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The Stepwise Interaction of [(phen)(Ph_3P)Cu(O_2COH)] with Pyrazoles and CO_2: Synthesis and Reactivity of Copper(I) Pyrazolecarboxylates

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Abstract

Reactions between [(phen)(Ph_3P)Cu(O_2COH)] (A, phen = 1,10-phenanthroline) and 3,5-dimethylpyrazole (pzH) or pyrazole (PzH) in acetone afford the insoluble copper(I) pyrazolates $[Cu(pz)]_n$ or $[Cu(Pz)]_n$ and red solutions. The action of CO_2 on these suspensions at low temperature yields new copper(I) pyrazolecarboxylates of formula [(phen)(Ph_3P)Cu(O_2Cpz)(H_2O)] (**1a**) or [(phen)(Ph_3P)Cu(O_2CPz)(H_2O)] (**1b**) respectively. When heated at 80 °C under vacuum as solid, **1a** gives [(phen)(Ph_3P)Cu(pz)] (**2**). The latter can be also obtained by N_2 bubbling at 0 °C through suspensions of **1a**. At higher temperatures the decarboxylation reaction of **1a** is accompanied by the loss of phen and PPh_3, $[Cu(pz)]_n$ being recovered as the final product. By stirring an acetone suspension of **1a** under a CO_2 atmosphere, free pzH and an orange product analysing as [(phen)(Ph_3P)Cu(O_2COH)] (**3**) were isolated. Complex **3**, although having the same stoichiometry as A, was shown to exhibit spectroscopic and some chemical properties quite different from those of A. The action of pzH under an inert atmosphere on **3** (molar ratio pzH/**3** = 1), allowed the isolation of **1a**, without carbon dioxide evolution.

Excess phen on polymeric $[Cu(pz)]_n$ causes the formation of $[(phen)Cu(pz)]_2$ (**4**), probably containing a bridging pyrazolate group. The latter has been reacted with CO_2 in the presence of pzH (molar ratio pzH/**4** > 1) obtaining the pyrazolecarboxylato complex **5**, [(phen)(pzH)Cu(O_2Cpz)]. The neutral pyrazole ligand present in **5**, weakly bound to the metal center, can be easily displaced by triphenylphosphine, with formation of **1a**, or by cyclohexylisocyanide. In the latter case, displacement of both pzH and phen has been observed, and the new pyrazolyl complex **6** $[(CyNC)Cu(pz)]_2$, formed.

Gas volumetric and thermogravimetric measurements and IR spectra are reported and discussed. A plausible mechanism by which complexes **1** are formed, is also reported.

Introduction

The reactions of CO_2 with metal amides, [M(NR_2)], to provide metallocarbamates, [M(O_2CNR_2)], have been studied in considerable detail, mainly in the case of the early transition metal amides [1]. In general, these reactions do not involve activation of CO_2 by prior coordination to the metal center [2], the formation of the carbamate products proceeding by the interaction of the carbamic acid and the amide [1]. Research on the coordination chemistry of pyrazole and pyrazole-derived ligands has received growing interest in recent years [3]. In particular, pyrazoledithiocarboxylates of transition metals have been reported [4, 5]. They are obtained by reacting potassium pyrazoledithiocarboxylates, $pzCS_2K$, (prepared from potassium pyrazolides, pzK and carbon disulphide) with transition metal ions. Potassium pyrazolides readily form 1:1 adducts with CO_2, ArNCO, RNCNR. The CO_2 adduct, $pzCO_2K$, stable in the solid state, extrudes CO_2 upon reaction with transition metal ions, yielding metal pyrazolate derivatives [4].

In a series of studies involving the reactivity of the hydrogen–carbonate–copper(I) complex, [(phen)(Ph_3P)Cu(O_2COH)] (A, phen = 1,10-phenanthroline) [6], we have found that its stepwise reactions with pyrazole (PzH) or 3,5-dimethyl-pyrazole (pzH) and CO_2 occur quite readily. In this paper we report the synthesis, characterization, and the reactivity of some copper(I) pyrazolecarboxylate complexes. These products represent, to our knowledge, the first example of pyrazolecarboxylate groups stabilized through coordination on a transition metal.

