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Reactions of Tetrahydrogenoboratebis(triphenylphosphine)copper(I) Complex with Nitrophenols

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Copper complexes with phenoxo-groups as ligands were until recently unknown. A recent study reports on the synthesis and the structure determination of the complex $[(p\text{-}MeC_6H_4NC)_4Cu_2(OPh)_2]$ in which the phenoxo-group acts as a bridging ligand [1]. We report here on the synthesis of five complexes of general formula $[(PPh_3)_2CuL]$, {where L = $2\text{-}NO_2C_6H_4O$, $2,x\text{-}(NO_2)_2C_6H_3O$ (x = 4,5,6), $2,4,6\text{-}(NO_2)_3C_6H_2O$}, of one complex of $[(PPh_3)_3Cu_2L_2]$ formula {where L = $4\text{-}NO_2C_6H_4O$}, and on the X-ray structure determination of three of them (compounds *1, 2, 3* of Table I). These complexes have been obtained by reaction of the cited nitrophenols with tetrahydrogenoboratebis(triphenylphosphine)-copper(I), which generally reacts with acids [2, 3] to give the corresponding bis(triphenylphosphine)copper(I) salts. In the same conditions the *meta*-nitrophenol does not react. The list of the complexes studied, their analytical results and melting points are reported in Table I.

Experimental

All chemicals were reagent grade and were used as received. The tetrahydrogenoboratebis(triphenylphosphine)copper(I) complex $[(PPh_3)_2CuBH_4]$ was prepared according to the literature [4]. The complexes were prepared by adding to a tetrahydrofurane solution of $[(PPh_3)_2CuBH_4]$ an ethanolic solution of LH {(LH = 2,x-dinitrophenol (x = 4,5,6), 2,4,6-trinitrophenol} or a tetrahydrofurane solution of L′H {L′H = 2-nitrophenol, 4-nitrophenol}. In all cases the molar ratio LH, L′H:$[(PPh_3)_2CuBH_4]$ was 1:1. After magnetic stirring at room temperature for about 12 hours, the complexes were isolated by adding light petroleum to the solution, filtered off and dried *in vacuo*. Crystals suitable for X-ray structure determination were obtained by slow diffusion of light petroleum through a methylene chloride solution of the complexes.

Crystal Data

Compound (*1*). $C_{42}H_{34}CuNO_3P_2$, M = 726.23, monoclinic, space group $P2_{1/n}$, a = 14.355(3), b = 16.073(2), c = 16.128(3), β = 107.75(2), V = 3544.1 Å^3, Z = 4, D_c = 1.36 g cm^{-3}, μ(Mo-Kα) = 7.44 cm^{-1}.

Compound (*2*). $C_{66}H_{53}Cu_2N_2O_6P_3$, M = 1190.17, monoclinc, space group $P2_{1/c}$, a = 15.184(3), b = 38.506(13), c = 19.921(5), β = 98.69(2), V = 11513.8 Å^3, Z = 8, D_c = 1.37 g cm^{-3}, μ(Mo-Kα) = 8.74 cm^{-1}.

Compound (*3*). $C_{42}H_{33}CuN_2O_5P_2$, M = 771.24, triclinic, space group P_1, a = 13.351(3), b = 13.386(2), c = 13.050(2), α = 115.96(2), β = 90.99(2), γ = 112.95(2), V = 1880.4 Å^3, Z = 2, D_c = 1.36 g cm^{-3}, μ(Mo-Kα) = 7.10 cm^{-1}.

Intensity data for compounds *1, 2* and *3* were collected on a CAD-4 diffractometer by the ω-scan technique in the 2θ range 3–50° for compounds *1* and *3* and 3–46° for compound *2*. The observations used

TABLE I. Analytical Data.

Compound	No.	Colour	M.p., °C	Elemental Analysis[a]		
				C%	H%	N%
$[(PPh_3)_2Cu(2\text{-}NO_2C_6H_4O)]$	*1*	red	153	69.98(69.46)	4.93(4.72)	1.78(1.93)
$[(PPh_3)_3Cu_2(4\text{-}NO_2C_6H_4O)]_2$	*2*	pale-yellow	170	67.19(66.61)	4.56(4.46)	2.24(2.35)
$[(PPh_3)_2Cu(2,4\text{-}(NO_2)_2C_6H_3O)]$	*3*	red	180	65.40(65.40)	4.33(4.31)	3.71(3.63)
$[(PPh_3)_2Cu(2,5\text{-}(NO_2)_2C_6H_3O)]$	*4*	red	140	65.17(65.40)	4.32(4.31)	3.60(3.63)
$[(PPh_3)_2Cu(2,6\text{-}(NO_2)_2C_6H_3O)]$	*5*	orange-red	160	66.50(65.40)	4.40(4.31)	3.52(3.63)
$[(PPh_3)_2Cu(2,4,6\text{-}(NO_2)_3C_6H_2O)]$	*6*	amaranth-red	155	62.34(61.76)	3.85(3.92)	5.15(5.14)

[a] Calculated values in parentheses.

