

## *trans*-[Dichlorobis(triphenylphosphine)nickel(II)] · (C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>)<sub>2</sub>: a Clathrate of the Allogon of Venanzi's Tetrahedral Complex

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Received November 27, 1984

### Abstract

The synthesis of the clathrate compound [NiCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] · (C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>)<sub>2</sub> and a complete X-ray analysis are described. [NiCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] · (C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>)<sub>2</sub> is orthorhombic with *a* = 23.486(6), *b* = 20.298(6), *c* = 8.290(3) Å, space group *Pbca*, *Z* = 4; *R* = 0.063. The inclusion compound contains square-planar moieties *trans*-[NiCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] and dichloroethane molecules which do not appear to interact chemically. The X-ray structure of tetrahedral [NiCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] has been re-investigated and relevant relationships of molecular parameters between the two allogons are reported.

### Introduction

The stereochemistry of [NiX<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>] complexes (X = halide, pseudohalide; PR<sub>3</sub> = substituted phosphine) has been thoroughly investigated [1]. In particular, the role of steric and electronic factors of the ligand set was carefully examined and the distorted tetrahedral configuration of [NiCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>], **1**, has been ascribed to a combination of steric bulkiness and of relatively low ligand-field strength of PPh<sub>3</sub> [2]. In fact, **1** has always been known as a tetrahedral species in the solid state [3].

We were interested in using **1** as a starting reagent for preparative purposes, and noticed that treatment of the green-mauve microcrystalline material [2] with sym-C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub> (but not CHCl<sub>3</sub>, CCl<sub>4</sub>) under certain conditions led to a red crystalline product analyzing as [NiCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] · (C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>)<sub>2</sub>, **2**. The obvious hypothesis was that we had accidentally prepared an allogonic form of Venanzi's tetrahedral [NiCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] complex, and this

prompted us to undertake a full X-ray analysis of the red species. Moreover, in order to make a reliable comparison with the structural data of the corresponding tetrahedral allogon, we carried out an X-ray re-investigation.

### Experimental

Crystals of **2** suitable for X-ray analysis were obtained by dissolving 130 mg of **1** in 4.5 ml of anhydrous sym-C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> under nitrogen. A red solution with green reflexes was obtained, from which, after ca. 2 min at 20 °C, in absence of stirring, dark red prisms of [NiCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] · (C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>)<sub>2</sub>, **2**, were obtained in quantitative yield. *Anal. Calcd.* for C<sub>40</sub>H<sub>38</sub>Cl<sub>6</sub>P<sub>2</sub>Ni: C, 56.38; H, 4.49; Cl 24.96. *Found:* C, 55.8; H 4.38; Cl 23.6%. A similar procedure, although not restricted to the detailed conditions mentioned above, always gave a crystalline red precipitate. Operation in open atmosphere generally gave red crystals, mixed with a white amorphous precipitate. Prolonged contact of the red crystals with C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>, even under air exclusion, led to slow decomposition to a white precipitate in contact with a greenish solution. Crystals of **2** under vacuum (ca. 10<sup>-3</sup> torr) at 20 °C show after a few hours a gradual colour change from red to greenish-mauve, a material which analyzes as NiCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>. A similar change occurs if dry crystals of **2** are left for several days in an open atmosphere, or even under nitrogen in a flask of convenient size (100 ml for 50 mg). The only way to store **2** was in a C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>-saturated nitrogen atmosphere at room temperature. Conversion of **1** to **2** appears to be completely reversible and storage of **1** in a C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>-saturated nitrogen atmosphere slowly forms again **2** quantitatively. Moreover, the contact of crystals of **2** with n-hexane or toluene (in which **1** and **2** are insoluble) gives rapid conversion of **2** into **1**.

