Chem.* **50**, 553–565.
- Bradley, D. C., Hursthouse, M. B., Smallwood, R. J. & Welch, A. J. (1972). *J. Chem. Soc. Chem. Commun.* pp. 872–873.
- Brammer, L. & Stevens, E. D. (1988). *Acta Cryst.* **C45**, 400–403.
- Cassidy, J. M. & Whitmire, K. H. (1991). *Acta Cryst.* **C47**, 2094–2098.
- Dick, D. G., Stephan, D. W. & Campana, C. F. (1990). *Can. J. Chem.* **68**, 628–632.
- Dunitz, J. D. (1995). *X-ray Analysis and the Structure of Organic Molecules*, 2nd ed. Basel: VCH.
- Enraf-Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf-Nonius, Delft, The Netherlands.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Hope, H., Olmstead, M. M., Murray, B. D. & Power, P. P. (1985). *J. Am. Chem. Soc.* **107**, 712–713.
- Litz, K. E., Bender, J. E. IV, Kampf, J. W. & Banaszak Holl, M. M. (1997). *Angew. Chem. Int. Ed. Engl.* **36**, 496–498.
- Mealli, C., Dapporto, P., Sriyonyongwat, V. & Albright, T. A. (1983). *Acta Cryst.* **C39**, 995–996.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Soolingen, J. van (1995). PhD thesis, Utrecht University, The Netherlands.
- Spek, A. L. (1997). *HELENA*. Utrecht University, The Netherlands.
- Spek, A. L. (2000). *PLATON*. Utrecht University, The Netherlands.