bonds in $(Bz_3PO)_2CoCl_2$ (Santos & Mascarenhas, 1979) but longer than those in $(Ph_3PO)_2CoCl_2$ (Mangion, Smith & Shore, 1976). As in other metal halide adducts of trimethylphosphine oxide a slight lengthening of the P–O bond [1·508 (3) Å in $(Me_3PO)_2CoCl_2$] compared to uncoordinated Me_3PO [1·476 (2) Å] (Wilkins, Hagen, Hedberg, Shen & Hedberg, 1975) is observed. The average P–C bond length in $(Me_3PO)_2CoCl_2$ is 1·771 (4) Å. Fig. 2 shows the contents of the unit cell.

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Structure of 3-(η^2,η^2-1,5-Cyclooctadiene)-3-pallada-1,2-dicarba-*closo*-dodecaborane(11)

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Abstract. $[3\text{-}(\eta^2,\eta^2\text{-}C_8H_{12})\text{-}3,1,2\text{-}PdC_2B_9H_{11}]$, $M_r = 346·9$, orthorhombic, *Pbca*, $a = 13·2485$ (18), $b = 11·549$ (3), $c = 19·589$ (3) Å, $V = 2997·3$ (12) Å^3, $Z = 8$, $D_x = 1·538$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0·71069$ Å, $\mu = 1·20$ mm^{-1}, $F(000) = 1392$, room temperature, $R = 0·035$ for 3217 unique observed reflections. Crystallographic study of the title compound yields slipping distortion parameters which imply that the previously suggested correlation with B(8) chemical shift may not be fully applicable.

Introduction. The title compound, (1), is one of a number of products isolated from the reaction between $[(cod)Pd(\eta\text{-}C_5H_5)]BF_4$ (cod = 1,5-cyclooctadiene) and $Tl[TlC_2B_9H_{11}]$ at room temperature in CH_2Cl_2 (Smith & Welch, 1986*a*). Separation by thin layer chromatography (CH_2Cl_2, *n*-hexane 2:1 eluant) afforded the product as a purple band ($R_f = 0·7$) in low yield (< 5%). Although the compound has previously been synthesized by a different route (Colquhoun, Greenhough & Wallbridge, 1985) no diffraction study was reported. However, the structure of this species is important in respect of the conformation and slipping distortion of the {Pd(ene)$_2$} fragment relative to the $C_2B_9H_{11}$ cage, and therefore we have undertaken the crystallographic determination described herein.

Experimental. Purple irregular plate (0·5 × 0·3 × 0·05 mm), from solvent diffusion using CH_2Cl_2 and *n*-hexane; CAD-4 diffractometer, 25 reflections centred ($13·5 < \theta < 14·5°$), graphite-monochromated Mo $K\alpha$; for data collection $\theta_{max} = 30°$, ω–2θ scans in 96 steps, ω-scan width 0·8° + 0·35° tanθ, rapid prescan after which reflections with $I > 0·67\sigma(I)$ remeasured such that final net intensity had $I > 5\sigma(I)$ subject to a maximum measuring time of 75 seconds; two octants of data (*hkl* and *−h−kl*, 7942 reflections) measured over 111 X-ray hours with no detectable decay or movement; systematic absences (0*kl*: $k = 2n + 1$, *h*0*l*: $l = 2n + 1$, *hk*0: $h = 2n + 1$) uniquely define space group. 4360 unique data, $R_{int} = 0·0263$; for structure solution and refinement 3217 reflections with $F > 2\sigma(F)$ retained (*h* 0→18, *k* 0→16, *l* 0→27), Patterson synthesis (Pd) and difference-Fourier methods; post-solution empirical absorption correction (*DIFABS*, Walker & Stuart, 1983), full-matrix least-squares refinement on *F*,

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$w = [\sigma^2(F) + 0{\cdot}000096(F)^2]^{-1}$, anisotropic thermal parameters for non-H atoms, isotropic for grouped H atoms, $R = 0{\cdot}0347$, $wR = 0{\cdot}0308$, $S = 1{\cdot}499$, data: variable ratio 13:1, max. peak and min. trough in final ΔF synthesis 0·545 and −0·633 e Å^{-3} respectively, max. shift/e.s.d. in final cycle 0·017; inlaid neutral scattering factors for H, B, C and neutral scattering factors for Pd from *International Tables for X-ray Crystallography* (1974). Computer programs *SHELX76* (Sheldrick, 1976), *CALC* (Gould & Taylor, 1986), *EASYORTEP* (Mallinson, 1984; see also Johnson, 1976) and *PLUTO* (Motherwell, 1978).