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The size of the crystal used for X-ray analysis was approximately  $0.3 \times 0.2 \times 1.0 \text{ mm}^3$ . The crystal was sealed in a thin capillary during X-ray measurements. The intensities and cell dimensions were measured on a Philips four-circle automatic diffractometer with  $\text{MoK}\alpha$  radiation ( $\lambda = 0.7107 \text{ \AA}$ ) monochromated by a graphite plate at room temperature. Crystal data:  $\text{C}_{36}\text{H}_{30}\text{P}_2\text{Cl}_2\text{Ni} \cdot (\text{C}_2\text{H}_4\text{Cl}_2)_2$  crystallizes in the orthorhombic system; space group  $Pbca$  (N. 61) with  $a = 23.486(6) \text{ \AA}$ ,  $b = 20.298(6) \text{ \AA}$ ,  $c = 8.290(3) \text{ \AA}$ ;  $Z = 4$ ;  $\rho(\text{calcd}) = 1.43 \text{ g cm}^{-3}$ . The intensity data were collected in the  $\theta - 2\theta$  scan mode up to  $2\theta = 50^\circ$ . Of the 3403 unique collected reflections, 2231 with  $I \geq 3\sigma(I)$  were used for the structure determination. Corrections for absorption were neglected [ $\mu(\text{MoK}\alpha) = 9.36 \text{ cm}^{-1}$ ]. The structure was solved by the heavy-atom method. The position of the metal atom was fixed at the inversion center (special position). The positions of all other non-hydrogen atoms were determined by successive Fourier syntheses. Several cycles of the block-diagonal least squares refinement with  $w = 1$  reduced the  $R$  value to 0.063. The non-hydrogen atoms thermal parameters were refined anisotropically. Hydrogen atoms were revealed on the Fourier  $\Delta F$  map and isotropically refined during the last cycle. All the computations were carried out by an IBM-144 computer (Centro di Calcolo, Università di Padova) using SHELX-76 programs (G. Sheldrick, University of Cambridge). Final fractional atomic coordinates for the 25 non-hydrogen atoms in  $[\text{NiCl}_2(\text{PPh}_3)_2] \cdot (\text{C}_2\text{H}_4\text{Cl}_2)_2$  are listed in Table II.\* During the data collection, two standard reflections were measured every 180 min to check the stability and the alignment of the crystal and the electronics.

Crystals of **1** were obtained by dissolution in hot anhydrous acetic acid, slow cooling to room temperature, and subsequent slow solvent evaporation at ambient conditions. The greenish-blue crystals were filtered off and dried *in vacuo*. The size of the crystal used for X-ray analysis was approximately  $0.1 \times 0.1 \times 0.05 \text{ mm}^3$ . The general experimental procedure, as well as the data processing and calculations, were analogous to those reported above. Crystal data:  $\text{C}_{36}\text{H}_{30}\text{P}_2\text{Cl}_2\text{Ni}$  crystallizes in the monoclinic system; space group  $P2/a$  (N. 13) with  $a = 17.399(6) \text{ \AA}$ ,  $b = 8.198(4) \text{ \AA}$ ,  $c = 11.644(5) \text{ \AA}$ ;  $\beta = 107.0(3)^\circ$ ;  $Z = 2$ ;  $\rho(\text{calcd}) = 1.367 \text{ g cm}^{-3}$ . Of the 2697 unique collected reflections, 628 with  $I \geq 3\sigma(I)$  were used for the structure determination. Hydrogen atoms were neglected. The final  $R$  value was reduced to 0.103.

\*Tables of thermal parameters, hydrogen positions and observed and calculated structure factors are available as supplementary material.

## Results and Discussion

The molecular structure of *trans*- $[\text{NiCl}_2(\text{PPh}_3)_2]$  is depicted in Fig. 1. The molecule is planar and the nickel atom is on a symmetry center. Selected bond distances and angles are summarized on Table I and fractional coordinates are reported in Table II. The corresponding data referring to **1** are reported in Tables III and IV.

The Ni–P (2.242(3) Å) and Ni–Cl (2.155(3) Å) distances are both shorter than the corresponding distances determined for the tetrahedral allgon **1**: Ni–P (2.320(9) Å) and Ni–Cl (2.206(9) Å). These observations are in agreement with those referring to the pair of allgons given by the complex  $[\text{NiBr}_2(\text{P}(\text{CH}_2\text{Ph})\text{Ph}_2)_2]$  [4]. However, while the shortening of the Ni–X bonds is similar (*ca.* 0.05 Å), the shrinking of the Ni–P bonds is more pronounced on going from **1** to **2** (*ca.* 0.08 Å) than in the other case (*ca.* 0.05 Å).

Partial views of the cell of **2** are shown in Fig. 2. The relative position of the  $\text{NiCl}_2\text{P}_2$  molecular unit with respect to the eight  $\text{C}_2\text{H}_4\text{Cl}_2$  molecules surrounding it is clearly apparent. The solvent molecules *do not* interact chemically with the nickel complex, as shown by the shortest contact distance (C(20)–Cl(1) ( $\frac{1}{2} - x, -y, \frac{1}{2} + z$ )) determined by the crystal structure analysis (*i.e.* 3.579 Å, see Fig.

