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New organophosphorus ligands with SPNSO skeleton and their copper(I) complexes

Crystal and molecular structures of $(SPPh_2)(O_2SPh)NH$, $[(Ph_3P)_2Cu\{(SPPh_2)(O_2SMe)N\}]$ and $[(Ph_3P)_2Cu\{(SPPh_2)(O_2SC_6H_4Me\text{-}4)N\}] \cdot 0.5C_6H_5CH_3$

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Abstract

The new phosphorus ligand $(SPPh_2)(O_2SPh)NH$ (**1**) was prepared by reacting $Li[HN(S)PPh_2]$ and $PhSO_2Cl$ and was easily converted into its potassium salt, $K[(SPPh_2)(O_2SPh)N]$ (**2**), by treatment with *t*-BuOK. Copper(I) complexes, $[(Ph_3P)_2Cu\{(SPPh_2)(O_2SR)N\}]$ [R = Me (**3**), Ph (**4**), C_6H_4Me-4 (**5**)], were obtained from $(Ph_3P)_2CuNO_3$ and the potassium salt of the corresponding acid in a 1:1 molar ratio. All compounds were characterized by multinuclear (^1H, ^{13}C, ^{31}P) NMR spectroscopy. The molecular structures of the free acid **1**, as well as of complexes **3** and $\mathbf{5} \cdot 0.5C_6H_5CH_3$, were established by single-crystal X-ray diffraction. The acidic proton in **1** is attached to nitrogen and the molecular units are associated through intermolecular $S=O \cdots H–N$ hydrogen bonding [$H \cdots O$ 2.098 Å], resulting in dimeric units. For the copper complexes, monomeric structures with bidentate $[(SPPh_2)(O_2SR)N]^-$ ligands were found.

Keywords: Thiophosphorus ligands; Copper complexes; X-ray crystal structures

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1. Introduction

Tetraorganodichalcogenoimidodiphosphinato anions, $[(XPR_2)(YPR'_2)N]^-$ (X, Y = O, S, Se; R, R′ = alkyl, aryl, OR), are proved to be versatile ligands towards Main Group or transition metals [1–3]. Usually they behave as bidentate moieties, generating six-membered carbon-free metallacycles (**A**). However, due to the high flexibility of the XPNPY skeleton, other coordination patterns were also observed [1–3].

Copper complexes containing $[(XPR_2)(YPR'_2)N]^-$ ligands raised considerable interest as structural model compounds for the active sites in copper-containing enzymes and proteins [4–6], compounds with nonlinear optical properties [7] or precursors for solid state materials [8]. Mononuclear copper(I) and copper(II) complexes with chelating *O*,*O*-, *O*,*S*- or *S*,*S*-ligands were described and they display different structures, *i.e.* trigonal $[(Ph_3P)Cu\{(XPPh_2)_2N\}]$ (X = S [9], Se [10]), or tetrahedral $[(Ph_3P)_2Cu\{(XPR_2)_2N\}]$ (R = Me, X = S; R = Ph, X = O) [11], and $[Cu\{(XPR_2)(YPR_2)N\}_2]$ (R = Ph, X = Y = O; R = Ph, X = S, Y = O) [11], $[Cu\{\{OP(OPh)_2\}_2N\}_2]$ [12]. A few polynuclear copper(I) complexes with bimetallic triconnective ligand units were also reported, *i.e.* neutral trinuclear $[Cu\{(XPR_2)(YPR'_2)N\}]_3$ (R, R′ = Pr^i, Ph; OEt, OPh, $OC_6H_4Bu^t$-2; X = Y = S, Se [8,13,14]), ionic tetranu-

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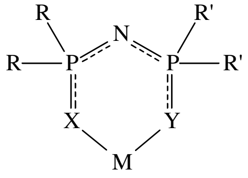
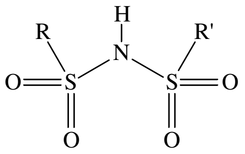


A



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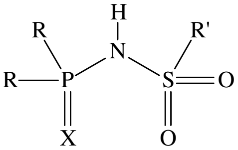

C

clear $[Cu_4\{(SPPh_2)_2N\}_3][X]$ ($X = [CuCl_2]^-$ [15,16], $[BF_4]^-$ [17], $[I_3]^-$ [18]) or $[Cu_4\{(SePPh_2)_2N\}_3][BF_4]^-$ [17], and neutral tetranuclear $[Cu\{(OPMe_2)(SPPh_2)N\}]_4$ [19].

Bis(organosulfonyl)imides, $(O_2SR)(O_2SR')NH$ (**B**), have also attracted some interest as ligands towards metal centres [20]. Only two copper(II) complexes with such ligands are structurally characterized by X-ray diffraction studies, *i.e.* $[Cu(L)_4\{(O_2SMe)_2N\}_2]$ ($L = H_2O$ [21], pyridine [22]), and they display polymeric networks built by hydrogen bonding. However, the ligands act as monodentate units towards the metal centre and the octahedral coordination sphere is completed by water or pyridine molecules.

We previously reported the synthesis and spectroscopic characterization of two members of a new class of organophosphorus ligands of type **C**, *i.e.* $(SPPh_2)(O_2SR)NH$ [R = Me, C_6H_4Me-4], along with their alkali metal (Li, Na, K) salts [20]. Here we report on the synthesis and spectroscopic characterization of a new member of this series of ligands and its potassium salt, *i.e.* $(SPPh_2)(O_2SPh)NH$ (**1**) and $K[(SPPh_2)(O_2SPh)N]$ (**2**), as well as on the copper(I) complexes of type $[(Ph_3P)_2Cu\{(SPPh_2)(O_2SR)N\}]$ [R = Me (**3**), Ph (**4**), C_6H_4Me-4 (**5**)]. The molecular structures of **1**, **3** and **5** $\cdot 0.5C_6H_5CH_3$ are also reported.

