Inorganica Chimica Acta, 104 (1985) L19–L23

Bis(triphenylphosphine)copper(I)*o*- and *p*-nitrobenzoates, Synthesis and X-ray Structure

M. A. CABRAS, L. NALDINI

Istituto di Chimica Generale ed Inorganica dell'Università, Via Vienna 2, 07100 Sassari, Italy

M. A. ZORODDU

Istituto C.N.R. per l'Applicazione delle Tecniche Chimiche Avanzate ai Problemi Agrobiologici, Via Vienna 2, 07100 Sassari, Italy

F. CARIATI

Dipartimento di Chimica Inorganica e Metallorganica and Centro C.N.R., Via Venezian 21, 20133 Milan, Italy

F. DEMARTIN, N. MASCIOCCHI and M. SANSONI

Istituto di Chimica Strutturistica Inorganica, Via Venezian 21, 20133 Milan, Italy

Received May 25, 1985

The synthesis and the structure determination of the complexes $[(PPh_3)_2CuL]$, $[(PPh_3)_2CuL']$ and $[(PPh_3)_2CuL'(H_2O)]\cdot 0.5C_4H_8O$ where L = $2\text{-}NO_2C_6H_4CO_2$, L′ = $4\text{-}NO_2C_6H_4CO_2$ are described below. These complexes have been obtained by the reaction of 2- and 4-nitrobenzoic acid with tetrahydrogenoboratebis(triphenylphosphine)copper(I) which generally reacts with acids [1–3] to give the corresponding bis(triphenylphosphine)copper(I) salts.

The list of those compounds synthetized and their analytical results are to be found 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].

Compound (1) was prepared by adding 20 ml of a $CHCl_3$ solution containing 0.167 g (1 mmol) of 2-nitrobenzoic acid to 10 ml of a $CHCl_3$ solution containing 0.602 g (1 mmol) of $[(PPh_3)_2CuBH_4]$. After magnetic stirring at room temperature, the compound was isolated by adding hexane to the solution. Crystals suitable for X-ray structure determination were obtained by slow diffusion of hexane through a chloroform solution of the complex. Crystals contain some non stoichiometric amount of $CHCl_3$ which appears to be disordered in the crystal lattice.

Compound (2) was prepared as compound (1) by using 4-nitrobenzoic acid.

Compound (3) was prepared by adding 30 ml of a tetrahydrofurane/water (1/1 in vol.) solution containing 0.617 g (1 mmol) of 4-nitrobenzoic acid to 10 ml of tetrahydrofurane solution containing 0.603 g (1 mmol) of $[(PPh_3)_2CuBH_4]$. After magnetic stirring at room temperature the compound precipitated and was filtered off. Crystals suitable for X-ray determination were obtained by slow diffusion of water/tetrahydrofurane (1/1) through a tetrahydrofurane solution of the complex.

The thermogravimetric analysis diagram of compound (3) shows a weight loss of about 2.5% between 50 °C and 65 °C (minimum value of DTG diagram 60 °C) due to dehydration (calc. 2.23%) and weight loss of about 4.5% between 85 °C and 105 °C (minimum value of DTG diagram 97.5 °C) due to tetrahydrofurane loss. The presence of tetrahydrofurane and water in the compound (3) was determined also by PMR spectroscopy. In fact the PMR spectrum of this compound in $CDCl_3$ shows two multiplets centered at $\delta = 3.75$ and $\delta = 1.85$ ppm which must be attributed to THF and one broad signal at $\delta = 2.08$ ppm which must be attributed to H_2O. All these signals are in the expected ratios with respect to signal areas found for the other protons of the molecule.

It should be noted that compound (2) can also be prepared by adding hexane to a chloroform solution of compound (3) and that, on the contrary, by adding hexane to a tetrahydrofurane/water (1/1 vol.) solution of compound (2), compound (3) is formed. Compound (1) dissolved in tetrahydro-

TABLE I. Analytical Data.