Results and Discussion

The hydrogen–carbonate–copper(I) complex, [(phen)(Ph_3P)Cu(O_2COH)] (A), reacts, as expected, with mineral and organic acids leading to a large series of copper(I) derivatives having halides or carboxylato groups as the anions [6a]. Similarly, A reacts with phenol under an inert atmosphere, giving the copper(I)–phenoxo complex [(phen)(Ph_3P)Cu(OPh)]

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$$\begin{tikzcd}
 & {[\mathrm{Cu(pz)}]_n \overset{\text{(i)}}{\rightleftharpoons} [\mathrm{(phen)(Ph_3P)Cu(pz)}]} \arrow[dl, "\text{(ii)}"'] \arrow[dr, "\text{(iii)}"] & \\
{\underset{\textbf{A}}{[\mathrm{(phen)(Ph_3P)Cu(O_2COH)}] + \mathrm{pzH}}} & & {\underset{\textbf{1a}}{[\mathrm{(phen)(Ph_3P)Cu(O_2Cpz)(H_2O)}] + \mathrm{pzH}}}
\end{tikzcd}$$

(i) phen, PPh_3; (ii) CO_2/H_2O (H_2CO_3); (iii) $CO_2(H_2O)$/pzH ($pzCO_2H$).

Scheme 1.

[6b]. Reactions were also observed when **A** was treated with activated alkanes in the absence or in the presence of CO_2 [6c].

A reacts under an inert atmosphere with 3,5-dimethyl-pyrazole (pzH) or pyrazole (PzH) at 50 °C, carbon dioxide being evolved, eqn. (1) (reaction (i))

$$\begin{tikzcd}
\mathbf{A} + \mathrm{pzH} \arrow[r, "\text{(i) } N_2/50\ ^\circ C"] & {[\mathrm{Cu(pz)}]_n + \text{red solution}} \arrow[d, "\text{(ii) } CO_2/0\ ^\circ C"] \\
 & {\underset{\textbf{1a}}{[\mathrm{(phen)(Ph_3P)Cu(O_2Cpz)(H_2O)}]}}
\end{tikzcd} \qquad (1)$$

From reaction (i) the already known $[Cu(pz)]_n$ [7a] as an insoluble white product and a red solution were obtained. Analogously, when reaction (i) is carried out by using pyrazole (PzH), the polymeric white derivative $[Cu(Pz)]_n$ [7b] together with a red solution formed. By bubbling CO_2 at 0 °C through the suspension obtained as in reaction (i), the formation of an insoluble yellow product **1a**, was observed, eqn. (1) (reaction (ii)).

A molar ratio pzH/**A** $\geqslant 3$ was shown to be essential in order to isolate **1a** in an analytically pure form; if reaction (ii) was carried out with an initial lower pzH/**A** molar ratio, the starting complex **A** was recovered. When pyrazole was used instead of 3,5-dimethyl-pyrazole, the corresponding yellow product **1b** was obtained. Reactions (i) and (ii) were carried out in acetone but the same course was observed if toluene was used.

To the yellow products **1a** and **1b**, which were shown to be diamagnetic, formulations as pyrazolecarboxylate derivatives are assigned on the basis of their elemental analyses, IR spectra and reactivity.

Complexes **1a** and **1b** are stable enough in the solid state at room temperature and at atmospheric pressure, but they were shown to be rather unstable even in suspension (see later), thus preventing NMR measurements and molecular weight determinations. Because of this, we gave up any attempt to prepare single crystals for X-ray crystallographic studies.

Thermogravimetric measurements carried out on **1a** always gave graphs having two distinct steps for the CO_2 loss. This behaviour could be explained by supposing that in a first stage one mole CO_2 per two moles Cu is lost with concomitant formation of a dimeric species; the latter should be responsible for the second CO_2 loss. Moreover, repeated quantitative gas volumetric analyses confirmed for **1a** a molar ratio $CO_2/Cu = 1$. On the other hand, oxygen analyses always gave a molar ratio $O/Cu = 3$, thus suggesting the presence of one mole H_2O per mole Cu, although the IR spectra of complexes **1a** and **1b** (see later) did not show unambiguous bands assignable to ν(OH). The hydrogen–carbonate–copper(I) complex **A** gave $[Cu(pz)]_n$ (reaction (i)) in 93% yield, thus suggesting that in the red solution a copper-containing product is present which most probably should be the reactive species towards CO_2 (reaction (ii)).