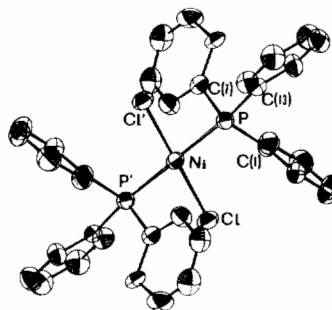


Fig. 1. ORTEP drawing of the *trans*- $[\text{NiCl}_2(\text{PPh}_3)_2]$  moiety of  $[\text{NiCl}_2(\text{PPh}_3)_2] \cdot (\text{C}_2\text{H}_4\text{Cl}_2)_2$ .

TABLE I. Selected Bond Distances (Å) and Bond Angles (deg) for *trans*- $[\text{NiCl}_2(\text{PPh}_3)_2] \cdot (\text{C}_2\text{H}_4\text{Cl}_2)_2$ .<sup>a</sup>

Ni–Cl	= 2.155(3)	Cl–Ni–P	= 93.2(1)
Ni–P	= 2.242(3)	Ni–P–C(1)	= 119.9(3)
P–C(1)	= 1.839(11)	Ni–P–C(7)	= 110.3(4)
P–C(7)	= 1.827(11)	Ni–P–C(13)	= 113.8(4)
P–C(13)	= 1.821(11)	C(1)–P–C(7)	= 102.7(5)
		C(1)–P–C(13)	= 101.1(5)
		C(7)–P–C(13)	= 107.8(5)

<sup>a</sup>Numbers in parentheses in this and following table refer to the estimated standard deviations in the least significant digits.

TABLE II. Fractional Coordinates for *trans*- $[\text{NiCl}_2(\text{PPh}_3)_2] \cdot (\text{C}_2\text{H}_4\text{Cl}_2)_2$ .

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Ni	0.0000	0.0000	0.0000
P	0.0652(1)	0.0611(1)	0.1292(3)
Cl	0.0436(1)	-0.0910(1)	0.0510(4)
C <sub>1</sub>	0.1208(5)	0.0207(5)	0.2500(15)
C <sub>2</sub>	0.1239(5)	0.0275(6)	0.4153(15)
C <sub>3</sub>	0.1677(6)	-0.0022(7)	0.5041(15)
C <sub>4</sub>	0.2070(5)	-0.0399(7)	0.4222(19)
C <sub>5</sub>	0.2043(5)	-0.0479(6)	0.2577(19)
C <sub>6</sub>	0.1611(5)	-0.0177(6)	0.1711(16)
C <sub>7</sub>	0.0307(5)	0.1151(5)	0.2760(13)
C <sub>8</sub>	0.0510(3)	0.1831(3)	0.2785(8)
C <sub>9</sub>	0.0178(6)	0.2166(6)	0.4175(15)
C <sub>10</sub>	-0.0195(6)	0.1864(7)	0.5211(16)
C <sub>11</sub>	-0.0332(5)	0.1212(7)	0.5019(16)
C <sub>12</sub>	-0.0087(5)	0.0858(6)	0.3796(15)
C <sub>13</sub>	0.1080(4)	0.1124(5)	-0.0038(14)
C <sub>14</sub>	0.0944(5)	0.1195(6)	-0.1654(14)
C <sub>15</sub>	0.1285(5)	0.1573(6)	-0.2675(14)
C <sub>16</sub>	0.1760(5)	0.1888(6)	-0.2067(15)
C <sub>17</sub>	0.1898(5)	0.1827(6)	-0.0472(14)
C <sub>18</sub>	0.1561(4)	0.1451(5)	0.0540(13)
Cl <sub>2</sub>	0.3379(2)	0.2783(2)	0.2876(5)
Cl <sub>3</sub>	0.2693(2)	0.1361(3)	0.3565(6)
C <sub>19</sub>	0.3381(6)	0.1467(9)	0.2737(25)
C <sub>20</sub>	0.3689(7)	0.2001(7)	0.3194(23)

