

Ilia A. Guzei,<sup>a\*</sup> Makwena J. Moloto<sup>b</sup> and James Darkwa<sup>b</sup>

<sup>a</sup>2124 Chemistry Department, University of Wisconsin-Madison, 1101 University Ave, Madison, WI 53706, USA, and <sup>b</sup>Department of Chemistry, University of Western Cape, Private Bag X17, Belville 7535, South Africa

Correspondence e-mail: iguzei@chem.wisc.edu

#### Key indicators

Single-crystal X-ray study

$T = 173\text{ K}$

Mean  $\sigma(\text{C}-\text{C}) = 0.005\text{ \AA}$

$R$  factor = 0.043

$wR$  factor = 0.126

Data-to-parameter ratio = 19.3

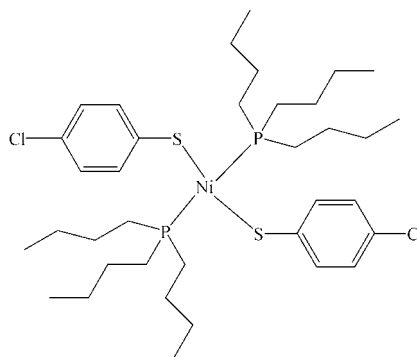
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

## Bis(*p*-chlorothiophenolato)bis(tri-*n*-butylphosphine)nickel(II)

The title complex,  $[\text{Ni}(\text{C}_6\text{H}_4\text{ClS})_2(\text{C}_{12}\text{H}_{27}\text{P}_3)_2]$ , resides on a crystallographic inversion center in a triclinic unit cell. The structural features of the complex compare well with those of similar square planar Ni(O) complexes reported in the Cambridge Structural Database.

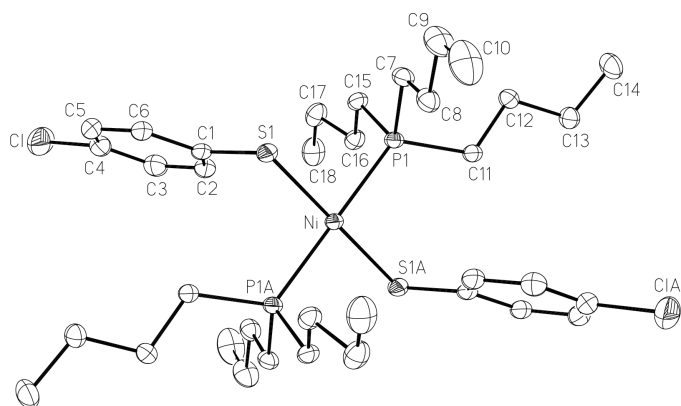
#### Comment

Dihalogeno diphosphino nickel compounds,  $\text{Ni}(\text{PR}_3)_2\text{X}_2$  ( $X = \text{Cl}, \text{Br}, \text{I}; R = \text{Ph}, ^n\text{Bu}$ ), are a ready source of phosphine ligands in the preparation of nickel phosphino complexes. This is usually achieved *via* metathesis reactions between the halo phosphino complex and another nickel compound. However, products from tributylphosphine invariably turn out to be oils and thus it is difficult to separate the new phosphino compound from remnants of  $\text{Ni}(\text{P}^n\text{Bu}_3)_2\text{X}_2$  which may be present. We have used the metathesis approach to prepare starting materials for the synthesis of cyclopentadienylnickel and diethyldithiocarbamate nickel complexes (Darkwa *et al.*, 1993, 1998, 1999; Babikanyisa & Darkwa, 1997; Nevondo *et al.*, 2000). Recently, in one such experiment, small amounts of unreacted  $\text{Ni}(\text{P}^n\text{Bu}_3)_2\text{Br}_2$  were found to have reacted with  $\text{LiSC}_6\text{H}_4\text{Cl}$ -4, producing the title complex, (I) (Fig. 1).



