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(3-Acetylpyridine-*κN*)chlorobis(triphenylphosphine-*κP*)copper(**I**): a suitable candidate for absolute asymmetric synthesis?

Anders Lennartson,* Kent Salo and Mikael Håkansson

Department of Chemistry, Göteborg University, SE-412 96 Göteborg, Sweden

Correspondence e-mail: anle@chem.gu.se

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Key indicators

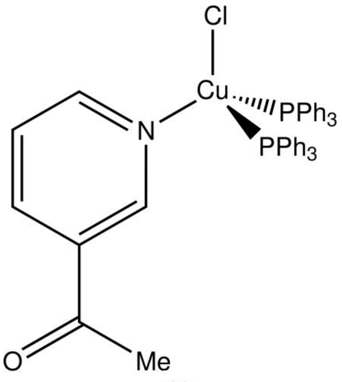
Single-crystal X-ray study
T = 290 K
Mean σ(C–C) = 0.006 Å
R factor = 0.064
wR factor = 0.139
Data-to-parameter ratio = 15.9

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

It was found that 3-acetylpyridine is capable of displacing triphenylphosphine from [CuCl(PPh$_3$)$_3$], forming the title compound, [CuCl(C$_7$H$_7$NO)(C$_{18}$H$_{15}$P)$_2$]. The two triphenylphosphine ligands possess the same sense of chirality, and the molecules are therefore conformationally chiral. The compound was found to crystallize as a racemate (centrosymmetric space group) under the crystallization conditions employed. The molecular structure shows that the carbonyl C atom is blocked at one side by a triphenylphosphine ligand, while the other face is open for nucleophilic attack. Obtaining chiral crystals of the title compound is thus a future objective. In the crystal structure, C—H···O(=C)-bonded dimers are formed, which are further stabilized by π–π interactions. The dimers form infinite chains through weak C—H···π interactions.

Comment

Recently, we reported the structure of *catena*-poly[[(3-acetylpyridine)copper(I)]μ_3-chloro] (Lennartson *et al.*, 2005), a coordination polymer obtained from CuCl and 3-acetylpyridine. This complex was prepared in order to find a ketone or aldehyde complex crystallizing in a Sohncke (Flack, 2003) space group. Solid-state reduction of such a complex might result in an enantiomeric excess in the resulting alcohol product. However, the polymeric nature of the copper(I) halide–acetylpyridine complexes made it difficult to prepare and characterize this compound; the introduction of neutral spectator ligands was expected to give soluble monomeric species. We present here the crystal structure of the title compound, (I).



(I)

The coordination geometry around the Cu^{I} centre in (I) is best described as tetrahedral (Fig. 1 and Table 1), and both triphenylphosphine ligands have the same sense of chirality,

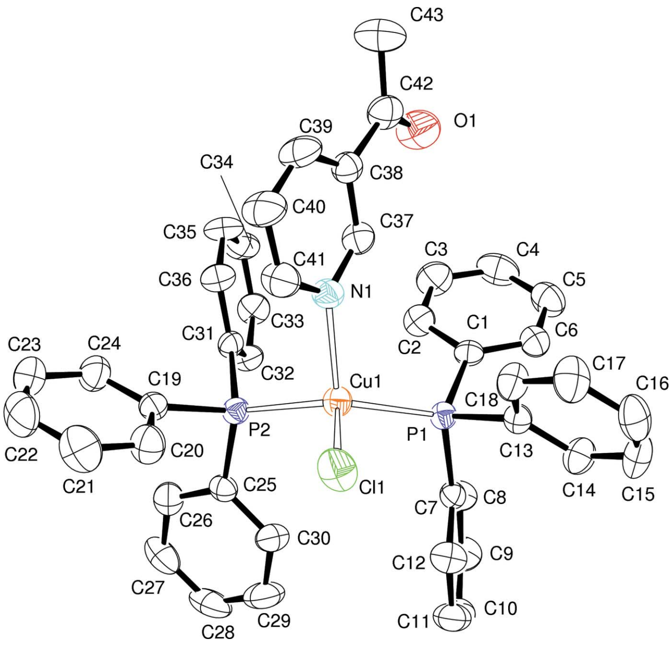


Figure 1
A plot of (I), showing the crystallographic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. All H atoms have been omitted.

