

axial positions on either side of the N-Ga-C₂ basal plane. As the O(1)-Ga(3)-O(4) bond angle is 157.2 (2)°, the coordination environment about Ga(3) may be described as distorted trigonal bipyramidal. It is interesting to note that the Ga(3)-N(1) bond distance of 2.024 (5) Å is noticeably shorter than the terminal Ga-N bond distances of 2.164 (5) and 2.171 (6) Å for Ga(1)-N(1) and Ga(2)-N(2), respectively. The Ga-O bond distances are 2.450 (5) and 2.278 (5) Å for Ga(3)-O(1) and Ga(3)-O(4), respectively. These Ga-O bond distances in the title compound are exceedingly long and, when compared to those in other organogallium-oxygen compounds,²³ must be considered among the longest reported. Furthermore, considering the great affinity that gallium has for oxygen, in addition to the fact that the aza crown contains twice as many oxygen atoms as nitrogen atoms, it is interesting to note that the trimethylgallium units preferred nitrogen over oxygen. The conformation of the crown in [Ga(CH₃)₂][C₁₂H₂₆N₂O₄][Ga(CH₃)₃]₂ is also noteworthy. The conformation of dibenzo-18-crown-6 in [Ga(CH₃)₃]₂[dibenzo-18-crown-6]²³ was observed to be exodentate. Indeed, the conformation of crown ethers is predominantly found to be exodentate in group 13 metal-crown ether complexes. However, the conformation of diaza-18-crown-6 in the title compound is determined to be endodentate. This may be regarded as a consequence of the stabilizing influence of the central dimethylgallium unit as well as N-H...O hydrogen bonding

present in the compound.³¹ From a comparison of other pentacoordinate organogallium moieties,^{24-26,32,33} it appears that trigonal bipyramidal is the preferred mode of coordination geometry. Forthcoming studies from this laboratory will further examine factors affecting the organometallic coordination chemistry of gallium.

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Registry No. [Ga(CH₃)₂][C₁₂H₂₆N₂O₄][Ga(CH₃)₃]₂, 126876-15-1; Ga(CH₃)₃, 1445-79-0; C₁₂H₂₆N₂O₄, 23978-55-4.

Supplementary Material Available: A summary of the data collection and refinement, plots of molecules, and tables of crystal data, bond distances and angles, final fractional coordinates, and thermal parameters (12 pages); a listing of observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

(31) Although not included in the model, hydrogen atoms placed in idealized positions for either the major (atom N(2)) or minor (atom N(1)) disorder component site are involved in bifurcated hydrogen bonding with atoms O(2) and O(3) of the major component or atoms O(1) and O(4) of the minor component. This interaction is characterized by N...O distances ranging from 2.85 to 2.90 Å, H...O distances ranging from 2.48 to 2.51 Å, N-H...O angles ranging from 104 to 107°, and O...H...O angles of 136°.

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Fully Regioselective Catalytic Carbonylation of Acrylic Derivatives: Synthesis of Methylmalonic Acid by Iron Pentacarbonyl Catalyzed Hydrocarboxylation of Acrylic Acid

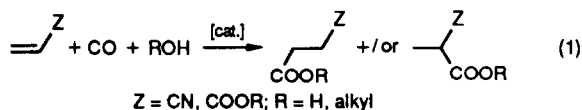
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Laboratoire de Chimie de Coordination du CNRS, Unité No. 8241 liée par conventions à l'Université Paul Sabatier et à l'Institut National Polytechnique, 205 route de Narbonne, 31077 Toulouse Cedex, France

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Summary: The catalytic, fully regioselective hydrocarboxylation of acrylic acid to methylmalonic acid is reported for the first time. This reaction, which involves Fe(CO)₅ as catalyst precursor in the presence of Ca(OH)₂ in a H₂O-iPrOH mixture as solvent, is brought about at 70 °C under atmospheric carbon monoxide pressure.

The catalytic oxacarbonylation of olefins with carbon monoxide and alcohols or water in the presence of transition metals has been known to occur since 1940.¹ Since that time, a great deal of work has been devoted to the designing of systems for the precise control of the regioselective oxacarbonylation of α-olefins.² However, acrylic derivatives (eq 1) have been given far less attention.



