OH· radicals produced from water radiolysis react with formate giving $COO^{-}\cdot$ radicals. Then $COO^{-}\cdot$ and e_{aq}^{-} react with O_2 to generate $O_2^{-}\cdot$ as the sole radical species:[11]

$$H_2O \rightarrow OH\cdot,\ H\cdot,\ e_{aq}^{-},\ H_2,\ H_2O_2 \tag{4}$$

$$OH\cdot + HCOO^{-} \rightarrow H_2O + COO^{-}\cdot \tag{5}$$

$$H\cdot + HCOO^{-} \rightarrow H_2 + COO^{-}\cdot \tag{6}$$

$$COO^{-}\cdot + O_2 \rightarrow O_2^{-}\cdot + CO_2 \tag{7}$$

$$e_{aq}^{-} + O_2 \rightarrow O_2^{-}\cdot \tag{8}$$

At pH 7.6, $O_2^{-}\cdot$ disappears essentially by reaction 1,[9] and if $^1O_2$ is produced, it will react with RTS[12] or will be quenched either by $O_2^{-}\cdot$ or by water (reactions 3, 2, and 9, respectively).

$$^1O_2 \xrightarrow{H_2O} {}^3O_2 \tag{9}$$

Assuming that $^1O_2$ yield is 100% for reaction 1, the radiolytic yield of RTS disappearance is expressed as

$$G(\text{-RTS}) = G(O_2^{-}\cdot)k_3[\text{RTS}]/[2(k_3[\text{RTS}] + k_9)]$$

where $G(O_2^{-}\cdot) = 6$ molecules per 100 eV and $k_9/k_3 = 1.5 \times 10^{-3}$ M;[12] thus $G(\text{-RTS}) = 0.35$. The experimental value obtained with oxygen saturated solutions is $G(\text{-RTS}) = 0.05 \pm 0.01$ molecule per 100 eV (3×10^{18} eV cm^{-3} < dose < 30×10^{18} eV cm^{-3}).

This low yield cannot be attributed to the generation of $^1O_2$ because no endoperoxide $RTSO_2$, which had been shown to be stable under these conditions, could be detected by HPLC. Furthermore, we have observed higher G values in presence of air; so it must be assumed that *another reaction occurred between RTS and one of the radicals* $COO^{-}\cdot$ *or* e_{aq}^{-}.

In order to check this hypothesis, the effects of these species upon RTS were investigated by using a pulse radiolysis method. Electron pulses were produced by an accelerator (Febetron 708), and the kinetics were followed by rapid spectrophotometry.[14] The doses were homogeneously delivered in solutions saturated with nitrogen or nitrous oxide in order to produce e_{aq}^{-} and $COO^{-}\cdot$ (reactions 4, 5, 6) or $COO^{-}\cdot$[13] alone (reactions 4–6, 10).

$$e_{aq}^{-} + N_2O + H_2O \rightarrow OH\cdot + N_2 + OH^{-} \tag{10}$$

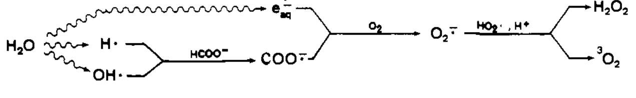
Under such conditions, no reaction could be detected between $COO^{-}\cdot$ and RTS. On the contrary, e_{aq}^{-} reacted efficiently with RTS, leading to a rapid one-electron reduction followed by a dismutation of the intermediate:

$$\text{RTS} + e_{aq}^{-} \rightarrow \text{RTS}^{-}\cdot \tag{11}$$

$$2\text{RTS}^{-}\cdot + 2H_2O \rightarrow \text{RTSH}_2 + \text{RTS} + 2OH^{-} \tag{12}$$

Kinetic study of the competing reactions involved in the decay of e_{aq}^{-} with or without RTS led to the value $k_{11} = (3 \pm 1)10^9$ M^{-1} s^{-1}.