Discussion. The final fractional coordinates are listed in Table 1, and Fig. 1 presents a perspective view of the molecule demonstrating the atomic numbering scheme adopted (Casey, Evans & Powell, 1983). Bond distances and selected bond angles are listed in Table 2.* There are no significant intermolecular contacts using the coordinates of Table 1, but when C—H and B—H bond distances are extended to idealized values six intermolecular H···H contacts less than 2·4 Å result, details of which are deposited.

The cyclooctadiene ring adopts a C_2 twist boat conformation more or less identical to that found in (cod)PdCl$_2$, (2), (Rettig, Wing & Wiger, 1981) and to the gas phase conformation and the minimum energy conformation found by molecular orbital calculations on the free diene. The metal–diene interactions of (1) are somewhat weaker than those of (cod)PdCl$_2$ as demonstrated by the shorter olefinic bond lengths and longer Pd—C distances found in (1). This is chemically reasonable, as the $C_2B_9H_{11}$ ligand is a weak π acceptor and will therefore be in competition with the diene for back-donation, whereas Cl is a weak π donor. Within (1), the slight difference (0·04 Å) between the Pd—Z(1) and Pd—Z(2) distances [Z(1) is the midpoint of C(21)C(22) and Z(2) the midpoint of C(25)C(26)] can be ascribed to intramolecular steric forces. The angles α and β (Ittel & Ibers, 1976) describing the geometry of the two double bonds and their substituents are: C(21)C(22), α = 19°, β = 79°, 79° and C(25)C(26), α = 19°, β = 79°, 82°. The twist, torque and tilt angles (Rettig, Wing & Wiger, 1981) describing the orientation of the alkenes with respect to the metal are: twist = 11°, 12°, torque = 7°, 4° and tilt = 1°, 0°. While the olefinic C=C bonds are out of parallel by a comparable angle (8°) to that in (2) (9°) and the tilt angles are as small (*cf.* 0°, 0°), the twist angles are considerably larger; however, these larger angles are probably merely the result of the greater metal-to-ligand distance and do not imply any greater distortion of the ligand.

Table 1. *Fractional coordinates of atoms* (*e.s.d.'s in parentheses*) *and equivalent isotropic thermal parameters* (Å^2)

