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Synthesis, spectroscopic and structural characterization of adducts of stoichiometry CuX:dppe (1:2) (X = I, ClO₄, BH₄, O₃SCF₃, SCN, $dppe = Ph_2P(CH_2)_2PPh_2$)

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Abstract

Syntheses and spectroscopic features (IR, NMR and ESI MS) are reported for five 1:2 adducts of CuX with dppe (X = I, ClO₄, NCS, O₃SCF₃ (\equiv tfs) BH₄; dppe = Ph₂P(CH₂)₂PPh₂). ESI MS and ³¹P NMR spectroscopy indicate that these species dissociate in solution yielding free diphosphine and 3:2 species. A single crystal X-ray structure determination has been carried out on Cu(dp-pe)₂NCS defining a four-coordinate complex of the form [(*P*,*P*'-dpex)M(*P*-dpex)X] for M = Cu, the thiocyanate being N-bound; the ionic [Cu(*P*,*P*'-dppe)₂]tfs has also been structurally characterized. © 2005 Elsevier B.V. All rights reserved.

Keywords: Silver; ³¹P NMR; X-ray crystal structure; Diphosphine; ESI MS

1. Introduction

Previous contributions [1–7] in the present sequence have described the structural characterization of adducts of stoichiometry MX:dpex (1:1) [1–5] or $(2:3)_{(n)}$ [6] or (2:1) [7], M = univalent coinage metal (copper(I), silver(I)), X = simple anion, usually (pseudo)halide or, where possible, oxyanions ClO₄, NO₃, carboxylate (spanning a range of basicities), dpex = Ph₂E(CH₂)_xEPh₂, bis(diphenylpnicogeno)alkane (or, on occasion, bis(diphenylphosphino)-ferrocene, 'dppf') [5]. Structurally defined adducts of the form MX:L (1:2) are few in number, all defined as E = P. The majority are ionic, with mononuclear cations of the form [M(*P*-dppx-*P'*)₂]X, the metal being four-coordi-

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nate: for 'dppe' (=bis(diphenylphosphine)ethane = Ph_2P - $(CH_2)_2PPh_2$ [Cu(dppe)₂](ClO₄) [8], [Cu(dppe)₂](NO₃) [9], ('tfa' (= CF_3^{-})) [10], (PF_6) [11], [Ag(dppe)_2](NO_3) [12], for 'dppp' (=bis(diphenylphosphino)propane = $Ph_2P(CH_2)_3PPh_2$, [Cu(dppp)₂](ClO₄) [13,14], (BF₄) [8], $[Ag(dppp)_2](SCN)$ [15], for 'dppf' (=bis-(diphenylphosphino)ferrocene) $[Ag(dppf)_2](ClO_4)$ [16]. (BF₄) [17]; an ionic binuclear form is defined for $[(P,P'-dppe)Ag(P-dppe-P')_2Ag(P,P'-dppe)](NO_3)_2 [18].$ A neutral mononuclear four-coordinate form (erroneously described by us as three-coordinate on p. 721 of [1]) is found in [(P,P'-dppp)Ag(P-dppp)X], X =Cl, Br, I, CN [15]. Thus far, there have been no reports of structurally characterized adducts of the form CuX:ppx (1:2) for any X = halide or pseudo-halide, although a hint as to the possible accessibility of a [(P,P'-dppx)Cu(P-dppx)X] array is provided by the isolation and structural characterization of the adduct CuCl:dppe (2:3) as $[{(P,P'-dppe)CuCl}_2(P-dppe-P')]$

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[19], where the four-coordinate environment is filled by a combination of uni-and bi-dentate dppe.

Adducts of the form CuX:dppe (1:2) have been of interest in respect of their biological activity against P388 leukaemia, M5076 reticulum cell sarcoma and B16 melanoma [20]. In particular, for X = halide, much of their chemistry is ill-defined, with a poverty of structural data. We have synthesized a number of CuX:dppe (1:2) adducts and characterized them as described herein. In undertaking single crystal X-ray characterization, we were intrigued by the dichotomy described above between the forms obtained for AgX:dppp (1:2) for X = SCN (ionic) and X = Cl, Br, I, CN (neutral mononuclear molecules). With the CuX:dppe (1:2) array, the thiocyanate, obtained adventitiously crystalline, being shown to be of the form [(P, P'-dppe)Cu(NCS)(P-dppe)], provides a platform for the understanding of the remainder of its less tractable halide counterparts.