In Scheme 1 a plausible mechanism for the formation of the pyrazolecarboxylate complex **1a** is reported. The fact that the overall reaction leading to **1a** (eqn. (1)) requires excess pyrazole, is tentatively related to the essential formation, in solution, of the free pyrazole–carboxylic acid, pzCOOH. The latter will react with the copper-containing species present in the red solution (reaction (i), eqn. (1)). Although not definitively, we put forward the hypothesis that this species is the orange pyrazolyl complex $[(phen)(Ph_3P)Cu(pz)]$. In fact, this product, obtained by us as will be described later (complex **2**), when added to an acetone solution of 3,5-Me_2pyrazole, previously saturated with CO_2, gave **1a** quantitatively. On the basis of this, one could suggest that the insoluble $[Cu(pz)]_n$ should gradually convert into $[(phen)(Ph_3P)Cu(pz)]$ by reacting with free phen and PPh_3, formed in the course of reaction (i). However, it has been verified that no evident reactions occurred when $[Cu(pz)]_n$ was reacted: (1) with phen and PPh_3 in the absence of CO_2; (2) with phen, PPh_3 and pzH again in the absence of CO_2. It is to be pointed out that this lack of reactions is in agreement with the chemical behaviour of the pyrazolato complex $[(phen)(Ph_3P)Cu(pz)]$ (**2**) (see later). Thus the concomitant presence of CO_2 was shown to be essential in order to involve the polymeric $[Cu(pz)]_n$ in subsequent reactions. In fact, by reacting an acetone suspension of $[Cu(pz)]_n$ with phen, PPh_3, pzH and CO_2 at 0 °C, the formation of **1a** was observed (see 'Experimental'). Moreover, $[Cu(pz)]_n$ gave the hydrogen–carbonato–copper(I) complex **A** when reacted with phen and PPh_3 in the presence of CO_2 (reaction (ii), Scheme 1). These results seem to confirm that, in the absence of CO_2, the equilibrium $[Cu(pz)]_n \rightleftharpoons [(phen)(Ph_3P)Cu(pz)]$ (Scheme 1) is strongly shifted towards the left side. Finally, the mode by which pzH reacts with **A** (reaction (i), eqn. (1)) ruled out the alternative possibility that in reaction (iii) (Scheme 1) complex **A** is the intermediate species leading to **1a** in the presence of pzH.

Reactions of 1a

Complex **1a** completely loses CO_2 in the solid state at 80 °C under vacuum (10^{-2} Torr), producing an orange compound which does not show in its IR spectrum bands assignable to the carboxylate group and which analyses as $[(phen)(Ph_3P)Cu(pz)]$ (**2**) eqn. (2) (reaction (i))

$$\begin{tikzcd}
 & {\underset{\mathbf{2}}{[(phen)(Ph_3P)Cu(pz)]} + CO_2 + H_2O} \arrow[d, "(iii)"] \\
\mathbf{1a} \arrow[ur, "(i)"] \arrow[dr, "(ii)"'] & \\
 & {[Cu(pz)]_n + phen + PPh_3 + CO_2 + H_2O}
\end{tikzcd} \qquad (2)$$

(i) 80 °C (10^{-2} Torr) as solid or by N_2 bubbling through suspensions having a high **1a**/acetone ratio; (ii) 120 °C (10^{-2} Torr) as solid or by N_2 bubbling through suspensions having low **1a**/acetone ratios; (iii) 120 °C (10^{-2} Torr) as solid or by stirring suspensions having a low **2**/acetone ratio.

If **1a** is heated under vacuum as solid at 120 °C, complex **2** cannot be isolated, $[Cu(pz)]_n$ being recovered as the only copper-containing final product, and the concomitant release of both phen and PPh_3 was verified (eqn. (2), reaction (ii)). On the other hand the pyrazolate complex **2** gives place to $[Cu(pz)]_n$ when heated at 120 °C (10^{-2} Torr) as solid.

The pyrazolecarboxylate complex **1a**, when in suspension, gives place to $[(phen)(Ph_3P)Cu(pz)]$ (**2**) or to $[Cu(pz)]_n$ depending on the experimental conditions (eqn. (2), reaction (iii)). In fact, complex **2** can be obtained only if low temperatures and high ratios **1a**/solvent are used (eqn. (2), reaction (i)). Low ratios **1a**/solvent allowed the isolation of only $[Cu(pz)]_n$ in 91% yield (eqn. (2)), reaction (ii)). By stirring acetone suspensions of **2**, the fast formation of the polymeric $[Cu(pz)]_n$ has been observed (eqn. (2), reaction (iii)).

The formation of the already known copper(I) pyrazolate $[Cu(pz)]_n$ [7a] from **1a** is accompanied by a red solution, in which the presence of a copper-containing species again seems a plausible hypothesis.

In view of the rarity of five-coordinate copper(I) complexes, two alternative structures can be proposed for complex **2**: (1) a pyrazolyl derivative having a monodentate pyrazolato group with 1,10-phenanthroline acting as a bidentate ligand, (2) a pyrazolyl derivative containing a bridging pz^- group and a monodentate phenanthroline. Complexes containing monodentate pyrazolato groups, although not numerous, are known [8]. On the other hand, 1,10-phenanthroline, which has been verified in most cases to behave as a bidentate ligand, can act, although much less frequently, as a monodentate ligand at least in the solid state [9]. On the basis of its spectroscopic properties (see later), we formulate complex **2** as containing a monodentate pyrazolato group.

