
Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1355). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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anti,mer-[Bis(2-diphenylphosphinoethyl)(*n*-propyl)amine-*N*,*P*,*P*′](phenylethynyl)[(Z)-1-*p*-tolyl-4-phenyl-η^3-but-1-en-3-ynyl]ruthenium(II) Chloroform Solvate

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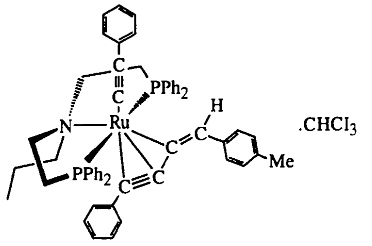
Abstract

The title structure, $[Ru(C_8H_5)(C_{17}H_{13})(C_{31}H_{35}NP_2)].CHCl_3$, consists of discrete *anti,mer*-[Ru(C≡CPh){η^3-PhC≡C—C═CH(*p*-tolyl)}(PNP)] neutral molecules, where PNP is $CH_3CH_2CH_2N(CH_2CH_2PPh_2)_2$, and $CHCl_3$ solvate molecules. The Ru^{II} metal centre is pseudo-octahedrally coordinated by a meridional tridentate PNP ligand, a phenylethynyl ligand and a η^3-bonded (Z)-1-*p*-tolyl-4-phenyl-η^3-but-1-en-3-ynyl ligand. The butenynyl moiety is *anti* with respect to the *n*-propyl tail on the N-atom donor of the aminodiphosphine ligand and lies in a plane almost perpendicular to that containing the Ru(PNP) moiety.

Comment

In recent years, there has been considerable interest in the synthesis, structure and reactivity of Ru^{II}–enynyl complexes (Hill, 1995). In particular, we have reported recently that the Ru^{II}–vinylidene complexes *fac,cis*- and *mer,trans*-[$RuCl_2${C═C(H)*R*}(PNP)], where *R* is Ph or *p*-tolyl and PNP is $CH_3CH_2CH_2N(CH_2CH_2PPh_2)_2$, react with LiC≡CPh in tetrahydrofuran to afford enynyl and dienynyl complexes, respectively (Bianchini, Innocenti, Peruzzini, Romerosa & Zanobini, 1996).

As a complement to our studies of C—C coupling reactions involving 1-alkynes, we report here the X-ray diffraction analysis of the Ru^{II}–enynyl complex *anti,mer*-[Ru(C≡CPh){η^3-PhC≡C—C═CH(*p*-tolyl)}(PNP)].$CHCl_3$, (I), prepared by treatment of *fac,cis*-[$RuCl_2${C═C(H)(*p*-tolyl)}(PNP)] in tetrahydrofuran with two equivalents of LiC≡CPh (Bianchini, Innocenti, Peruzzini, Romerosa & Zanobini, 1996). The structure of this complex is of great relevance in confirming that the C—C bond-forming reaction leading to the enynyl fragment involves vinylidene and σ-alkynyl ligands.



(I)

An *ORTEP*II (Johnson, 1976) drawing of the title compound with the atomic numbering scheme is shown in Fig. 1. For clarity, the phenyl substituents of the PNP ligand have been omitted. The crystal structure consists of discrete *anti,mer*-[Ru(C≡CPh){η^3-PhC≡C—C═CH(*p*-tolyl)}(PNP)] molecules and clathrated chloroform molecules. The metal atom is pseudo-octahedrally coordinated by the three donor atoms of a meridional PNP ligand, by a phenylethynyl ligand and by a η^3-PhC≡C—C═CH(*p*-tolyl) group.