2. Experimental

2.1. Materials and methods

All syntheses, handling and measurements were carried out as described in the preceding paper [1]. For the ESI-MS data, masses and intensities were compared to those calculated by using the IsoPro Isotopic Abundance Simulator Version 2.1 [21]; peaks containing copper ions are identified as the centres of isotopic clusters.

2.2. Syntheses of the copper complexes

2.2.1. CuI:dppe (1:2) (1)

dppe (0.79 g, 2.0 mmol) was added at room temperature to a chloroform suspension (20 ml) of CuI (0.19 g, 1.0 mmol). The suspension was stirred until a clear solution was obtained. After 48 h, the solution was evaporated under vacuum and the residue washed with a mixture of ethanol/diethyl ether at a ratio of 1:1. A clear precipitate has been obtained which was filtered off and washed with diethyl ether to give complex 1 as a colourless solid in 60% yield; m.p. 277 °C dec. ¹H NMR (CDCl₃, 293 K): δ 2.4 (br, 4H, PCH₂), 7.2–7.7 (m br, 20H, C₆H₅). ³¹P {¹H} NMR (CDCl₃, 293 K): δ -11.9, -5.7, +6.6. IR(nujol, cm⁻¹): 3042w, 1584w, 1570w, 1480m, 511s, 489m, 478m, 462m, 453w, 420w, 412w, 362w, 342w, 264w, 244w 203w, 174w. ESI MS (+): 502 [65] $[Cu(MeCN)(dppe)]^+$; 859 [100] $[Cu(dppe)_2]^+$. Anal. Calc. for C₅₂H₄₈CuIP₄: C, 63.26; H; 4.90. Found: C, 62.91.45; H, 5.15%. $\Lambda_{\rm m}$ (CH₂Cl₂, 10⁻³ M): 39.5 Ω^{-1} mol² cm⁻¹.

2.2.2. $CuO_3SCF_3:dppe(1:2)(2)$

dppe (0.79 g, 2.0 mmol) was added at room temperature to a chloroform suspension (20 ml) of Cu(O₃SC- F₃)·1/2C₆H₆ (0.25 g, 1.0 mmol). The suspension was stirred until a clear solution was obtained. After 48 h, the solution was slowly evaporated until a microcrystalline precipitate formed, which was washed with a mixture of ethanol/diethyl ether at a ratio of 1:1 to give complex **2** as a colourless solid in 80% yield; m.p. 198– 201 °C dec. ¹H NMR (CDCl₃, 293 K): δ 2.44 (m br, 8H, PCH₂), 7.2–7.7 (m br, 40H, C₆H₅). ³¹P {¹H} NMR (CDCl₃, 293 K): δ 5.6br, 32.97s. IR(nujol, cm⁻¹): 3058w, 1587w, 1571, 1236s, 1145s, 571w, 553w, 522m, 510m, 482m, 471sh, 421w, 415w, 370w. ESI MS (+): 502 [18] [Cu(MeCN)(dppe)]⁺; 859 [100] [Cu-(dppe)₂]⁺. *Anal.* Calc. for C₅₃H₄₈CuF₃O₃SP₄: C, 63.06; H; 4.79; S, 3.18. Found: C, 63.39; H, 4.93; S, 2.98%. Λ_m (CH₂Cl₂, 10⁻³ M): 48 Ω⁻¹ mol² cm⁻¹. Recrystallization from chloroform–ethanol yields 95% of **2**·H₂O.

