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Dinuclear μ -alkylidene complexes of transition metals as models for the transformation of CH_2X_2 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) into malonic acid derivatives by double carbonylation reactions

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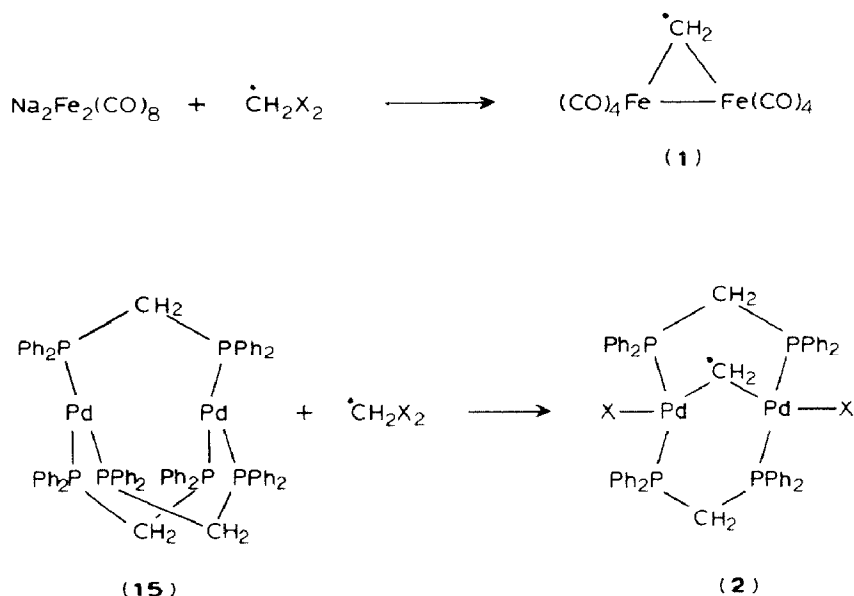
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Abstract

The carbonylation of the μ -alkylidene complexes $\text{Fe}_2(\text{CO})_8\text{CH}_2$ (**1**) and $\text{Pd}_2\text{I}_2(\text{PPh}_2\text{CH}_2\text{PPh}_2)_2\text{CH}_2$ (**2**) has been studied under a variety of conditions. In the presence of an alcohol ROH, complex **1** gives mainly the acetate $\text{CH}_3\text{CO}_2\text{R}$, the product of monocarbonylation, whereas under the same conditions complex **2** gives the malonate $\text{CH}_2(\text{CO}_2\text{R})_2$, the product of dicarbonylation. The mechanisms of both reactions are discussed. From the fraction involving **1** a mononuclear complex resulting from the dimerization of ketene has been isolated, and its structure established by an X-ray diffraction study. Olefins such as ethene and norbornene are able to trap the ketene intermediate. The possible participation of such μ -alkylidene complexes in the direct transformation of CH_2X_2 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) into malonic acid derivatives is discussed.

I. Introduction

The chemistry of mononuclear alkyl and alkylidene complexes of transition metals has been thoroughly studied. Their involvement in a large number of useful reactions is well documented [1]. This is not the case for μ -alkylidene complexes, in which one carbon atom bridges two metal centres, and only in recent years have they been made and studied. Interest in them lies mainly in the fact that such species have been suggested to be intermediates in reactions such as Fischer–Tropsch syntheses [2] olefin metathesis [3], and polymerisations [4].



Scheme 1

We describe here another, novel use of these dinuclear species, namely in carbonylation. In the presence of alcohols this leads, depending on the conditions and on the nature of the metal centres, either to acetates, the products of monocarbonylation, or to malonic acid derivatives, the products of dicarbonylation [5,6,7,8].

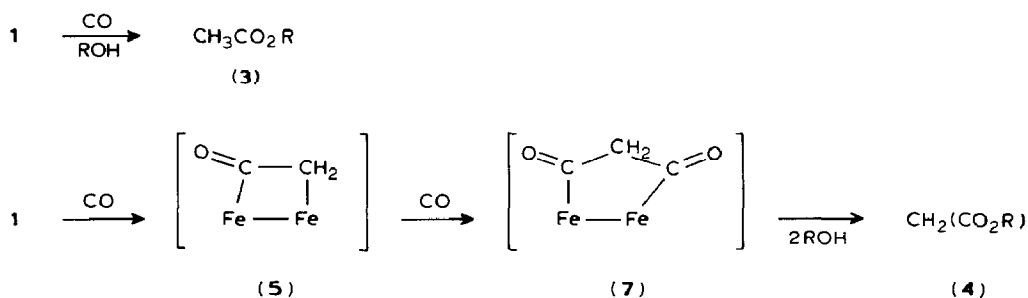
The reactions of two complexes of this type are described in this paper, namely a μ -methylene complex of iron, **1**, and a μ -methylene complex of palladium, **2**. The reasons for this choice are: (i) the two complexes are readily synthesized; (ii) Fe and Pd are involved in many carbonylation reactions; and (iii) the reactions through which these complexes are synthesized resemble the first step of some catalytic cycles. Thus, in the case of the iron complex, a substitution reaction of an anionic organometallic compound with dihalide gives the starting complex **1**, and in the case of palladium, an oxidative addition of CH_2X_2 to a Pd^0 complex leads to the A-frame derivative **2** (Scheme 1).

II. Results and discussion

A. Reaction of $\text{Fe}_2(\text{CO})_8\text{CH}_2$ with CO in the presence of alcohols

In the light of a report by Keim and his coworkers [5], who described the transformation of complex **1** into methyl acetate in a carbonylation/methanol solvolysis reaction (Scheme 2), we carried out carbonylations with the same complex but varying the nature of the alcohol. Thus, reaction of **1** under 40 atm of CO in toluene at 70°C in the presence of the more basic lauryl alcohol gave, in addition to the expected ester **3** (41% yield), malonate **4** in 3% yield.

The conversion of **1** into **4** corresponds formally to the insertion of one CO group into each C-Fe σ bond of the bridging carbene function, followed by a double solvolysis reaction (Scheme 2). In order to try to improve the malonate/acetate ratio, the CO pressure, the temperature of the reaction, the nature of the solvent,



Scheme 2

and the nature of the alcohol were varied and the effects of various additives examined.

(a) *Effect of the CO pressure and of the temperature.* Although complex 1 is only sparingly soluble at room temperature, in common solvents such as hexane and toluene, all reactions were carried out in such solvents since its stability in polar solvents such as tetrahydrofuran and acetone is very low.

As can be seen in Table 1, increase in the CO pressure (up to 90 atm) raises the total yield of the reaction, though the best yield is only ca. 50%; however, no effect on the selectivity towards malonate was observed. The rate of the reaction at a given pressure (40 atm at room temperature) increases when the temperature is raised from 50 to 70°C (Table 1), but there is a fall in the total yield at temperatures over 100°C, probably owing to thermal decomposition of complex 1. The optimum conditions (standard) are thus 40 atm at 70°C.