The two diphenylphosphine ends of the PNP ligand are bent towards the N atom [P(1)—Ru(1)—N(1) 82.0 (2) and P(2)—Ru(1)—N(1) 84.2 (2)°] as a consequence of the chelate-ring bite. The Ru(1)—N(1) [2.267 (6) Å], Ru(1)—P(1) and Ru(1)—P(2) distances [2.319 (2) and 2.307 (2) Å, respectively], although somewhat shorter than those found in *anti,mer*-[Ru(C≡CPh)(η^3-PhC≡C—C═CHPh)(PNP)] (Bianchini, Innocenti, Peruzzini, Romerosa & Zanobini, 1996), are in the range of those found for related Ru(PNP) complexes

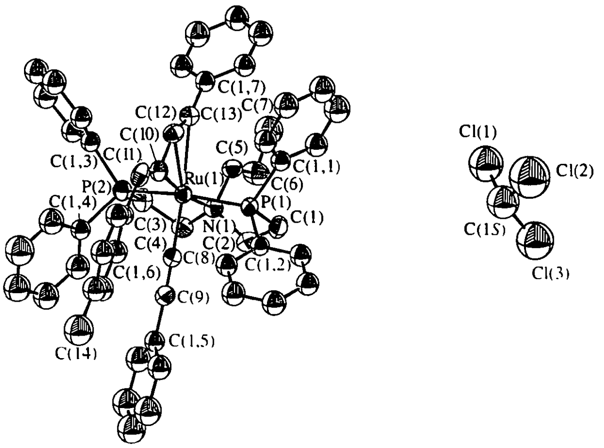


Fig. 1. An *ORTEP*II (Johnson, 1976) drawing of (I) showing the atom-labelling scheme. Displacement ellipsoids are shown at 50% probability levels. The phenyl substituents of the PNP ligand have been omitted for clarity.

(Bianchini, Masi, Peruzzini, Romerosa & Zanobini, 1995; Bianchini, Innocenti, Masi, Peruzzini & Zanobini, 1992). The Ru atom is displaced by 0.053 (2) Å from the least-squares plane through atoms P(1), P(2), N(1) and Ru(1) towards the enynyl ligand. The practically linear phenylethynyl ligand [C(8)—C(9)—C(1,5) 177.1 (8)°] is *cis* with respect to the three donor atoms of the PNP ligand [C(8)—Ru(1)—N(1) 84.1 (2)°] and *trans* to the η^3-PhC≡C—C=CH(*p*-tolyl) group [C(8)—Ru(1)—C(13) 173.6 (3), C(8)—Ru(1)—C(12) 143.5 (3) and C(8)—Ru(1)—C(10) 105.3 (3)°]. The Ru(1)—C(8) distance [1.999 (8) Å] is shorter than that of the Ru—C_{sp} single bond (2.127 Å), but similar to that found in the related compound *anti,mer*-[Ru(C≡Ph)(η^3-PhC≡C—C=CHPh)(PNP)]. The *n*-propyl chain on the central N-atom donor of the PNP ligand and the phenylethynyl ligand are mutually *anti*. The title compound thus adopts an *anti,mer* stereochemistry identical to that found in the complex *anti,mer*-[Ru(C≡CPh)(η^3-PhC≡C—C=CHPh)(PNP)]. The enynyl fragment is linked to the metal atom through the C(13)—C(12)—C(10) three-atom sequence, as confirmed by the corresponding bond lengths of 2.423 (8) [Ru(1)—C(13)], 2.205 (7) [Ru(1)—C(12)] and 2.050 (8) Å [Ru(1)—C(10)]. The torsion angle at the phenylethynyl end [C(12)—C(13)—C(1,7)] is as large as 158.6 (8)°. The amplitude of this angle is commonly taken as a diagnostic parameter for establishing the nature of the alkyne bonding (Alcock, Hill, Melling & Thompsett, 1993). In the present case, it is slightly larger than that found in *anti,mer*-[Ru(C≡CPh)(η^3-PhC≡C—C=CHPh)(PNP)] [154 (1)°], indicating that in this case also there may be a modest perturbation of the *sp* character of the alkynyl C atoms. This agrees with a weak bonding interaction of the Ru atom with the C≡CPh group of the butenynyl ligand. Atoms C(10), C(12), C(13) and Ru(1) are coplanar, with the largest deviation being only 0.015 (8) Å for the C(12) atom. This confirms that some degree of electronic delocalization may exist in the RuC_3 moiety as has been suggested previously (Bianchini, Peruzzini, Zanobini, Frediani & Albinati, 1991). The angle between the C(10), C(12), C(13), Ru(1) plane and that containing the Ru(PNP) assembly is 89.4 (2)°. The rest of the metrical parameters pertaining to the molecule are in good agreement with those determined previously for analogous structures.