Compound	Colour	M.p. (°C)	Elemental analysis^a		
			C%	H%	N%
$[(PPh_3)_2Cu(2\text{-}NO_2C_6H_4CO_2)]$ (1)	pale yellow	204	68.13(68.52)	4.53(4.52)	1.87(1.85)
$[(PPh_3)_2Cu(4\text{-}NO_2C_6H_4CO_2)]$ (2)	lemon-yellow	180	68.62(68.52)	4.64(4.51)	1.93(1.85)
$[(PPh_3)_2Cu(4\text{-}NO_2C_6H_4CO_2)(H_2O)]\cdot 0.5C_4H_8O$ (3)	amber-yellow	145	67.20(66.87)	4.94(4.95)	1.73(1.73)

^{a}Calculated values in parentheses.

0020-1693/85/$3.30

furane/water (1/1 vol.) solution, does not afford the analogous of compound (**3**), containing a coordinate molecule of water and a 2-nitrobenzoate ligand.

C, H and N were determined by using a Perkin-Elmer 240B elemental analyser. Thermal studies were performed on a Perkin-Elmer thermogravimetric apparatus in nitrogen atmosphere. IR spectra were recorded with a Perkin-Elmer 683 spectrophotometer. Proton NMR spectrum was obtained on a Varian CFT 20 spectrometer.

Crystal Data

Intensity data were collected on a Nonius CAD-4 diffractometer with graphite monochromated MoK_α radiation ($\lambda = 0.71073$ Å) within a 2θ sphere of 50° for compounds (2) and (3), with 46° for compound (1).

The structures were solved by conventional Patterson and Fourier methods and refined by full-matrix least-squares. Some relevant crystallographic parameters are shown in Table II. Perspective views of compounds (1), (2) and (3) are shown in Figs. 1, 2 and 3 respectively.

Results and Discussion

As can be seen from Fig. 1, in compound (1) the 2-nitrobenzoate anion behaves as a symmetrical bidentate carboxylate ligand. The conformational features of the ligand arise from the need to maintain normal intramolecular contacts and can be accomplished (i) by rotating the carboxylate group around the C(1)–C(2) axis (torsional angle O(1)–C(1)–C(2)–C(3) 21.1°) in order to minimize the interaction O(1)····H(7) and O(2) with the nitro-group, and (ii) by rotating the nitro-group around the C(3)–N direction so that the N, O(3), O(4) plane can face O(2) with a minimum contact of 2.77 Å with the nitrogen atom. The 4-nitrobenzoate ligand in compound (2) is asymmetrically bidentate (the two Cu–O distances being 2.145(3) and 2.304(3) Å) while in compound (3) the same is monodentated with a shorter interaction with the metal atom (Cu–O(1) distance 2.067(3) Å). Again the carboxylate and nitro-groups can rotate around C(1)–C(2) and N–C(5) directions respectively. The extent of rotation of the carboxylate with respect to the phenyl ring is larger in compound (2) than in compound (3), mainly due to packing effects rather than to the intramolecular interaction between the carboxylic oxygen atoms and the aromatic hydrogen atoms. Moreover, the packing forces are probably responsible for the tilting between the planes C(1), C(2), O(1), O(2) and Cu, O(1), O(2) of 13.5° in compound (2), which is only 3.2° in compound (1).

The infrared data of compound (1), (2) and (3) are in Table III. Investigations have been limited to the bands which presented less complicated problems of assignments, that is to the stretching vibrations $\nu_{as}(CO_2)$, $\nu_s(CO_2)$, $\nu_{as}(NO_2)$ and $\nu_s(NO_2)$ of the nitrobenzoic anions and the bending vibration $\delta(H_2O)$. All these vibrations are between 1700 and 1200 cm^{-1}, as in Fig. 4, [5, 6]. It is important to note that the infrared spectra do not emphasize the structural difference found between compound

TABLE II. Crystal Data and Intensity Collection Parameters.

	Compound **1**	Compound **2**	Compound **3**
Formula	$C_{43}H_{34}CuNO_4P_2 \cdot 0.5CHCl_3$	$C_{43}H_{34}CuNO_4P_2$	$C_{43}H_{36}CuNO_5P_2 \cdot 0.5C_4H_8O$
Mol. weight (uma)	813.9	754.2	808.3
System	monoclinic	monoclinic	triclinic
Space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$
a (Å)	15.345(2)	11.439(5)	13.149(5)
b (Å)	12.673(3)	20.190(7)	13.283(9)
c (Å)	22.496(3)	12.152(5)	14.007(8)
α (°)			110.85(3)
β (°)	107.51(2)	112.54(3)	106.43(3)
γ (°)			103.85(3)
U (Å^3)	4172	3619	2029
Z	4	4	2
D_c (g cm^{-3})	1.296	1.384	1.323
$\mu(MoK_\alpha)$ (cm^{-1})	7.35	7.33	6.61
Final R	0.067	0.052	0.064
Final R_w	0.076	0.065	0.084
Number of independent reflections collected	5656	6626	6688
Number of reflections having $I > 3\sigma(I)$	1815	3865	3748