All experimental results observed by γ radiolysis may be explained by the following scheme:



According to this scheme

$$G(\text{-RTS}) = G_{e_{aq}^{-}}k_{11}[\text{RTS}]/(k_{11}[\text{RTS}] + k_8[O_2])$$

where $G_{e_{aq}^{-}} = 2.7$ molecules per 100 eV, $[O_2] = 1.2 \times 10^{-3}$ M, and $k_8 = 2.10^{10}$ M^{-1} s^{-1}. The observed linear variation of $1/G(\text{-RTS})$ vs. 1/[RTS] led to the experimental value $k_{11} = (2.5 \pm 0.5)10^9$ M^{-1} s^{-1}; this rate constant is in agreement with results obtained by pulse radiolysis.

In conclusion, the slow disappearance of RTS during γ radiolysis of oxygen saturated solutions is not due to the reaction between $^1O_2$ and RTS but to a side reaction between the substrate and e_{aq}^{-}. Therefore, noncatalyzed disproportionation of $O_2^{-}\cdot$ in neutral solutions does not yield $^1O_2$.

Supplementary Material Available: $1/G(\text{-RTS})$ vs. 1/[RTS] for γ radiolysis and high-performance liquid chromatograms (5 pages). Ordering information is given on any current masthead page.

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[11] Behar, D.; Czapski, G.; Rabani, J.; Dorfman, L. M.; Schwarz, H. A. *J. Phys. Chem.* **1970**, *74*, 3809–3814.

[12] Aubry, J. M.; Rigaudy, J.; Cuong, N. K. *Photochem. Photobiol.* **1981**, *33*, 155–158.

[13] Buxton, G. V.; Sellers, R. M. *Trans. Faraday Soc.* **1973**, *69*, 555–559. Hoffman, M. Z.; Simic, M. *Inorg. Chem.* **1973**, *12*, 2471–2472.

[14] Houee-Levin, C.; Gardes-Albert, M.; Ferradini, C.; Pucheault, J. *Radiat. Res.* **1980**, *83*, 270–278. Lesigne, B.; Sauneuf, R. *Rev. Sci. Instrum.* **1976**, *47*, 1063–1064.

Rh(I)–Cu(II) Catalyzed Oxidation of 1-Hexene by O_2 Using Immobilized, Site-Separated Organosulfide Complexes

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A new class of catalytic oxidations involving metal centered oxygen atom transfer to terminal olefins from dioxygen has been discovered in the past seven years.[1] Most recently Mimoun has reported a homogeneous system involving Rh(I), Cu(I) or Cu(II), and H^+ as cocatalysts for the oxidation of terminal olefins to methyl ketones with >98% specificity and unusually high turnovers (110 in 4 h).[1a] Several workers have proposed the sequential coordination of O_2 and terminal olefin, followed by the formation of a five-membered peroxy metallocycle,[1a–c,2] as the first steps in their oxidation reaction mechanisms. The relatively short lifetimes of the homogeneous catalysts active in this class of oxidations encouraged us to seek a functionalized solid support to site isolate the rhodium complexes, on the assumption that the catalyst deactivation process was multiordered in rhodium. The presumed need to coordinate both O_2 and olefin to rhodium led us to consider the use of immobilized monodentate,[3] anionic[4] ligands which would be stable to oxidation[5] and form strong bonds with group 8 transition metals. We report here (1) the preparation of novel monomeric organosulfide–rhodium carbonyl complexes which do not have a counterpart in solution chemistry and (2) the effectiveness of the organosulfide supported Rh(I)–Cu(II) system in the catalytic oxidation of 1-hexene to 2-hexanone using dioxygen.

A series of silica gel bound organosulfide samples ([SG]–SH) were produced varying only in their sulfide concentrations (0.20, 0.10, 0.050 and 0.025 mmol of S per gram of [SG]) by reacting

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[1] (a) Mimoun, H.; Machirant, M. M. P.; de Roch, I. S. *J. Am. Chem. Soc.* **1978**, *100*, 5437. (b) Mimoun, H.; Igersheim, F. *Nouv. J. Chim.* **1980**, *4*, 161. (c) Read, G.; Walker, P. J. C. *J. Chem. Soc., Dalton Trans.* **1977**, 883. Farrar, J.; Holland, D.; Milner, D. J. *Ibid.* **1975**, 815. *Ibid.* **1975**, 2440.