Finally, the crystal packing appears to be governed by normal van der Waals interactions with no anomalous intermolecular contacts.

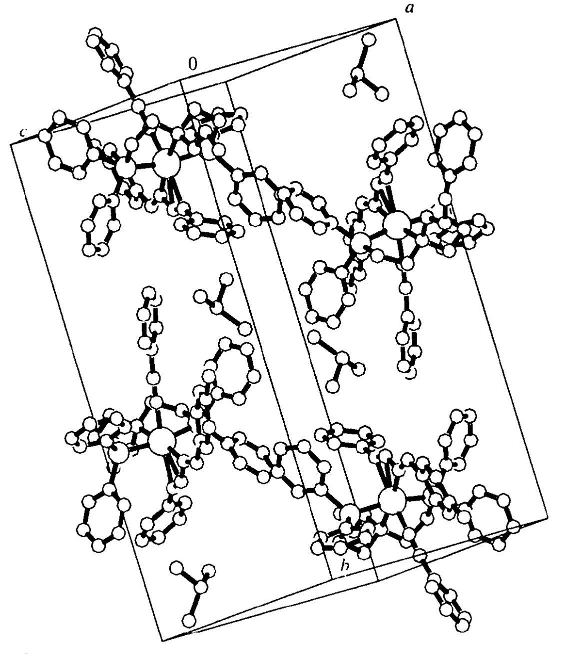


Fig. 2. The cell-packing diagram for (I).

Experimental

Deep-orange crystals of (I) were grown by slow diffusion of ethanol into a diluted chloroform solution of the crude microcrystalline material prepared as previously described by Bianchini, Innocenti, Peruzzini, Romerosa & Zanobini (1996).

Crystal data

$[Ru(C_8H_5)(C_{17}H_{13})-(C_{31}H_{35}NP_2)].CHCl_3$
$M_r = 1022.37$
Monoclinic
$P2_1/n$
$a = 12.987\ (2)$ Å
$b = 24.929\ (2)$ Å
$c = 15.472\ (2)$ Å
$\beta = 92.00\ (2)°$
$V = 5006.1\ (11)$ Å^3
$Z = 4$
$D_x = 1.355$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 12$–$17°$
$\mu = 0.575$ mm^{-1}
$T = 293\ (2)$ K
Small prism
0.52 × 0.27 × 0.22 mm
Orange

