

## Oxidative Decomplexation of Chromium Fischer Carbene Complexes Induced by Dioxiranes

Mariona Gibert, Marta Ferrer, Anna-Maria Lluch, Francisco Sánchez-Baeza, and Angel Messeguer\*

Department of Biological Organic Chemistry, I.I.Q.A.B. (C.S.I.C.). J. Girona, 18. 08034 Barcelona, Spain

Received October 14, 1998

The reaction course of the oxidative decomplexation of Fischer carbene complexes with dioxiranes was examined. The portionwise addition of 2.2 equiv of dimethyldioxirane (DMD) to Fischer carbene complex **1** afforded ethyl phenylpropiolate in 90% yield. When the reaction was carried out using a CO<sub>2</sub>-free DMD solution in a N<sub>2</sub> atmosphere ester **2** was formed in 40% yield, whereas in the presence of an O<sub>2</sub> atmosphere the yield increased to 70%. This same assay performed in the presence of <sup>18</sup>O<sub>2</sub> atmosphere afforded the ester **2** partially labeled at the C=O moiety (approximately 50%, GC-MS) with <sup>18</sup>O. On the other hand, treatment of Fischer carbene complex **1** with a [<sup>18</sup>O<sub>2</sub>]dimethyl-dioxirane solution led to the formation of <sup>18</sup>O-labeled CO<sub>2</sub> (trapped as BaCO<sub>3</sub> and detected by IRMS). From these results it can be suggested that the oxidative decomplexation of Fischer carbene complexes by dioxiranes involves an initial attack of the dioxirane to the metal coordination sphere. In this step a CO ligand is oxidized to CO<sub>2</sub> thus leaving an unstable chromium tetracarbonyl intermediate which would react with O<sub>2</sub> to give the final ester product and chromium(III) oxide.

### Introduction

The capability of dioxiranes, in particular of dimethyldioxirane (DMD) and trifluoromethyl(methyl)dioxirane (TFMD), to transfer an oxygen atom to a wide variety of substrates under mild, controlled conditions, accounts for the numerous applications that these reagents have found in organic synthesis.<sup>1</sup> These oxidation reagents have exhibited also interesting applications in the organometallic field. In a pioneering work, Wolowiec and Kochi used DMD for the generation of highly unstable oxometal species from Mn(II) and Fe(II) porphyrins<sup>2</sup> and for the oxidative decarbonylation of tricarbonylrhenium and molybdenum complexes.<sup>3</sup> However, is in the release of organic ligands from metal transition complexes and on the selective oxidation of ligands present in these complexes where the reactivity of dioxiranes has been most widely explored.<sup>4,5</sup>

Concerning the release of organic ligands, we reported the use of DMD for the decomplexation of arene tricarbonylchromium(0) compounds.<sup>6</sup> In this case, excellent

conversions to the arene derivative were obtained, although the scope of the decomplexation was limited by the presence of organic ligands more sensitive to the dioxirane action, inter alia, the thioether moiety. Conversely, the slow reaction rates observed for the reaction of DMD with tricarbonyl( $\eta^4$ -diene)iron and  $\mu$ -( $\eta^2$ -alkyne)-hexacarbonyldicobalt complexes and the chemoselectivity problems encountered on the models studied raised serious doubts on the efficiency of dioxiranes for the decomplexation of these iron and cobalt compounds in comparison with the use of more conventional reagents, i.e., amine oxides.<sup>7</sup>

By contrast, dioxiranes appear to be valuable reagents for the oxidative decomplexation of Fischer carbene complexes. In a preliminary communication we described the use of DMD for the decomplexation of selected chromium carbene compounds.<sup>8</sup> Later, Barluenga et al. reported the successful use of TFMD for the release of the organic ligand present in Diels–Alder products from reactions of –BF<sub>2</sub>– adducts of functionalized Fischer vinylcarbene complexes with chiral 2-amino-1,3-dienes.<sup>9</sup> More recently, we carried out a study on the decomplexation of a Fischer carbene complex bearing a conjugated enamino moiety.<sup>10</sup>

Herein we report our results on the reaction course of the oxidative decomplexation of Fischer carbene complexes with dioxiranes. The studies on the decomplexation mechanism of metal carbonyl complexes have been mainly referred to metal carbonyls and metal carbonyl clusters.<sup>11,12</sup> In these studies, amine *N*-oxides were used

(1) For reviews on dioxiranes, see: (a) Adam, W.; Curci, R.; Edwards, J. *Acc. Chem. Res.* **1989**, *22*, 205–211. (b) Murray, R. W., *Chem. Rev.* **1989**, *89*, 1187–1201. (c) Curci, R.; Dinoi, A.; Rubino, M. F. *Pure Appl. Chem.* **1995**, *67*, 811–822. (d) Adam, W.; Hadjiarapoglou, L. P.; Curci, R.; Mello, R. In *Organic Peroxides*; Ando, W., Ed.; John Wiley: Chichester, 1992; pp 195–219. (e) Adam, W.; Smerz, A. K. *Bull. Soc. Chim. Belg.* **1996**, *105*, 581599.

(2) Wolowiec, S.; Kochi, J. K. *J. Chem. Soc., Chem. Commun* **1990**, 1782–1784.

(3) Wolowiec, S.; Kochi, J. K. *Inorg. Chem.* **1991**, *30*, 1215–1221.

(4) Messeguer, A. *Acros Chim. Acta* **1995**, *1*, 71–73.