The action of water on **1a** readily gives place to the formation of the starting complex **A**, free pzH being released, eqn. (3)

$$\begin{tikzcd}
 & \mathbf{A} \\
\underset{\mathbf{1a}}{[(phen)(Ph_3P)Cu(O_2Cpz)(H_2O)]} \arrow[ur, "H_2O"] \arrow[dr, "CO_2"'] & \\
 & \text{orange product} + pzH
\end{tikzcd} \qquad (3)$$

When a well dried acetone suspension of **1a** was stirred under a CO_2 atmosphere, the formation of free pzH and of an orange insoluble product was observed (eqn. (3)). The IR spectrum of this orange material (see later) and its elemental analyses confirmed the absence of the pyrazolate group. Moreover, this product was shown to be rather stable under vacuum at 80 °C as solid. On the basis of analytical and IR data and on its reactivity, we assign to this complex a formulation containing a hydrogen–carbonate group, $[(phen)(Ph_3P)Cu(O_2COH)]$ (**3**).

Owing to its rather low solubility in the common organic solvents, no NMR data could be obtained. Repeated molecular weight measurements in methanol always gave low values with respect to that of the monomeric species.

Complex **3**, although having the same composition as **A**, exhibits spectroscopic and some chemical properties quite different from those of **A**. The existence of more than one type of hydrogen–carbonate–copper(I) complex with the same composition, $[(Ph_3P)_2Cu(O_2COH)]$, has already been observed and the presence of different associated species has been postulated [10]. The plausible structure of **3** will be discussed below. It is to be pointed out that complex **3** reacts with pzH under nitrogen, even with a molar ratio pzH/**3** = 1, giving again the pyrazolecarboxylato derivative **1a** without decarboxylation. It is noteworthy that the already reported complex **A**, when treated with pzH under the same molar ratio pzH/**A** = 1, leads to the formation of $[Cu(pz)]_n$ with CO_2 evolution, as described above (eqn. (1), reaction (i)).

Moreover, complex **3**, when reacted with CyNC (Cy = cyclohexyl), gives place to the already reported ionic copper(I) complex, $[(phen)Cu(CyNC)_2](HCO_3)$, as does **A** [6a]. The latter reaction confirms the nature of **3** as containing a HCO_3^- group. As regards the role of CO_2 in the $\mathbf{1a} \rightarrow \mathbf{3}$ conversion, one can presume that carbon dioxide works in order to prevent the decarboxylation of the starting **1a** (see eqn. (3)). The subsequent stoichiometric hydrolysis (one mole H_2O per mole Cu is present in **1a**) leads to the formation of **3**.

Pyrazolecarboxylate Complexes from $[Cu(pz)]_n$

By reacting the polymeric $[Cu(pz)]_n$ [7a] with excess 1,10-phenanthroline, the pyrazolato derivative $[(phen)Cu(pz)]_n$ (**4**) is quantitatively isolated. Complex **4** was shown to be much more stable than **2** when heated under vacuum as solid; even at 120 °C it was recovered unchanged. Its spectroscopic properties and chemical behaviour seem to suggest a dimeric structure for **4** with bridging pyrazolato groups and phen behaving as a bidentate ligand.

Complex **4** reacts with CO_2 in the presence of pzH (molar ratio $pzH/\mathbf{4} > 1$) giving the brick-red pyrazolecarboxylato derivative **5**, eqn. (4)

$$\underset{\mathbf{4}}{[(phen)Cu(pz)]_n} \xrightleftharpoons[80\ ^{\circ}C/10^{-2}\ Torr]{CO_2/pzH} \underset{\mathbf{5}}{[(phen)(pzH)Cu(O_2Cpz)]} \qquad (4)$$

Analytical, IR data and its reactivity support the formulation assigned to complex **5**. By heating at 80 °C under vacuum in the solid state, the pyrazolecarboxylato complex **5** restores **4** quantitatively, CO_2 and pzH being released, (eqn. (4)).

The neutral pyrazole ligand pzH of **5** being weakly bound to the metal center, is easily displaced by neutral ligands such as PPh_3 and CyCN. Triphenylphosphine, when reacted with **5**, gives place to $[(phen)(Ph_3P)Cu(O_2Cpz)(H_2O)]$ (**1a**) (see 'Experimental').