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: refined from ΔF (Walker & Stuart, 1983)
$T_{\min} = 0.675$, $T_{\max} = 1.000$
7222 measured reflections
6930 independent reflections
4519 observed reflections $[I > 2\sigma(I)]$
$R_{\rm int} = 0.0481$
$\theta_{\max} = 22.99°$
$h = -14 \rightarrow 14$
$k = 0 \rightarrow 27$
$l = 0 \rightarrow 16$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0625$
$wR(F^2) = 0.1516$
$S = 1.017$
6892 reflections
257 parameters
$w = 1/[\sigma^2(F_o)^2 + (0.0649P)^2 + 36.1124P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.531$
$\Delta\rho_{\max} = 1.28$ e Å^{-3}
$\Delta\rho_{\min} = -1.21$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from Cromer & Waber (1974)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Ru(1)	0.3016 (1)	0.1269 (1)	0.5774 (1)	0.031 (1)
P(1)	0.4747 (1)	0.1246 (1)	0.5454 (1)	0.035 (1)
P(2)	0.1265 (2)	0.1126 (1)	0.5831 (1)	0.036 (1)
N(1)	0.2858 (4)	0.0824 (2)	0.4498 (4)	0.035 (1)
C(1)	0.4791 (6)	0.0806 (3)	0.4498 (5)	0.047 (2)
C(2)	0.3801 (6)	0.0482 (3)	0.4411 (5)	0.043 (2)
C(3)	0.0992 (6)	0.0775 (3)	0.4804 (5)	0.044 (2)
C(4)	0.1943 (6)	0.0469 (3)	0.4518 (5)	0.044 (2)
C(5)	0.2762 (6)	0.1205 (3)	0.3749 (5)	0.041 (2)
C(6)	0.2727 (8)	0.0979 (4)	0.2858 (5)	0.063 (3)
C(7)	0.2536 (10)	0.1402 (5)	0.2200 (8)	0.101 (4)
C(8)	0.3154 (5)	0.0534 (3)	0.6281 (5)	0.035 (2)
C(9)	0.3182 (6)	0.0078 (3)	0.6550 (5)	0.041 (2)
C(10)	0.3168 (5)	0.1784 (3)	0.6804 (5)	0.037 (2)
C(11)	0.3334 (6)	0.1904 (3)	0.7649 (5)	0.043 (2)
C(12)	0.2987 (6)	0.2130 (3)	0.6101 (5)	0.039 (2)
C(13)	0.2790 (6)	0.2192 (3)	0.5317 (5)	0.043 (2)
C(14)	0.3995 (9)	0.0447 (5)	1.0525 (7)	0.089 (3)
C(2,1)	0.5483 (4)	0.2263 (2)	0.5784 (3)	0.053 (2)
C(3,1)	0.5935 (5)	0.2754 (2)	0.5606 (3)	0.064 (3)
C(4,1)	0.6291 (5)	0.2857 (2)	0.4786 (4)	0.067 (3)
C(5,1)	0.6196 (5)	0.2469 (2)	0.4143 (3)	0.073 (3)
C(6,1)	0.5745 (4)	0.1977 (2)	0.4321 (3)	0.053 (2)
C(1,1)	0.5388 (4)	0.1874 (2)	0.5141 (3)	0.040 (2)
C(2,2)	0.5433 (3)	0.0841 (2)	0.7052 (3)	0.048 (2)
C(3,2)	0.6167 (4)	0.0659 (2)	0.7658 (3)	0.060 (2)
C(4,2)	0.7192 (4)	0.0618 (2)	0.7439 (3)	0.060 (2)
C(5,2)	0.7484 (3)	0.0757 (2)	0.6613 (3)	0.053 (2)
C(6,2)	0.6750 (4)	0.0939 (2)	0.6007 (3)	0.047 (2)
C(1,2)	0.5725 (3)	0.0981 (2)	0.6226 (3)	0.038 (2)
C(2,3)	0.0458 (3)	0.2097 (2)	0.6368 (3)	0.049 (2)
C(3,3)	−0.0300 (4)	0.2487 (2)	0.6443 (3)	0.061 (2)
C(4,3)	−0.1230 (4)	0.2437 (2)	0.5979 (4)	0.061 (2)
C(5,3)	−0.1404 (3)	0.1997 (2)	0.5440 (4)	0.062 (2)
C(6,3)	−0.0646 (4)	0.1608 (2)	0.5366 (3)	0.052 (2)
C(1,3)	0.0285 (3)	0.1658 (2)	0.5830 (3)	0.039 (2)
C(2,4)	0.0566 (5)	0.0156 (2)	0.6539 (3)	0.057 (2)
C(3,4)	0.0184 (5)	−0.0157 (2)	0.7198 (4)	0.071 (3)
C(4,4)	−0.0015 (5)	0.0073 (3)	0.7993 (3)	0.076 (3)
C(5,4)	0.0166 (5)	0.0616 (3)	0.8129 (3)	0.089 (3)
C(6,4)	0.0548 (5)	0.0930 (2)	0.7469 (4)	0.067 (3)
C(1,4)	0.0748 (4)	0.0699 (2)	0.6674 (3)	0.041 (2)
C(2,5)	0.2453 (4)	−0.0835 (2)	0.6615 (3)	0.062 (2)
C(3,5)	0.2433 (5)	−0.1345 (2)	0.6979 (4)	0.080 (3)
C(4,5)	0.3142 (5)	−0.1482 (2)	0.7636 (4)	0.080 (3)
C(5,5)	0.3870 (5)	−0.1109 (2)	0.7929 (4)	0.077 (3)
C(6,5)	0.3890 (4)	−0.0600 (2)	0.7565 (4)	0.057 (2)
C(1,5)	0.3181 (4)	−0.0463 (2)	0.6908 (3)	0.043 (2)
C(2,6)	0.3194 (4)	0.0989 (2)	0.8305 (3)	0.054 (2)
C(3,6)	0.3364 (5)	0.0643 (2)	0.9000 (4)	0.063 (3)
C(4,6)	0.3819 (5)	0.0833 (2)	0.9766 (3)	0.060 (2)
C(5,6)	0.4103 (4)	0.1369 (2)	0.9838 (3)	0.060 (2)
C(6,6)	0.3933 (4)	0.1715 (2)	0.9143 (3)	0.055 (2)
C(1,6)	0.3478 (4)	0.1525 (2)	0.8376 (3)	0.039 (2)
C(2,7)	0.3361 (3)	0.2696 (2)	0.4060 (3)	0.050 (2)
C(3,7)	0.3157 (4)	0.2947 (2)	0.3270 (3)	0.062 (2)
C(4,7)	0.2153 (4)	0.2972 (2)	0.2931 (3)	0.061 (2)
C(5,7)	0.1353 (3)	0.2747 (3)	0.3382 (3)	0.066 (3)
C(6,7)	0.1557 (3)	0.2496 (2)	0.4172 (3)	0.054 (2)
C(1,7)	0.2561 (4)	0.2471 (2)	0.4511 (3)	0.041 (2)
C(1*S*)	0.8091 (11)	0.0807 (6)	0.0547 (9)	0.107 (4)
Cl(1)	0.8585 (4)	0.0256 (2)	0.0004 (3)	0.143 (2)
Cl(2)	0.9030 (4)	0.1286 (2)	0.0741 (4)	0.172 (2)
Cl(3)	0.7059 (3)	0.1083 (2)	−0.0055 (3)	0.124 (1)