2.2.3. CuSCN:dppe (1:2) (3)

dppe (1.60 g, 4.0 mmol) was added at room temperature to an ethanol suspension (20 ml) of CuSCN (0.12 g, 1.0 mmol). The suspension was stirred for 48 h. The colourless precipitate was filtered and washed with a mixture of ethanol/diethyl ether 1:1 to give complex **3** as a colourless solid in 80% yield; m.p. 226 °C dec. ¹H NMR (CDCl₃, 293 K): δ 2.1, 2.3 (br, 4H, PCH₂), 7.0–7.7 (m br, 20H, C₆H₅). ³¹P {¹H} NMR (CDCl₃, 293 K): δ –5.7 br. IR(nujol, cm⁻¹): 3042w, 2067s (CN), 1583w, 1570w, 1482sh, 518s, 509s, 491m, 481m, 443w, 420w, 363w, 340w, 236w. ESI MS (+): 502 [15] [Cu(MeCN)(dppe)]⁺; 859 [100] [Cu(dppe)₂]⁺. *Anal.* Calc. for C₅₃H₄₈CuNP₄S: C, 69.31; H; 5.27; N, 1.53; S, 3.49%. Found: C, 68.89; H, 5.23; N, 1.89; S, 3.76%. A_m (CH₂Cl₂, 10⁻³ M): 40.0 Ω⁻¹ mol² cm⁻¹.

2.2.4. CuClO₄:dppe (1:2) (4)

dppe (1.60 g, 4.0 mmol) was added at room temperature to an ethanol suspension (20 ml) of (PPh₃)₄Cu-(ClO₄) (1.21 g, 1.0 mmol). A colourless precipitate formed which was filtered off and washed with ethanol to give complex **4** as a colourless solid in 40% yield; m.p. 140–143 °C dec. ¹H NMR (CDCl₃, 293 K): δ 2.42 (t, 4H, PCH₂), 7.2–7.5 (m br, 20H, C₆H₅). ³¹P {¹H} NMR (CDCl₃, 293 K): δ –12.1, 5.8 br. IR(nujol, cm⁻¹): 3065w, 3046w, 1684w, 1569w, 1480sh, 1082s br, 622s (ClO₄), 514s, 506m, 489m, 475m, 443w, 369w, 337w, 203br. ESI MS (+): 502 [15] [Cu(MeCN)(dppe)]⁺; 859 [100] [Cu(dppe)₂]⁺. *Anal.* Calc. for C₅₂H₄₈ClCu-O₄P₄: C, 65.07; H; 5.04%. Found: C, 65.27; H, 5.23%. A_m (CH₂Cl₂, 10⁻³ M): 40.0 Ω⁻¹ mol² cm⁻¹.

2.2.5. CuBH₄:dppe (1:2) (5)

dppe (1.60 g, 4.0 mmol) was added at room temperature to an ethanol suspension (20 ml) of $Cu(PPh_3)_2$ -(BH₄) (0.60 g, 2.0 mmol). A colourless precipitate formed which was filtered off and washed with ethanol to give complex **5** as a colourless solid in 80% yield;

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m.p. 263 °C dec. ¹H NMR (CDCl₃, 293 K): δ 2.51 (t, 4H, PCH₂), 7.5, 7.7 (m br, 20H, C_6H_5). ³¹P {¹H} NMR (CDCl₃, 293 K): δ -12.1, 5.8 br. IR(nujol, cm⁻¹): 3073w, 3051w, 1589, 1482m, 532s, 511m, 500m, 455m, 409m, 392m, 310w, 301w, 288w, 269w, 251w, 198m, 188m, 171w. ESI MS (+): 431 [48] [(dppe- O_2 + H]⁺; 859 [100] [(dppe-O)₂Na]⁺. Anal. Calc. for C₅₂H₅₂BCuP₄: C, 71.36; H; 5.99%. Found: C, 71.59; H, 5.98%. $\Lambda_{\rm m}$ (CH₂Cl₂, 10⁻³ M): 1.0 Ω^{-1} mol² cm⁻¹.

2.3. Structure determination

Full spheres of CCD area-detector diffractometer data (Bruker AXS instrument, ω-scans, monochromatic Mo K α radiation, $\lambda = 0.7107_3$ Å) were measured yielding N_{total} reflections, these merging to N unique (R_{int} cited) after 'empirical'/multiscan absorption correction (proprietary software), $N_{\rm o}$ with $F > 4\sigma(F)$ being considered 'observed' and used in the full matrix least squares refinement, refining anisotropic displacement parameter forms for the non-hydrogen atoms, $(x, y, z, U_{iso})_{H}$ being constrained at estimates. Conventional residuals R, R_w are cited at convergence (weights: $(\sigma^2(F) +$ $(0.0004F^2)^{-1}$), neutral atom complex scattering factors being employed within the XTAL 3.7 program system [22]. Pertinent results are given below and in the text, tables and figures, the latter showing 50% probability amplitude displacement ellipsoids for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 A. Full .cif depositions (excluding structure factor amplitudes) reside with the Cambridge Crystallographic Data Centre (CCDC 271376, 273448).