The hydroesterification of acrylonitrile in the presence of base-promoted cobalt catalyst systems can be selectively

(>92%) directed either to 2- or to 3-cyanopropionates by the appropriate choice of the base promoter and process conditions.³

In contrast, no catalytic oxacarbonylation of acrylates or acrylic acid at the α-position has been reported so far. In the case of ethyl acrylate, only cobalt-catalyzed reactions leading to diethyl succinate have been reported.^{4,5} Similarly, in the case of acrylic acid itself, only a nickel-catalyzed hydrocarboxylation to succinic acid has been known.⁶ No catalytic carbonylation to methylmalonic acid (MMA) or its derivatives has been reported so far.

Interestingly, however, Takegami et al.,⁷ and later Collman et al.,⁸ reported that the stoichiometric addition of NaHFe(CO)₄ to methyl acrylate, in THF, was highly regioselective, leading to an alkyltetracarbonylferrate (isolated as the PPN⁺ salt) with the iron moiety linked α to the methoxycarbonyl group. Both groups, however, observed that the addition was strongly inhibited by a

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Table I. Iron Pentacarbonyl Catalyzed Hydrocarboxylation of Acrylic Acid^a

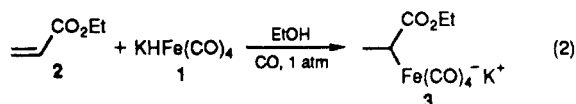
run no.	amt of AA, ^b mmol	base, ^c (amt, mmol)	amt of Fe(CO) ₅ , mmol	solvent (amt, mL)	cosolvent (amt, mL)	MMA rel to AA, ^b %	TON ^f
1	9.0	KOH (18.3)	1.44	H ₂ O (50)		66 ^d	4
2	9.3	KOH (39.8)	1.44	H ₂ O (50)		19 ^d	1
3	9.2	Ca(OH) ₂ (19.8)	1.44	H ₂ O (50)		66 ^d	4
4	9.2	Ca(OH) ₂ (20.1)	1.44	H ₂ O (40)	tBuOH (10)	78 ^d /(73) ^e	5
5	17.1	Ca(OH) ₂ (26.0)	1.44	H ₂ O (40)	tBuOH (10)	67 ^d	8
6	35.3	Ca(OH) ₂ (56.8)	0.76	H ₂ O (80)	tBuOH (20)	43 ^e	20
7	35.0	Ca(OH) ₂ (57.0)	0.76	H ₂ O (80)	iPrOH (20)	63 ^{d,g}	29

^a Reaction conducted for 48 h at 70 °C under CO (1 atm), 750 rpm. ^b AA = acrylic acid, MMA = methylmalonic acid. ^c Total amount of base used. ^d Determined by GLC analysis after esterification with diazomethane.²³ ^e Isolated yields. ^f Turnover number. ^g The only side reaction (formation of propionic acid) never exceeded 4–5% relative to the engaged AA.

carbon monoxide atmosphere, a discouraging situation for catalytic purposes. In contrast, the reaction of KHF₂(CO)₄ (1) with ethyl acrylate (2) in ethanol is not inhibited by a carbon monoxide atmosphere and appears also to be highly regioselective.⁹ Indeed, oxidation of the reaction medium by iodine leads to diethyl methylmalonate with a high selectivity.^{9,10} This oxidation step, however, precludes performing the reaction in a catalytic manner since the iron carbonyl species are simultaneously destroyed.¹⁰

During studies aimed at the development of the use of tetracarbonylhydridoferrates [M]⁺[HFe(CO)₄]⁻ in organic synthesis,^{10–16} we also explored the possibility for the use of these complexes for the catalytic oxacarbonylation of ethyl acrylate and acrylic acid at the α-position.

The case of ethyl acrylate was initially considered. We first confirmed that the reaction of ethanolic solutions of 1 with 2 under carbon monoxide (1 atm) gave the expected alkyltetracarbonylferrate 3 (eq 2), which is slowly protonated by ethanol (to give ethyl propionate)¹⁰ but could nevertheless be isolated as its PPN⁺ salt and characterized by NMR¹⁰ and X-ray diffraction studies.¹¹

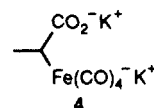


We then investigated the reaction of 2 with catalytic amounts of 1 in ethanol under carbon monoxide. However, only traces of diethyl methylmalonate could be observed under either atmospheric or higher (20 bar) carbon monoxide pressure.¹⁰