Cyclohexylisocyanide causes the displacement of both pzH and phen, and the new pyrazolato derivative **6**, $[(CyNC)Cu(pz)]_2$ formed. The latter, when heated at 140 °C under vacuum as solid, gave the polymeric $[Cu(pz)]_n$ quantitatively.

Preliminary results on the structure of complex **6**, determined by X-ray diffraction, confirmed the presence of bridging pyrazolato groups in dimeric molecules.

Mass Spectra of Complexes $[Cu(pz)]_n$, 2, 4 and 6

Preliminary results on the EI mass spectra of the new pyrazolate complexes **2**, **4** and **6** and of $[Cu(pz)]_n$ show the presence, as the species having the highest nuclearity, of the trimer $[Cu(pz)]_3$, whereas the CI mass spectra of complexes **2** and **6** showed the presence, as the species having the highest nuclearity, of the hexamer $[Cu(pz)]_6$.

Infrared Spectra

The presence in complex **1a** of a coordinated 3,5-Me_2-pyrazolecarboxylato group is also supported by its IR spectrum. In fact, taking into account that the IR spectrum of sodium 3,5-Me_2-pyrazolecarboxylate, $pzCO_2Na$, exhibits two strong bands at 1685 and 1450 cm^{-1} which can be assigned to the $\nu_{as}(CO_2)$ and $\nu_s(CO_2)$ stretchings respectively, and that the IR spectrum of the related $pz^{13}CO_2Na$ (absorptions at 1630 and 1340 cm^{-1}) confirmed the above attributions, for complex **1a** we can assign the bands which appear in its IR spectrum at 1579 and 1350 cm^{-1} to the $\nu_{as}(CO_2)$ and $\nu_s(CO_2)$ stretching vibrations respectively (Fig. 1). It is to be pointed out that the IR spectrum of **1a** always showed the presence of an unexpected band at 1620 cm^{-1}. It could be attributed to a $\nu_{as}(CO_2)$ vibration, but repeated elemental analyses confirmed the presence in **1a** of only one $pzCO_2^-$ per copper atom. Moreover, the IR spectrum of **1a** exhibits solely the splitting of the $\nu_{as}(CO_2)$ band, while the $\nu_s(CO_2)$ absorption is not splitted. On the other hand, the IR spectrum of the related pyrazolecarboxylato complex $[(phen)(Ph_3P)Cu(O_2CPz)(H_2O)]$ (**1b**) did not show the splitting of the $\nu_{as}(CO_2)$ band ($\nu_{as}(CO_2) = 1615$ cm^{-1}, $\nu_s(CO_2) = 1385$ cm^{-1}). This fact seems to support the hypothe-

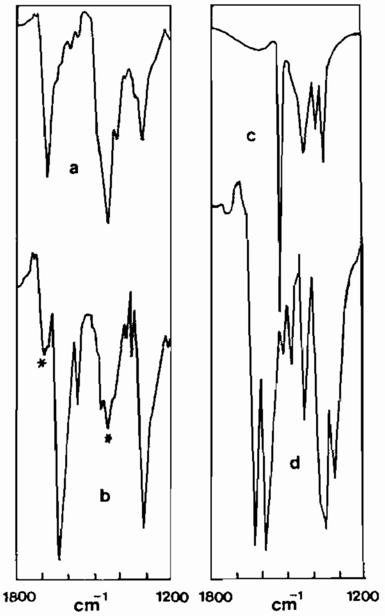

Fig. 1. IR spectra (1800–1200 cm^{-1} region) of powdered solid samples spread on NaCl disks. (a) $pzCO_2Na$; (b) $pz^{13}CO_2Na$ (bands signed * are due to a $pzCO_2Na$ impurity); (c) $[Cu(pz)]_n$; (d) $[(phen)(Ph_3P)Cu(O_2Cpz)(H_2O)]$ (**1a**) (pz = 3,5-Me_2pyrazolate, $C_5H_7N_2$).

TABLE 1. Analytical Data

Compound[a]	Colour	Melting point (°C)	Found (calc.) (%)		
			C	H	N
1a [(phen)(Ph_3P)Cu(O_2Cpz)(H_2O)] [b]	yellow	92(dec)	65.06 (65.21)	4.94 (4.83)	8.32 (8.45)
2 [(phen)(Ph_3P)Cu(pz)] [c]	orange	139	69.53 (69.94)	4.96 (5.00)	9.42 (9.33)
3 [(phen)(Ph_3P)Cu(O_2COH)] [d]	orange	167	65.73 (65.67)	4.38 (4.24)	5.06 (4.94)
4 $[(phen)Cu(pz)]_n$	violet	186	59.88 (60.27)	4.51 (4.43)	16.53 (16.54)
5 [(phen)(pzH)Cu(O_2Cpz)]	brick-red	65(dec)	58.16 (57.68)	4.63 (4.81)	17.61 (17.55)
6 $[(CyNC)Cu(pz)]_2$	white	232(dec)	53.93 (53.83)	6.85 (6.73)	15.63 (15.70)