[2] Sheldon, R. A.; Van Doorn, J. A. *J. Organomet. Chem.* **1975**, *94*, 115.

[3] Our use of a bidentate polystyrene–2,2′-bipyridine supported rhodium complex [[P]–bpyRhXCl (where X denotes μ-Cl, $P(C_6H_5)_3$, or monodentate [P]–bpy)] resulted in an inactive system for the catalytic oxidation reported by Mimoun. The preparation and characterization of [P]–bpyRhXCl is described in a paper to be published in *Inorg. Chem.* ([P] represents a polymer support.)

[4] Mimoun reported, and we have further investigated, the role of chloride in improving the catalyst lifetimes. The homogeneous system's activity (used for comparison in this report) may be improved to 193 turnovers in 24 h simply by adding 3 equiv of chloride. The reaction in this case proceeded identical with that when using Mimoun's precursors: $RhCl_3\cdot 3H_2O$ and $Cu(NO_3)_2\cdot 2.5H_2O$. We feel this is a result of chloride coordination inhibiting rhodium complex aggregation. Indeed, this effect is maximized at 5 equiv of chloride, resulting in 343 turnovers in 24 h, with all the improvement coming from much slower catalyst deactivation (the initial rates with 3 and 5 equiv of Cl^- were identical).

[5] For example, a polystyrene–diphenylphosphine support $[[P]\text{–}P(C_6H_5)_2]$ was unsuitable due to the facile oxidation of the phosphine to phosphine oxide.[1c]

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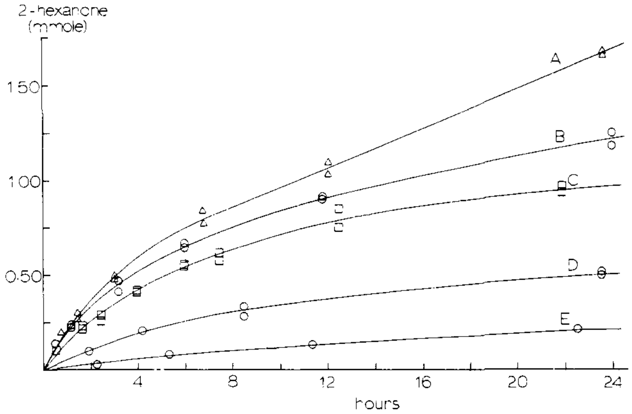

Figure 1. All reactions were run at 70 °C under 52 psi of O_2 after mixing components at room temperature. Used for each run were 0.074 mmol of $Rh(CO)_2S'_nBF_4$ (as a freshly prepared EtOH solution), 0.16 mmol of S (as [SG]–SH), 0.074 mmol of $Cu(NO_3)_2{\cdot}2.5H_2O$, 0.148 mmol of H_2SO_4 or 0.222 mmol of $HClO_4$ (see below), 0.568 mmol of 2-hexanone (as an internal standard), 45 mL of EtOH (distilled over $CaCO_3$), and 15.0 mL of 1-hexene (distilled over CaH_2, passed through alumina). Curve A: 0.222 mmol of $HClO_4$ as the proton source; 0.025 mmol of S per gram of [SG] as the support. Curve B: 0.148 mmol of H_2SO_4 as the proton source; 0.025 mmol of S per gram of [SG]. Curve C: 0.148 mmol of H_2SO_4; 0.050 mmol of S per gram of [SG]. Curve D: 0.148 mmol of H_2SO_4; 0.10 mmol of S per gram of [SG]. Curve E: 0.148 mmol of H_2SO_4; 0.20 mmol of S per gram of [SG]. 2-Hexanone production was monitored by using GLC, with 2-heptanone as an internal standard.

