

C–C coupling of activated alkanes with carbon dioxide by [(phen)(Ph₃P)Cu(O₂COH)]

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(Received November 16th, 1987)

Abstract

The reactions of the bicarbonatocopper(I) complex, [(phen)(Ph₃P)Cu(O₂COH)] (**A**, phen = 1,10-phenanthroline), with activated alkanes CH₂(R)(R') (R = R' = CN; R = R' = COOEt; R = CN, R' = COOEt), in the presence and in the absence of carbon dioxide have been studied. Reaction of malonodinitrile with **A** under an inert atmosphere gives the organocopper complex, [(phen)(Ph₃P)Cu{CH(CN)₂}] (**1**), whereas in the presence of CO₂ C–C coupling occurs to give the carboxylated derivative [(phen)(Ph₃P)Cu{O₂CCH(CN)₂}] (**2**). Complex **2** can be obtained by bubbling CO₂ through solutions of **1**. Complex **1** is readily formed when dinitrogen is bubbled through suspensions of **2** or when **2** is kept under vacuum at room temperature. Ethyl cyanoacetate reacts with **A** under an inert atmosphere to give [(phen)(Ph₃P)Cu{OC(OEt)=CHCN}] (**3**), and in the presence of carbon dioxide to give [(phen)(Ph₃P)Cu{O₂CCH(CN)(COOEt)}] (**4**). The latter can be also obtained by the action of CO₂ on complex **3**.

The reaction of diethyl malonate with **A** gives the unexpected carboxylato complex [(phen)(Ph₃P)Cu{O₂CCH₂COOEt}] (**5**) under nitrogen or under a carbon dioxide. A possible mechanism for formation of **5** is discussed.

Introduction

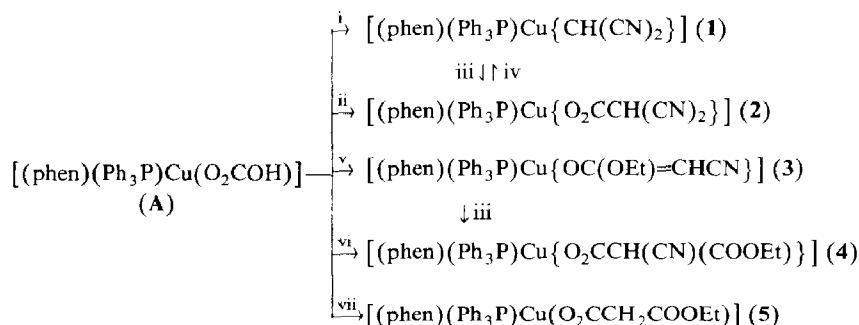
Insertions of small molecules (CO, CS₂, C₂H₄, etc.) into metal–carbon σ-bonds are key steps in a variety of important stoichiometric and catalytic chemical processes [1]. The reaction of carbon dioxide with σ-bonded organotransition metal compounds is also important in exploitation of CO₂ in the catalytic synthesis of organic molecules [2]. By analogy with the main group organometallic compounds, the anticipated products would be expected to be the corresponding mono- or bi-dentate carboxylates [2].

In extension of our studies on the reactions of the bicarbonatocopper(I) complex, [(phen)(Ph₃P)Cu(O₂COH)] (**A**, phen = 1,10-phenanthroline) [3], we have found that it

reacts readily with alkanes containing C–H bonds activated by electron-withdrawing substituents, both in the absence and in the presence of carbon dioxide. The results of the reactions are described below.

Results and discussion

The products of the reactions described here are shown in Scheme 1.



Scheme 1. i: $\text{CH}_2(\text{CN})_2$; ii: $\text{CO}_2/\text{CH}_2(\text{CN})_2$; iii: CO_2 ; iv: under vacuum at r.t. or by N_2 bubbling; v: $\text{CH}_2(\text{CN})(\text{COOEt})$; vi: $\text{CO}_2/\text{CH}_2(\text{CN})(\text{COOEt})$; vii: $\text{CH}_2(\text{COOEt})_2$ or $\text{CO}_2/\text{CH}_2(\text{COOEt})_2$.