[a] pz = 3,5-dimethyl-pyrazolato, $C_5H_7N_2$; phen = 1,10-phenanthroline. [b] O, 7.18; (7.25); Cu, 9.42 (9.59); P, 4.46 (4.68). [c] Cu, 11.00 (10.57). [d] O, 8.41 (8.47); complex **3**, although having the same composition as **A**, exhibits different spectroscopic and chemical behaviour (see text).

sis that for complex **1a**, in the solid state, two types of molecules exist; these, though having the same number of coordinative bonds, exhibit different geometries or merely different geometric distortions with respect to a tetrahedral geometry, as a consequence of packing steric effects.

By comparing the $\Delta\nu(\nu_{as}(CO_2) - \nu_s(CO_2))$ of 3,5-Me_2pzCO_2Na, **1a**, **1b** and **5**, the following values are found: 3,5-Me_2pzCO_2Na, $\Delta\nu = 235$ cm^{-1}; **1a**, $\Delta\nu = 229$ cm^{-1}; **1b**, $\Delta\nu = 230$ cm^{-1}; **5**, $\Delta\nu = 230$ cm^{-1}. Therefore, the $\Delta\nu$ are practically irrespective of the fact that the free and the coordinated pyrazolecarboxylato anion is considered. This behaviour could be explained supposing the presence in **1a**, **1b** and **5** of a bidentate pyrazolecarboxylato group, analogously to what has been observed in the case of carboxylato complexes [11]. An alternative hypothesis is the presence of a monodentate pyrazolecarboxylato group in which the oxygen of the C=O is involved in a hydrogen bond with the water molecule (complexes **1a** and **1b**) or with the NH of the pzH ligand (complex **5**). This situation has already been found in some carboxylato complexes of transition metals containing coordinated water molecules [12].

Figure 2 reports the $\nu_{as}(CO_2)$ and $\nu_s(CO_2)$ absorptions for the hydrogen–carbonate complexes **A** and **3**, which display different colours and chemical properties, as has been pointed out. The overall infrared spectrum of **A** has already been discussed [6a]. In the 1800–1000 cm^{-1} region the IR spectra of the two products do not exhibit marked differences. Nevertheless, complex **A** and **3** show interesting differences in their IR spectra, when the 900–600 cm^{-1} region is considered (Fig. 3). In this range phen γ(CH) bands [13] and PPh_3 γ(CH) and ϕ(CC) bands [14] are found. By comparing the IR spectra of **A** and **3**, one can realize that the latter exhibits more phen γ(CH) vibrations with respect to the IR spectrum of **A**. This fact suggests that the phen ligand appears in complex **3** with a number of symmetry operations lower than in complex **A**. This difference can be tentatively related with the presence of a bidentate phen in **A** and with a monodentate phen in **3**. It is noteworthy that, as phen γ(CH) vibrations are concerned, the IR spectra of complex **A** and of [(phen)(Ph_3P)CuCl] in the 900–600 cm^{-1} region are nearly identical (Fig. 3). On the basis of its spectroscopic properties and on its reactivity, we assume that in complex **3** the hydrogen–carbonate group acts as a bidentate ligand on the metal center.

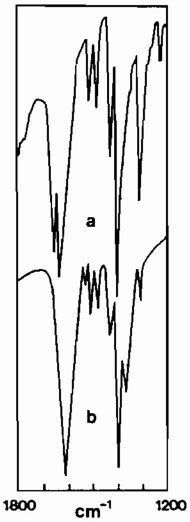

Fig. 2. IR spectra (1800–1200 cm^{-1} region) of powdered solid samples spread on NaCl disks. (a) [(phen)(Ph_3P)Cu(O_2COH)] (**A**); (b) [(phen)(Ph_3P)Cu(O_2COH)] (**3**).

Finally, the IR spectra of complexes **2** and of [(phen)(Ph_3P)CuCl] being similar in the 900–600 cm^{-1} region, we suppose that, among the two possibilities (monodentate phen or monodentate pyrazolato), complex **2** represents an example of a monodentate pyrazolato derivative. Its chemical behaviour seems to support this hypothesis. A bidentate phen also seems to be present in complex **1a**, as its IR spectrum in the 900–600 cm^{-1} region appears very similar to that of **2**.