(I)

The Ni atom resides on a crystallographic inversion center. Complex (I) is isostructural with compounds  $\text{Ni}(\text{SPh})_2(\text{P}^n\text{Bu}_3)_2$ , (II) (Cao *et al.*, 1995), and  $\text{Ni}(\text{S-}p\text{-tolyl})_2(\text{P}^n\text{Bu}_3)_2$ , (III) (Jiang *et al.*, 1991). Interestingly, complexes (I)–(III) all exist in the triclinic form in the solid state but compound (III) also crystallizes in a monoclinic cell. The coordination geometry about the Ni center in (I) is slightly distorted square planar with two S and two P atoms in *trans* positions. The Ni–S distance in (I) [2.2093 (7) Å] is somewhat shorter than that in (II) or (III) [2.217 (2) and 2.213 Å, respectively], but slightly



**Figure 1**  
Molecular structure of (I). The displacement ellipsoids are shown at the 30% probability level.

longer than the average Ni–S single bond of 2.18 (4) Å. The latter value was obtained by averaging 1594 Ni–S single bonds in complexes found in the Cambridge Structural Database (CSD; Allen & Kennard, 1993). While the differences in the Ni–S bond distances in (I)–(III) are subtle, it is noteworthy that the length of the Ni–S bond increases as the substituent in the *para* position of the phenyl ring becomes a better  $\sigma$ -donor of electron density. Thus, the Ni–S bond length increases left to right according to the sequence Ph-tolyl–C<sub>6</sub>H<sub>4</sub>Cl-4. The Ni–P bond in (I) [2.2361 (7) Å] is in good agreement with that in (III) [2.237 Å] but significantly shorter than the corresponding bond in (II) [2.245 (2) Å]. Interestingly, all three Ni–P bond distances are much longer than the average Ni–P bond length of 2.20 (5) Å, obtained by averaging 1362 Ni–P bonds in suitable complexes found in the CSD. The angles about the Ni center in (I) range from 86.57 (3) to 93.43 (3)°. The butyl groups exhibit the normal zigzag conformation, with the four C atoms of each butyl group coplanar within 0.07 Å.

## Experimental

Triethylamine (1.0 ml) was added to a purple solution of Ni(P<sup>n</sup>Bu<sub>3</sub>)<sub>2</sub>Br<sub>2</sub> (0.45 g, 0.72 mmol) and HSC<sub>6</sub>H<sub>4</sub>Cl-4 (0.21 g, 1.45 mmol) in toluene (30 ml). The solution gradually changed to red-brown over 20 min and was further stirred for 3 h. The red-brown solution was filtered and the filtrate evaporated to dryness, leaving a brown residue. The residue was extracted with hexane and concentrated to about 20 ml. On cooling at 258 K red-brown needle-like crystals were formed. Yield = 0.18 g (40%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.81 (*d*, 4H,  $J_{\text{HH}} = 8.4$  Hz, SC<sub>6</sub>H<sub>4</sub>Cl-4), 7.03 (*d*, 4H,  $J_{\text{HH}} = 8.4$  Hz, SC<sub>6</sub>H<sub>4</sub>Cl-4), 1.41 (*m*, 36H, P<sup>n</sup>Bu<sub>3</sub>), 0.89 (*m*, 18H, P<sup>n</sup>Bu<sub>3</sub>).

## Crystal data

C<sub>36</sub>H<sub>62</sub>Cl<sub>2</sub>NiP<sub>2</sub>S<sub>2</sub>  
 $M_r = 750.53$   
 Triclinic,  $P\bar{1}$   
 $a = 8.6314$  (7) Å  
 $b = 10.3062$  (8) Å  
 $c = 11.9720$  (9) Å  
 $\alpha = 75.4198$  (10)°  
 $\beta = 83.3078$  (10)°  
 $\gamma = 84.9883$  (10)°  
 $V = 1021.81$  (14) Å<sup>3</sup>

$Z = 1$   
 $D_x = 1.220$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 564 reflections  
 $\theta = 2.0$ – $24.0^\circ$   
 $\mu = 0.81$  mm<sup>-1</sup>  
 $T = 173$  (2) K  
 Block, red  
 0.50 × 0.40 × 0.40 mm

## Data collection

Bruker SMART CCD area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: empirical (SADABS; Blessing, 1995)  
 $T_{\text{min}} = 0.688$ ,  $T_{\text{max}} = 0.738$   
 3843 measured reflections

3843 independent reflections  
 3133 reflections with  $I > 2\sigma(I)$   
 $\theta_{\text{max}} = 26.4^\circ$   
 $h = -10 \rightarrow 10$   
 $k = -12 \rightarrow 12$   
 $l = 0 \rightarrow 14$

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.043$   
 $wR(F^2) = 0.126$   
 $S = 1.07$   
 3843 reflections  
 199 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0676P)^2 + 0.4884P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 1.80$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.45$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

Ni–S1	2.2093 (7)	Ni–P1	2.2361 (7)
S1–Ni–P1	86.57 (3)		

Data collection: SMART (Bruker, 1997); cell refinement: SAINT (Bruker, 1997); data reduction: SHELXTL (Bruker, 1997); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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