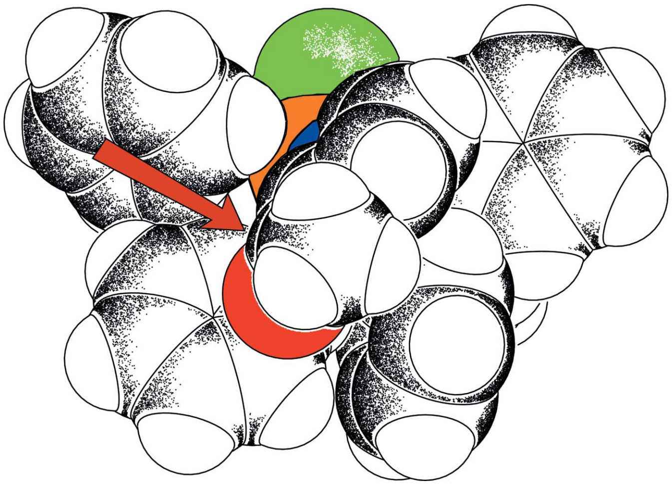


Figure 2
A space-filling plot, showing the most favourable side for nucleophilic attack at the carbonyl C atom.

which may be described in terms of helicity (Zelewsky, 1996). As a result, the complex as such is conformationally chiral. A search in the Cambridge Structural Database (CSD; Version 5.27; Allen, 2002) revealed only four similar structures: [Cu*X*(PPh$_3$)$_2$(pyridine)], with X = Cl, Br or I (Engelhardt *et al.*, 1989), and [CuI(PPh$_3$)$_2$(imidazole)] (CSD refcode: DAFLAY; Wu *et al.*, 2004). These four structures display the same arrangement of ligands around the Cu atom as does (I), except for [CuBr(PPh$_3$)$_2$(pyridine)], where the two triphenylphosphine ligands are mirror images of each other, making the complex achiral. An interesting feature of (I) is obvious from a space-filling plot (Fig. 2): the 3-acetylpyridine ligand is located in a pocket formed by the conformationally chiral triphenylphosphine ligands, and one of the carbonyl faces is much more shielded than the other. In the future, we hope to crystallize (I) as a conglomerate and perform a subsequent solid-state reduction or alkylation of the enantiopure crystals. A similar approach has been successful in the case of an aluminium complex (Johansson & Håkansson, 2005).

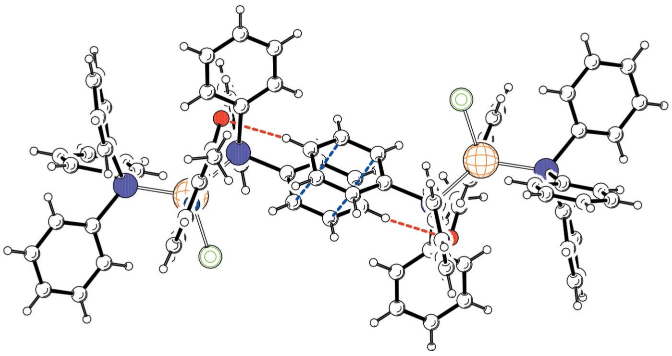


Figure 3
The intermolecular O$\cdots$H interactions (red dashed lines) and intermolecular π–π interactions (blue dashed lines) in (I). The structure is viewed approximately perpendicular to the *ac* diagonal.

