

REACTION OF CARBON DIOXIDE WITH ARYLCOPPER(I) COMPLEXES CONTAINING TERTIARY PHOSPHINES

N. MARSICH, A. CAMUS and G. NARDIN

Istituto di Chimica, Università di Trieste, 34127 Trieste (Italy)

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Summary

ArCu^{I} compounds (Ar = phenyl, *o*-, *m*-, or *p*-tolyl) do not react with carbon dioxide at appreciable rate, but in the presence of triphenylphosphine in appropriate solvents undergo insertion to give the corresponding carboxylato complexes $\text{ArCO}_2\text{Cu}(\text{PPh}_3)_2$. In the presence of diphos the carbon dioxide absorption was very slow and mainly gave $(\text{ArCO}_2\text{Cu})_2\text{diphos}_3$ complexes. The (diphenylphosphino)methane (DPM) derivatives $[\text{ArCO}_2\text{CuDPM}]_2$ and $(\text{ArCO}_2\text{Cu})_2\text{DPM}$ were prepared by other methods for comparison. The X-ray structure of $\text{HCO}_2\text{Cu}(\text{PPh}_3)_2$ is reported.

Introduction

Since De Pasquale and Tamborsky [1] first studied the interactions between fluoroorganocopper compounds and carbon dioxide, the number of papers in this field has increased rapidly, reflecting the considerable interest in all reactions between transition metal compounds and CO_2 . These reactions are known to involve a simple coordination of CO_2 , with formation of adducts or an insertion of CO_2 into a metal–carbon bond, with formation of carboxylates. The interaction of CO_2 with transition metals is often investigated in connection with the objective of bringing about catalytic insertion of CO_2 into organic substrates. Some reversible reactions of CO_2 with copper(I) and copper(II) compounds have been reported recently [2]. Usually, however, the reaction with organocopper gives final products derived from insertion. Most of these studies were by Yamamoto et al. [3] or Normant et al. [4] and were concerned almost exclusively with organocopper compounds of the aliphatic series. We describe here the reaction between carbon dioxide and some arylcopper complexes containing tertiary phosphines.

Results and discussion

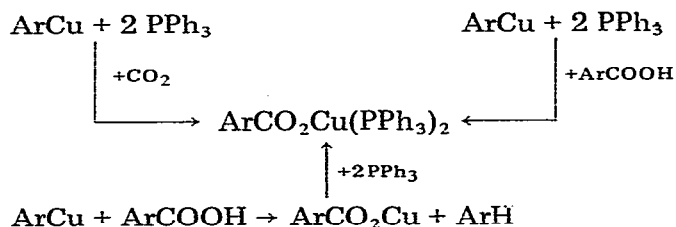
The rate of absorption of CO_2 by solutions or suspensions of ArCu (Ar = phenyl, *o*-, *m*-, or *p*-tolyl; solvent* = toluene or ether) at 0°C was negligible, but was increased in the presence of tertiary phosphines (triphenylphosphine and 1,2-bis(diphenylphosphino)ethane (diphos)). The maximum ratio of absorbed CO_2 to Cu was 1. For the triphenylphosphine derivatives the reaction was complete in some hours, but a longer time was needed for diphos complexes. The highest rate of absorption was observed at a P/Cu ratio of 3, while catalytic amounts of the ligand and also a P/Cu ratio of 1 had negligible effects. P(Ph)_3 was ineffective for the CO_2 insertion.

The analytical data for the isolated products, which were white or cream diamagnetic compounds, with a stoichiometry depending mainly on the ligand, are given in Table 1 (T = tolyl). When dried and kept under nitrogen these complexes are stable for months, but they are also reasonably stable in the air.

Infrared data for copper(I) carboxylato complexes are given in Table 2.

Complexes with triphenylphosphine

The reaction between ArCu^{I} compounds and triphenylphosphine gives complexes with Cu/PPh_3 ratios of 2 and 3 [6]. In contrast, in the reaction with CO_2 , stable products were formed only for the stoichiometry $\text{ArCO}_2\text{Cu(PPh}_3)_2$, the same complexes also being obtained starting from 1/1 and 1/3 ratios. The occurrence of insertion, previously observed for alkylcopper complexes [7], is demonstrated by the identity of products with those obtained in other ways (Scheme 1).