Table 2. *Selected geometric parameters (Å, °)*

Ru(1)—C(8)	1.999 (8)	Ru(1)—C(13)	2.423 (8)
Ru(1)—C(10)	2.050 (8)	C(8)—C(9)	1.211 (10)
Ru(1)—C(12)	2.205 (7)	C(10)—C(11)	1.352 (10)
Ru(1)—N(1)	2.267 (6)	C(10)—C(12)	1.401 (11)
Ru(1)—P(2)	2.307 (2)	C(12)—C(13)	1.240 (11)
Ru(1)—P(1)	2.319 (2)		
C(8)—Ru(1)—C(10)	105.3 (3)	C(8)—Ru(1)—C(13)	173.6 (3)
C(8)—Ru(1)—C(12)	143.5 (3)	C(10)—Ru(1)—C(13)	68.8 (3)
C(10)—Ru(1)—C(12)	38.2 (3)	C(12)—Ru(1)—C(13)	30.6 (3)
C(8)—Ru(1)—N(1)	84.1 (2)	N(1)—Ru(1)—C(13)	101.8 (2)
C(10)—Ru(1)—N(1)	170.4 (3)	P(2)—Ru(1)—C(13)	92.7 (2)
C(12)—Ru(1)—N(1)	132.3 (3)	P(1)—Ru(1)—C(13)	94.0 (2)
C(8)—Ru(1)—P(2)	85.3 (2)	C(9)—C(8)—Ru(1)	175.5 (7)
C(10)—Ru(1)—P(2)	97.8 (2)	C(8)—C(9)—C(1,5)	177.1 (8)
C(12)—Ru(1)—P(2)	96.7 (2)	C(11)—C(10)—C(12)	129.2 (8)
N(1)—Ru(1)—P(2)	84.2 (2)	C(11)—C(10)—Ru(1)	153.9 (6)
C(8)—Ru(1)—P(1)	89.2 (2)	C(12)—C(10)—Ru(1)	76.9 (4)
C(10)—Ru(1)—P(1)	96.5 (2)	C(13)—C(12)—C(10)	149.3 (8)
C(12)—Ru(1)—P(1)	95.6 (2)	C(13)—C(12)—Ru(1)	84.4 (5)
N(1)—Ru(1)—P(1)	82.0 (2)	C(10)—C(12)—Ru(1)	64.9 (4)
P(2)—Ru(1)—P(1)	165.61 (7)	C(12)—C(13)—Ru(1)	64.9 (5)