(b) *Influence of external ligands and of the nature of the nucleophiles.* It is known that the carbonylation of alkylmetal derivatives containing CO ligands can be

Table 1

Influence of temperature and CO pressure on the carbonylation/solvolytic reactions of $\text{Fe}_2(\text{CO})_8\text{CH}_2^a$ (Scheme 2)

$T(^{\circ}\text{C})$	$P(\text{CO})$ atm	Yield acetate (%)	Yield malonate (%)	Ratio malonate/acetate	Total yield	Time (h)
70	90	46	5	0.10	51	16
70	70	52	5	0.09	57	16
70	50	45	4	0.08	49	16
70	30	19	2	0.10	21	19
70	12	19	2	0.10	21	22
70	1	5	traces		5	37
50	40	34	2	0.05	36	66
60	40	41	3	0.07	44	4
80	40	33	2	0.07	35	5
120	40	19	1	0.05	20	4

^a Experimental conditions: $\text{Fe}_2\text{CH}_2(\text{CO})_8$ (5.7×10^{-4} mol) and $\text{CH}_3(\text{CH}_2)_{11}\text{OH}$ (11.4×10^{-4} mol) in hexane (70 ml) at 60°C.

Table 2

Influence of external ligands on the carbonylation/solvolytic reactions of $\text{Fe}_2(\text{CO})_8\text{CH}_2$ ^a (Scheme 2)

<i>P</i> (CO)	Ligand	Alcohol	Yield acetate (%)	Malonate (%)	Ratio malonate/acetate	Total yield (%)
	PMe_2Ph	Lauryl alcohol	26	3	0.1	29
	$(\text{Ph}_2\text{P})_2\text{CH}_2$	Lauryl alcohol	38	2	0.05	40
	PPh_3	Lauryl alcohol	21	1	0.03	22
	Et_3N	Lauryl alcohol	78	1	0.007	79
	$(\text{Me}_2\text{NCH}_2)_2$	Lauryl alcohol	71	1	0.01	72
	–	Lauryl alcohol	41	3	0.07	44
40	Et_3N	Lauryl alcohol	25	17	0.7	42
40	Bu_3N	Lauryl alcohol	28	10	0.36	38
40	PPh_3	Lauryl alcohol	16	1	0.06	17
40	PMe_2Ph	Lauryl alcohol	18	0.2	0.01	18
40	Et_2N	Decanol-4				
40	Et_3N	Triethylcarbinol	3	10 5	3.03	13 5
40	Et_3N	Butoxyethanol	57	11	0.2	68
40	Et_3N	Phenol	30	0	0	30

^a Experimental conditions: $\text{Fe}_2\text{CH}_2(\text{CO})_8$ (5.7×10^{-4} mol) and $\text{CH}_3(\text{CH}_2)_{11}\text{OH}$ (11.4×10^{-4} mol) in hexane (40 ml) with the ligand then added.

promoted, in the absence of CO, by additives such as amines and phosphines [9]. As can be seen in Table 2, this is also true in the present case, the yield of acetate being substantially increased when a tertiary amine was added to the mixture in a reaction at room temperature in the absence of CO.

Like tertiary amines, primary amines can induce the insertion of CO into the bridging carbon atom, the amine acts as a nucleophile to give the corresponding methylamide. No diamide resulting from a dicarbonylation reaction was observed.

A similar result was obtained when the reaction was carried out under 40 atm of CO, or when lauryl alcohol was added to the reaction mixture in the absence of CO. In the case of phosphines the yields of acetate are much lower. It should be noted that in the absence of CO, the yields of malonate are always low.

A complete change in the selectivity of malonate is observed when the carbonylation is carried out under the standard conditions, but in the presence of a tertiary amine (Table 2). The best results are observed in the case of Et_3N , the malonate/acetate ratio being 0.68, compared with 0.07 in the absence of an amine. Under these conditions, the nature of the alcohol is also important; as can be seen from Table 2, the presence of a secondary alcohol of moderate bulk, such as

4-decanol, raises the malonate/acetate ratio to 3.3, but lowers the total yield (13 vs. 79%), whereas more acidic alcohols, such as butoxyethanol and phenol, lower the ratio, phenol giving only the acetate.

B. Reaction of $Pd_2I_2(PPh_2CH_2PPh_2)_2CH_2$ with CO in the presence of alcohols

Use of palladium compounds in single carbonylation reactions is well documented [10,11,12]. Since double carbonylation reactions induced by this metal and leading to α -ketoesters or to α -ketoamides have recently been described [13], we decided to examine the carbonylation reactions of the dinuclear μ -alkylidene complex **2**. This complex, which was first described by Balch [14], is obtained by oxidative addition of CH_2X_2 ($X = I, Br, Cl$) to a dinuclear Pd^0 complex **15**. Dicarboxylation of complex **2** is thus of special interest in connection with the not fully solved problem of the mechanism of the direct transformation of CH_2Cl_2 into malonic acid derivatives [15].

(a) *Influence of the reaction conditions.* Unsuccessful attempts were made by Balch to insert CO into complex **2**, at low CO pressure and in the absence of nucleophiles [14]. We therefore used the conditions of carbonylation we had found to be best for complex **1**.

Complex **2** is only sparingly soluble in alkanes, but more soluble in aromatic and halogenated solvents. The carbonylations were again carried out at 70 °C under 40 atm of CO, in the presence of excess lauryl alcohol. Table 3 presents the results of these reactions. It can be seen that no carbonylation takes place in hexane, probably because of the lack of solubility of **2**. In CH_2Cl_2 , the acetate is the main product, and in toluene, an excellent selectivity towards malonate is observed (malonate/acetate 7.17). As far as the influence of the pressure is concerned, it can be seen that at low pressure (< 10 atm) the degree of conversion is very low, and that above 10 atm of CO, the reactivity of complex **2** and the selectivity towards malonate do not depend on the pressure. The reaction is slower than that of complex **1**, the maximum yield (50%) being observed only after 50 h. Longer reaction times lead to the formation of a third product, the dilauryl ether. In

Table 3

Influence of the reaction conditions on the carbonylation/solvolysis reactions of $Pd_2I_2(PPh_2CH_2PPh_2)_2CH_2$ ^a

Run	$P(CO)$ atm	Time (h)	Solvent	Yield acetate (%)	Yield malonate (%)	Ratio malonate/acetate	Total yield
1	1	20	toluene	4	6.5	1.6	10.5
2	10	20	toluene	11	27	2.45	38
3	20	20	toluene	12	26	2.16	38
4	40	20	toluene	9	25	2.77	34
5	60	20	toluene	9	22	2.44	31
6	85	20	toluene	6.5	25	3.8	31.5
7	40	50	hexane	0	0		0
8	40	50	dichloro-methane	80	15	0.18	95
9	40	50	toluene	6	43	7.17	49

^a Experimental conditions: $Pd_2I_2(PPh_2CH_2PPh_2)_2CH_2$ (2×10^{-4} mol) and $CH_3(CH_2)_{11}OH$ (4×10^{-4} mol) in the appropriate solvent (70 ml) at 70 °C, under CO (40 atm).