2. Experimental

2.1. General methods

Starting materials, *i.e.* $Ph_2P(S)NH_2$ [23], $K[(SPPh_2)(O_2SR)N]$ (R = Me, C_6H_4Me-4) [20] and $(Ph_3P)_2CuNO_3$ [24], were prepared according to the literature methods. Other reagents including Bu^nLi, $PhSO_2Cl$, Ph_3P and $Cu(NO_3)_2$ were purchased from Aldrich and used without further purification. All manipulations involving air sensitive compounds were carried out under vacuum or argon using Schlenk techniques. Solvents were dried and distilled prior to use. Solutions in dry $CDCl_3$ (**1**, **3**–**5**) or DMSO-d_6 (**2**) were used for NMR studies. The ^1H-, ^{13}C- and 2D-NMR spectra were recorded on a BRUKER DRX 400 instrument operating at 400.13 and 100.61 MHz, while ^{31}P NMR spectra were recorded on a BRUKER 300 Avance instrument operating at 121.4 MHz. The chemical shifts are reported in δ units (ppm) relative to the residual peak of the deuterated solvent (ref. $CHCl_3$: ^1H 7.26, ^{13}C 77.0 ppm; DMSO-d_6: ^1H 2.50, ^{13}C 39.43 ppm) and H_3PO_4 85%. The ^1H and ^{13}C chemical shifts were assigned based on 2D experiments using standard BRUKER XWIN-NMR pulse sequences.

2.2. Syntheses

2.2.1. Preparation of $(SPPh_2)(O_2SPh)NH$ (**1**)

A solution of *n*-BuLi in *n*-hexane (8.375 mL 1.6 M, 0.0134 mol) was added dropwise at room temperature to a stirred solution of $Ph_2P(S)NH_2$ (6.246 g, 0.0268 mol) in 100 mL of anhydrous tetrahydrofurane, under an argon atmosphere. The reaction mixture was stirred for 2 h. Then a solution of $PhSO_2Cl$ (1.75 mL, 0.0134 mol) in 50 mL of anhydrous tetrahydrofurane was added dropwise. The reaction mixture was stirred for 12 h and then the solvent was removed under vacuum. Toluene (50 mL) was added to the resulting oily product and the obtained suspension was treated with water (200 mL). From the organic phase the solvent was removed under vacuum and half of the initial $Ph_2P(S)NH_2$ was recovered (3.12 g). The aqueous phase was treated with HCl 0.5 N (50 mL) and the resulting colourless solid product was separated by suction filtration and dried under vacuum. Recrystallisation from a chloroform/*n*-hexane mixture (1/4, v/v) gave the title compound as a microcrystalline solid. Yield: 2.52 g (54%), m.p. 170–172 °C. ^1H NMR: δ 6.50s,br [1H, NH], 7.32t [2H, P-C_6H_5-*para*, $^3J(HH)$ 8.0 Hz], 7.41dt [4H, P-C_6H_5-*meta*, $^3J(HH)$ 8.0, $^4J(PH)$ 3.6 Hz], 7.51m [3H, S-C_6H_5-*meta*+*para*], 7.58d [2H, S-C_6H_5-*ortho*, $^3J(HH)$ 7.3 Hz], 7.87dd [4H, P-C_6H_5-*ortho*, $^3J(PH)$ 14.6, $^3J(HH)$ 7.2 Hz]. ^{13}C NMR: δ 127.12s [C_m, S-C_6H_5], 128.44d [C_m, P-C_6H_5, $^3J(PC)$ 14.1 Hz], 128.78s [C_o, S-C_6H_5], 132.05d [C_i, $^1J(PC)$ 100.0 Hz], 132.10d [C_o, P-C_6H_5, $^2J(PC)$ 12.3 Hz], 132.44d [C_p, P-C_6H_5, $^4J(PC)$ 3.2 Hz], 133.07s [C_p, S-C_6H_5], 140.76s [C_i, S-C_6H_5]. ^{31}P NMR: δ 53.9s.

2.2.2. Preparation of $K[(SPPh_2)(O_2SPh)N]$ (**2**)

A reaction mixture of $(SPPh_2)(O_2SPh)NH$ (1.12 g, 3 mmol) and Bu^tOK (0.336 g, 3 mmol) in 100 mL of anhydrous diethyl ether was stirred at room temperature for 24 h. The resulting solid was separated by filtration and then dried under vacuum. The title compound was obtained as a white powder. Yield: 1.12 g (92%), m.p. 224–225 °C. ^1H NMR: δ 7.31m (9H, P-C_6H_5-*meta*+*para* + S-C_6H_5-*meta*+*para*), 7.84m (6H, P-C_6H_5-*ortho* + S-C_6H_5-*ortho*). ^{13}C NMR: δ 126.05s (C_m, S-C_6H_5), 127.55d [C_m, P-C_6H_5, $^3J(PC)$ 12.3 Hz], 127.74s (C_o, S-C_6H_5), 129.46s (C_p, S-C_6H_5), 129.59d [C_p, P-C_6H_5, $^4J(PC)$ 2.6 Hz], 130.79d [C_o, P-C_6H_5, $^2J(PC)$ 10.7 Hz], 141.27d [C_i, P-C_6H_5, $^1J(PC)$ 105.9 Hz], 148.42s (C_i, S-C_6H_5). ^{31}P NMR: δ 36.9s [$^1J(PC)$ 105.7 Hz].