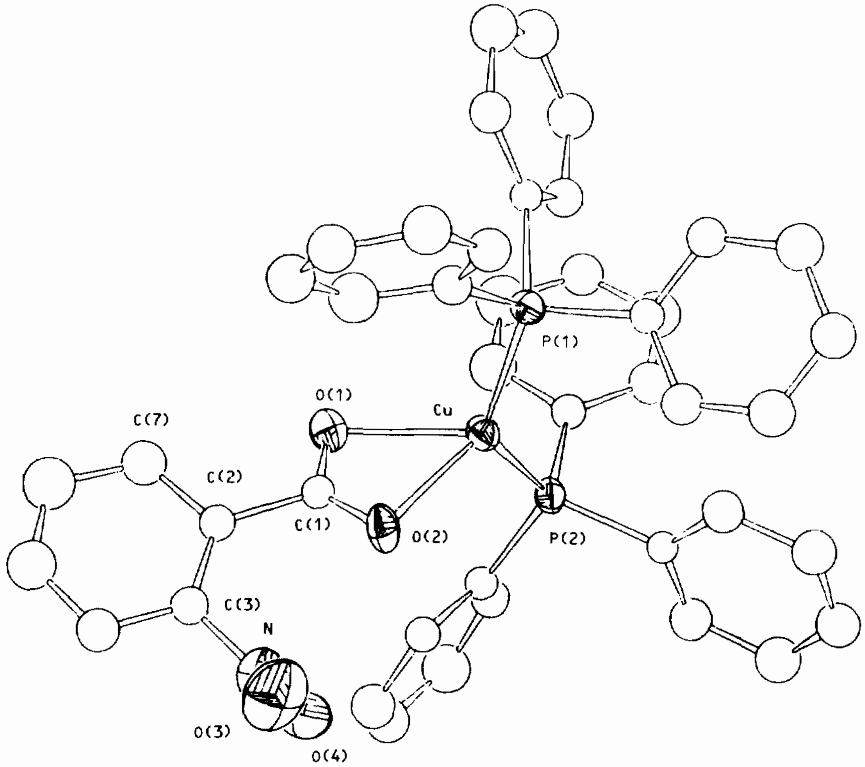

Fig. 1. ORTEP drawing of the [$(PPh_3)_2Cu(2\text{-}NO_2C_6H_4CO_2)$] molecule. Selected bond distances (Å) and angles (°) within the molecule: Cu–O(1) 2.244(7), Cu–O(2) 2.251(7), Cu–P(1) 2.247(3), Cu–P(2) 2.243(3), C(1)–O(1) 1.238(12), C(1)–O(2) 1.235(12), C(1)–C(2) 1.519(14), C(3)–N 1.540(19), N–O(3) 1.221(13), N–O(4) 1.222(13), P(1)–Cu–P(2) 130.3(1), O(1)–Cu–O(2) 58.4(3), N···O(2) 2.77(2), O(3)···O(2) 2.88(2).