The absorption corrections were calculated from a ΔF refinement because suitable reflections for an empirical ψ scan were not available. This procedure gave a small improvement of both the displacement parameters and the geometrical data. The structure was solved by direct and Fourier methods and full-matrix least-squares refinement was based on F^2 values, with $\Sigma w(F_o^2 - F_c^2)^2$ minimized and anisotropic displacement parameters for the Ru, P, N and C atoms (except for those of the phenyl rings and terminal methyl groups). All phenyl rings were treated as rigid bodies with D_{6h} symmetry (C—C 1.39 Å) and the H atoms were introduced at calculated positions (C—H 0.96 Å for methyl C atoms and 0.93 Å for sp^2 and phenyl C atoms).

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: local software. Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai & Pritzkow, 1994).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1221). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Zinc–*meso*-tetra-*p*-tolylporphyrin and its Chlorotoluene Channel-Type Clathrate with π–π and C—H···π Interaction Modes Stabilizing the Porphyrin Host Lattice

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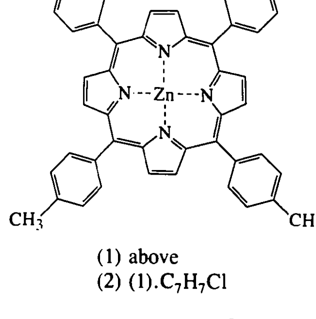
Abstract

The title compound, (*meso*-5,10,15,20-tetra-*p*-tolylporphyrinato-*N*,*N′*,*N″*,*N‴*)zinc(II), $[Zn(C_{48}H_{36}N_4)]$, displays a high tendency to form complexes and clathrates with other components from various environments, and is a useful building block for the construction of heteromolecular solids. Modes of its intermolecular assembly in the pure compound and in its clathrate with *m*-chlorotoluene, $[Zn(C_{48}H_{36}N_4)].C_7H_7Cl$, have been characterized by X-ray crystal-structure analysis. The clathrate appears to be stabilized by π–π stacking and cooperative C—H···π interactions between the tolyl substituents and contains large interporphyrin channels extending throughout the crystal.

Comment

This study is part of an ongoing investigation of the crystalline architectures afforded by functionalized tetraphenylmetalloporphyrins and of the potential utility of these materials for the development of simple chemical models of self-assembly *via* weak intermolecular forces (Goldberg, Krupitsky, Stein, Hsiou & Strouse, 1995; Krupitsky, Stein & Goldberg, 1995). The tetra-*p*-tolylporphyrin compound readily forms crystalline adducts with metal ions in different oxidation states. The crystal structures of the non-metallated tetra-*p*-tolylporphyrin (Butcher, Jameson & Storm, 1985), and of its numerous five- and six-coordinate metal complexes with various axial ligands and Cr, Fe, Mo, Os, V, Ti, Sc, Sb and Re ions in the porphyrin center, have been reported previously (October 1995 release of the Cambridge Structural Database; Allen & Kennard, 1993). The metal complexes reveal intermolecular architectures common to the tetraphenylporphyrin 'sponges' (Byrn, Curtis, Goldberg, Hsiou, Khan, Sawin, Tendick & Strouse, 1991; Byrn, Curtis, Hsiou, Khan, Sawin, Tendick, Terzis & Strouse, 1993) and consistently crystallize as solvates. It was of further interest in the present context to investigate the intermolecular organization in crystalline solids based on the four-coordinate zinc–tetra-*p*-tolylporphyrin framework.

The crystallization mode of the title compound is affected by the solvent environment, yielding a homomolecular solvent-free solid, (1), from guaiacol, and a clathrate, (2), from the more lipophilic *m*-chlorotoluene. The molecular structures of zinc–tetra-*p*-tolylporphyrin in the two crystals are depicted in Fig. 1 and they do not exhibit unusual features. In both compounds,



(1) above
(2) (1).C_7H_7Cl

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