2.3.1. Crystallrefinement data

2.3.1.1. Cutfs:dppe (1:2) ' H_2O ' ($2 \cdot H_2O$). $C_{53}H_{50}Cu$ - $F_3O_4P_4S$, M = 1027.5. Monoclinic, space group $P2_1/n$ $(C_{2h}^5, \text{ No. 14; variant}), a = 15.068(2) \text{ Å}, b = 18.778(3)$ Å, c = 18.584(3) Å, $\beta = 91.283(3)^\circ$, V = 5257 Å³. $D_c(Z = 4) = 1.29_6$ g cm⁻³. $\mu_{Mo} = 6.3$ cm⁻¹; specimen: $0.62 \times 0.48 \times 0.28$ mm; 'T'_{min/max} = 0.90. $2\theta_{max} = 55^{\circ}$; $N_{\rm t} = 45565, N = 11992$ ($R_{\rm int} = 0.030$), $N_{\rm o} = 8161$; R =0.058, $R_w = 0.099$. T ca. 300 K.

Variata. The tfs anion was modelled as disordered over two sets of sites, occupancies refining to 0.661(9) and complement. A difference map residue was assigned as a water molecule oxygen, site occupancy set at unity after trial refinement, associated H not located.

2.3.1.2. CuSCN: dppe (1:2) (3). $C_{53}H_{48}CuNP_4S \cdot 3/2$ $C_6H_{13}N$, M = 1067.3. Monoclinic, space group C2/c $(C_{2b}^6, \text{No. 15}), a = 46.355(5), b = 10.783(1), c = 22.306$ (2) Å, $\beta = 91.871(2)^{\circ}$, $V = 11144 \text{ Å}^3$. $D_c(Z = 8) =$ 1.27₂ g cm⁻³. $\mu_{Mo} = 5.9$ cm⁻¹; specimen: 0.25 × 0.20 × 0.10 mm; 'T'_{min/max} = 0.85. $2\theta_{max} = 58^{\circ}$; $N_t = 54937$, $N = 14270 \ (R_{\text{int}} = 0.039), N_{\text{o}} = 10226; R = 0.045, R_{w} =$ 0.052. T ca. 153 K.

Variata. Difference map residues were modelled in terms of cyclohexylamine molecules, one comprising a pair of overlapping half-weighted components, the other disordered about one of the crystallographic 2-axes (isotropic displacement parameter forms).

3. Results and discussion

3.1. Syntheses

The reaction in solution at room temperature of one equivalent of CuX (X = I, O₃SCF₃, SCN) with at least two equivalents of 1,2-bis(diphenylphosphino)ethane (dppe) at room temperature has given rise to the 1:2 adducts CuX:dppe 1-3 (Chart 1). Derivatives 4 and 5 formed when the triorganophosphine copper(I) complexes [(PPh₃)₄Cu]ClO₄ and [(PPh₃)₂CuBH₄] were reacted with excess of the dppe donor. The P-donor ligand to metal ratio employed is an important determinant for the syntheses of the compounds, different species being generally formed when equimolar quantities, or donor excesses were employed. For example, when the reaction between dppe and CuX (X = Cl or Br)was carried out in a 1:2 equimolar ratio, the previously reported trinuclear species CuX:dppe (2:3) formed [6]. The choice of the solvent is also important: the adducts



Chart 1.

1–5 have been obtained when the reaction was carried out in ethanol, whereas in MeCN adducts of stoichiometries 1:1 were generally obtained. The materials are difficult to obtain suitably crystalline from the usual solvents, the specimen of the thiocyanate used for the X-ray work being obtained from cyclohexylamine.

