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The First Six Membered Genuine Heterocycle: $[Ph_3PCu\{Ph_2P(S)\text{-}N\text{-}C(O)Ph\}]$

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The synthesis and X-Ray structure of the first six membered non-ionic genuine heterocycle is reported. The non-planar ring is formed by Cu, O, C, N, P, and S and its conformation is described as pseudo boat.

Keywords: genuine; heterocycle; copper

INTRODUCTION

The term "genuine heterocycles" [1] (GH) was used first time to describe ring systems which contain only one atom of each element in the cyclic skeleton and to distinguish them from multielement heterocycles which are derivatives of a homocyclic, or heterocatenate form [2]. Considering the 12 elements most commonly observed in cyclic environments (B, C, N, O, Al, Si, P, S, Ga, Ge, As, Se), one can envisage as many as 220 different three-membered systems. Interestingly, fewer than 40 examples of genuine heterocyclic frameworks (containing these elements) have been isolated and spectroscopically identified, only 10 examples have been characterized by X-ray crystallography [3]. The first example of a five-membered GH containing lithium and chlorine was reported [4].

EXPERIMENTAL

General

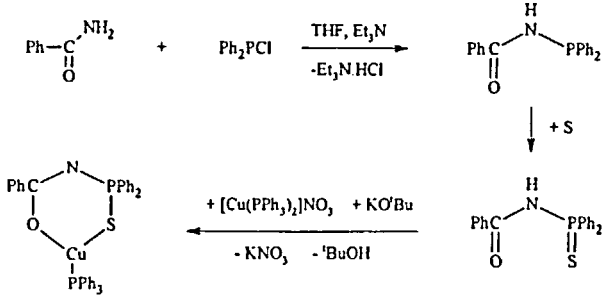
All reactions were performed under argon in anhydrous conditions. NMR spectra were recorded in $CDCl_3$ using a Bruker AVANCE DRX 500 instrument, and were referenced to H_3PO_4 (85%) or Me_4Si. Microanalyses were performed using a Fisons EA 1108 instrument at the Palacky University, Olomouc, Czech Republic.

Synthesis of $Ph_2P(S)$-NH-C(O)Ph

The ligand was prepared by a published method [5]. To $PhC(O)NH_2$ (3.2 g, 7.7 mmol) dissolved in tetrahydrofurane (150 ml) was added Et_3N (3.9 ml, 30 mmol), 4-dimethylaminopyridine (200 mg, 20 mmol) and neat Ph_2PCl (5 ml, 27.9 mmol). After an overnight reflux, sulphur powder (1.78 g, 55.7 mmol) was added and stirred overnight. The solution was filtered and the filtrate was reduced to dryness to a white powder. It was then triturated with ether (200 ml) to give a a white precipitate (see Figure 1).

Yield: 6.43 g (34 %). Mp: 186–188° C. Calcd. for $C_{19}H_{16}NOPS$: C 67.64, H 4.78, N 4.15 %. Found: C 67.25, H 4.54, N 4.02 %. ^{31}P-{^1H} NMR ($CDCl_3$): 56.0 ppm.

FIGURE 1. The synthesis of $[(PPh_3)Cu\{Ph_2P(S)\text{-}N\text{-}C(O)Ph\}]$.



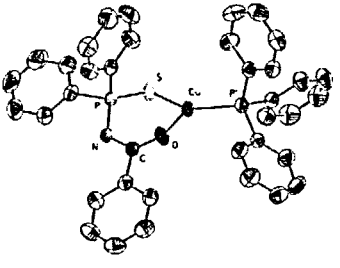
Synthesis of $[(PPh_3)Cu\{Ph_2P(S)\text{-}N\text{-}C(O)Ph\}]$

To a suspension of $Ph_2P(S)$-NH-C(O)Ph (0.21 g, 0.62 mmol) in methanol (20 ml) KO^tBu (0.07 g, 0.62 mmol) was added with stirring. Consequently, a solution of $[Cu(Ph_3P)_2]NO_3$ (0.40 g, 0.62 mmol) in $CHCl_3$ (25 ml) was added dropwise and the mixture was refluxed for 2

hours. The white precipitate was filtered off, washed with ether and dried in vacuum (see Figure 1) [5].
Yield: 0.24 g (59.0 %). Mp: 204–206° C. Calcd. for $C_{37}H_{30}NP_2OCu$: C 67.11, H 4.57, N 2.12, S 4.84 %. Found: C 67.10, H 4.65, N 2.02, S 4.80 %. ^{31}P-{^1H} NMR (CH_2Cl_2): 28.4 ppm.

X-ray determination
Crystals were grown from the diffusion of hexane into a dichloromethane solution of [(PPh_3)Cu{Ph_2P(S)-N-C(O)Ph}]. Diffraction data were collected using a KUMA KM-4 κ-axis diffractometer with Mo-Kα radiation. Structures were solved by direct methods and refined by full-matrix least-squares methods using anisotropic thermal parameters for the non-hydrogen atoms. The programs used were: DATPROC9 for the data reduction [6], SHELXS-86 for the structure solution [7], SHELXL-93 for the structure refinement [8], and the drawings were made by ORTEP [9].

FIGURE 2. The structure of [(PPh_3)Cu{Ph_2P(S)-N-C(O)Ph}].



MOLECULAR STRUCTURE

In [(PPh_3)Cu{Ph_2P(S)-N-C(O)Ph}] the X-ray structure (see Figure 2, Table 1) reveals that copper is trigonal (Cu lies 0.03 Å out of the Cu-O-S-P' mean plane) and that the Cu-S-P-N-C-O ring is non-planar in what can best be described as a pseudo boat conformation. The P-S-Cu-O mean plane [max. deviation 0.16 Å for Cu] is inclined by 142° to the O-C-N-P mean plane (max. deviation 0.01 Å for C).
TABLE 1. Selected data [Å, deg] for [(PPh_3)Cu{Ph_2P(S)-N-C(O)Ph}].

Cu-O	2.013(2)	P-N	1.621(3)
Cu-P'	2.1897(10)	N-C	1.326(4)
Cu-S	2.2230(10)	C-O	1.270(3)
S-P	2.0111(12)		
O-Cu-P'	112.43(7)	N-P-S	119.00(10)
O-Cu-S	106.18(7)	C-N-P	121.1(2)
P'-Cu-S	141.27(4)	O-C-N	126.4(3)
P-S-Cu	92.31(5)	C-O-Cu	125.68(19)

Acknowledgments

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