SCHEME 1

The same products have also been prepared by treating copper(II) carboxylates with the ligand in alcoholic solution [8].

The $\text{PhCO}_2\text{Cu(PPh}_3)_2$ complex I, when refluxed in toluene with excess methyl iodide** for 30 min, gave an almost theoretical yield of methylbenzoate and a copper derivative identical with $[\text{CuI}_3][\text{MePPh}_3]_2$ [10], according to the

* Other solvents such as methanol [5a], dichloroethane [5b], nitromethane [5c], pyridine [5d], carbon disulfide [5e] are known to react with these organocopper compounds or their complexes with tertiary phosphines.

** For ester formation by reaction between $\text{RCO}_2\text{Cu}^{\text{I}}$ and methyl iodide see ref. 9.

ANALYTICAL DATA FOR COPPER(II) CARBOXYLATO COMPLEXES

Formula	m.p. (dec.) (°C)	Analysis (found(calcd.)) (%)				Mol. wt. (found calcd.)		%w/w
		C	H	Cu	P	DCE	Toluene	
$\text{PhCO}_2\text{Cu}(\text{PPh}_3)_2$	212–214	72.6 (72.82)	4.87 (4.98)	8.98 (8.96)	8.7 (8.74)	685 (709.2)		1.3
$o\text{-TCO}_2\text{Cu}(\text{PPh}_3)_2$	200–202	72.6 (73.06)	5.00 (5.15)	8.83 (8.78)	8.6 (8.57)	740 (723.2)		1.4
$m\text{-TCO}_2\text{Cu}(\text{PPh}_3)_2$	192–194	72.8	5.15	8.81	8.5	715		1.3
$p\text{-TCO}_2\text{Cu}(\text{PPh}_3)_2$	194–196	73.0	5.10	9.01	8.4	736		2.3
$p\text{-TCO}_2\text{Cu}(\text{diphos})$	280–282	68.0	5.38	10.58	10.2	too low solubility		
$(\text{PhCO}_2\text{Cu})_2\text{diphos}_3 \cdot 2\text{Tol.}$	239–242	(68.39)	(5.23)	(10.64)	(10.38)	too low solubility		
$(o\text{-TCO}_2\text{Cu})_2\text{diphos}_3^a$	188–192	73.5 (72.88)	5.69 (5.64)	7.34 (7.27)	10.5 (10.64)	too low solubility		
$(m\text{-TCO}_2\text{Cu})_2\text{diphos}_3^a$	215–218	69.5 (70.89)	5.22 (5.44)	7.83 (7.98)	11.6 (11.67)	too low solubility		
$(p\text{-TCO}_2\text{Cu})_2\text{diphos}_3$	224–226, ~275	70.4	5.48	8.08	11.8	too low solubility		
$\text{PhCO}_2\text{CuDPM}$	218–223 ^b	71.0 (67.1)	5.46 (4.85)	7.89 (11.15)	11.9 (10.8)	too low solubility		1.3
$o\text{-TCO}_2\text{CuDPM}$	166–167	67.7 (67.97)	5.01 (5.01)	10.92 (10.90)	10.3 (10.63)	859 (583.1)		1.7
$m\text{-TCO}_2\text{CuDPM}$	231–233	67.5	4.63	10.97	10.5	840		1.3
$p\text{-TCO}_2\text{CuDPM}^a$	229–230	67.7	5.07	11.06	10.4	531		1.3
$(\text{PhCO}_2\text{Cu})_2\text{DPM}$	^c	62.5 (62.15)	4.32 (4.28)	16.42 (16.86)	8.3 (8.22)	too low solubility		
$(o\text{-TCO}_2\text{Cu})_2\text{DPM}$	^c	63.0 (62.99)	4.82 (4.64)	16.01 (16.26)	8.1 (7.92)	686 (781.7)		1.2
$(m\text{-TCO}_2\text{Cu})_2\text{DPM}$	^c	63.7	4.90	16.20	7.8	749		1.5
$(p\text{-TCO}_2\text{Cu})_2\text{DPM}$	^c	63.6	4.34	16.19	8.1	too low solubility		