Compounds 1–5 are generally air-stable, colourless materials, moderately soluble not only in strongly ionizing solvents such as DMSO, dimethylformamide and acetone, but also in chlorinated solvents such as CH_2Cl_2 or $CHCl_3$. Conductivity measurements, as expected, indicated that 1, 2 and 4 are 1:1 electrolytes in dichloromethane, Λ_m being always in the range 39–48 Ω^{-1} cm² mol⁻¹. This suggests the absence of any strong interaction between Cu and the counterions in solution. The BH₄ complex 5 is a non-electrolyte in solution, presumably in consequence of rapid oxidation of the dppe and partial dissociation of the complex in solution according to the following equilibrium (Eq. (1)).

$$(dppe)_2CuBH_4 + O_2 \leftrightarrow dppe-O_2 + dppeCuBH_4$$
 (1)

The conductivity value found for compound **3** suggests ionic dissociation Eq. (2) in solution as confirmed also by ESI-MS and NMR spectroscopy (see below).

$$[(dppe)_2Cu]^+ + SCN \leftrightarrow [(dppe)_2Cu]^+SCN^-$$
(2)

3.2. Spectroscopy

The infrared spectra of 1-5 (see Section 2) are consistent with the formulations proposed, showing all of the bands required by the presence of the counterion and of the phosphorus or arsenic donor [23], the bands due to the phosphine ligands being only slightly shifted with respect to those of the free donors. In the far-IR spectra of derivatives 1–5, the broad absorptions near 500 cm^{-1} and those at $450-400 \text{ cm}^{-1}$ are due to Whiffen's y and t vibrations, respectively. In the case of 3 the absorption at 2067 cm⁻¹ due to SCN is in accordance with those reported in the literature for monodentate N-bound pseudohalide groups [24,25] (Chart 1a). The trifluoromethanesulfonate and perchlorate complexes 2 and 4 exhibit absorptions which are not useful in distinguishing between monodentate or ionic counterions. However, on the basis of a previous report [8] and, in the case of 2, on the basis of the diffraction studies, a four-coordinate ionic structure (Chart 1b) can be assigned to both complexes.

In the ¹H NMR spectra of 1-5 in CDCl₃ (see Section 2), the signals due to the diphosphine ligands show different patterns with respect to those found for the free donors, confirming the existence of complexes in solution. The bridging methylene resonances in 1-5 appear as broad signals generally between 2.50 and 2.70 ppm

downfield shifted with respect to those found in the free donors.

The ³¹P NMR room temperature spectra of compounds 1-5 (CDCl₃ solution) exhibit broad singlets shifted downfield with respect to the signal of the free donor. This suggests that dissociation occurs in solution, yielding species having a smaller ligand to metal ratio (1:1 or 3:2) and the free dppe. In order to investigate dissociative processes, we have added dppe to the NMR tube containing solutions of compound 1. Three different resonances were immediately distinguishable at ca. -12, -6 and +6 ppm. The sharp signal at ca -12 ppm is attributable to free dppe, whereas those at ca + 6and -6 ppm are most likely due to species having CuP₃ and CuP₂ cores. On the addition of further dppe, the signal at +6 ppm increases in intensity and shifts downfield to 10.0 ppm in accordance with the formation of a $[Cu(dppe)_2]^+$ cation. Oxidation of the dppe occurs mainly in the solutions containing ClO₄, BH₄ and MeSO₃ counterions.

The positive electrospray mass spectra of 1–4 (the most relevant data are reported in Section 2) clearly support the existence of the ionic 1:2 form in acetonitrile solution, indicating, also, considerable dissociation in that solvent. It is noteworthy that the major peaks in the positive ion spectra of all species always arise from the cationic species $[Cu(dppe)_2]^+$, consequent upon the breaking of bridging bonds, and the loss of X counterions. However, peaks due to $[Cu(MeCN)(dppe)]^+$ species have always been detected; compound **5** is completely dissociated in solution, peaks due to oxidized dppe only being found.