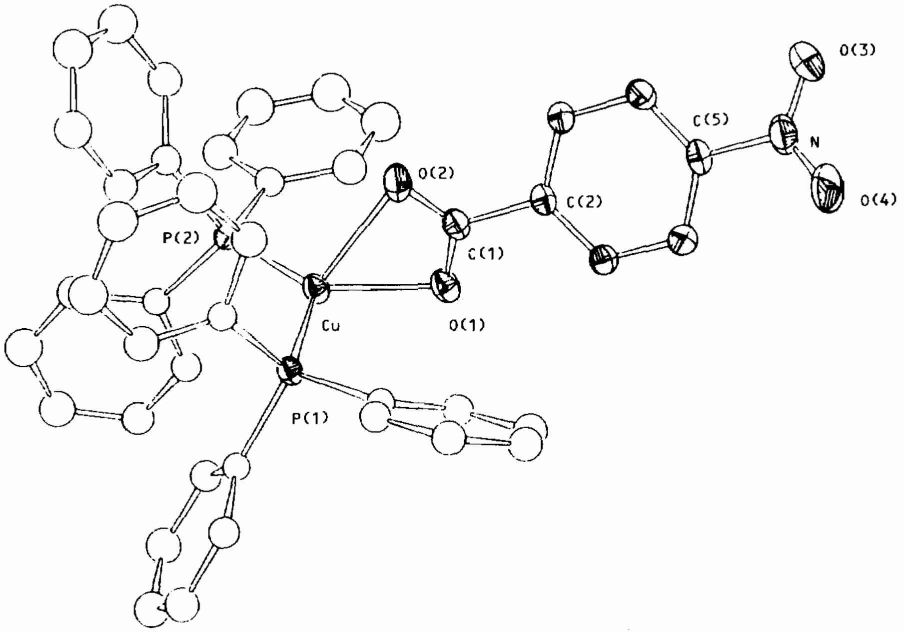

Fig. 2. ORTEP drawing of the [$(PPh_3)_2Cu(4\text{-}NO_2C_6H_4CO_2)$] complex. Selected bond distances (Å) and angles (°) within the molecule: Cu–O(1) 2.145(3), Cu–O(2) 2.304(3), Cu–P(1) 2.251(1), Cu–P(2) 2.223(1), C(1)–O(1) 1.247(5), C(1)–O(2) 1.251(5), C(1)–C(2) 1.507(5), C(5)–N 1.471(5), N–O(3) 1.227(5), N–O(4) 1.200(5), P(1)–Cu–P(2) 128.59(4), O(1)–Cu–O(2) 58.9(1).