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TABLE II. Infrared Stretching Frequencies (cm^{-1}).[a]

Compound	$\nu_{as}(NO_2)$	$\nu_s(NO_2)$	$\nu(CO)$
$[(PPh_3)_2Cu(2\text{-}NO_2C_6H_4O)]$	1545s	1326m	1246s
$[(PPh_3)_3Cu_2(4\text{-}NO_2C_6H_4O)]_2$	1586s	1337m	1291vs
$[(PPh_3)_2Cu(2,4\text{-}(NO_2)_2C_6H_3O)]$	1564s 1529s	1327vs	1255s
$[(PPh_3)_2Cu(2,5\text{-}(NO_2)_2C_6H_3O)]$	1543s	1333mw	1261s
$[(PPh_3)_2Cu(2,6\text{-}(NO_2)_2C_6H_3O)]$	1530s	1335ms	1250vs
$[(PPh_3)_2Cu(2,4,6\text{-}(NO_2)_3C_6H_2O)]$	1568s 1549s	1325s 1318s	1265s

[a] s = strong; m = medium; w = weak; v = very.

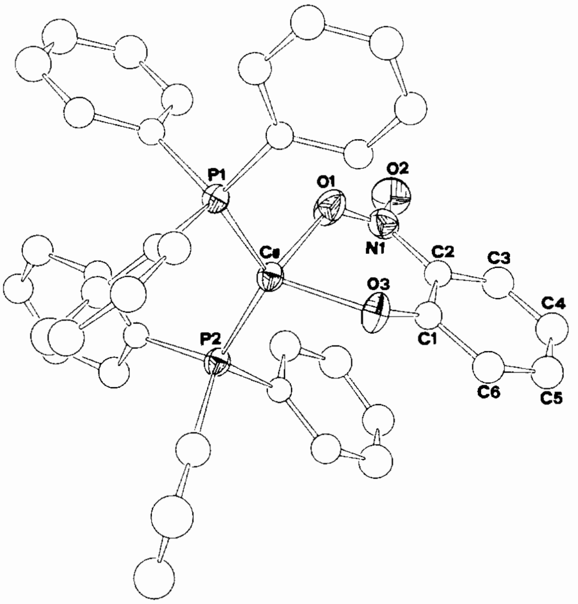

Fig. 1. Perspective view of $[L_2Cu(2\text{-}NO_2C_6H_4O)]$ complex. Selected bond distances (Å) within the molecule are: Cu–P1 = 2.220(2); Cu–P2 = 2.250(2); Cu–O1 = 2.227(6); Cu–O3 = 2.004(5); N1–O1 = 1.217(8); N1–O2 = 1.232(8); N1–C2 = 1.432(9); C1–O3 = 1.261(8); C1–C2 = 1.421(10).

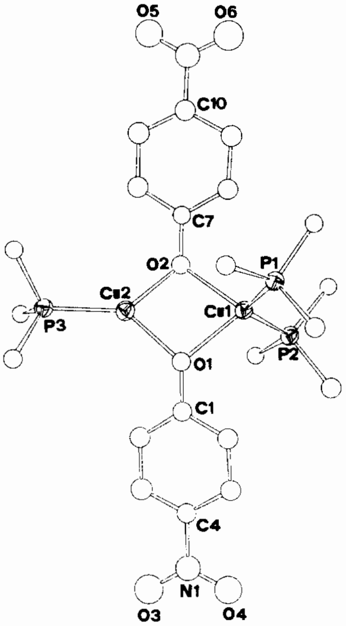

Fig. 2. Perspective view of $[L_3Cu_2(4\text{-}NO_2C_6H_4O)_2]$ complex. Average bond distances (Å) are: Cu1–O1 = 2.132; Cu1–O2 = 2.175; Cu2–O1 = 1.998; Cu2–O2 = 2.005; Cu1–P1 = 2.259; Cu1–P2 = 2.259; Cu2–P3 = 2.153; O1–C1 = 1.32; O2–C7 = 1.32; C4–N1 = 1.47; N1–O3 = 1.22; N1–O4 = 1.22; C10–N2 = 1.45; N2–O5 = 1.22; N2–O6 = 1.22.

in the solution and refinement of the structures, corrected for Lorentz and polarization effects were limited to independent reflections having $I \geqslant 3\sigma(I)$ [1741 for compound *1*, 6212 for compound *2* and 4041 for compound *3*]. The structures were solved by usual Patterson and Fourier methods and full-matrix refined down to R values of 0.043, 0.059 and 0.053 for compound *1*, *2* and *3* respectively. Principal bond parameters are reported in the figures captions. Perspective views of compounds *1*, *2* and *3* are shown in Figs. 1, 2 and 3 respectively. In compound *1* the copper atom is in a distorted tetrahedral environment, with the nitrophenolate ligand coordinated in a chelating fashion through one nitrogroup oxygen atom and the phenolic oxygen, in order to form a six-membered ring. For compound *2* the asymmetric unit in the cell consists of two independent molecules with only small differences in bonding and conformational parameters. Figure 2 may represent either of the two independent molecules with only the first phenylic carbon atoms of the triphenylphosphine ligands shown for clarity. Each molecule