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\,\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Pd(3)	0·13021 (1)	0·11776 (2)	0·16576 (1)	0·0291 (1)
C(1)	0·01845 (20)	0·1385 (3)	0·26348 (15)	0·0395 (16)
C(2)	0·11321 (23)	0·20605 (24)	0·27479 (15)	0·0367 (15)
B(4)	0·0523 (3)	−0·0021 (3)	0·23349 (18)	0·0439 (20)
B(5)	0·0024 (3)	0·0316 (4)	0·31732 (18)	0·0464 (20)
B(6)	0·0444 (3)	0·1676 (3)	0·34597 (18)	0·0470 (21)
B(7)	0·22370 (23)	0·1245 (3)	0·25969 (16)	0·0384 (17)
B(8)	0·1869 (3)	−0·0185 (3)	0·24185 (18)	0·0427 (20)
B(9)	0·1092 (3)	−0·0622 (3)	0·30885 (18)	0·0460 (20)
B(10)	0·1058 (3)	0·0419 (3)	0·37454 (17)	0·0411 (18)
B(11)	0·1768 (3)	0·1628 (3)	0·34280 (17)	0·0454 (20)
B(12)	0·2174 (3)	0·0177 (4)	0·32645 (18)	0·0465 (20)
C(21)	0·1688 (3)	0·2728 (3)	0·09981 (16)	0·0487 (19)
C(22)	0·24701 (25)	0·1974 (3)	0·09709 (16)	0·0493 (19)
C(23)	0·2667 (3)	0·1113 (4)	0·04219 (21)	0·068 (3)
C(24)	0·1776 (3)	0·0430 (4)	0·01824 (19)	0·067 (3)
C(25)	0·0958 (3)	0·0236 (3)	0·07006 (16)	0·0478 (18)
C(26)	0·0179 (3)	0·0976 (3)	0·08215 (16)	0·0495 (19)
C(27)	0·0006 (3)	0·2121 (4)	0·04891 (20)	0·068 (3)
C(28)	0·0912 (4)	0·2894 (4)	0·04459 (20)	0·067 (3)
H(1)	−0·0336 (22)	0·1717 (24)	0·2440 (14)	0·040 (60)
H(2)	0·1129 (20)	0·2749 (25)	0·2630 (15)	0·040 (60)
H(4)	−0·0032 (22)	−0·0518 (24)	0·2027 (14)	0·049 (49)
H(5)	−0·0683 (24)	0·003 (3)	0·3214 (15)	0·050 (36)
H(6)	0·0039 (22)	0·235 (3)	0·3699 (15)	0·050 (36)
H(7)	0·2955 (22)	0·1685 (24)	0·2481 (14)	0·049 (49)
H(8)	0·2333 (22)	−0·075 (3)	0·2193 (14)	0·049 (49)
H(9)	0·0954 (23)	−0·143 (3)	0·3187 (15)	0·050 (36)
H(10)	0·0980 (21)	0·0182 (25)	0·4277 (15)	0·050 (36)
H(11)	0·2170 (22)	0·219 (3)	0·3731 (14)	0·050 (36)
H(12)	0·2890 (22)	−0·010 (3)	0·3531 (13)	0·050 (36)
H(21)	0·166 (3)	0·327 (3)	0·1288 (17)	0·057 (52)
H(22)	0·2945 (25)	0·204 (3)	0·1247 (16)	0·057 (52)
H(23)	0·295 (3)	0·143 (3)	0·0103 (19)	0·080 (64)
H(23′)	0·315 (3)	0·052 (3)	0·0572 (19)	0·080 (64)
H(24)	0·149 (3)	0·081 (4)	−0·0165 (20)	0·080 (64)
H(24′)	0·195 (3)	−0·031 (3)	0·0003 (18)	0·080 (64)
H(25)	0·0887 (24)	−0·052 (3)	0·0902 (16)	0·057 (52)
H(26)	−0·035 (3)	0·072 (3)	0·1073 (16)	0·057 (52)
H(27)	−0·042 (3)	0·254 (3)	0·0779 (19)	0·090 (69)
H(27′)	−0·029 (3)	0·201 (3)	0·0051 (21)	0·090 (69)
H(28)	0·116 (3)	0·273 (4)	0·0049 (21)	0·090 (69)
H(28′)	0·065 (3)	0·363 (3)	0·0483 (21)	0·090 (69)

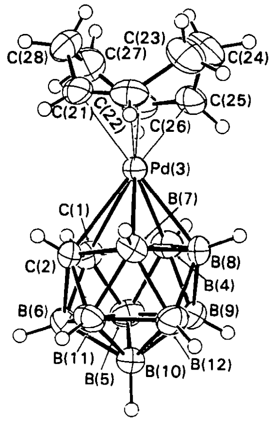

Fig. 1. Perspective view of (1). Thermal ellipsoids at 50% probability level except for H atoms, which are given a fixed radius of 0·1 Å for clarity.

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* Lists of structure factors, anisotropic thermal parameters, intermolecular contacts, a full list of angles and b-axis projection packing diagram have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43221 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The slip and fold parameters Δ, σ, φ and θ that conveniently define the distortion of a pentagonal ligand face η^5 bound to a metal have been developed by ourselves and others (Mingos, Forsyth & Welch, 1978; Faller, Crabtree & Habib, 1985; Smith & Welch, 1986*b*) and are illustrated in Fig. 2. For (1), $\Delta = 0{\cdot}24$, $\sigma = -7{\cdot}4°$, $\varphi = 5{\cdot}9°$ and $\theta = 4{\cdot}9°$. Δ here is measured with respect to the centroid of the lower pentagonal belt of boron atoms. Colquhoun, Greenhough & Wallbridge (1985) have defined an alternative slip parameter *d* which takes into account the fact that this lower belt is often folded into an envelope conformation. For (1), $d = 0{\cdot}10$ (5) Å.