Table 4

Reactivity of PdI₂dppm and related Pd^{II} complexes with various solvents

Complex	Solvent	Yield acetate (%)	Yield malonate (%)	Ratio malonate/acetate
PdCl ₂ (PPh ₃) ₂ ^a	CH ₂ Cl ₂	84	2	0.02
		117	4	0.03
PdCl ₂ (PPh ₃) ₂ ^a	C ₆ H ₅ CH ₃	67	14	0.2
PdCl ₂ (PhCN) ₂ ^a	CH ₂ Cl ₂	17	6	0.3
PdCl ₂ (PhCN) ₂ ^a	C ₆ H ₅ CH ₃	9	3	0.3
PdCl ₂ (PPh ₃) ₂ ^b	CH ₂ Cl ₂	10	2	0.2
Pd ₂ dppm ₃ ^b	CH ₂ Cl ₂	4	2	0.2
PdI ₂ dppm ₃ ^a	C ₆ H ₅ CH ₃	34	2	0.06

^a Experimental conditions: L₂PdX₂ (2 × 10⁻⁴ mol), CH₂I₂ (10⁻³ mol), CH₃(CH₂)₁₁OH (2 × 10⁻³ mol), Et₃N (10⁻³ mol) in toluene (70 ml) at 70 °C, under CO (40 atm) for 21 h. ^b Similar conditions but without CH₂I₂.

addition to the organic products, PdI₂dppm was isolated in all cases, and it appears that a dismutation occurs during the carbonylation/solvolysis reaction.

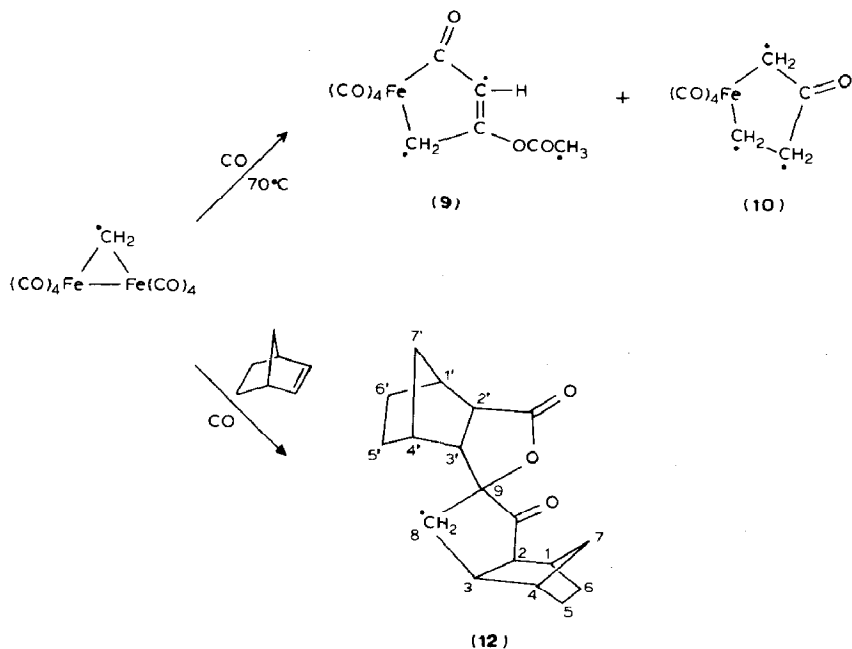
(b) *Reactivity of Pd^{II} complexes.* Since PdI₂dppm is formed during the carbonylation of complex **2**, we examined the behaviour of this complex and of other Pd^{II} complexes towards CH₂I₂ (or CH₂Cl₂), CO, and lauryl alcohol in the presence of Et₃N. Table 4 shows that Pd^{II} complexes mainly give the acetate, and that the malonate/acetate ratio depends on the nature of the ligand on the metal. Moreover, even CH₂Cl₂ can be carbonylated to give the acetate, though in low yield.

B. Reaction of complexes **1** and **2** with CO in the absence of nucleophiles

In order to try to detect intermediates in these mono- and di-carbonylation reactions, several reactions were carried out in the absence of nucleophiles. Complexes **1** and **2** were exposed to CO under our standard conditions, and the reaction was also carried out in the presence of reactive olefins that might interact with any CO mono- and di-insertion products.

(a) *Reaction of **1** with CO: detection of mononuclear derivatives of ketene.* After complex **1** in hexane had been kept under CO (40 atm) at 70 °C for 17 h two new complexes were isolated by silica gel chromatography. The faster moving product, obtained as pale yellow needles from hexane/dichloromethane (m.p. 69 °C, 2%), was identified as complex **9** (Scheme 3). The IR spectrum shows the presence of an iron carbonyl fragment ($\nu(\text{CO})$, 2100, 2040 cm⁻¹), an organic ester grouping ($\nu(\text{CO})$ 1775 cm⁻¹), and a conjugated ketone ($\nu(\text{CO})$ 1680 cm⁻¹). The mass spectrum ([M]⁺ at *m/z* 294) is consistent with a structure containing a Fe(CO)₄ group linked to a trimer of ketene.

The ¹H NMR spectrum shows three signals, at δ (6.06 ppm 1H, triplet, *J* 1.8 Hz), 2.55 (2H, doublet, *J* 1.8 Hz), and 2.26 (3H, singlet). The structure which agrees best with the spectroscopic data is the enol ester of a ferracyclopentanedione, **9**. This structure was confirmed by an X-ray study. An ORTEP view of the complex appears in Fig. 1, and shows that the four CO groups and the organic ligand are arranged around the iron centre to form a slightly distorted octahedron. The C(4)–Fe(1)–C(1) angle is smaller (81°) than the mean of the angles between the CO



Scheme 3

Table 5

Interatomic distances (Å) and bond angles for compound **9**: e.s.d.s in parentheses refer to the last significant digit