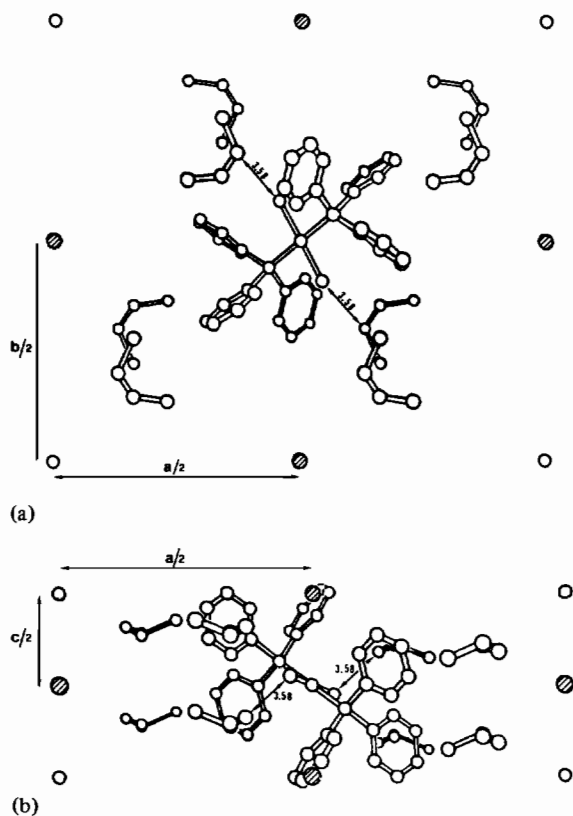
TABLE III. Selected Bond Distances (Å) and Angles (deg) for Tetrahedral  $[\text{NiCl}_2(\text{PPh}_3)_2]$ , 1.

Ni-Cl	= 2.206(9)	Cl-Ni-P	= 104.6(3)
Ni-P	= 2.320(9)	Cl-Ni-P'	= 93.2(1)
P-C(1)	= 1.827(17)	Cl-Ni-Cl'	= 126.6(3)
P-C(7)	= 1.846(19)	P-Ni-P'	= 111.5(4)
P-C(13)	= 1.849(16)	Ni-P-C(1)	= 119.9(8)
		Ni-P-C(7)	= 107.2(9)
		Ni-P-C(13)	= 116.1(7)
		C(1)-P-C(7)	= 104.6(11)
		C(1)-P-C(13)	= 105.5(11)
		C(7)-P-C(13)	= 101.4(12)

2). In Fig. 3 another partial view of the crystal lattice is depicted. In this figure the allocation of the  $\text{C}_2\text{H}_4\text{Cl}_2$  molecules is clearly understandable, *i.e.* they lie in wider channels, which extend along the *z* axis. An approximate estimate of the sectional area of the channels is 34 (Å) [2]. The facile release of  $\text{C}_2\text{H}_4\text{Cl}_2$  from the crystal lattice at ambient conditions and its recovery from an atmosphere containing  $\text{C}_2\text{H}_4\text{Cl}_2$  at partial pressure of *ca.* 60 torr indicates that the contribution of the trapped solvent to the free energy of the system  $[\text{NiCl}_2(\text{PPh}_3)_2] \cdot (\text{C}_2\text{H}_4\text{Cl}_2)_2$  has to be comparatively very small.

TABLE IV. Fractional Coordinates for Tetrahedral  $[\text{NiCl}_2(\text{PPh}_3)_2]$ .

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Ni	0.2500	1.2078(7)	0.0000
Cl	0.1384(6)	1.3287(11)	0.0081(9)
P	0.2887(5)	1.0486(10)	0.1721(7)
C <sub>1</sub>	0.2133(11)	0.9325(25)	0.2188(19)
C <sub>2</sub>	0.1676(11)	0.8232(25)	0.1342(19)
C <sub>3</sub>	0.1074(11)	0.7314(25)	0.1607(19)
C <sub>4</sub>	0.0930(11)	0.7489(25)	0.2718(19)
C <sub>5</sub>	0.1387(11)	0.8581(25)	0.3563(19)
C <sub>6</sub>	0.1989(11)	0.9499(25)	0.3299(19)
C <sub>7</sub>	0.3335(15)	1.1867(26)	0.2993(19)
C <sub>8</sub>	0.2890(15)	1.3265(26)	0.3047(19)
C <sub>9</sub>	0.3147(15)	1.4328(26)	0.4021(19)
C <sub>10</sub>	0.3850(15)	1.3993(26)	0.4939(19)
C <sub>11</sub>	0.4295(15)	1.2595(26)	0.4885(19)
C <sub>12</sub>	0.4037(15)	1.1532(26)	0.3912(19)
C <sub>13</sub>	0.3723(11)	0.9047(24)	0.1828(19)
C <sub>14</sub>	0.3676(11)	0.7421(24)	0.2153(19)
C <sub>15</sub>	0.4295(11)	0.6340(24)	0.2149(19)
C <sub>16</sub>	0.4960(11)	0.6886(24)	0.1820(19)
C <sub>17</sub>	0.5006(11)	0.8512(24)	0.1494(19)
C <sub>18</sub>	0.4388(11)	0.9593(24)	0.1498(19)