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

C(21)–C(28)	1·505 (6)	B(7)–B(11)	1·797 (5)
C(21)–C(22)	1·355 (5)	B(7)–B(12)	1·800 (5)
C(22)–C(23)	1·487 (6)	B(8)–B(9)	1·742 (5)
C(23)–C(24)	1·495 (6)	B(8)–B(12)	1·756 (5)
C(24)–C(25)	1·502 (5)	B(9)–B(10)	1·761 (5)
C(25)–C(26)	1·360 (5)	B(9)–B(12)	1·739 (5)
C(26)–C(27)	1·493 (5)	B(10)–B(11)	1·795 (5)
C(27)–C(28)	1·498 (6)	B(10)–B(12)	1·775 (5)
Pd(3)–C(21)	2·267 (4)	B(11)–B(12)	1·789 (5)
Pd(3)–C(22)	2·247 (4)	C(1)–H(1)	0·88 (3)
Pd(3)–C(25)	2·215 (3)	C(2)–H(2)	0·83 (3)
Pd(3)–C(26)	2·225 (3)	B(4)–H(4)	1·11 (3)
Pd(3)–C(1)	2·432 (3)	B(5)–H(5)	1·00 (3)
Pd(3)–C(2)	2·377 (3)	B(6)–H(6)	1·06 (3)
Pd(3)–B(4)	2·178 (4)	B(7)–H(7)	1·10 (3)
Pd(3)–B(7)	2·219 (3)	B(8)–H(8)	1·00 (3)
Pd(3)–B(8)	2·294 (4)	B(9)–H(9)	0·97 (3)
C(1)–C(2)	1·495 (4)	B(10)–H(10)	1·08 (3)
C(1)–B(4)	1·785 (5)	B(11)–H(11)	1·03 (3)
C(1)–B(5)	1·637 (5)	B(12)–H(12)	1·13 (3)
C(1)–B(6)	1·686 (5)	C(21)–H(21)	0·85 (3)
C(2)–B(6)	1·724 (5)	C(22)–H(22)	0·83 (3)
C(2)–B(7)	1·765 (4)	C(23)–H(23)	0·82 (4)
C(2)–B(11)	1·654 (5)	C(23)–H(23′)	0·99 (4)
B(4)–B(5)	1·813 (5)	C(24)–H(24)	0·89 (4)
B(4)–B(8)	1·800 (5)	C(24)–H(24′)	0·96 (4)
B(4)–B(9)	1·797 (5)	C(25)–H(25)	0·96 (3)
B(5)–B(6)	1·758 (5)	C(26)–H(26)	0·90 (3)
B(5)–B(9)	1·789 (5)	C(27)–H(27)	0·94 (4)
B(5)–B(10)	1·774 (5)	C(27)–H(27′)	0·95 (4)
B(6)–B(10)	1·755 (5)	C(28)–H(28)	0·86 (4)
B(6)–B(11)	1·756 (5)	C(28)–H(28′)	0·92 (4)
B(7)–B(8)	1·757 (5)		