Fe(1)–C(11)	1.815(3)	C(1)–C(2)	1.471(4)
Fe(1)–C(12)	1.842(3)	C(2)–C(3)	1.327(4)
Fe(1)–C(13)	1.817(3)	C(2)–O(5)	1.391(3)
Fe(1)–C(14)	1.795(3)	C(3)–C(4)	1.457(4)
Fe(1)–C(1)	2.066(3)	C(4)–O(4)	1.201(3)
Fe(1)–C(4)	2.044(3)	O(5)–C(6)	1.351(4)
C(11)–O(11)	1.128(4)	C(6)–C(7)	1.478(5)
C(12)–O(12)	1.124(3)	C(6)–O(81)	1.223(8)
C(13)–O(13)	1.125(3)	C(6)–O(82)	1.211(6)
C(14)–O(14)	1.129(4)		
C(12)–Fe(1)–C(11)	95.8(1)	O(13)–C(13)–Fe(1)	177.9(3)
C(13)–Fe(1)–C(11)	93.9(1)	O(14)–C(14)–Fe(1)	177.2(3)
C(13)–Fe(1)–C(12)	97.5(1)	C(2)–C(1)–Fe(1)	107.4(2)
C(14)–Fe(1)–C(11)	164.6(1)	C(3)–C(2)–C(1)	122.5(3)
C(14)–Fe(1)–C(12)	96.2(1)	O(5)–C(2)–C(1)	110.8(3)
C(14)–Fe(1)–C(13)	94.2(1)	O(5)–C(2)–C(3)	126.8(3)
C(1)–Fe(1)–C(11)	85.8(1)	C(4)–C(3)–C(2)	114.6(3)
C(1)–Fe(1)–C(12)	88.5(1)	C(3)–C(4)–Fe(1)	112.4(2)
C(1)–Fe(1)–C(13)	174.0(1)	O(4)–C(4)–Fe(1)	124.2(2)
C(1)–Fe(1)–C(14)	84.8(1)	O(4)–C(4)–C(3)	123.4(3)
C(4)–Fe(1)–C(11)	83.8(1)	C(6)–O(5)–C(2)	124.6(3)
C(4)–Fe(1)–C(12)	171.6(1)	C(7)–C(6)–O(5)	110.4(4)
C(4)–Fe(1)–C(13)	90.9(1)	O(81)–C(6)–O(5)	121.7(5)
C(4)–Fe(1)–C(14)	82.9(1)	O(81)–C(6)–C(7)	121.6(5)
C(4)–Fe(1)–C(1)	83.1(1)	O(82)–C(6)–O(5)	120.8(4)
O(11)–C(11)–Fe(1)	177.5(3)	O(82)–C(6)–C(7)	125.7(4)
O(12)–C(12)–Fe(1)	177.2(3)		

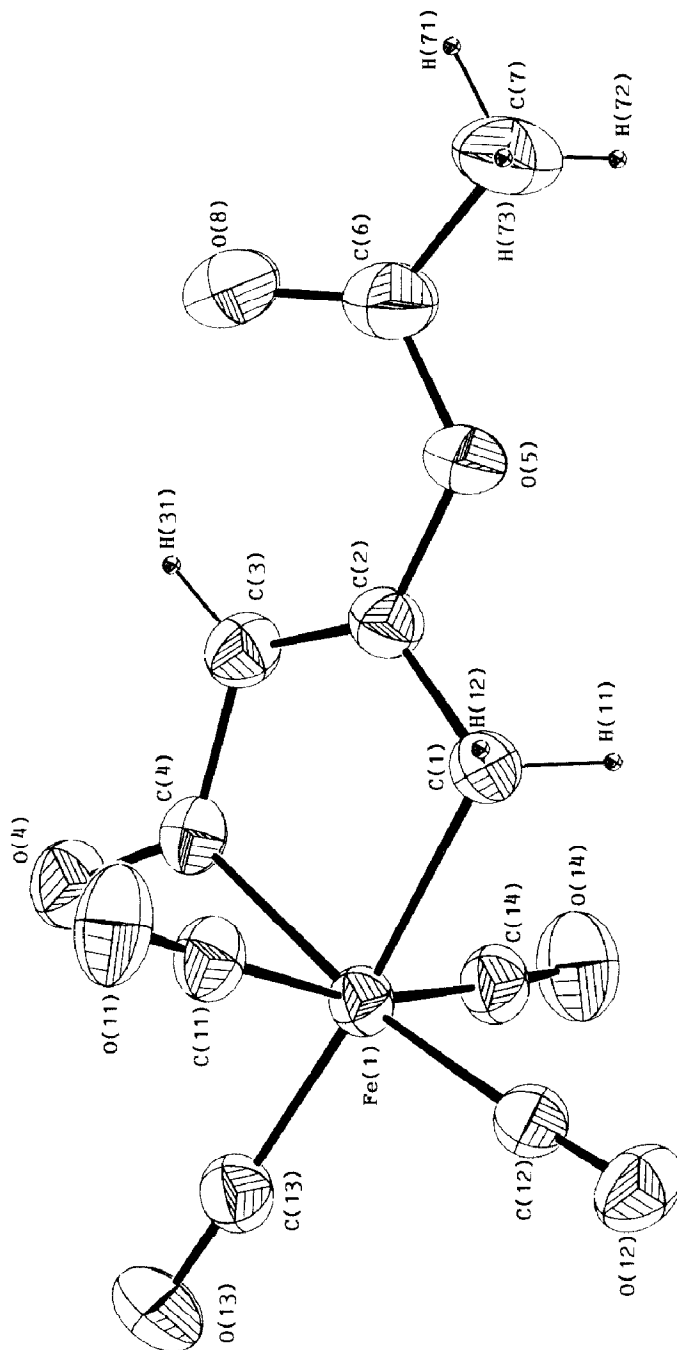


Fig. 1. ORTEP view of compound 9.

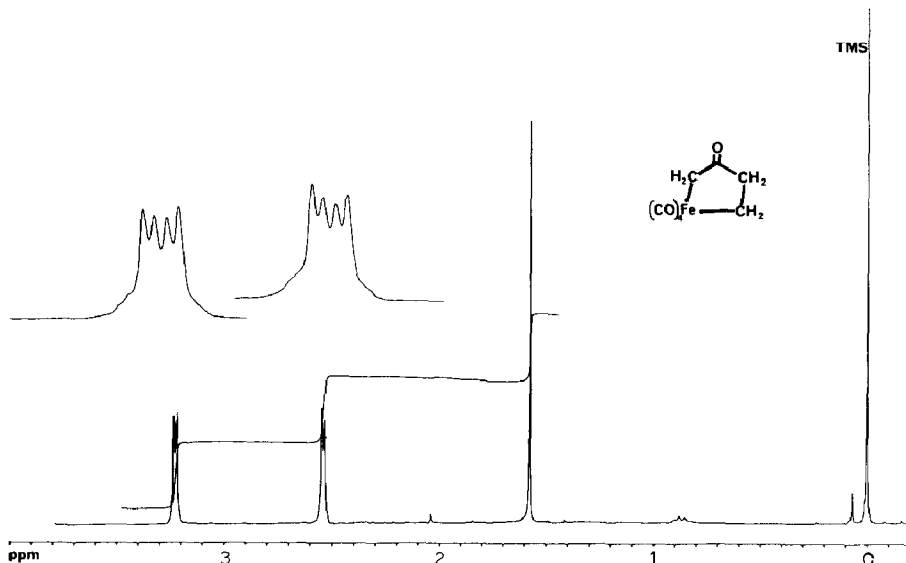


Fig. 2. ^1H NMR spectrum of compound **10**.

ligands (95°) as a result of the ring strain. The bond distances and bond angles are given in Table 5, and are consistent with literature data [16].