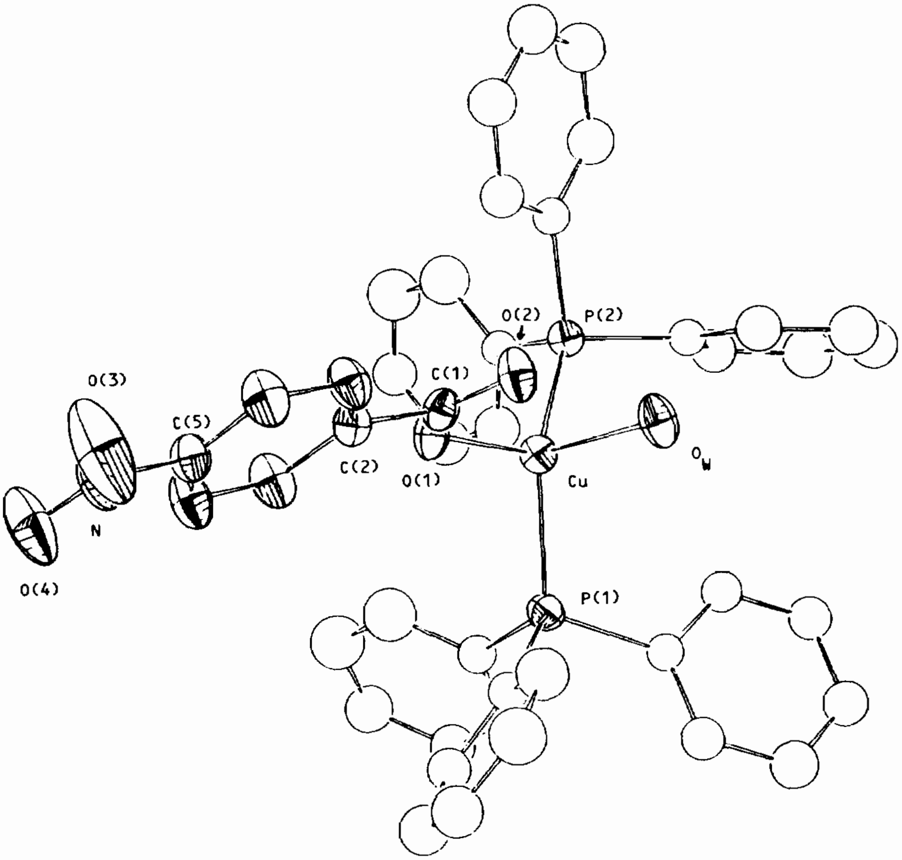

Fig. 3. ORTEP drawing of the $[(PPh_3)_2Cu(4\text{-}NO_2C_6H_4CO_2)(H_2O)]$ molecule. Selected bond distances (Å) and angles (°) within the molecule: Cu–O(1) 2.067(3), Cu···O(2) 3.318(3), Cu–O_w 2.227(3), Cu–P(1) 2.252(1), Cu–P(2) 2.246(1), C(1)–O(1) 1.249(5), C(1)–O(2) 1.243(5), C(1)–C(2) 1.518(6), C(5)–N 1.497(7), N–O(3) 1.170(8), N–O(4) 1.185(5), O_w···O(2) 2.658(5), P(1)–Cu–P(2) 126.85(5), O(1)–Cu–O_w 93.7(1).

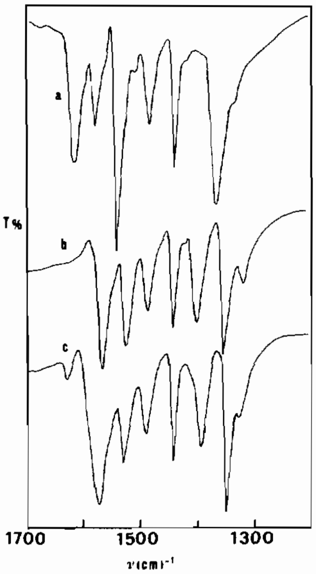

Fig. 4. Infrared spectra of solid samples spread on NaCl plates of: (a) $[(PPh_3)_2Cu(2\text{-}NO_2C_6H_4CO_2)]$; (b) $[(PPh_3)_2Cu(4\text{-}NO_2C_6H_4CO_2)]$; (c) $[(PPh_3)_2Cu(4\text{-}NO_2C_6H_4CO_2)(H_2O)]\cdot 0.5C_4H_8O$.

(**2**), in which the carboxylic group is bicoordinated to the copper atom ($\Delta\nu = \nu_{as}(CO_2) - \nu_s(CO_2) = 214$ cm^{-1}) and compound (**3**) in which the carboxylic group is monocoordinated ($\Delta\nu = 223$ cm^{-1}). On the other hand, these results are in agreement with the X-ray measurements which show that the C–O bond distances have similar values in compound (**2**) and (**3**) probably due to the hydrogen bonding interation between O(2) and O_w in compound (**3**) (O(2)···O_w 2.658(5) Å).

References

1 F. Cariati and L. Naldini, *J. Inorg. Nucl. Chem., 28,* 2243 (1966).

2 F. Cariati, L. Naldini, A. Panzanelli, F. Demartin and M. Manassero, *Inorg. Chim. Acta, 69,* 117 (1983).

3 L. Naldini, A. Panzanelli, G. Rassu, F. Cariati, F. Demartin, M. Manassero and N. Masciocchi, *Inorg. Chim. Acta, 83,* L71 (1984).

4 F. Cariati and L. Naldini, *Gazz. Chim. Ital., 95,* 3 (1965).

5 G. B. Deacon and R. J. Phillips, *Coord. Chem. Rev., 33,* 227 (1980).

6 A. Kuwae and K. Machida, *Spectrochim. Acta, Part A:, 35,* 27 (1979).

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

Compound	$\delta(H_2O)$	$\nu_{as}(CO_2)$	$\nu_{as}(NO_2)$	$\nu_s(CO_2)$	$\nu_s(NO_2)$[b]
$[(PPh_3)_2Cu(2\text{-}NO_2C_6H_4CO_2)]$		1615s	1539vs	1368vs	1340sh
$[(PPh_3)_2Cu(4\text{-}NO_2C_6H_4CO_2)]$		1566vs	1525s	1352vs	1320m
$[(PPh_3)_2Cu(4\text{-}NO_2C_6H_4CO_2)(H_2O)]\cdot 0.5C_4H_8O$[c]	1624w	1571vs	1527s	1348vs	1325m

[a] s = strong; m = medium; w = weak; sh = shoulder; v = very. [b] Tentatively assigned because this band should be obscured by the more strong $\nu_s(CO_2)$ band. [c] $\nu_{as}(H_2O)$ and $\nu_s(H_2O)$ are present as a broad band at about 3420 cm^{-1}. Characteristic bands of THF are not easily detectable.