Thus, at least under the conditions used, 3 does not easily insert carbon monoxide. The reluctance of some alkyl ligands to migrate has been recently shown not to be connected with a strengthening of the metal–carbon bond but rather with an unfavorable charge distribution that reduces the possibility of nucleophilic attack of the alkyl group on a carbonyl ligand.¹⁷

Thus it appears that, in complex 3, the alkyl migration is difficult because of the presence of the electron-withdrawing carboxy group ($\sigma(\text{Hammett}) = +0.44$),¹⁸ which probably causes an unfavorable charge density on the first

carbon atom of the alkyl ligand. These considerations led us to explore the possible carbonylation of acrylic acid salts which, on reaction with KHF₂(CO)₄, could conceivably lead to the alkyltetracarbonylferrate complex 4.



In such a complex, the electron-withdrawing properties of the carboxylate group would be less unfavorable ($\sigma(\text{Hammett}) = +0.11$)¹⁸ and the alkyl migration could be expected to occur more easily.

The first experiments were conducted by reacting potassium acrylate (1.4 mmol) with equimolar quantities of 1 in water (50 mL) for 4 h at 70 °C under carbon monoxide (1 atm). Under these conditions, methylmalonic acid could be isolated in good yield¹⁹ without any oxidative treatment. These stoichiometric experiments confirmed our hypothesis because they showed that the carbon monoxide insertion does occur spontaneously under very mild conditions. As a result, catalytic experiments were explored and the main results are summarized in Table I.

The first experiments indicated that the reaction was potentially catalytic (410% / Fe for a possible maximum of 620%, run 1) and very reproducible, provided that the temperature was at least 70 °C. Furthermore, the regioselectivity was 100%, as no trace of succinic acid could be detected and only traces (<5%) of propionic acid were formed.

Investigations aimed at increasing the turnover number created a problem with the hydroxide ion concentration (run 2). Indeed, under high-pH conditions, HFe(CO)₄⁻ behaves as an acid ($\text{p}K_a = 12.7$)²⁰ to give the Fe(CO)₄²⁻ dianion, as confirmed by IR analysis. These observations led us to consider Ca(OH)₂ as a base, for it is only slightly soluble in water and gives a buffered solution at pH 12.6 (20 °C).²¹

As may be seen in Table I (run 3), the use of Ca(OH)₂ allows the reaction to reach a turnover number of 4, even when excess base is present in the reaction medium as an insoluble solid.

Some possible cosolvents were tested in order both to improve the contact between Fe(CO)₅ and the aqueous base during the formation of HFe(CO)₄⁻ and to increase the reaction rate. Among these, *tert*-butyl alcohol was selected and proved to have a beneficial effect (run 4).

Increasing the ratio of acrylic acid to Fe(CO)₅ resulted

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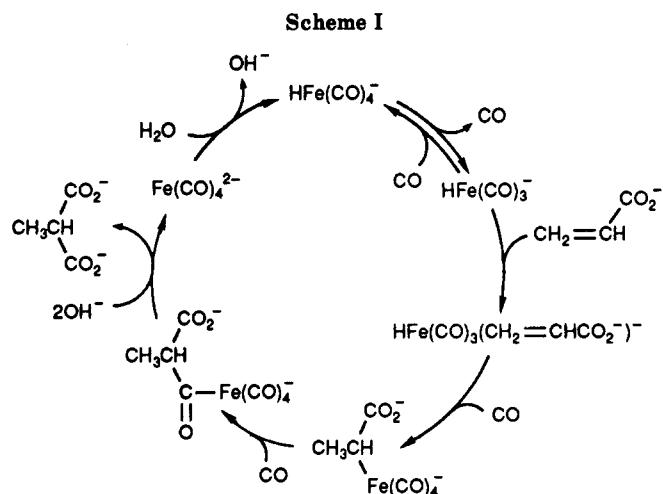
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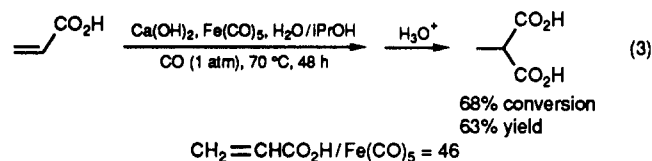
(19) Because of its high solubility in water, extraction of MMA from the acidified reaction medium can be performed in only 85% yield, as shown by separate experiments with commercial MMA under the same conditions.