The second complex, obtained as white-yellowish needles (15% yield, m.p. 109°C), was tentatively assigned structure **10**. The infrared spectrum again reveals the presence of an iron carbonyl moiety ($\nu(\text{CO})$, 2065, 2005 and 1980 cm^{-1}) and an organic carbonyl group ($\nu(\text{CO})$, 1750 cm^{-1}), which can be identified as a cyclopentanone. The ^1H NMR spectrum (Fig. 2) is very simple. It shows three signals of equal intensity. Two of these signals are due to vicinal CH_2 groups at δ 3.23 and 2.54 (dd, J 3 and 1.5 Hz), whereas the third one corresponds to an isolated CH_2 group, at δ 1.57. Irradiation experiments confirmed the assignment. The mass spectrum ($[M]^+$ at m/z 238) is in agreement with the proposed structure **10**. The ^{13}C NMR spectrum shows signals at δ 214.4 (CO ketone), 209.7, 204.1 (CO's), 45.9, 21.2 and 21.1 (CH_2 's). Unfortunately, no crystals suitable for an X-ray analysis could be obtained.

(b) *Trapping of the acyl intermediate with norbornene.* It is known that acyl derivatives of mononuclear transition metal complexes can react with olefins to give insertion products, and we used this reaction to try to detect the products of CO insertion into **1**. Thus, reaction of **1** with CO under standard conditions, but in the presence of bicyclohept-2-ene (norbornene), gave two isomeric organic compounds in 40% yield. Repeated recrystallization of the mixture from $\text{CH}_2\text{Cl}_2/\text{EtOH}$ yielded one of the derivatives in a pure form.

This product (m.p. 198°C) shows no IR absorptions attributable to an iron carbonyl moiety. Absorptions at 1785 and 1750 cm^{-1} can be attributed to a γ -lactone and a cyclopentanone, respectively. The presence of these two groupings is confirmed by the ^{13}C NMR spectrum, in which signals appear at 177 and 214 ppm. The mass spectrum ($[M]^+$ at m/z 286), and the elemental analysis are in agreement with the incorporation of two norbornene units and three CO groups into the starting complex **1**.

The ^{13}C NMR spectrum shows 17 signals (18 s are expected); ^{13}C - ^1H correlation experiments allowed the assignment of all the signals and confirmed the presence of two overlapping signals at 28 ppm, the data being consistent with structure **12**. The assignments were further confirmed by the use of lanthanide shift reagent, complexation taking place preferentially at the ester carbonyl group.

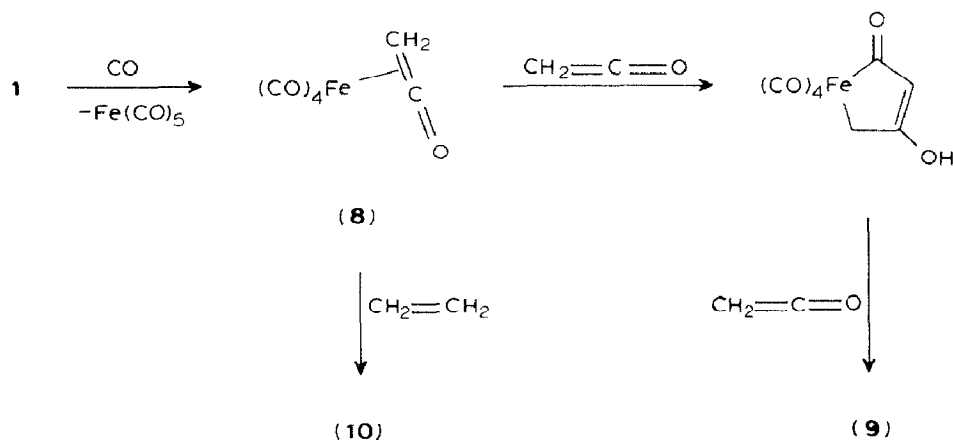
The values of the coupling constants between H(7) and H(2)-H(3), H(2')-H(3'), and H(2), H(3), indicate strongly that the purified compound is the *exo-exo* isomer.

C. Discussion

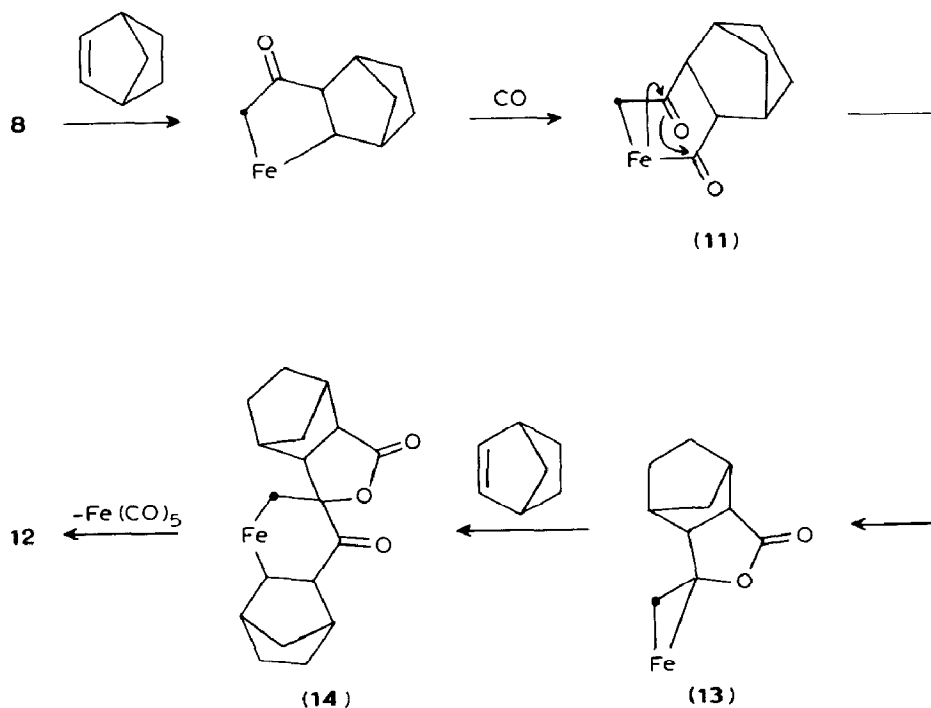
The most important observation is the difference in the nature of the reactions of **1** and **2** towards CO, both in the presence and in the absence of alcohols. In the case of complex **1**, the trapping experiments confirmed that the main reaction involves monoinsertion of CO, no products due to a double carbonylation, being detected. A common intermediate in all the reactions may be complex **8**, a cleavage product of the dinuclear complex. Thus, reaction of **8** with free ketene (from the decomposition of **8**) would give **9** via a dimer of ketene, whereas reaction of **8** with ethene (formed by dimerization of two CH_2 units of **1**) might give **10**. Such a reaction mechanism (Scheme 4) would be in agreement with results obtained by Pettit and coworkers, who observed the cleavage of the dinuclear framework by phosphines [17].