The bicarbonatocopper(I) complex, [(phen)(Ph₃P)Cu(O₂COH)] (**A**) [3a], reacts, as expected, with mineral and organic acids HX (X = Cl, Br, I, RCOO) to give a large series of copper(I) derivatives having halides or carboxylato groups as the anions [3a]. Similarly, **A** reacts with phenol under N₂ to give the phenoxocopper(I) complex [(phen)(Ph₃P)Cu(OPh)] [3b]. Reactions were also observed when **A** was treated with activated alkanes in the absence or presence of carbon dioxide.

Reaction of **A** with $\text{CH}_2(\text{CN})_2$

A reacts with $\text{CH}_2(\text{CN})_2$ under N₂ at room temperature to give the metallated complex [(phen)(Ph₃P)Cu{CH(CN)₂}] (**1**) (Scheme 1, reaction i). The IR spectrum (Table 1) shows bands at 2180, 2130 and 2090 cm⁻¹ assigned to the nitrile vibrations. In the parent complex [(Ph₃P)₂Cu{CH(CN)₂}], obtained by treating the methylcopper(I) derivative [(Ph₃P)₂Cu(CH₃)] with malonodinitrile, the nitrile bands are reported to lie at 2150 and 2095 cm⁻¹ [4]. The ¹³C NMR spectrum of **1** in CD₂Cl₂ solution shows a signal at δ 137.8 ppm; that is assigned to the nitrile-C, but the signal due to the methyne-C could not be detected.

When **A** was treated with malonodinitrile and CO₂, the dicyanoacetatecopper(I) complex, [(phen)(Ph₃P)Cu{O₂CCH(CN)₂}] (**2**), was formed (Scheme 1, reaction ii). Conductivity measurements in nitrobenzene confirmed that **2** is a non-electrolyte. No ¹³C NMR data could be obtained for **2** owing to its too low solubility in the common organic solvents. Its IR spectrum (Table 1) has its C=O bands at the same frequencies as those reported for the ionic iridium complex [H₂Ir(PMe₃)₄]⁺[O₂CCH(CN)₂]⁻ (1612 and 1330 cm⁻¹), whose structure has been determined [5]. The latter, as a solid, was shown to contain the dicyanoacetate anion as an anionic carboxylic acid, (NC)₂C⁻-COOH, derived from a proton migration to the oxygen atom. On the basis of this, we tentatively assign to **2** a structure containing an unidentate dicyanoacetate group, (NC)₂CH-COOCu.

Table 1

Analytical and IR data ^a

Compound	M.p. (°C)	Analyses (Found (calcd.) (%))				IR significant bands (cm ⁻¹)
		C	H	N	O	
[(phen)(Ph ₃ P)Cu{CH(CN) ₂ }] (1)	165	69.55 (69.41)	4.30 (4.20)	9.67 (9.81)		2180m, 2130s, 2090sh, 1140m,
[(phen)(Ph ₃ P)Cu{O ₂ CCH(CN) ₂ }] (2)	145 (dec)	66.10 (66.39)	3.84 (3.90)	9.17 (9.11)	5.10 (5.20)	2200m, 2180s, 2130m, 1610s, 1320s, 1140m
[(phen)(Ph ₃ P)Cu{OC(OEt)=CHCN}]·C ₆ H ₆ (3)	127	70.84 (70.74)	5.02 (5.03)	6.14 (6.03)	4.52 (4.60)	2180s, 1610vs, 1140vs, 1040m
[(phen)(Ph ₃ P)Cu{O ₂ CCH(CN)(COOEt)}] (4)	128	65.07 (65.30)	4.35 (4.38)	6.48 (6.34)	9.62 (9.67)	2200s, 1690s, 1600s, 1320s
[(phen)(Ph ₃ P)Cu{O ₂ CCH ₂ COOEt}] ^b (5)	137	65.62 (65.98)	4.61 (4.71)	4.40 (4.39)	9.88 (10.05)	1720s, 1620s, 1340ms, 1280ms, 1230ms, 1140ms, 1030m

^a In Nujol mulls. ^b The IR spectrum of the potassium salt EtO₂CCH₂CO₂K shows significant bands at 1735s, 1600s, 1380ms, 1320m, 1235m, 1160ms and 1050m cm⁻¹.