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in an increase of the reaction rate (runs 5 and 6), which suggests that the acrylate moiety is involved in the rate-determining step of the reaction. Finally, *i*PrOH proved to be an even more efficient cosolvent than *t*BuOH (run 7, eq 3).



A simple catalytic scheme can be proposed (Scheme I) on the basis of the following observations.

(i) The reaction of eq 3 was quite inhibited when carried out under 20 bar of carbon monoxide pressure. This result

suggested that the dissociative process $\text{HFe(CO)}_4^- \rightarrow \text{HFe(CO)}_3^- + \text{CO}$, previously proposed by several authors, was occurring.^{7,8,22}

(ii) A stoichiometric reaction conducted on a 1.4-mmol potassium acrylate scale was monitored by quenching small aliquots with hydrochloric acid. The reaction never led to significant amounts of propionic acid (HPLC analysis), thus indicating that the concentration of the alkylferrate 4 was low throughout the reaction and that the rate-determining step is the formation of 4 from 1 and potassium acrylate. This hypothesis is supported by the fact that the reaction rate does depend on the acrylate concentration (*vide supra*).

(iii) Monitoring the reaction of eq 4 by IR analysis indicated that HFe(CO)_4^- was the only detectable iron carbonyl species and that its concentration was almost constant throughout the reaction.

In summary, we have found the first catalytic hydrocarboxylation of acrylic acid into methylmalonic acid. The full regioselectivity and the mildness of reaction conditions must be emphasized. Work is in progress to develop further applications of this catalytic system.

Acknowledgment. We wish to thank Rhône-Poulenc for a studentship to E.P. and for financial support. Fruitful discussions with P. Leconte, R. Perron, and L. Krumenacker are gratefully acknowledged.

Registry No. KHFe(CO)_4 , 17857-24-8; potassium acrylate, 10192-85-5; methylmalonic acid, 516-05-2; propionic acid, 79-09-4; iron pentacarbonyl, 13463-40-6; acrylic acid, 79-10-7.

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Oxidative Addition/Decarbonylation of α,ω -Alkanedioyl Dichlorides. Metallacycle Formation via Intramolecular Reductive Cyclization of a Pendant Acid Chloride with Samarium(II) Iodide

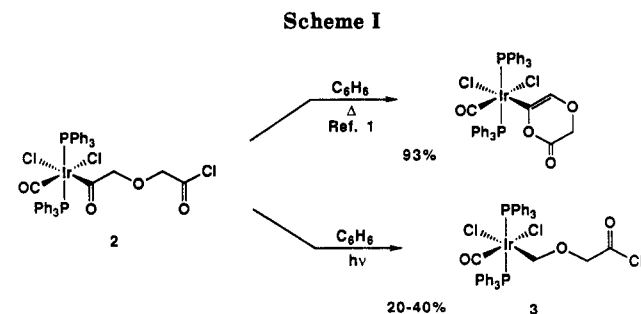
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Summary: Controlled oxidative addition and decarbonylation at one end of α,ω -alkanedioyl dichlorides is reported with $(\text{Ph}_3\text{P})_2\text{Ir}(\text{N}_2)\text{Cl}$, giving Ir(III) alkyl complexes bearing a pendant acid chloride functionality. The use of the di-nitrogen complex enables suppression of competitive intramolecular lactonization processes. Use of 2 equiv of samarium(II) diiodide uniquely promotes intramolecular reductive cyclometalation of one of these complexes, forming a cyclic acyl complex. This cyclization is highly sensitive to both electronic factors in the substrate and the nature and stoichiometry of the reducing agent.

We recently reported the controlled oxidative addition of one end of diglycolyl dichloride (1) to Vaska's complex, giving the monometalated acyl complex 2, free from competitive double metalation (Scheme I).¹ Decarbonylation



of this complex was anticipated to provide a substituted alkyl ligand bearing pendant acid chloride functionality, required as a precursor to novel oxygen-substituted metallacycle complexes. Attempted thermal decarbonylation of complex 2 instead resulted in an intramolecular cyclization of the pendant acid chloride onto the acyl functionality, giving an interesting but undesired metallo-enol lactone complex.² In this communication, we describe a

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