Davison Grade 62 silica gel with $(CH_3O)_3Si(CH_2CH_2CH_2SH)$ in refluxing xylenes. These were reacted with freshly prepared $Rh(CO)_2S'_nBF_4$(I, S′ ≡ solvent) in THF[6] or EtOH under Ar, producing orange to lemon-yellow [SG]–SH supported rhodium complexes. Infrared spectra in the CO region for the supported rhodium complexes were recorded after bubbling CO through EtOH suspensions at room temperature for several hours.[7] The three band spectrum[8] for the [SG]–SH bound I using the 0.20 mmol of S per gram of [SG] support clearly identified the supported species as the dimer $(\mu\text{-[SG]–S})_2Rh_2(CO)_4$ (II).[9] This is produced from proximate silica gel bound sulfide groups. In contrast, the supported rhodium complex produced from I and the 0.050 mmol of S per gram of [SG] support was characterized as $\text{[SG]–SRh(CO)}_2S'_n$ (III) from its two band infrared spectrum.[10] The supported rhodium complex formed by using the 0.10 mmol of S per gram of [SG] support was shown by infrared spectroscopy to consist of a mixture of both the monomeric and dimeric rhodium carbonyl complexes. To our knowledge, III is the first example of a monomeric organosulfide transition-metal carbonyl complex which is stable in the absence of additional noncarbonyl ligands. A number of monomeric organosulfide carbonyl transition-metal complexes have been reported,[11] but all require stabilizing ligands, such as cyclopentadiene or phosphines, or strong electron-withdrawing groups, such as F_3CS^- or $F_5C_6S^-$, on the organosulfide. In the absence of these features any monomeric metal sulfide that may be formed in solution quickly reacts to form the dimers and lose CO. The replacement of CO with more inert ligands or the use of the much weaker fluorinated sulfide base may inhibit this process. The physical site isolation of the organosulfide ligands obtained with the 0.050 mmol of S per gram of [SG] support enables the formation of the coordinatively unsaturated III in the absence of either special ligands or weak base sulfides. Compound III can be heated overnight at 70 °C in the presence of all oxidation reaction components (vide infra) except O_2 and reformed by exposure to CO. The loss of CO is quite facile in the presence of O_2, but reversible.

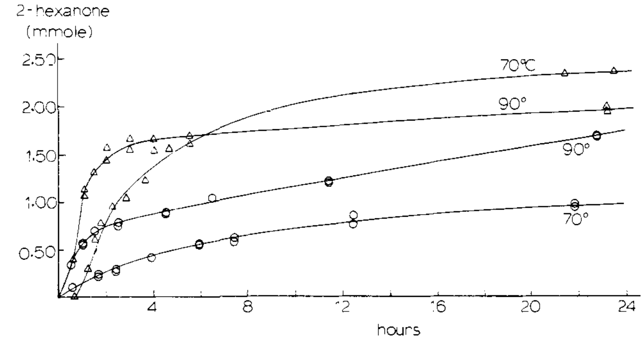

Figure 2. All reaction systems were prepared, as in Figure 1, at 70 °C or 90 °C as indicated near each curve. (Δ) homogeneous systems (no [SG]–SH added). (○) [SG]–SH supported systems, using 0.050 mmol of S per gram of [SG].