Complexes **1** and **2** can be readily converted into one another (Scheme 1, reactions iii/iv). Thus, complex **2** can be also obtained by bubbling carbon dioxide through a solution of **1**, and **2** loses CO₂ when dinitrogen is bubbled through its suspensions at room temperature or when the solid is kept under vacuum at room temperature. This loss of CO₂ has been confirmed by thermogravimetric measurements. In the light of the above results, the possibility that formation of complex **2** from **1** proceeds by direct insertion of carbon dioxide into the copper-carbon bond cannot be ruled out.

Reaction of A with CH₂(CN)(COOEt)

Ethyl cyanoacetate reacts with **A** under N₂ to give [(phen)(Ph₃P)Cu{OC(OEt)=CHCN}] (**3**) (Scheme 1, reaction v). The alternative formulation of complex **3** as a metallated species, viz. [(phen)(Ph₃P)Cu{CH(CN)(COOEt)}] can be ruled out on the basis of its spectroscopic data. Thus the IR spectrum of **3** shows an absorption at 1610 cm⁻¹, which would be an unusually low value for a ν_{as}(C=O) band of a COOEt group. The position of this band remained unchanged for solutions, confirming that complex **3** retains its structure in solution. Furthermore, molecular weight measurements gave values that exclude possible intermolecular interactions involving the carbonyl group of the COOEt. Finally no bands assignable to the *sym* stretching of the ester were found. All these facts indicate that the IR band at 1610 cm⁻¹ is to be attributed to a C=C stretch. For the previously reported metallated complex, [(Ph₃P)₂Cu{CH(CN)(COOEt)}] [**4**], the ν_{as}(C=O) was found to lie at 1670 cm⁻¹. Further support for the formulation assigned to **3** comes from the observation that **A** reacts with the ketone C₆H₅SO₂CH₂COCH₃ to give [(phen)-(Ph₃P)Cu{OC(CH₃)=CHSO₂C₆H₅}], which shows a strong band at 1620 cm⁻¹ in its IR spectrum [6]. We assume that the formation of complex **3** involves reaction of ethyl cyanoacetate with **A** in its enolic form, HOC(OEt)=CHCN.

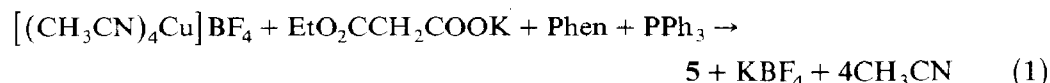
A reacts with $\text{CH}_2(\text{CN})(\text{COOEt})$ and carbon dioxide to give the carboxylato product, $[(\text{phen})(\text{Ph}_3\text{P})\text{Cu}\{\text{O}_2\text{CCH}(\text{CN})(\text{COOEt})\}]$ (**4**), (Scheme 1, reaction vi). The IR spectrum of **4** does have the $\nu_{\text{as}}(\text{C}=\text{O})$ band of the COOEt group in the expected region (Table 1).

Six resonances were present in the ^{13}C NMR spectrum of **4**, at 174.4, 171.3, 137.6, 77.4, 59.2 and 14.9 ppm; of these only the resonances at 137.6 and 14.9 ppm could be assigned unambiguously, to CN and CH_3 carbons, respectively.

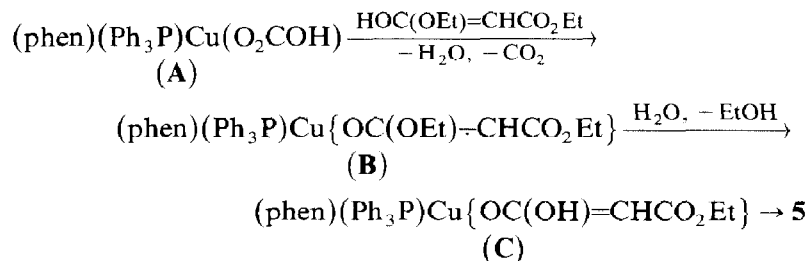
Complex **4** can be readily obtained from **3** by bubbling CO_2 through its solutions (Scheme 1). This carboxylation was shown to be irreversible. The formation of complex **4** appears thus to proceed by a route involving the carboxylato species $\text{O}_2\text{CCH}(\text{CN})(\text{COOEt})$, which is stabilized by coordination to the copper(I) center [7].