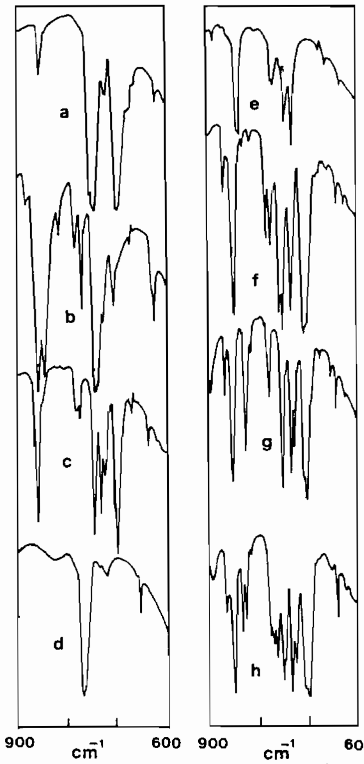

Fig. 3. IR spectra (900–600 cm^{-1} region) of powdered solid samples spread on NaCl disks. (a) PPh_3; (b) phen; (c) [(phen)(Ph_3P)CuCl]; (d) $[Cu(pz)]_n$; (e) $[(phen)Cu(pz)]_n$ (4); (f) [(phen)(Ph_3P)Cu(pz)] (2); (g) [(phen)(Ph_3P)Cu(O_2COH)] (A); (h) [(phen)(Ph_3P)Cu(O_2COH)] (3).

Experimental

Pyrazole (PzH) and 3,5-dimethyl-pyrazole (pzH) were reagent grade quality and were used without further purification. Solvents were purified and dried by standard methods. [(phen)(Ph_3P)Cu(O_2COH)] (**A**) was obtained as already described [6a]. All reactions were carried out under an inert atmosphere, unless noted otherwise. Infrared spectra were obtained by using a Perkin-Elmer Mod. 783 spectrometer.

Reaction of [(phen)(Ph_3P)Cu(O_2COH)] A with PzH and pzH

To an acetone solution (10 ml) of pyrazole (PzH) (1.59 mmol), **A** (0.53 mmol) was added under stirring. The yellow suspension was heated to 50 °C, carbon dioxide being evolved while an insoluble white product and a red solution formed. The insoluble white material was shown to be the already known polymeric copper(I) complex $[Cu(Pz)]_n$ [7b], by means of elemental analyses and its IR spectrum which was identical to that of an authentic sample. $[Cu(Pz)]_n$ was obtained in 93% yield. For the nature of the copper(I) species present in the red solution, see 'Results and Discussion'. No reaction occurred when **A** and PzH were reacted at room temperature, even by using the above molar ratio PzH/**A**.

Analogous results were achieved when **A** was reacted with 3,5-dimethyl-pyrazole (pzH) under the same experimental conditions. $[Cu(pz)]_n$ was recovered as the white insoluble material.

Stepwise Interaction of A with Pyrazoles and CO_2

The acetone suspensions, obtained as described above, were cooled at 0 °C and maintained for 4 h under a carbon dioxide atmosphere. The colour of the suspended solid gradually changed from white to yellow. It was recovered by filtration under a CO_2 atmosphere, washed with acetone (previously saturated with CO_2) and dried at atmospheric pressure. **1a** and **1b** were obtained in an 88% yield (based on **A**). When pyrazoles PzH and pzH were reacted with **A** by using a molar ratio PzH/**A** or pzH/**A** lower than 3, the subsequent reaction with carbon dioxide at 0 °C always gave the starting hydrogen–carbonate–copper(I) complex **A**.

Thermogravimetric determinations, carried out on **1a** or **1b**, always gave diagrams which showed two distinct steps assignable to the loss of two CO_2 units.

1a has been directly obtained by reacting an acetone suspension of $[Cu(pz)]_n$ with phen·H_2O, PPh_3 and pzH (molar ratio Cu:phen:PPh_3:pzH = 1:1:1:3) under a CO_2 atmosphere at 0 °C. 1,10-Phenanthroline must be added as the final ligand in order to obtain **1a** by this route.

Reactions of 1a

(1) **1a**, maintained at 80 °C in the solid state under vacuum (10^{-2} Torr) for 8 h, gave the orange product **2**, [(phen)(Ph_3P)Cu(pz)].

(2) Complex **2** was again the product obtained when dinitrogen was bubbled through an acetone suspension (3 ml) of **1a** (0.1 g), maintained at 0 °C. When more solvent was used, the polymeric $[Cu(pz)]_n$ (91% yield) was recovered. Complex **2** shows in its IR spectrum significant bands at 1515(w), 1100(s), 840(s), 750(s), 730(s) and 700(s) cm^{-1}.