The Rh(I), Cu(II), and H^+ catalyzed oxidation of 1-hexene to 2-hexanone was carried out by using the series of [SG]–SH supported rhodium species characterized above. The results are presented in Figure 1. It is apparent from this data that as the silica gel's surface sulfide concentration is decreased, the catalyst activity increases. Thus it appears that the active catalyst precursor is the monomer III, while the dimer II forms a much less active, or inactive, catalyst. The homogeneous system (no [SG]–SH added) in the presence of slightly more than 2 equiv of $(CH_3O)_3Si(CH_2CH_2CH_2SH)$ was almost completely inactive. The rhodium catalyst precursor formed in this solution is $[Rh(CO)_2(RS)]_2$ and is analogous to the supported rhodium dimer II. The homogeneous system in the absence of silane exhibited an induction period of 40 min and then catalyzed the oxidation at a very fast rate (the profile for this system can be seen in Figure 2). After 24 h, however, its activity had dropped to only 0.9% of the initial rate. In contrast, the activity of an analogous catalytic oxidation using III (with 0.025 mmol of S per gram of [SG]; curve B in Figure 1) after 24 h of reaction was 7.4% its initial rate. As a result the supported system III was actually twice as active as the homogeneous solution at 24 h. The most striking feature in Figure 1 is the complete inhibition of catalyst degradation after 7 h by using III with $HClO_4$ as the proton source (curve A). In this case the rate of 1-hexene oxidation is a constant 0.70 turnover/h over the final 17 h of reaction (19% of the initial rate). This is in marked contrast to the result obtained with the homogeneous system in which catalyst deactivation is rapid and dominant. The large improvement in the supported catalyst stability by using $HClO_4$ rather than H_2SO_4 (curve B) is likely the result of the poorer ligating ability of ClO_4^- relative to SO_4^{2-}. This would prevent the leaching of rhodium due to the proton's counterion coordination and the catalyst's subsequent oxidative and/or aggregative deactivation.

Enough [SG]–SH must be added to bind all Rh(I) and Cu(II), or extensive rhodium leaching into solution results from the competition by Cu(II) for sulfide groups. To further establish that the oxidation was catalyzed by the [SG]–SH bound rhodium complex, and not leached rhodium, the filtrate was syringed off under reaction conditions (52-psi O_2, 70 °C), 0.074 mmol of Cu(II) added, and the reaction restarted to check for catalytic activity. For the 0.050 mmol of S per gram of [SG] sample, leached rhodium accounted for only 14% of the total activity at 3.5 h, which considering the much greater initial activity of homogeneous I suggests that only 5% of the active rhodium complex was present in the solution under the reaction conditions. On mixing together the reaction components at room temperature, using any sample of [SG]–SH all Rh(I) and Cu(II) were bound to the support. The supported complex III (using 0.050 mmol of S per gram of [SG]) and homogeneous I (in the absence of silane) were also used for the oxidation of 1-hexene at 90 °C using

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(6) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 3089.

(7) This was required to achieve good reproducibility due to the facile loss of CO in the presence of dioxygen.

(8) Bands at 2075 (m), 2055 (s), and 2005 (s) cm^{-1}.

(9) Allum, K. G.; Hancock, R. D.; Howell, I. V.; McKenzie, S.; Pitkethly, R. C.; Robinson, P. J. *J. Organomet. Chem.* **1975**, *87*, 203.

(10) Bands at 2055 (m) and 2006 (s) cm^{-1}.

(11) (a) Review: Abel, E. W.; Crosse, B. C. *Organomet. Chem. Rev.* **1967**, *2*, 443. (b) Grobe, J.; Mohr, W. *J. Fluorine Chem.* **1976**, *8*, 145. (c) King, R. B.; Welcman, N. *Inorg. Chem.* **1969**, *8*, 2540. Knox, G. R.; Pryde, A. *J. Organomet. Chem.* **1974**, *74*, 105.

H_2SO_4 as the proton source. As seen in Figure 2 the supported catalyst is even more resistent to deactivation at 90 °C than it was at 70 °C when compared to the homogeneous system.

The inactivity of homogeneous organosulfide complexes in catalysis (outside of electron-transfer roles) is a direct result of sulfide's strong bridging ability which effectively eliminates necessary coordination sites. The demonstration of (1) the stability of the monomeric organosulfide rhodium carbonyl complexes reported here (with respect to dimerization) in cases of effective site isolation on silica gel, (2) the ability of the [SG]-SH supported Rh(I)-Cu(II) system to effectively catalyze the oxidation of 1-hexene, and (3) the inhibition of catalyst decomposition by site isolation of Rh(I) serve as yet another example of the unique role which may be served by functionalized polymers as supports for transition-metal complexes.[12] The greater resistance to catalyst deactivation with the site isolated monomeric III compared to either the dimer II or the homogeneous I may be a result of a stabilizing influence of the sulfide ligand to irreversible monomeric rhodium oxidation and/or the effectiveness of rhodium site isolation in inhibiting multiordered decomposition mechanisms. We are currently investigating the role of Cu(II) in this sytem by further diluting the silica gel surface in organosulfide to achieve site- separation of Rh(I) and Cu(II). The most dilute samples reported here (0.025 mmol of S per gram of [SG]) most likely allow some Rh(I)-Cu(II) interaction. A drop in supported catalyst activity with further dilution would implicate the need for the direct interaction of Rh(I) and Cu(II) in the reaction mechanism.