Reaction of **A** with $\text{CH}_2(\text{COOEt})_2$

Diethyl malonate reacts with **A** either under nitrogen or in the presence of carbon dioxide to give the unexpected *O*-metallated product $[(\text{phen})(\text{Ph}_3\text{P})\text{Cu}(\text{O}_2\text{CCH}_2\text{COOEt})]$ (**5**) (Scheme 1, reaction vii). The formation of complex **5** formally corresponds to dealkylation of the COOEt ester. Dealkylation reactions of COOR esters have been previously observed [8]. The IR spectrum of **5** (CH_2Cl_2 solution) shows significant strong bands at 1610 and 1730 cm^{-1} that can be assigned to the carbonyl asymmetric stretchings of the carboxylato and the ester moiety, respectively. The ^{13}C NMR spectrum of **5** shows signals at δ 171.4, 60.8 and 14.4 ppm that we tentatively assign to O_2C , OCH_2 and CH_3 carbons. Complex **5** has also been obtained by the alternative route shown in eq. 1 (see Experimental), and this conclusively confirms the formulation



Complex **5** reacts with EtBr to give $\text{CH}_2(\text{COOEt})_2$ as the only organic product. The mode of formation of **5** has been further investigated, and a possible mechanism of this reaction is as follows:



The diethylmalonate is assumed to react in the first step with **A** in its enolic form to give **B**, as it was suggested for the formation of **3**. Hydrolysis involving the COEt group of the *O*-bonded species **B** then takes place, and rearrangement of the product **C** to **5** represents the last step.

We were not able to isolate the intermediate derivatives **B** and **C**. GLC of the mother liquor from reaction vii, confirmed the presence of ethyl alcohol. The related ^{13}C -bicarbonatocopper(I) complex, $[(\text{phen})(\text{Ph}_3\text{P})\text{Cu}(\text{O}_2^{13}\text{COH})]$ was also used at the starting material, in reaction vii (Scheme 1): $^{13}\text{CO}_2$ was readily evolved, and the final product was shown to be identical to complex **5**.

It is noteworthy that the action of the alkyl halides RX ($R \neq Et$) on complex **5** allows stoichiometric formation of the mixed malonate esters, $RO_2CCH_2CO_2Et$, which are not readily prepared by the usual organic methods.

Experimental

Malonodinitrile, diethyl malonate and ethyl cyanoacetate were of reagent grade quality and were used without further purification. Solvents were purified and dried by standard methods. $[(phen)(Ph_3P)Cu(O_2COH)]$ was obtained as already described [3a]. IR spectra were recorded on a Perkin-Elmer Model 781 spectrometer. ^{13}C NMR spectra were recorded on a Bruker AC 200 multinuclear spectrometer.

$[(Phen)(Ph_3P)Cu\{CH(CN)_2\}]$ (**1**). To a stirred degassed toluene solution (10 ml) of triphenylphosphine (0.264 mmol), were added $[(phen)(Ph_3P)Cu(O_2COH)]$, complex **A**, (0.218 mmol), and $CH_2(CN)_2$ (0.348 mmol). After 2 h the yellow precipitate was filtered off, washed with toluene and diethyl ether, and dried in vacuo.

$[(Phen)(Ph_3P)Cu\{O_2CCH(CN)_2\}]$ (**2**). Method A. Carbon dioxide was bubbled through a toluene (10 ml) solution of triphenylphosphine (0.263 mmol), and $[(phen)(Ph_3P)Cu(O_2COH)]$ (0.217 mmol) and $CH_2(CN)_2$ (0.333 mmol) were added. After 2 h the yellow precipitate was filtered off, washed with toluene and diethyl ether previously saturated with CO_2 , then dried at atmospheric pressure under carbon dioxide.