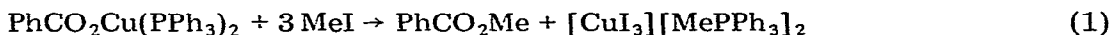
^a The following complexes with solvent of crystallization were also isolated, and gave good analyses: $(o\text{-TCO}_2\text{Cu})_2\text{diphos}_3 \cdot 1.5$ toluene; $(m\text{-TCO}_2\text{Cu})_2\text{diphos}_3 \cdot 2$ toluene; $p\text{-TCO}_2\text{CuDPM} \cdot 2$ toluene. The presence of solvent was confirmed quantitatively by GLC. ^b m.p. of the complex crystallized from CH_2Cl_2 or toluene and petroleum ether. The product crystallized from $\text{MeOH} + \text{petroleum ether}$, with the same analytical composition, but a completely different IR spectrum, melts at $151\text{--}153^\circ\text{C}$ (sample inserted at ca. 140°C). Upon recrystallization again from CH_2Cl_2 or toluene the original complex is regenerated. ^c The decomposition point is very different from the m.p.. Furthermore both are dependent on the immersion temperature of the capillary and heating rate.

TABLE 2
IR DATA ^a FOR COPPER(I) CARBOXYLATO COMPLEXES

Complex	$\nu(\text{CO}_2)_{\text{asym}}$ (s(br)) (cm^{-1})	$\nu(\text{CO}_2)_{\text{sym}}$ (s(br)) (cm^{-1})	$\Delta\nu$ (cm^{-1})
$\text{PhCO}_2\text{Cu}(\text{PPh}_3)_2$	1537	1390	147
<i>o</i> - $\text{TCO}_2\text{Cu}(\text{PPh}_3)_2$	1540	1392	148
<i>m</i> - $\text{TCO}_2\text{Cu}(\text{PPh}_3)_2$	1540	1382	158
<i>p</i> - $\text{TCO}_2\text{Cu}(\text{PPh}_3)_2$	1535	1400	135
<i>p</i> - TCO_2Cu diphos	1535	1383	152
$(\text{PhCO}_2\text{diphos}_3)_2\text{tol}$	1568 ^b	1362	206
(<i>o</i> - $\text{TCO}_2\text{Cu}_2\text{diphos}_3$)	1564 ^b	1352	204
(<i>m</i> - TCO_2Cu) ₂ diphos ₃	1564 ^b	1360	210
(<i>p</i> - TCO_2Cu) ₂ diphos ₃	1567 ^b	1353	214
$[\text{PhCO}_2\text{CuDPM}]_2$ ^c	1563 ^b	1372	191
$[\text{PhCO}_2\text{CuDPM}]_3$ ^d	1551 ^b	1386–1364	165–187
[<i>o</i> - $\text{TCO}_2\text{CuDPM}]_2$	1549	1363	186
[<i>m</i> - $\text{TCO}_2\text{CuDPM}]_2$	1564	1364	200
[<i>p</i> - $\text{TCO}_2\text{CuDPM}]_2$	1555	1365	190
$(\text{PhCO}_2\text{Cu})_2\text{DPM}$	1560	1385 ^b	175
(<i>o</i> - TCO_2Cu) ₂ DPM	1554	1388 ^b	166
(<i>m</i> - TCO_2Cu) ₂ DPM	1562	1385 ^b	177
(<i>p</i> - TCO_2Cu) ₂ DPM	1550	1385 ^b	165

^a Measured as KBr discs. The $\delta(\text{CO}_2)$ region (620–680 cm^{-1} [7]) is partially obscured by the phenyl groups of the ligands. ^b Peaks with shoulders. ^c Crystallized from toluene. ^d Crystallized from MeOH.

following equation:



Complex I did not liberate CO_2 when heated at 200°C and only small amounts of the gas were released at 280°C. The other complexes of this series showed even higher thermal stability.