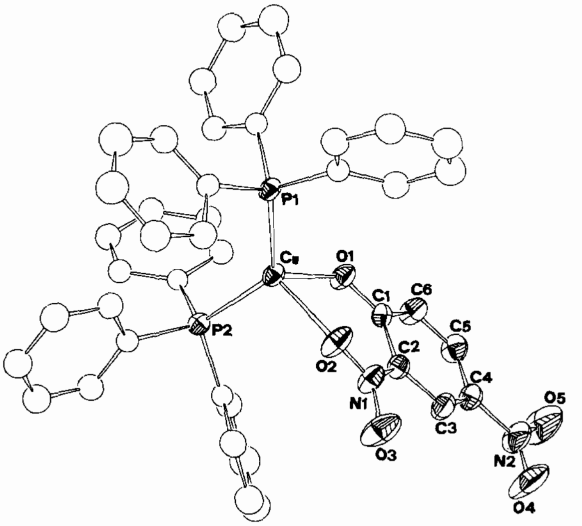

Fig. 3. Perspective view of $[L_2Cu(2,4\text{-}(NO_2)_2C_6H_3O)]$ complex. Selected bond distances (Å) within the molecule are: Cu–P1 = 2.224(1); Cu–P2 = 2.243(1); Cu–O1 = 2.023(3); Cu–O2 = 2.252(3); C1–O1 = 1.261(4); C1–C2 = 1.429(5); N1–C2 = 1.437(5); N1–O3 = 1.224(4); N1–O2 = 1.225(4); N2–O4 = 1.202(6); N2–O5 = 1.213(5).

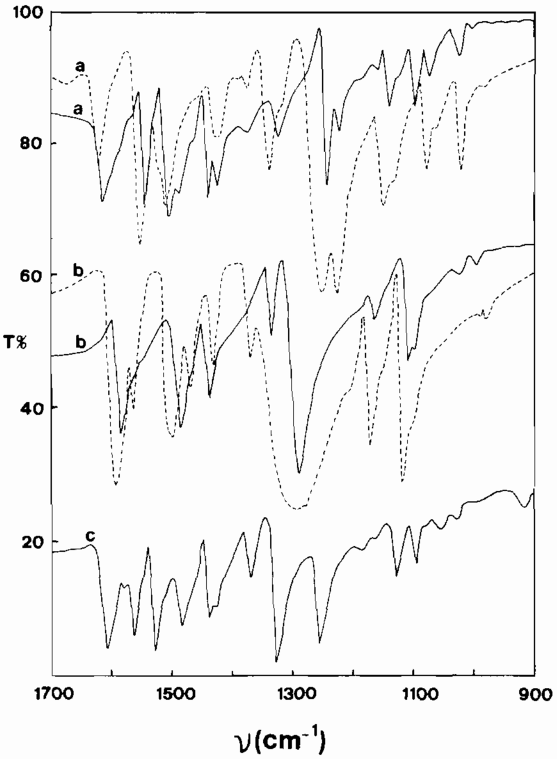

Fig. 4. Infrared spectra of solid samples spread on NaCl plates of: a) —— $[L_2Cu(2\text{-}NO_2C_6H_4O)]$; ----- $2\text{-}NO_2C_6H_4OK\cdot 0.5H_2O$; b) —— $[L_3Cu_2(4\text{-}NO_2C_6H_4O)_2]$; ----- $4\text{-}NO_2\text{-}C_6H_4OK\cdot H_2O$; c) —— $[L_2Cu(2,4\text{-}(NO_2)_2C_6H_3O)]$.

contains two copper atoms in a different coordination, one being three-coordinate with a planar geometry and the other one having a distorted tetrahedral coordination. The three-coordinate copper atom is bonded to a phosphorus atom of the triphenylphosphine molecule and to two oxygen atoms of the phenoxo groups, acting as bridging ligands between the two copper atoms. The tetracoordinate one is bonded to two triphenylphosphine ligands and to two oxygen atoms of the bridging phenoxo-groups. The molecular structure of *2* is similar to that of $[(PPh_3)_3Cu_2Cl_2]$ [5] in which the two copper atoms are bridged by two chlorine atoms. Compound *3* exhibits a molecular structure very similar to that of the complex *1*, with the nitro-group in *para* position to the phenoxo-group not involved in the coordination. The infrared data of the compounds studied are reported in Table II. Our investigation has been limited to the bands that seemed to present less complicated problems of assignment, that is to the bands of stretching vibrations $\nu_{as}(NO_2)$, $\nu_s(NO_2)$ and $\nu(CO)$ of the phenoxo ligands. In the spectra of the complexes studied the values of these vibrations have been determined, according to the data reported in the literature [6] in the following ranges: $\nu_{as}(NO_2)$ between 1529 and 1586 cm^{-1}, $\nu_s(NO_2)$ between 1318 and 1337 cm^{-1}, $\nu(CO)$ between 1246 and 1291 cm^{-1} (see Table II and Fig. 4). It is worth noting that the infrared spectra does not emphasize the structural difference found between complex *1*, in which the nitro-group is coordinated to the copper atom, and the complex *2* in which the nitro-group is not coordinated.

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