Such a mechanism could also operate for the reaction between **1** and norbornene (vide infra). In this case there is a sequential incorporation of the olefin and CO into-complex **1**. Such a process has already been observed in the case of acylmanganese derivatives [18,19], and more recently in the copolymerization of ethene and CO catalyzed by Pd complexes [20].

A mechanism, related to those operating with manganese derivatives is given in Scheme 5: successive insertions of norbornene and CO in complex **8** would give complexes **11**, **13** and **14**. An intramolecular nucleophilic attack by the carbonyl oxygen on the acyl carbon atom would then lead to the methylene lactone derivative **14**. Further insertions of CO and norbornene followed by a reductive coupling could then give the observed ketolactone **12**.



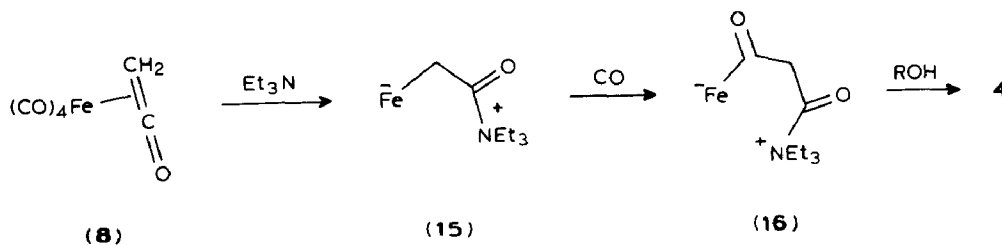
Scheme 4



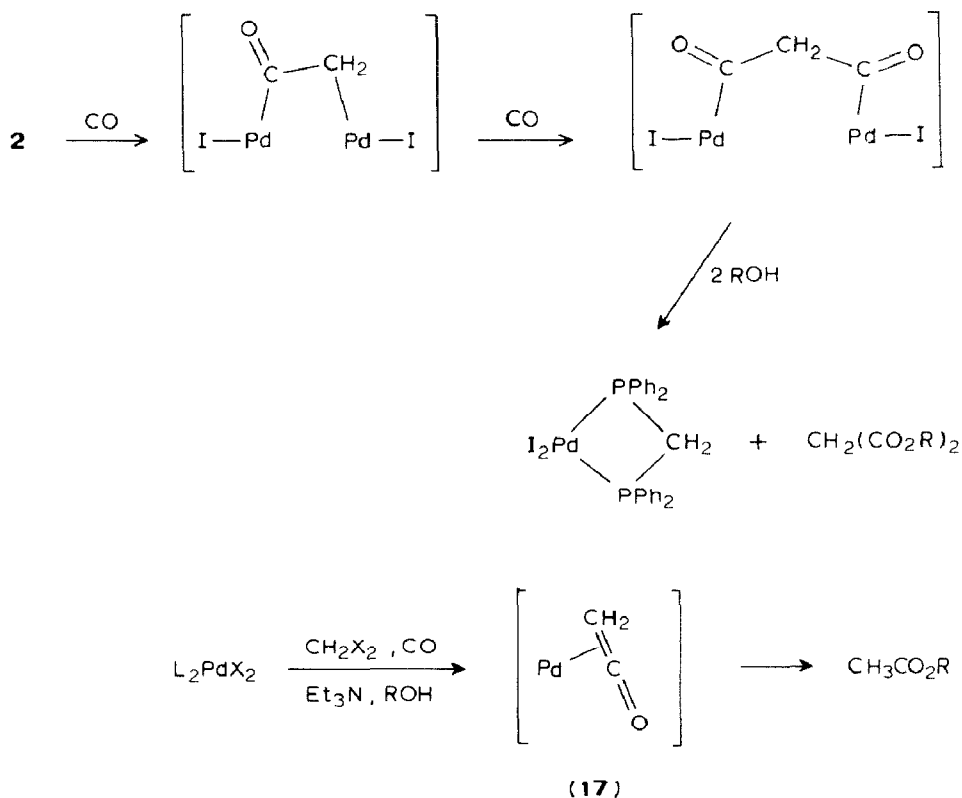
Scheme 5

As far as the reaction of **1** with CO and alcohols is concerned, the presence of a tertiary amine is essential for both the mono- and di-insertion reactions (Table 2). In the absence of CO, the presence of Et_3N favours the formation of the acetate. This type of influence on the insertion of CO into alkyl derivatives of transition metals is well known. In the present case, the role of the amine is two-fold to promote the formation of the ketene complex of the metal which contains a very reactive ketene carbonyl carbon and so could undergo nucleophilic attack to give a zwitterionic intermediate **15**. This suggestion is supported by the finding that secondary amines give amides even in the presence of alcohols. Intermediate **15** in turn could undergo a further CO insertion [21], and finally, by a double alcoholysis of **16**, give the malonate (Scheme 6).

It is evident that dinuclear species such as the dinuclear acyl complex of type **5** and a malonyl bridged **7** species of type **7** would lead to the same products after elimination of Fe(CO)_5 . Such species have indeed been reported [22,23,24,25].



Scheme 6



Scheme 7

Complex **2** like complex **1** gives a mixture of acetate and malonate in the CO insertion/alcoholysis reaction. The malonate/acetate ratio is again highly dependant on the reaction conditions, but, surprisingly, under optimum conditions a conversion of 50% can be obtained with a very good selectivity towards malonate.

As far as the mechanism of this reaction is concerned the following points must be considered.

(i) It is not possible to state whether the reaction occurs at one or on two metal centres, since no intermediates could be isolated in the absence of alcohol. It is likely, however, that the bidentate ligand would help to hold the dinuclear framework together until the end of the reaction, and it has been shown [26] that the dinuclear framework is preserved during carbonylation of $(\text{PPh}_3)_2\text{Cl}_2\text{Pd}_2\text{Ph}_2$ into $(\text{PPh}_3)_2\text{Cl}_2\text{Pd}_2(\text{OCPH})_2$.

(ii) Along with the organic products, $[\text{PdI}_2(\text{dppm})]$ could be isolated. It thus seems, that a dismutation occurs during the carbonylation/solvolysis reaction (Scheme 7).

The formation of PdI_2dppm prevents the regeneration of **2** after the carbonylation/alcoholysis reaction, but may account for the production of the acetate, since under the same conditions, PdI_2dppm , gives the lauryl acetate in 34% yield, with only trace amounts of malonate. Similar results were observed starting from other Pd^{II} complexes (Table 4).

The difference in selectivities between the carbonylation reactions of **2** and Pd^{II} complexes is an indication that the intermediates are not the same. In the first case

the formation of a malonyl bridge is probably followed by solvolysis to give the malonate. In the second case the formation of a mononuclear ketene complex **17**, which is only slowly carbonylated [27,28], leads, after solvolysis to the acetate. It is noteworthy that even CH_2Cl_2 can be converted into the acetate though in low yield (Table 4) (Scheme 7).