Conductivity measurements confirmed that the $\text{ArCO}_2\text{Cu}(\text{PPh}_3)_2$ compounds are monomeric and almost undissociated [8] in dichloroethane (DCE); they are, however, dimeric uni-univalent electrolytes in MeOH (37–41 $\Omega^{-1} \text{cm}^2 F^{-1}$). The IR frequencies observed for $\nu(\text{CO}_2)$ (Table 2) agree reasonably well with those reported by Hammond et al. [8], and the X-ray structure given in the Appendix confirms that the carboxylato group is bidentate, as suggested by the above authors on the basis of the separation ($\Delta\nu$) between the *sym* and *asym* CO_2 stretching frequencies.

The IR spectra of some of the compounds before crystallization showed, in addition to the $\text{ArCO}_2\text{Cu}(\text{PPh}_3)_2$ bands, medium broad absorption peaks at about 1615 and 1320 cm^{-1} *. As the insertion of the CO_2 into the Cu–C bond is assumed to proceed through the formation of CO_2 coordination complexes [7,11], these peaks were at first attributed to the presence of incompletely transformed intermediates. Later, however, from the reaction of CO_2 with the triphenylphosphine derivative of the *o*-tolyl copper two products were isolated:

* The original products could not be regenerated by bubbling CO_2 through a solution of recrystallized $\text{ArCO}_2\text{Cu}(\text{PPh}_3)_2$.

(A) a cream-coloured rather unstable powder, which separated spontaneously from the solution; (B) a white microcrystalline compound, which was isolated from the concentrated mother liquor. The IR spectra (Fig. 1) show clearly that B is the normal carboxylate, while A is responsible for the anomalous peaks. The IR spectral and other characteristics of A (m.p. 154–156°C; CO_2/Cu released on acidolysis and pyrolysis = 0.77) are the same as those for $\text{HOCO}_2\text{Cu}(\text{PPh}_3)_2$ [3]. Probably, owing to the long time of reaction, even traces of moisture in the CO_2 are sufficient to decompose the organometallic compound.

Complexes with diphos

Of the organocopper complexes involving diphos, the most easily formed are those of formula $(\text{ArCu})_2\text{diphos}_3$ [5b], which is also the preferred stoichiometry for the carboxylate derivatives. $(\text{ArCO}_2\text{Cu})_2\text{diphos}_3$ complexes were found to be uni-univalent electrolytes both in DCE ($32\text{--}34\ \Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$) and in MeOH ($72\text{--}79\ \Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$). In the solid state their structure probably resembles that of the chloride derivative $(\text{CuCl})_2\text{diphos}_3$ [12], with one diphos molecule bridging the two copper atoms, each of which is further coordinated by a chelating molecule of the ligand. The high values of $\Delta\nu$ observed in the IR spectra confirm the existence of severe steric hindrance at the copper atoms, which forces the carboxylato groups to be monodentate. The absorptions due to the $\nu(\text{CO}_2)$ can be readily identified by comparison with the IR spectra of $(\text{ArCu})_2\text{diphos}_3$ complexes [5b].

The products isolated from the reaction of ArCu and diphos in equimolecular amounts were mixtures. In spite of satisfactory analyses, their IR spectra showed the presence of side-products, with $\nu(\text{CO}_2)$ frequencies very close to