C(22)–C(21)–C(28)	125·2 (3)	B(9)–B(5)–B(10)	59·25 (21)
C(21)–C(22)–C(23)	126·3 (3)	C(1)–B(6)–C(2)	51·98 (18)
C(22)–C(23)–C(24)	116·2 (4)	C(1)–B(6)–B(5)	56·74 (20)
C(23)–C(24)–C(25)	115·9 (4)	C(2)–B(6)–B(11)	56·74 (20)
C(24)–C(25)–C(26)	124·8 (3)	B(5)–B(6)–B(10)	60·65 (21)
C(25)–C(26)–C(27)	126·7 (3)	B(10)–B(6)–B(11)	61·48 (21)
C(26)–C(27)–C(28)	115·4 (4)	Pd(3)–B(7)–C(2)	72·24 (15)
C(21)–C(28)–C(27)	115·5 (4)	Pd(3)–B(7)–B(8)	69·33 (16)
C(21)–Pd(3)–C(22)	34·93 (13)	C(2)–B(7)–B(11)	55·30 (18)
C(21)–Pd(3)–C(26)	79·28 (13)	B(8)–B(7)–B(12)	59·15 (20)
C(22)–Pd(3)–C(25)	80·55 (13)	B(11)–B(7)–B(12)	59·63 (20)
C(25)–Pd(3)–C(26)	35·68 (13)	Pd(3)–B(8)–B(4)	62·92 (16)
C(1)–Pd(3)–C(2)	36·19 (10)	Pd(3)–B(8)–B(7)	64·87 (16)
C(1)–Pd(3)–B(4)	45·13 (12)	B(4)–B(8)–B(9)	60·93 (21)
C(2)–Pd(3)–B(7)	45·01 (11)	B(7)–B(8)–B(12)	61·63 (21)
B(4)–Pd(3)–B(8)	47·39 (13)	B(9)–B(8)–B(12)	59·60 (21)
B(7)–Pd(3)–B(8)	45·80 (13)	B(4)–B(9)–B(5)	60·72 (21)
Pd(3)–C(1)–C(2)	69·92 (15)	B(4)–B(9)–B(8)	61·13 (21)
Pd(3)–C(1)–B(4)	59·88 (14)	B(5)–B(9)–B(10)	59·93 (21)
C(2)–C(1)–B(6)	65·32 (20)	B(8)–B(9)–B(12)	60·60 (21)
B(4)–C(1)–B(5)	63·80 (21)	B(10)–B(9)–B(12)	60·96 (21)
B(5)–C(1)–B(6)	63·84 (21)	B(5)–B(10)–B(6)	59·75 (21)
Pd(3)–C(2)–C(1)	73·89 (16)	B(5)–B(10)–B(9)	60·82 (21)
Pd(3)–C(2)–B(7)	62·75 (14)	B(6)–B(10)–B(11)	59·29 (21)
C(1)–C(2)–B(6)	62·70 (20)	B(9)–B(10)–B(12)	58·90 (21)
B(6)–C(2)–B(11)	62·61 (21)	B(11)–B(10)–B(12)	60·14 (21)
B(7)–C(2)–B(11)	63·34 (20)	C(2)–B(11)–B(6)	60·65 (20)
Pd(3)–B(4)–C(1)	74·99 (16)	C(2)–B(11)–B(7)	61·36 (19)
Pd(3)–B(4)–B(8)	69·68 (17)	B(6)–B(11)–B(10)	59·23 (21)
C(1)–B(4)–B(5)	54·15 (19)	B(7)–B(11)–B(12)	60·25 (20)
B(5)–B(4)–B(9)	59·44 (21)	B(10)–B(11)–B(12)	59·40 (20)
B(8)–B(4)–B(9)	57·94 (20)	B(7)–B(12)–B(8)	59·21 (20)
C(1)–B(5)–B(4)	62·05 (20)	B(7)–B(12)–B(11)	60·11 (20)
C(1)–B(5)–B(6)	59·42 (21)	B(8)–B(12)–B(9)	59·79 (21)
B(4)–B(5)–B(9)	59·84 (21)	B(9)–B(12)–B(10)	60·15 (21)
B(6)–B(5)–B(10)	59·60 (21)	B(10)–B(12)–B(11)	60·47 (21)

The structure of (1) may be compared with those recently reported (Colquhoun, Greenhough & Wallbridge, 1985) for [3-(tmen)-3,1,2-$PdC_2B_9H_{11}$], (3), (tmen = tetramethylethylenediamine) and [3,3-$(Me_3P)_2$-3,1,2-$PdC_2B_9H_{11}$], (4). In all three molecules the bis(exopolyhedral ligand)Pd plane is orthogonal to the metallabonded carborane ligand face and displays an effectively perpendicular conformation (Mingos, Forsyth & Welch, 1978); specifically, in (1) the dihedral angles between the plane defined by Pd(3)*Z*(1)*Z*(2) and those defined by C(1)C(2)B(7)B(8)B(4) and B(8)-B(10)B(6) are 88 and 78° respectively.