Method B. CH_2Cl_2 (10 ml) was saturated with CO_2 and triphenylphosphine (0.176 mmol) and **1** (0.175 mmol) were then added. After 0.5 h the yellow product was filtered off under CO_2 , and dried at atmospheric pressure.

$[(Phen)(Ph_3P)Cu\{OC(OEt)=CHCN\}]$ C_6H_6 (**3**). To a stirred degassed benzene solution (10 ml) of triphenylphosphine (0.395 mmol) were added **A** (0.350 mmol) and $CH_2(CN)(COOEt)$ (20 drops). After 1 h the yellow product **3** was filtered off, washed with benzene and diethyl ether, and dried in vacuo.

$[(Phen)(Ph_3P)Cu\{O_2CCH(CN)(COOEt)\}]$ (**4**). Method A. Benzene (10 ml) was saturated with CO_2 and triphenylphosphine (0.395 mmol), $[(phen)(Ph_3P)Cu(O_2COH)]$ (0.350 mmol) and $CH_2(CN)_2$ (20 drops) were added and the CO_2 atmosphere was maintained. After 2 h the yellow product **4** was filtered off, washed with benzene and diethyl ether, and dried in vacuo.

Method B. Carbon dioxide was bubbled through a CH_2Cl_2 solution (10 ml) of triphenylphosphine (0.097 mmol) and **4** (0.078 mmol) was added. The solution turned from red to yellow. After 1 h it was evaporated to dryness and the residue was treated with diethyl ether, previously saturated with carbon dioxide. The yellow precipitate was shown to be **4**.

$[(Phen)(Ph_3P)Cu(O_2CCH_2COOEt)]$ (**5**). Method A. Benzene (5 ml) was degassed and $CH_2(COOEt)_2$ (30 drops), triphenylphosphine (0.198 mmol), and $[(phen)(Ph_3P)Cu(O_2COH)]$ (0.176 mmol) were added. Rapid CO_2 evolution was noted, and a red solution was formed. After 4 h the yellow precipitate of **5** was filtered off, washed with benzene and diethyl ether, and dried in vacuo. The mother liquor was shown by GLC to contain ethyl alcohol.

Complex **5** was again the product when the reaction of **A** with $CH_2(COOEt)_2$ was carried out under CO_2 .

Method B. To a stirred acetone suspension (15 ml) of $[(\text{CH}_3\text{CN})_4]\text{BF}_4$ (0.318 mmol) under N_2 was added $\text{EtO}_2\text{CCH}_2\text{CO}_2\text{K}$ (0.376 mmol). An orange solution formed, and after 30 min it was filtered under nitrogen to remove the excess of $\text{EtO}_2\text{CCH}_2\text{CO}_2\text{K}$ and the formed KBF_4 . To the filtrate was added PPh_3 (0.636 mmol), a colourless solution then being formed. After 15 min 1,10-phenanthroline (0.318 mmol) was added, and the solution became orange. After 10 min it was evaporated to dryness and the residue treated with degassed ethyl ether to leave the insoluble complex **5**.

Decarboxylation of 2. A CH_2Cl_2 solution (10 ml) of triphenylphosphine (0.164 mmol) was degassed with dinitrogen and **2** (0.163 mmol) was added as N_2 was bubbled through. After 15 min a solution was obtained and was evaporated to dryness. The residue was treated with diethyl ether, and the insoluble product shown to be complex **1**. Similar decarboxylation of **2** to give **1** was achieved by keeping solid **2** under vacuum (10^{-1} torr) at room temperature for 1 h. The reverse reaction did not occur in the solid state under carbon dioxide at atmospheric pressure.

Reaction of 3 with MeI. To a stirred benzene suspension (10 ml) of **3** (0.157 mmol) MeI (2 ml) under N_2 was added. After 2 h the orange precipitate was filtered off, and shown to be the known $[(\text{phen})(\text{Ph}_3\text{P})\text{CuI}]$ from elemental analyses and the IR spectrum. The mother liquor was shown to contain $\text{CH}_3\text{CH}(\text{CN})\text{COOEt}$.

Reaction of 5 with EtBr. This reaction was carried out as described above for reaction of **3** with MeI. The mother liquor was shown to contain $\text{CH}_2(\text{COOEt})_2$.

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