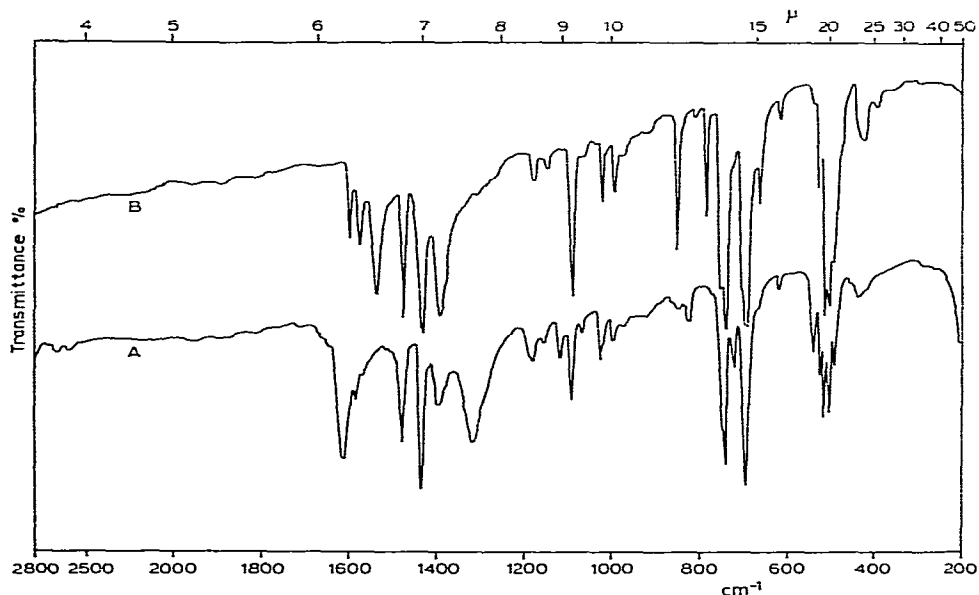


Fig. 1. IR spectra in Nujol and KI of the compounds isolated from the reaction of CO_2 with the triphenylphosphine derivative of the *o*-tolylcopper. A = side-product; B = $o\text{-TCO}_2\text{Cu}(\text{PPh}_3)_2$.

those of A. In the *p*-tolylCO₂Cudiphos, which is the only recrystallizable complex, the carboxylato group is bidentate.

Complexes with DPM

Some copper(I) carboxylato complexes containing (diphenylphosphino)methane (DPM) were also prepared for comparison. Usually DPM acts as monodentate, and the two expected series of derivatives, ArCO₂DPM and (ArCO₂Cu)₂DPM, were isolated (Table 1). Since the reaction between organocopper compounds and the ligand affords the [Cu(PPh₂CHPPh₂)₃·2S (S = solvent) (II) with elimination of the aromatic group originally bonded to the copper atom [13]^{*}, these complexes were made via the copper(I) carboxylates (Scheme 1). They were also prepared by treating II with the appropriate aromatic acid. The ArCO₂CuDPM complexes seem to exist in two forms in solution, since conductivity measurements indicate that they are uni-univalent electrolytes, but dimers in DCE (15–18 Ω⁻¹ cm² F⁻¹) and trimers in MeOH (26–30 Ω⁻¹ cm² F⁻¹). In the case of the PhCO₂CuDPM complex, it was possible to isolate two interconvertible modifications as solids by recrystallization from toluene and methanol, respectively. The presumed dimeric form, with IR spectrum consistent with monodentate carboxylato groups, is the preferred species for the tolyl derivatives. The trimeric form is probably similar to the chloride analogue [Cu₃Cl₂DPM₃]⁺ Cl⁻ [14]. The halide is tricoordinated, but in addition one oxygen of bridging carboxylato group can form a further bridge to another copper atom [15].

The (ArCO₂Cu)₂DPM complexes are monomers and non-electrolytes. Here the DPM bridges the two copper atoms, and the low steric hindrance allows the carboxylato groups to act as bidentate.

Experimental

All reactions were carried out under dry nitrogen. The solvents were dried and distilled under nitrogen immediately before use. The CO₂ was dried by passing it through a cooled trap (–60°C). The organocopper compounds were prepared by published methods [16].

PhCO₂Cu(PPh₃)₂. 1.0 g (3.8 mmol) of PPh₃ was added to a stirred toluene (30 ml) suspension of 0.53 g (3.8 mmol) of PhCu at 0°C. The deep-orange solution formed was filtered and CO₂ bubbled through it for a few hours. The white precipitate was filtered off, washed with toluene, and dried in vacuo.

The other complexes of this series were prepared in a similar way. In the case of the *o*- and *p*-tolyl derivatives the complexes did not separate, and were precipitated by adding ether to the previously concentrated solution.