Fig. 2. View along *z*, A and along *y*, B, axes of *trans*- $[\text{NiCl}_2(\text{PPh}_3)_2] \cdot (\text{C}_2\text{H}_4\text{Cl}_2)_2$ . ○ (Nickel at *c* = 0); ⊗ (Nickel at *c* = ½) in (A). ○ (Nickel at *b* = 0); ⊗ (Nickel at *b* = ½) in Fig. (B).

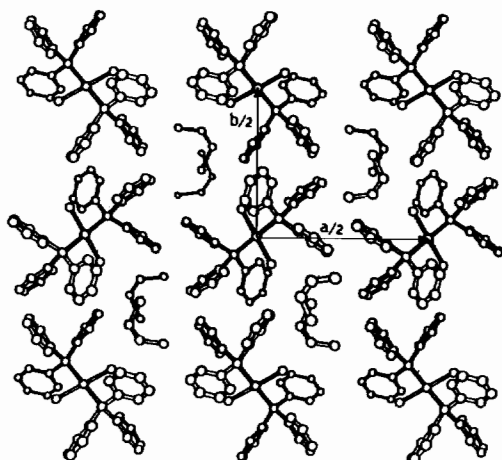


Fig. 3. View along  $z$  axis of the crystal lattice of  $trans$ - $[\text{NiCl}_2(\text{PPh}_3)_2] \cdot (\text{C}_2\text{H}_4\text{Cl}_2)_2$ .

Moreover, the availability of wider channels in the crystal lattice of **2** undoubtedly explains the kinetically easy removal of dichloroethane.

The easy removal of the trapped solvent molecules leads to the *complete* conversion of **2** into **1** and reveals that the free energy of solid tetrahedral  $[\text{NiCl}_2(\text{PPh}_3)_2]$  is minimally lower than that of solid square-planar  $[\text{NiCl}_2(\text{PPh}_3)_2]$ .

In connection with this observation, it can be reasonably considered that the stability of the solid tetrahedral allgon is the consequence of its relatively lower lattice free energy, which could arise from an appreciable dipole–dipole interaction [5].

On the other hand, the host lattice of the apolar square planar allgon undergoes an evident stabilization by the weaker (albeit decisive) dipole–dipole interaction due to the gusted dichloroethane molecules.

The free energies of the two allgonic molecular entities are in fact quite similar. This conclusion is in

line with theoretical calculations [6] and with the observation of the almost equi-energetic molecular structures of  $[\text{NiBr}_2(\text{P}(\text{CH}_2\text{Ph})\text{Ph}_2)_2]$  (tetrahedral) and *trans*- $[\text{NiBr}_2(\text{P}(\text{CH}_2\text{Ph})\text{Ph}_2)_2]$  [4].

#### Acknowledgements

We wish to thank Prof. L. Venanzi for his interest for this work as well as for the suggestion to re-investigate the X-ray structure of compound **1**. Helpful discussion with Prof. G. Zanotti is gratefully acknowledged.

#### Supplementary Material Available

Originals of fractional coordinates, thermal parameters and F lists for both compounds  $[\text{NiCl}_2(\text{PPh}_3)_2]$  and  $trans$ - $[\text{NiCl}_2(\text{PPh}_3)_2] \cdot (\text{C}_2\text{H}_4\text{Cl}_2)_2$  (10 pages).

#### References

- 1 L. Sacconi, 'Transition Metal Chemistry, Vol. IV', Marcel Dekker, New York, 1968, p. 241;
- 2 L. M. Venanzi, *J. Chem. Soc.*, 719 (1958);  
L. M. Venanzi, *J. Inorg. Nucl. Chem.*, 8, 137 (1958).
- 3 G. Garton, D. E. Henn, H. M. Powell and L. M. Venanzi, *J. Chem. Soc.*, 3625 (1963).
- 4 B. T. Kilbourn and H. M. Powell, *J. Chem. Soc. A.*, 1688 (1970).
- 5 M. C. Browning, J. R. Mellor, D. J. Morgan, S. A. Pratt, L. E. Sutton and L. M. Venanzi, *J. Chem. Soc.*, 693 (1962).
- 6 J. K. Burdett, *Inorg. Chem.*, 14, 375 (1975).