Acknowledgment. We gratefully acknowledge the support of this research by the Office of Naval Research.

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(12) One of the best examples is the demonstration of effective site isolation. See, for example: (a) Gubitosa, G.; Boldt, M.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1977**, *99*, 5174. (b) Wild, F. R. W. P.; Gubitosa, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1978**, *148*, 73. (c) Drago, R. S.; Gaul, J. H. *Inorg. Chem.* **1979**, *18*, 2019. (d) Grubbs, R.; Lau, C. P.; Cukier, R.; Brubaker, C., Jr. *J. Am. Chem. Soc.* **1977**, *99*, 4517. (e) Teal, O.; Anderson, D. L.; Bowman, R. G.; Basolo, F.; Burwell, R. L., Jr. *J. Am. Chem. Soc.* **1975**, *97*, 5125.

Synthesis and Molecular Structure of μ^4-Carbido-μ^2-carbonyl-dodecacarbonyltetrairon, a Neutral Iron Butterfly Cluster Bearing an Exposed Carbon Atom

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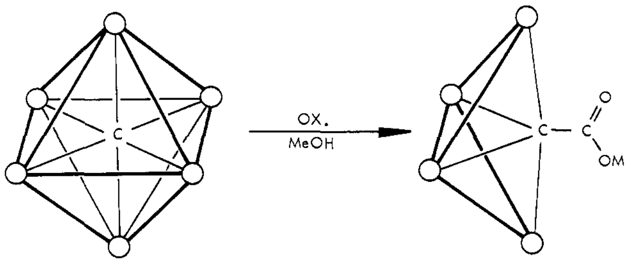
We recently reported[1] the first observation of the chemical reactivity of a cluster bound carbon atom in the synthesis from $Fe_6C(CO)_{16}^{2-}$ (I) of the butterfly (carbomethyoxy)methylidyne cluster $Fe_4(CO)_{12}CCO_2CH_3^-$ (II) in an oxidative fragmentation of the octahedral dianion I in methanol (eq 1).



$[Fe_6C(CO)_{16}]^{2-}$
I

$[Fe_4(CO)_{12}C\cdot CO_2Me]^-$
II

(1)

The remarkable reactivity of the hitherto encapsulated carbon atom in I when exposed by loss of two vertices from the original cluster is of immediate relevance to current conceptions of the hydrogenation of carbon monoxide on metal surfaces,[2] which propose the formation of surface carbon atoms via dissociative adsorption of CO. Our observation[1] of the facile assembly of a carbomethoxy group on such a carbon atom when its coordination number is reduced to four demonstrated for the first time the reactivity of cluster bound carbon atoms with low coordination number. This phenomenon has also been utilized by Muetterties et al. in the synthesis of $HFe_4(CO)_{12}CH$ from $Fe_4(CO)_{12}C^{2-}$. The hydrogenation of II to methyl acetate[1] provided a unique synthetic pathway to an organic oxygenate from CO and hydrogen mediated by a cluster reaction site, and we have continued our investigation into the promising reactivity of cluster bound carbon atoms.