$\Delta\{d\}$ values for (3) and (4) are 0·52 {0·36} and 0·26 {0·11} Å. Clearly the slipping distortion of (1) is very similar to that of (4), but substantially less than that of (3). It has been argued that the magnitude of the slipping distortion in a related series of $L_2MC_2B_9H_{11}$ compounds is a direct consequence of the π-acid character of the exopolyhedral ligand *L*; the greater the π-acceptor properties of *L*, the less slipping distortion expected (Mingos, 1977). Because cod and PMe_3 are both moderate π-acceptor ligands, whereas tmed is a pure σ donor, the correspondence of the slipping parameters of (1) with (4) but not with (3) is quite reasonable.

It has been tentatively suggested that the magnitude of the slipping distortion in $L_2MC_2B_9H_{11}$ species may be correlated with the chemical shift of the unique boron atom, B(8), and a compilation of ^{11}B NMR data for various $L_2PdC_2B_9H_{11}$ compounds including (1), (3) and (4) has been published (Colquhoun, Greenhough & Wallbridge, 1985). Unfortunately the results reported

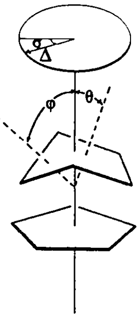

Fig. 2. Angles and distances describing the cage-slip distortion. Δ, the slip parameter, is the distance (Å) between the projection of the metal atom onto the plane of the lower pentagonal belt and the centre of the latter. σ is the angle (°) between the projections on the lower plane of (i) the slip direction and (ii) the upper belt atom made unique by envelope folding.

herein for (1) do not readily fit this correlation. Moreover, it is difficult to understand several of the observed chemical shifts for B(8) in terms of the accepted π-acidities of the ligands used in the compilation. In view of the above results it now seems likely that the chemical shifts of B(8) may not be diagnostic of the magnitude of the slipping distortion.

We thank the SERC for support.

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Structure of (Chloro)(di-2-pyridylmethane)(di-2-pyridylmethanol)copper(II) Perchlorate

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Abstract. $[CuCl(C_{11}H_{10}N_2)(C_{11}H_{10}N_2O)]ClO_4$, $M_r = 554{\cdot}87$, monoclinic, $P2_1/c$, $a = 13{\cdot}397\,(4)$, $b = 14{\cdot}663\,(2)$, $c = 13{\cdot}191\,(3)$ Å, $\beta = 116{\cdot}81\,(1)°$, $V = 2313\,(2)$ Å^3, $Z = 4$, $D_x = 1{\cdot}593$ Mg m^{-3}, $\lambda(\text{Mo }K\bar{\alpha}) = 0{\cdot}71073$ Å, $\mu = 1{\cdot}215$ mm^{-1}, $F(000) = 1132$, $T = 291$ K. Final $R = 0{\cdot}074$ for 2231 unique observed reflections. This high R value can be explained by the disordered perchlorate anion around which many low spurious peaks still remain after least-squares convergence. The coordination sphere of Cu can be described as an elongated octahedron owing to the Jahn–Teller effect. The basal plane is formed by four N atoms provided by the pyridine rings of the di-2-pyridylmethane and of the di-2-pyridylmethanol moieties respectively. The octahedron is completed by two large apical distances provided by the Cu—Cl(1) bond and by the Cu—O(1) bond, corresponding to the oxygen atom of the dipyridylmethanol.

Introduction. Synthetic copper complexes serve as suitable models for the natural copper centres in metalloproteins when they mimic some physical or chemical property of the protein site. In the case of the monooxygenases one atom of oxygen is reduced to water while the other is transferred to the substrate (Sigel, 1981). The title compound is an example of monooxygenase activity, since it is obtained as a product of the reaction of di-2-pyridylmethane with molecular oxygen. The hydroxylation reaction is catalysed by the presence of copper(II) and chloride ions.

Experimental. A 1 mmol sample of copper(II) perchlorate complex $[Cu(4N)_4(H_2O)_6](ClO_4)_2$ was dissolved with 1 mmol of copper(II) chloride in freshly distilled methanol and slightly refluxed. After this, 3 mmol of di-2-pyridylmethane dissolved in the same solvent were added to the warm reaction mixture and heated. The reaction mixture was air-saturated, since no precautions were taken to degas the solutions. When cooled, bright blue crystals were formed. The infrared

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