The complexes could be recrystallized from methanol. They also crystallized well from CH₂Cl₂ + ether, but the analytical results for C and H were somewhat

* [Cu(PPh₂CHPPh₂)₃] also reacted with CO₂ in toluene, absorbing one molecule of gas for each copper atom. After concentration of the solution and ether addition, an off-white powder was obtained (ν(CO₂) (cm⁻¹) 1535 s(br); 1378 s(br) with shoulder at ~1315 mw(br)). The product could not be recrystallized satisfactorily.

ow in this case, probably because of formation of small amounts of the corresponding halide derivatives.

$(PhCO_2Cu)_2diphos_3$. 1.75 g (4.4 mmol) of diphos were added to a stirred toluene (40 ml) suspension of 0.41 g (2.9 mmol) of $PhCu$ at $0^\circ C$, and CO_2 was bubbled through the white suspension for 8 h. Recrystallization was from hot toluene.

The other carboxylates containing diphos were prepared in the same way. The progress of the reaction could be easily observed in the case of the *p*-tolyl (*p*-T) derivative since $(p-TCu)_2diphos_3$ is soluble under these conditions. The yellow colour of the solution was discharged by reaction with the CO_2 and the white product began to separate after some hours.

$PhCO_2CuDPM$. 0.49 g (4.0 mmol) of benzoic acid were added to the orange solution obtained from 0.62 g (4.0 mmol) of *o*-TCu and 1.34 g (4.0 mmol) of DPM in toluene (30 ml) at $0^\circ C$. After 1 h the almost colourless solution was filtered and concentrated under vacuum. The complex was then precipitated by adding petroleum ether.

The same final product was obtained by first treating the organocopper suspension in toluene with benzoic acid and subsequently adding the DPM.

$(PhCO_2Cu)_2DPM$. 0.7 g (5.7 mmol) of benzoic acid were added to a toluene suspension (30 ml) of 0.88 g (5.7 mmol) of *o*-TCu at $0^\circ C$. A white solid separated slowly, while the solution turned pale blue. Upon addition of 0.95 g (2.85 mmol) of DPM, the solid dissolved to give a new silky off-white precipitate. Recrystallization was from toluene or acetone under nitrogen.

The other complexes of the two DPM series were prepared in the same way. They are more soluble than the DPE complexes in common solvents, but also less stable in the air, especially the 2/1 derivatives.

Appendix

The $ArCO_2Cu(PPh_3)_2$ complexes were refluxed with dimethoxyethane (DME) and the solutions then cooled to give white needles of a new product (m.p. $12-193^\circ C$ with gas release). The IR spectrum showed that the Ar groups bonded to the copper atom had disappeared, while the 1H NMR spectrum showed signals only in the triphenylphosphine region. The product did not release CO_2 on treatment with 6 *N* H_2SO_4 , but gave 1 mole of CO_2 per copper atom on pyrolysis at $200^\circ C$, leaving PPh_3 and metallic copper as the main solid products. It was as first thought that a compound similar to $Cu_2(CO_2)(PPh_3)_4$ [7] had been obtained, and it was, therefore, decided to determine its structure by X-ray diffraction. While this analysis was in progress, it was discovered that the compound was actually $HCO_2Cu(PPh_3)_2$, formed because of $HCHO/HCOOH$ impurities present in the DME used, which had been dried and deaerated without taking particular care in purifying it. $HCO_2Cu(PPh_3)_2$ is a known complex [8], which was recently obtained also by Beguin et al. [17] by inserting CO_2 into the $-Cu$ bond of $[HCuPPh_3]_6$; however, it is appropriate to report its structure since there is little published structural information for complexes of this type.