III. Conclusion

We have shown that μ -alkylidene complexes of transition metals can act as precursors of malonic acid derivatives, but even under optimum conditions some of the product of monoinsertion of CO, the acetate, is formed. Three important observations are worth of special mention:

(i) The μ -alkylidene complex of Pd is one of the most promising species for the dicarbonylation reaction.

(ii) In the case of the iron compound, a mononuclear diketene complex could be isolated, confirming the formation of a mononuclear (or dinuclear) ketene complex during the carbonylation.

(iii) The ketene complex reacts in the same way as alkylmetal complexes with olefins, to give either organometallic or organic-insertion products.

Experimental

General procedure

All reactions were carried out in oven-dried apparatus under an atmosphere of Ar or N_2 .

Benzene, diethyl ether, and tetrahydrofuran were distilled under argon from lithium aluminium hydride; dichloromethane was distilled from calcium hydride and hexane from sodium.

The IR spectra were recorded on a Beckman 4240 spectrophotometer, the ^1H and ^{13}C NMR spectra on either a JEOL 60HL or FX90, or Bruker AC200, WM250, or WM500 spectrometer. Melting points were determined with a Reichert apparatus and are uncorrected.

Reaction products were either purified by column chromatography on silica gel or by preparative thin layer chromatography. The organic products obtained in the carbonylations were analyzed with a Hewlett–Packard 1090 liquid chromatograph, with a IOTA refractometer as detector. The separations were carried out on a 30 cm silica gel column at 40°C , at a solvent rate of 1 ml/min with an ethyl acetate/heptane mixture (2.5/97.5) as eluent. The retention times of lauryl acetate and lauryl malonate were 6 and 9 min, respectively.

The carbonylation reactions were carried out in a 300 ml Engineers autoclave. Complexes **1** and **2** were prepared by published procedures [2,24].

Synthesis of complexes 9 and 10

A suspension of complex **1** (1 g, 2.8 mmol) in hexane (70 ml) was kept at 70°C , under CO (40 atm) for 17 h. After evaporation of the solvent, the residue was chromatographed on SiO_2 . Elution with petroleum ether/ether (95/5) first gave complex **9** (12 mg, 6%) as yellow needles (m.p. 69°C ; ν_{max} (cyclohexane) 2100, 2040, 1775, 1680 (CO); ^1H NMR (250 MHz, CDCl_3): 6.06 (1H, t, J 1.8 Hz), 2.55

(2H, d, J 1.8 Hz), 2.26 (3H, s). m/z 294 (M^+) then complex **10** (41 mg, 15%) as white yellowish crystals (m.p. 109 °C; ν_{\max} (cyclohexane) 2065, 2005, 1980, 1760 (CO); $^1\text{H NMR}$ (250 MHz, CDCl_3): 3.22 (2H, dd, J 3 and 1.5 Hz), 2.54 (2H, dd, J 3 and 1.5 Hz), 1.57 (2H, s). $^{13}\text{C NMR}$ (25 MHz, CDCl_3): 214.3 (CO), 209.7 (CO), 204.1 (CO), 46.1 (CH_2CH_2), 21.1 (CH_2). m/z 238 (M^+)).

Reaction of complex 1 with norbornene and CO

Norbornene (2 g, 21 mmol) was added to a suspension of **1** (0.5 g, 1.42 mmol) in hexane (70 ml). The mixture was stirred at 70 °C under CO (40 atm) for 15 h. After evaporation of the solvent, the residue was chromatographed on silica gel to give a mixture of two compounds as a white solid (162 mg, 40%). Recrystallization from ethanol/methylene chloride gave white needles of pure compound **11**. m.p. 198 °C; ν_{\max} (CCl_4): 1785, 1750 (CO), $^1\text{H NMR}$ (500 MHz, CDCl_3): 2.63 (1H, CH(1)), 2.66 (1H, CH_2), 2.67 (1H, CH(1')), 2.45 (2H, CH(8), CH(4')), 2.29 (1H, CH(2')), 2.23 (1H, CH(4)), 2.16 (1H, CH_3), 1.90 (1H, CH(3')), 1.61 (1H, CH(8)), 1.60 (4H, CH(5,6,5',6')), 1.30 (1H, CH(5)), 1.29 (2H, CH(7,7')), 1.20 (3H, CH(5,6,5')), 1.19 (1H, CH(7) or CH(7) or CH(7')), 1.13 (1H, CH(7) or CH(7')), $^{13}\text{C NMR}$ (50 MHz, CDCl_3): 214.1 (CO), 177 (COO), 89.8 (C(9)), 50.4 (C(2)), 49.3 (C(2')), 47.2 (C(3')), 42.2 (C(4)), 40.2 (C(1')), 38.8 (C(1)), 38.2 (C(4')), 37.8 (C(3)), 33.9 (C(7)), 34.4 (C(7')), 31.2 (C(8)), 28.4, 28.1 (2C), 27.3 (C(5), C(5')), C(6), C(6')). (Found: C, 75.6; H, 7.8, $\text{C}_{18}\text{H}_{10}\text{O}_3$ calcd.: C, 75.5; H, 7.7%.)

Preparation of laurylacetate 3 and laurylmalonate 4

These compounds were made from acetyl chloride and malonyl chloride and lauryl alcohol, respectively.

Lauryl acetate: Liquid ν_{\max} 1735 (CO); $^1\text{H NMR}$ (90 MHz, CDCl_3): 4.04 (2H, t, OCH), 2.0 (3H, s, CH_3C), 1.27 (20H, m, (CH_2)(10)), 0.87 (3H, m, CH_3); $^{13}\text{C NMR}$ (25 MHz, CDCl_3): 171.1 (CO), 64.6 (OCH), 31.9, 29.7, 29.4, 28.7, 26, 22.7 (CH_2), 20.9 (CH_2), 14.1 (CH_3); m/z : 228 (M^+).

Laurylmalonate: White solid; m.p. 32.5 °C; ν_{\max} 1730 (CO); $^1\text{H NMR}$ (90 MHz, CDCl_3): 4.16 (4H, t, OCH_2), 3.26 (2H, s, CH_3), 1.27 (40H, m, CH_2), 0.87 (6H, m, CH_3); $^{13}\text{C NMR}$ (25 MHz, CDCl_3): 166.7 (CO), 65.7 (C(3)), 41.8 ($\text{CH}_2\text{-CO}$), 32, 29.7, 29.3, 28.6, 25.9; 22.7 (CH_2), 14.1 (CH_3); m/z : 440 (M^+).

All other esters and malonates were prepared by the same procedure.

Reaction of 1 with hexylamine

A solution of hexylamine (0.1 ml, 1.1 mmol) in hexane (10 ml) was added to a suspension of complex **1** (100 mg, 0.28 mmol), in hexane (40 ml), at room temperature under argon. After 5 h the red solution was evaporated, and the residue subjected to preparative TLC to give hexylamide (14 mg, 38%) as an oil.