The intermolecular interactions in (I) are dominated by C—H$\cdots$O(=C) interactions, which give rise to weakly bound dimers (Fig. 3), with an O1$\cdots$C16$^{\rm i}$ separation of 3.410 (5) Å [symmetry code: (i) $2 - x, -y, 1 - z$]. Each molecule in the dimer contributes one donor and one acceptor atom. The dimers may receive further stabilization by π–π interactions (Fig. 3), as indicated by the distances C17$\cdots$C18$^{\rm i}$ and C18$\cdots$C17$^{\rm i}$ [3.699 (6) Å]. There are also indications of C—H$\cdots\pi$ interactions (Nishio, 2004; Cantrill *et al.*, 2000; Braga *et al.*, 1998). The distance between H40 and the centroid of the ring C25$^{\rm ii}$–C30$^{\rm ii}$ [symmetry code: (ii) $1 + x, y, z$] is 2.69 Å, indicative of an attractive interaction.

Experimental

CuCl (2.3 g, 23 mmol) was dissolved in degassed acetonitrile (200 ml). Triphenylphosphine (18 g, 70 mmol) was added to the solution, giving a white precipitate. The reaction mixture was refluxed for a few minutes and then cooled on ice. Removal of the mother liquor and drying *in vacuo* yielded [CuCl(PPh$_3$)$_3$] as white microcrystals (16 g, 18 mmol, 80%). 3-Acetylpyridine was then added dropwise to [CuCl(PPh$_3$)$_3$] (0.10 g, 0.11 mmol) with heating until a yellow solution was obtained. As the solution was cooled to 298 K, pale-yellow crystals of (I) appeared (0.055 g, 0.083 mmol, 75%).

Crystal data

[CuCl(C$_7$H$_7$NO)(C$_{18}$H$_{15}$P)$_2$]
M_r = 744.68
Monoclinic, $P2_1/c$
a = 9.7903 (18) Å
b = 37.266 (6) Å
c = 10.917 (2) Å
β = 115.547 (5)°
V = 3593.6 (11) Å^3
Z = 4
D_x = 1.376 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.81 mm^{-1}
T = 290 (2) K
Block, yellow
0.2 × 0.2 × 0.1 mm

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Data collection

Rigaku R-AXIS IIC image-plate diffractometer
φ scans
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2000)
$T_{\min} = 0.836$, $T_{\max} = 0.919$
25365 measured reflections
7029 independent reflections
5490 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.094$
$\theta_{\max} = 26.0°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.064$
$wR(F^2) = 0.139$
$S = 1.11$
7029 reflections
442 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0575P)^2 + 0.8762P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.38$ e Å^{-3}
$\Delta\rho_{\min} = -0.41$ e Å^{-3}

Table 1

Selected geometric parameters (Å, °).

Cu1—N1	2.151 (3)	Cu1—P2	2.2784 (10)
Cu1—P1	2.2687 (10)	Cu1—Cl1	2.3205 (11)
N1—Cu1—P1	109.10 (8)	C13—P1—Cu1	113.20 (11)
N1—Cu1—P2	99.83 (8)	C7—P1—Cu1	114.67 (11)
P1—Cu1—P2	124.61 (4)	C1—P1—Cu1	118.18 (12)
N1—Cu1—Cl1	102.32 (9)	C19—P2—Cu1	117.29 (12)
P1—Cu1—Cl1	106.49 (4)	C25—P2—Cu1	117.29 (12)
P2—Cu1—Cl1	112.12 (4)	C31—P2—Cu1	110.84 (11)

The crystals obtained (see *Experimental*) formed aggregates, and finding single crystals suitable for structural determination was difficult. The crystal quality is reflected in the rather high values for the $R_{\rm int}$ and R indices. All H atoms were included in calculated positions and refined with C—H bond lengths constrained to 0.93 (aromatic CH) or 0.96 Å (methyl CH_3), and $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}$(carrier C) for aromatic CH or $1.5U_{\rm eq}$(C43) for the methyl group.

Data collection: *CrystalClear* (Rigaku, 2000); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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