Structure of $HCO_2Cu(PPh_3)_2$

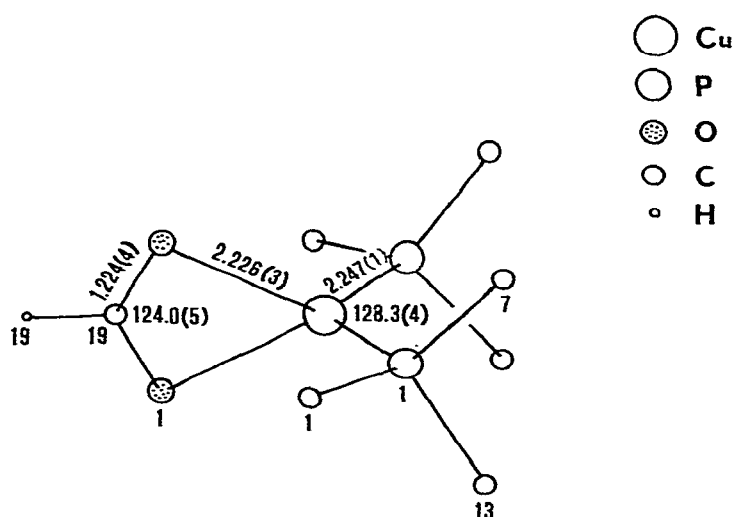
Crystal data: $C_{37}H_{31}CuO_2P_2$, $M = 633.1$, monoclinic, space group C_2/c (from

TABLE 3

ATOMIC FRACTIONAL COORDINATES ($\times 10^4$) FOR THE $\text{HCO}_2\text{Cu}(\text{PPh}_3)_2$ COMPLEX

Atom	x	y	z
Cu	0000	999(0)	2500
P(1)	913(0)	-78(1)	3024(1)
O(1)	4(1)	3138(3)	3201(2)
C(1)	1548(1)	1146(3)	3234(2)
C(2)	1534(1)	2542(4)	3589(3)
C(3)	2018(2)	3509(4)	3795(3)
C(4)	2509(2)	3087(5)	3656(3)
C(5)	2527(2)	1706(5)	3305(3)
C(6)	2046(1)	722(4)	3087(3)
C(7)	913(1)	-1382(3)	2128(2)
C(8)	803(2)	-841(4)	1218(2)
C(9)	721(2)	-1791(4)	466(2)
C(10)	743(2)	-3294(4)	6135(3)
C(11)	853(2)	-3844(4)	1509(3)
C(12)	942(2)	-2890(3)	2266(2)
C(13)	1174(1)	-1170(3)	4130(2)
C(14)	746(1)	-1894(4)	4334(2)
C(15)	922(2)	-2735(4)	5166(3)
C(16)	1524(2)	-2841(4)	5802(3)
C(17)	1952(2)	-2118(4)	5616(3)
C(18)	1783(1)	-1279(4)	4788(2)
C(19)	0000	3770(5)	2500
H(19)	0000	4893	2500

final refinement), a 24.582(9), b 9.100(5), c 15.469(7) Å, β 116.1(1)°, U 3106.3 Å³, D_m = 1.38, Z = 4, $F(000)$ = 1312, D_c = 1.35 g cm⁻³, μ_r (Mo- K_α) = 0.17, λ = 0.7107 Å. Cell parameters were determined from Weissenberg and precession photographs and refined with an on-line automatic single crystal

Fig. 2. A perspective drawing of complex $\text{HCO}_2\text{Cu}(\text{PPh}_3)_2$ showing the atom-numbering scheme.

Siemens diffractometer. A total of 1719 independent reflexions, having $I_o > 3\sigma(I_o)$ and $\theta \leq 27^\circ$ were collected using Mo- K_α radiation and corrected for Lorentz and polarization effects. No correction for absorption was applied. The structure was solved by the heavy-atom method. The final anisotropic least-squares refinement, including the contribution of hydrogen atoms, held constant, gave $R = 0.029$. Final coordinates are listed in Table 3. Calculated coordinates of the hydrogen atoms, observed and calculated structure factors and anisotropic temperature factors are available from the authors. Fig. 2 shows a view of the $\text{HCO}_2\text{Cu}(\text{PPh}_3)_2$ complex, with the bond distances and angles of interest. The copper atom is located on the two-fold crystallographic C_2 symmetry axis, so that the PPh_3 groups and the formiato group appear symmetrically arranged around the two-fold axis. The HCOO^- group is bonded to the metal through the oxygen atoms, acting as bidentate ligand ($\text{Cu}-\text{O}(1)$ 2.226(3) Å). The $\text{Cu}-\text{P}$ distances (2.247(1) Å) fall within the range characteristic of the presence of two copper-phosphorus bonds on the same Cu(1) atom [18].

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