We suggested a possible mechanism for the formation of II via carbonylation of the carbon atom in a μ^4-carbide intermediate to yield a ketenediyl cluster, $Fe_4(CO)_{12}CCO$, which then reacted with solvent methanol to yield II. We report here the results of our efforts to obtain evidence supporting this postulate and further investigations in the iron carbide system which have led to the isolation of $Fe_4(CO)_{13}C$, a tetranuclear iron species containing a carbon atom bound to four metal atoms.[4]

Our first aim was to establish the intermediacy of a ketenediyl cluster in the formation of II. In view of the reaction of a related (carbomethoxy)methylidynetricobalt cluster with acid to yield the corresponding acylium ion[5] (eq 2), we investigated the protonation of $Fe_4(CO)_{12}CCO_2CH_3^-$ as a route to $Fe_4(CO)_{12}CCO$.

$$Co_3(CO)_9CCO_2R \xrightarrow{HPF_6} Co_3(CO)_9CCO^+ \qquad (2)$$

When trifluoromethanesulfonic acid (1.0 mL) was added to a suspension of $Et_4N[Fe_4(CO)_{12}CCO_2CH_3]$ (1.0 g) in methylcyclohexane, under nitrogen, the green-black starting material dissolved in the acid layer immediately. Addition of degassed water and gentle warming resulted in the total extraction of the dark brown product into the organic phase, which was decanted via cannula onto molecular sieves. Filtration and evaporation under reduced pressure yielded a black, gummy solid which was extracted into hexane. Slow evaporation under nitrogen yielded the product (0.45 g) as a black, air-sensitive crystalline solid (III).

The infrared spectrum of III [cyclohexane, 2062 (s), 2051 (s), 2040 (s), 2035 (s), 2015 (w), 2000 (w), 1990 (m), 1901 (m) cm^{-1}] confirmed the removal of the carboxylic ester function from II [$\nu_{CO}(CO_2CH_3)$ 1655 cm^{-1}), a conclusion confirmed by the absence of ^1H resonances in the 90-MHz NMR spectrum of III. The ^{13}C NMR spectrum (22.5 MHz, CD_2Cl_2) of III contained only two resonances (30 °C), at 469 and 208 ppm (Me_4Si) in an intensity ratio of 1:13.[6] The prospect of a fluxional process averaging Fe–CO and C=CO environments in the target molecule $Fe_4(CO)_{12}CCO$ seemed unlikely, if intriguing, but the presence of 13 carbonyls and a unique carbon atom, confirmed by a parent ion at *m/e* 600 ($Fe_4C(CO)_{13}^+$) in the mass spectrum of III, suggested either a ketenediyl structure or one in which all the carbonyls were bound to iron atoms and a lone carbon atom was present.

Since the spectroscopic evidence was insufficient to establish unambiguously the identity of III, an X-ray structure determination[7] was performed on a single crystal grown by repeated

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(1) J. S. Bradley, G. B. Ansell, and E. W. Hill, *J. Am. Chem. Soc.*, **101**, 7417 (1979).

(2) V. Ponec, *Catal. Rev.-Sci. Eng.*, **18**, 151 (1978); P. Bileon, J. N. Helle, W. M. H. Sachtler, *J. Catal.*, **58**, 95 (1978).

(3) (a) M. Tachikawa and E. L. Muetterties, *J. Am. Chem. Soc.*, **102**, 4541 (1980). (b) M. A. Beno, J. M. Williams, M. Tachikawa, and E. L. Muetterties, *ibid.*, **102**, 4542 (1980).

(4) The structural characterizations of two other examples of Fe_4C clusters have recently been reported: $HFe_4(CO)_{12}C^-$ (D. F. Shriver and E. Holt, *J. Organomet. Chem.*, in press) and $Fe_4(CO)_{12}C^{2-}$ (J. H. Davis, M. A. Beno, J. M. Williams, J. Zimmie, M. Tachikawa, and E. L. Muetterties, *Proc. Natl. Acad. Sci. U.S.A.* **78**, 668 (1981)).

(5) D. Seyferth, J. E. Hallgren, and C. S. Eschbach, *J. Am. Chem. Soc.*, **96**, 1730 (1974).

(6) ^{13}C NMR spectra were obtained with samples prepared from ^{13}CO enriched $Fe(CO)_5$ as before.

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