(3) **1a** (0.2 g) was suspended in acetone (5 ml) at 30 °C under a CO_2 atmosphere. The colour of the suspended solid rapidly changed from yellow to orange. After 4 h the orange complex **3** was filtered off, washed with acetone and dried under vacuum. The mother liquor was shown to contain free 3,5-Me_2pzH.

(4) **1a** (0.170 g) was suspended in acetone (10 ml) containing 3 drops of water. After 0.5 h stirring, the formation of the hydrogen–carbonate–copper(I) complex **A** was observed, while the presence of free pzH in the reaction medium was verified.

Reaction of 2 with CO_2

(a) In the presence of H_2O. To acetone containing water, maintained under a CO_2 atmosphere, **2** was

added. A fast reaction takes place and a yellow insoluble product formed. It was recognised to be the hydrogen–carbonate copper(I) derivative **A**, while the mother liquor showed the presence of free pzH.

(b) In the presence of pzH. To an acetone solution (10 ml) of pzH (0.4 mmol) containing water (0.2 mmol), maintained under a CO_2 atmosphere, **2** (0.2 mmol) was added with stirring. A fast reaction takes place and the yellow pyrazolecarboxylato complex **1a** was recovered by filtration.

Reaction of [Cu(pz)]$_n$ with 1,10-Phenanthroline

[Cu(pz)]$_n$ (1.26 mmol) was suspended in acetone (10 ml) and phen·H_2O (6.30 mmol) was added under stirring at room temperature. After 5 h the violet complex **4**, [(phen)Cu(pz)]$_2$, (86% yield), was filtered off, washed with acetone and dried under vacuum. The same product **4** was obtained by heating **5** in the solid state at 80 °C under vacuum with concomitant elimination of pzH and CO_2.

Its IR spectrum shows bands at 1520(mw), 840(s) and 730(s) cm^{-1}.

Reaction of 3 with pzH

By adding **3** to an acetone solution of pzH (molar ratio 3/pzH = 1), at room temperature, the copper(I)–pyrazolecarboxylate (**1a**) was obtained.

Reaction of 4 with pzH and CO_2

By reacting **4** with an acetone solution of pzH (molar ratio pzH/4 > 2) under a CO_2 atmosphere for 2 h, the brick-red complex **5** was isolated.

The IR spectrum of **5** (voltalef oil mull) exhibits significant IR absorptions at 3250(m), 3194(m), 3094(m), 3027(m), 1610(vs), 1390(s), 1150(m), 840(s) and 730(s) cm^{-1}. The free pzH shows in its IR spectrum (4000–3000 cm^{-1}) bands at 3200(s), 3130(s), 3103(s) and 3040(s) cm^{-1}.

Reactions of 5 with PPh_3 and CyNC

(a) PPh_3. To an acetone solution of PPh_3 containing water (molar ratio PPh_3/H_2O = 1), **5** was added at room temperature (molar ratio PPh_3/**5** = 1). After 5 h **1a** was quantitatively obtained.

(b) CyNC. Complex **5** (0.68 mmol) was added to a diethyl ether solution of CyNC (0.3 ml). After 8 h the white product **6**, [(CyNC)Cu(pz)]$_2$, was recovered by filtration. The mother liquor showed the presence of phen and pzH.

The same complex **6** was obtained by directly reacting [Cu(pz)]$_n$ (0.3 g) with CyNC (0.6 ml) in degassed diethyl ether (5 ml). The IR spectrum of **6** shows bands at 2164(vs), 2131(sh) and 1520(mw) cm^{-1}.

Preparation of [Cu(pz)]$_n$

To an acetone solution (10 ml) of pzH (3.18 mmol), $[Cu(CH_3CN)_4]BF_4$ (1.59 mmol) was added under stirring at room temperature. To the colourless solution, triethylamine (0.5 ml) was slowly added. A white insoluble product formed. After 30 min it was filtered off, washed with acetone and diethyl ether and dried under vacuum.

Preparation of 3,5-Me_2pzCO_2Na

To a diethyl ether solution (10 ml) of pzH (5.21 mmol), Na (10.87 mmol) was added. When hydrogen evolution stopped (~1 h), the solution was recovered and maintained under a CO_2 atmosphere for 1 h. The insoluble white product was filtered off, washed with diethyl ether and dried at atmospheric pressure.

3,5-$Me_2pz^{13}CO_2Na$ was analogously prepared by using $^{13}CO_2$.

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