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# *trans*-Dichlorobis(triphenylphosphine)nickel(II) bis(dichloromethane) solvate: redetermination at 120 K

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Re-investigation of $[NiCl_2(PPh_3)_2]\cdot 2CH_2Cl_2$ at 120 K yielded much more accurate geometric parameters than the earlier room temperature study and confirmed the main conclusion of the latter: the Ni—P and Ni—Cl bonds in this centrosymmetric square-planar complex [2.2439 (5) and 2.1672 (5) Å] are significantly shorter than in the tetrahedral solvent-free $[NiCl_2(PPh_3)_2]$.

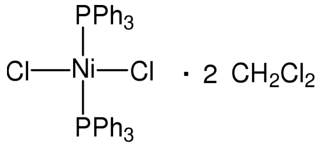
**Key indicators**

Single-crystal X-ray study
*T* = 120 K
Mean $\sigma$(C–C) = 0.002 Å
*R* factor = 0.029
*wR* factor = 0.074
Data-to-parameter ratio = 17.3

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

## Comment

In a solvent-free crystal, $[NiCl_2(PPh_3)_2]$, (II), adopts a tetrahedral coordination of the Ni atom (Garton *et al.*, 1963; Bruins Slot *et al.*, 1984; Corain *et al.*, 1985; Brammer & Stevens, 1989) and a green–blue colour. However, the $[NiCl_2(PPh_3)_2]\cdot 2ClCH_2CH_2Cl$ solvate, (III), is deep-red and shows a *trans* square-planar coordination (Corain *et al.*, 1985) with both Ni—P and Ni—Cl bonds significantly shorter than in (II). The same coordination was found in the $[NiCl_2(PPh_3)_2]\cdot 2CH_2Cl_2$ solvate, (I), the pseudo-polymorph of (III), but the precision of the room-temperature crystallographic study of (I) (Sletten & Kovacs, 1993) was not very high (*R* = 0.107).



$$trans\text{-}[NiCl_2(PPh_3)_2]\cdot 2\,CH_2Cl_2$$

(I)

Presently, we redetermined the structure of (I) at 120 K, which appeared essentially the same as at room temperature. The unit cell and the arrangement of the complex molecules bear a close semblance to those of (III). The Ni atom is located at an inversion centre and hence has a rigorously planar *trans*-coordination (Fig. 1). Thus, (I) and (III) can be described as allogons of (II). The Ni—P and Ni—Cl bond distances we found in (I), 2.2439 (5) and 2.1672 (5) Å, practically coincide with those reported by Sletten & Kovacs (1993) (2.241 and 2.164 Å), as well as with the corresponding distances in (III), *viz*. 2.242 (3) and 2.155 (3) Å (Corain *et al.*, 1985). The most accurate study (at 94 K) of the tetrahedral allogon (Brammer & Stevens, 1989) gave the distances Ni—P = 2.3180 (2) and Ni—Cl = 2.2075 (2) Å, longer than in (I) by 0.07 and 0.04 Å, respectively. The P—C bond lengths change contrary to the Ni—P, averaging 1.827 (4) Å in (III) against 1.816 (4) Å in the tetrahedral allogon, in accordance with the view that nickel *d*-electrons are back-donated into the $\sigma^*$(P—C) orbitals rather than into the pure *d*-orbitals of the P atoms (Xiao *et al.*, 1983; Marynick, 1984). Shorter P—C distances in (I) at room

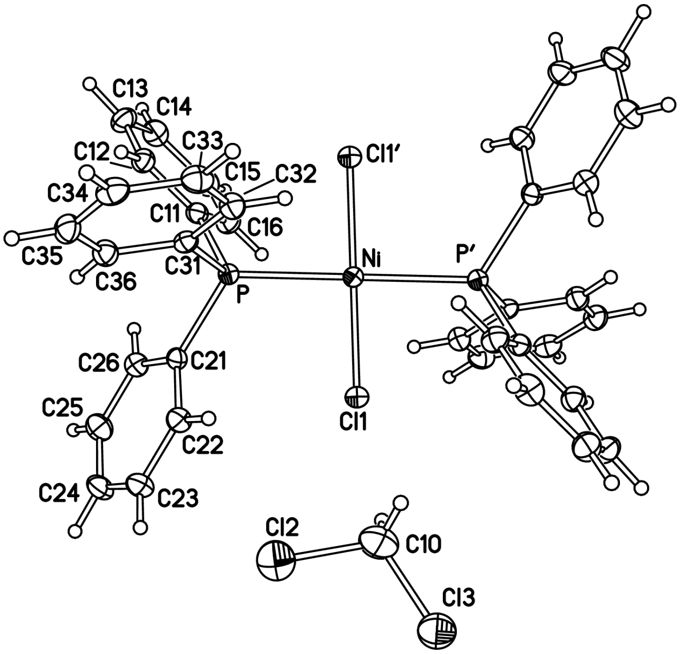


**Figure 1**
The molecules of $[NiCl_2(PPh_3)_2]$ and $CH_2Cl_2$ in (I). Displacement ellipsoids are drawn at the 50% probability level.

temperature, averaging 1.815 (9) Å, are obviously a spurious effect of thermal motion.

## Experimental

Green–mauve (II) was dissolved in $CH_2Cl_2$. After 48 h at 253 K, an orange–red precipitate of (II) formed, including crystals of X-ray quality. On drying *in vacuo*, (I) recovered the green colour of the starting (II).

*Crystal data*

$[NiCl_2(C_{18}H_{15}P)_2]\cdot 2CH_2Cl_2$
$M_r = 824.00$
Orthorhombic, *Pbca*
$a = 22.970\ (6)$ Å
$b = 20.005\ (4)$ Å
$c = 8.048\ (2)$ Å
$V = 3698.2\ (15)$ Å$^3$
$Z = 4$
$D_x = 1.480$ Mg m$^{-3}$

Mo $K\alpha$ radiation
Cell parameters from 879 reflections
$\theta = 12.0–23.4°$
$\mu = 1.07$ mm$^{-1}$
$T = 120\ (2)$ K
Prism, red
0.70 × 0.25 × 0.20 mm

*Data collection*

SMART 1 K CCD area-detector diffractometer
$\omega$ scans
Absorption correction: by integration (*XPREP SHELXTL*; Bruker, 1998), $R_{int} = 0.049$ before correction
$T_{min} = 0.659$, $T_{max} = 0.821$

26 505 measured reflections
4885 independent reflections
4081 reflections with $I > 2\sigma(I)$
$R_{int} = 0.040$
$\theta_{max} = 29.0°$
$h = -31 \rightarrow 24$
$k = -25 \rightarrow 26$
$l = -10 \rightarrow 7$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.074$
$S = 1.07$
4885 reflections
282 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0309P)^2 + 2.4862P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.44$ e Å$^{-3}$
$\Delta\rho_{min} = -0.30$ e Å$^{-3}$

$Csp^3$—H bond distances vary from 0.92 (3) to 0.98 (4) Å and $Csp^2$—H distances from 0.90 (2) to 0.99 (2) Å.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1999); program(s) used to solve structure: *SHELXTL* (Bruker, 1998); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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