ν_{\max} 1680 cm^{-1} (CO); $^1\text{H NMR}$ (90 MHz, CDCl_3): 6 (1H, m, NH), 1.92 (3H, s, CH_3CO), 1.32 (8H, m, (CH_2)), 0.86 (3H, m, CH_3), $^{13}\text{C NMR}$ (25 MHz, CDCl_3): 170 (CO), 39.8 (CH_2NH), 31.5, 29.6, 26.6, 23.2, 22.6 (CH_2), 20.2 ($\text{CH}_3(\text{O})$), 13.9 (CH_3); m/z : 143 (M^+).

X-Ray studies

Preliminary unit cell dimensions and symmetry informations were derived from precession photographs. Orientation and indexing operations as well as data collec-

tion were carried out on a Nonius CAD4 diffractometer. Accurate cell parameters are based on a least-squares analysis of 25 reflections in well-separated regions of reciprocal space ($24 < 2\theta < 28$).

Details of crystal data and the data collection parameters are given in Table 1. The intensities of two standard reflections monitored every hours decayed uniformly to final values about 40% less than their initial values. The data were scaled accordingly. The Ψ -scans of close to axial reflections showed no significant intensity variations so no absorption correction was applied. Corrections were made for Lorentz and polarization effects.

Computations were performed by use of the CRYSTALS system [29] adapted for a MicroVAX II. Atomic scattering factors for neutral Fe, C, O and H atoms were taken from ref. 30. Anomalous dispersion was taken into account.

The position of Fe atom was determined by Harker vector analysis of three dimensional Patterson map. All remaining non-hydrogen atoms were found from an electron density map. Hydrogen atoms were located on difference electron density map; their atomic coordinates were introduced into the refinements, and they were assigned a refineable overall isotropic thermal parameter. Final refinements were by

Table 6

Crystal data

Empirical formula	$C_{10}H_6O_7Fe$
Molecular wght	294
Crystal system	monoclinic
Space group	$P2_1/c$
a , Å	15.217(2)
b , Å	6.258(2)
c , Å	12.710(2)
β , °	97.64(1)
V , Å ³	1200
Z	4
Cryst. size, mm	$0.38 \times 0.14 \times 0.08$
$\mu(Mo-K\alpha)$, cm^{-1}	12.75
ρ (calcd), $g. cm^{-3}$	1.628
Temperature, °C	20
Radiation	Mo- $K\alpha$ (graphite monochromator)
Scan type	$\omega/0.66\theta$
Scan range θ , deg	$0.8 + 0.345 \tan\theta^a$
2θ range, deg	3–50
Speed range, $deg\ min^{-1}$	1.3–5.5
Standard reflections	4 1 6; 2 $\bar{4}$ 2
$F(000)$	592
Reflections collected	2574
Reflections merged (R_m)	2105(0.048)
Reflections used	1362 ($1 \geq 3\sigma(1)$)
R^b	0.0239
R_w	0.0233
rms (shift/esd)	0.14
Ratio of obs. to param.	7

^a Scan extended by 25% on either side for background determination. ^b $R = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$, $R_w = \{\Sigma w(F_o - F_c)^2 / \Sigma w(F_o)^2\}^{1/2}$.

Table 7

Fractional atomic coordinates with e.s.d. s in parentheses, and equivalent isotropic thermal parameter U_{eq} for compound **9** $U_{\text{eq}} = [U_{11} \times U_{22} \times U_{33}]^{1/3}$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Fe(1)	0.66758(3)	0.23146(7)	0.61368(3)	0.0469
C(11)	0.6127(2)	0.3387(5)	0.4894(3)	0.0585
O(11)	0.5808(2)	0.4017(4)	0.4103(2)	0.0808
C(12)	0.6584(2)	0.4769(5)	0.6915(2)	0.0549
O(12)	0.6564(2)	0.6280(4)	0.7389(2)	0.0730
C(13)	0.5684(2)	0.0997(5)	0.6466(2)	0.0583
O(13)	0.5081(2)	0.0122(4)	0.6666(2)	0.0801
C(14)	0.7406(2)	0.0925(5)	0.7134(2)	0.0564
O(14)	0.7889(2)	0.0045(4)	0.7733(2)	0.0814
C(1)	0.7828(2)	0.3528(5)	0.5675(2)	0.0537
C(2)	0.8169(2)	0.1926(5)	0.4986(2)	0.0529
C(3)	0.7756(2)	0.0088(5)	0.4740(2)	0.0550
C(4)	0.6946(2)	−0.0218(5)	0.5216(2)	0.0504
O(4)	0.6499(1)	−0.1801(3)	0.5092(20)	0.0633
O(5)	0.8963(1)	0.2606(4)	0.4666(2)	0.0650
C(6)	0.9369(3)	0.1642(7)	0.3911(3)	0.0758
C(7)	1.0180(3)	0.2821(9)	0.3745(3)	0.0953
O(81)	0.9294(7)	−0.028(1)	0.374(1)	0.0948
O(82)	0.8969(4)	0.040(1)	0.3290(6)	0.0864
				U_{iso}
H(11)	0.829(2)	0.378(6)	0.629(3)	0.102(5)
H(12)	0.771(2)	0.484(6)	0.527(3)	0.102(5)
H(31)	0.792(2)	−0.094(6)	0.429(3)	0.102(5)
H(71)	1.043(2)	0.232(6)	0.317(3)	0.102(5)
H(72)	1.057(2)	0.285(6)	0.436(3)	0.102(5)
H(73)	0.999(2)	0.408(6)	0.342(3)	0.102(5)

least squares with approximation (in four blocks) to the normal matrix (with all non-hydrogen atoms anisotropic). The criteria for a satisfactory completed analysis were the rms shift to standard deviation, and no significant features in the final difference map. The main features of the refinement are outlined in Table 6. Atomic coordinates are given in Table 7, and bond lengths and angles in Table 5. Tables of least squares planes, distances and angles involving hydrogen atoms, anisotropic thermal parameters for heavy atoms, and lists of observed and calculated structure factors can be obtained from the authors.

It must be pointed out that the oxygen atom of the carbonyl of the enol ester group is disordered. It may be regarded as statistically distributed on two sites related through the plane containing the O(5), C(6) and C(7) atoms: O(81) is 0.48 Å above this plane whereas O(82) is 0.34 Å below it. This disorder might be caused by electronic repulsion between the very electron-poor oxygen and the H(31) hydrogen atom. Indeed the O–H distances, 2.33 Å, are the shortest observed for the compound (Table 8); it would be even shorter if the oxygen exactly in the plane (2.26 Å). Allowance for the disorder lead to a more accurate C(6)–O distance for the carbonyl group, which increased from 1.15 Å (with the oxygen in the plane) to 1.22 Å, and improved the *R* value by 0.21% (2.60 to 2.39%).

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