3.3. X-ray diffraction study

The single crystal X-ray structure determination of the thiocyanate 3 was carried out on a specimen obtained from cyclohexylamine solution, a fortuitous product from a crystallization directed towards the acquisition of a mixed ligand CuSCN/dppe/N-base complex. One molecule, devoid of crystallographic symmetry, comprises the asymmetric unit of the structure. The results of the study are of considerable interest, the first structural definition of a complex of the form [(P,P'-dpex)M(P-dpex)X] (four-coordinate metal) for M = Cu (Fig. 1; Table 1), previously only known for the AgX/dppp (X = halide, CN) adducts. It is further of interest in that the thiocyanate is now bound to the metal atom (=Cu), whereas in AgSCN:dppp (1:2) it remains ionic. The role of the solvent and the denticity and bite of the ligand remain imponderables in accessing the present complex – the P_3MX system has been defined for silver(I) with thiocyanate, N-bound, [26]; the present, N-bound, is compatible with the only example showing a similar environment for copper(I) [27]. In the present, four-coordinate array,



Fig. 1. Projection of CuSCN:dppe (1:2) (3).

Table 1			
Selected	molecular	geometries	of 3

Atoms	Parameter	
Distances (Å)		
Cu–P(1)	2.2844(7)	
Cu–P(2)	2.2952(7)	
Cu–P(3)	2.2686(7)	
Cu–N	1.996(2)	
N–C	1.151(3)	
C–S	1.638(3)	
Angles (°)		
N-Cu-P(1)	115.90(7)	
N-Cu-P(2)	114.43(7)	
N-Cu-P(3)	98.09(6)	
Cu–N–C	154.9(2)	
P(1)-Cu-P(2)	90.14(2)	
P(1)–Cu–P(3)	120.65(3)	
P(2)–Cu–P(3)	119.11(3)	
N–C–S	178.8(2)	
Torsion angles (°) (carbon atoms der	noted by number only)	
P(2)-Cu-P(1)-1	-18.58(8)	
Cu–P(1)–1–2	45.4(2)	
1–2–P(2)–Cu	34.9(2)	
2–P(2)–Cu–P(1)	-5.17(8)	
Cu–P(3)–3–4	-63.4(2)	
P(3)-3-4-P(4)	-174.2(1)	
P(1) = 1 - 2 - P(2)	-544(2)	

Cu–P(1,2) are somewhat longer than Cu–P(3), in keeping with their incorporation in the chelate, the difference being less marked than in the AgX:dppp (1:2) arrays (X = Cl, Br, I, CN) of [15].

Table 2	
Selected cation geometries, Cutfs: dppe $(1:2)(::H_2O')$ $(2:H_2O)$	

Atoms	Parameter
•	1 drameter
Distances (A)	
Cu–P(1)	2.295(1)
Cu–P(2)	2.298(1)
Cu–P(3)	2.294(1)
Cu–P(3)	2.297(1)
Angles (°)	
P(1)-Cu-P(2)	89.03(4)
P(1)-Cu-P(4)	128.19(4)
P(1)-Cu-P(3)	122.42(4)
P(3)-Cu-P(4)	88.36(4)
P(2)-Cu-P(3)	115.40(4)
P(2)-Cu-P(4)	116.02(4)
Torsion angles (°) (carbon atoms deno	ted by number only)
Cu-P(1)-10-20	-39.0(3)
P(1)-10-20-P(2)	59.1(3)
10-20-P(2)-Cu	-49.1(3)
Cu - P(3) - 30 - 40	-50.0(3)
P(3) - 30 - 40 - P(4)	50.6(4)
30-40-P(4)-Cu	-25.3(3)



Fig. 2. The cation of $[Cu(dppe)_2](F_3CSO_3)(H_2O')$ (2 \cdot H_2O).

The structure of the triflate adduct **2**, modelled as a monohydrate, Cutfs:dppe (1:2) (:'H₂O'), with the possibility of the anion or solvent behaving as donors, is, in the event, unsurprising, being simply ionic $[Cu(P-dppe-P')_2]^+(tfs^-)$.'H₂O'. The cation geometry is similar to those previously established in the perchlorate, nitrate, trifluoroacetate, and hexafluorophosphate salts [8–12], Cu–P spanning a very narrow range (Table 2),

although the non-'bite' P–Cu–P angles are diverse and only poorly approximate 222-symmetry, despite the similarity in torsion strings in the chelate rings, the conformation of the latter differing appreciably from that of the chelate in the thiocyanate (see Fig. 2).

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