(5) For recent references on the oxidation of organic ligands, see: (a) Adam, W.; Schuhmann, R. M. *J. Organomet. Chem.* **1995**, *487*, 273–277. (b) Malisch, W.; Schmitzer, S.; Lankat, R.; Neumayer, M.; Prechtel, F.; Adam, W. *Chem. Ber.* **1995**, *128*, 1251–1255. (c) Schulz, M.; Kluge, R.; Schübler, M.; Hoffmann, G. *Tetrahedron* **1995**, *51*, 3175–3180. (d) Suns, S.; Edwards, J. O.; Sweigart, D. A.; D'Accolti, L.; Curci, R. *Organometallics* **1995**, *14*, 4, 1545–1547. (e) Adam, W.; Smerz, A. K. *Tetrahedron* **1996**, *52*, 5799–5804. (f) Adam, W.; Schuhmann, R. M. *J. Org. Chem.* **1996**, *61*, 874–878. (g) Malisch, W.; Hindahl, K.; Grün, K.; Adam, W.; Prechtel, F.; Sheldrick, W. S. *J. Organomet. Chem.* **1996**, *509*, 209–14. (h) Möller, S.; Fey, O.; Malisch, W.; Seelbach, W. *J. Organomet. Chem.* **1996**, *507*, 239–244.

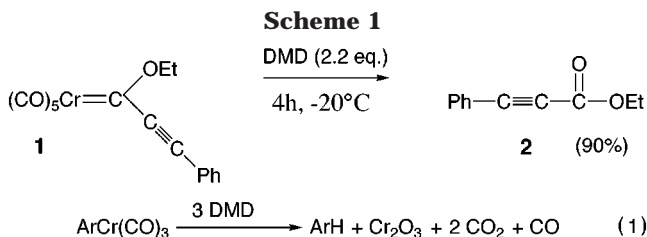
(6) Lluch, A. M.; Sanchez-Baeza, F.; Camps, F.; Messeguer, A. *Tetrahedron Lett.* **1991**, *32*, 5629–5630.

(7) Lluch, A. M.; Jordi, L.; Sanchez-Baeza, F.; Ricart, S.; Camps, F.; Moretó, J. M.; Messeguer, A. *Anal. Quim.* **1994**, *90*, 407–411.

(8) Lluch, A. M.; Jordi, L.; Sanchez, B. F.; Ricart, S.; Camps, F.; Messeguer, A.; Moreto, J. M. *Tetrahedron Lett.* **1992**, *33*, 3021–3022.

(9) Barluenga, J.; Canteli, R.-M.; Florez, J.; Garcia-Granda, S.; Gutierrez-Rodriguez, A. *J. Am. Chem. Soc.* **1994**, *116*, 6949–6950.

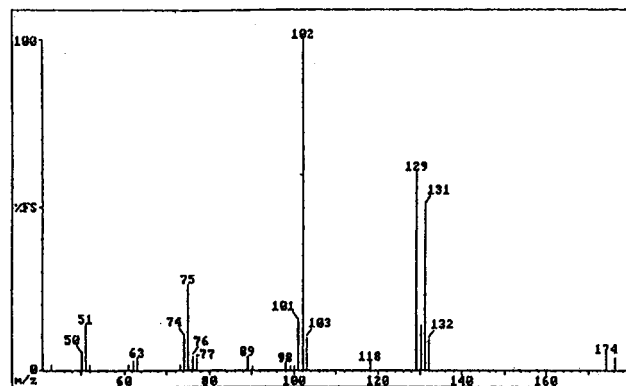
(10) Lluch, A.-M.; Gibert, M.; Sánchez-Baeza, F.; Messeguer, A. *Tetrahedron* **1996**, *52*, 3973–3982.



as oxidation reagents.<sup>13</sup> However, to our knowledge, the case of Fischer carbene complexes had not been examined in detail. Moreover, the consensus reached on the electrophilic character of dioxirane reactivity<sup>14–17</sup> makes difficult to extrapolate the results found for the reactivity of amine *N*-oxides in the above studies to the decomplexation reactions promoted by dioxiranes on Fischer carbene derivatives. Thus, it was interesting to ascertain whether the attack of the dioxirane would involve the reaction of an oxygen atom with the carbene moiety or it would create a vacant on the metal coordination sphere by the oxidative removal of a CO ligand, similarly to which occurs in the *N*-oxides mechanism. Furthermore, the roles of the dioxirane and that of O<sub>2</sub> (a molecule always present in the solutions of these oxidation reagents) in the subsequent steps of the decomplexation process would also be interesting to clarify. In this regard, the decomplexation experiments carried out in <sup>18</sup>O<sub>2</sub> atmosphere or by using for the first time an <sup>18</sup>O-labeled dioxirane, i.e., [<sup>18</sup>O]dimesityldioxirane, were crucial for supporting our conclusions.

### Results and Discussion

The Fischer carbene complex **1** was selected for the present study (Scheme 1). The preliminary assays carried out to determine the stoichiometry of the decomplexation reaction showed that, in contrast to the case of the arenetricarbonylchromium(0) complexes where 3 equiv of the dioxirane were needed to release the arene (eq 1),<sup>6</sup> the amount of DMD required for the complete conversion of the carbene complex **1** was highly dependent on the temperature and on the addition procedure of the dioxirane to the reaction mixture. Thus, 6–7 equiv of DMD was needed if the reagent was added all at once to a solution of **1**. This amount was reduced to 2.2 equiv when the addition was carried out portionwise and at –20 °C. Under these conditions, ethyl phenylacrylate (**2**) was isolated in 90% yield. Likewise, the addition of 2 molar equiv of TFMD (0.5 equiv added at 30 min intervals at –20 °C) to a solution of **1** afforded ester **2** in 91% yield. In both cases, the analysis of the insoluble material formed in the crude reaction mixture revealed that the chromium was present as Cr(III).<sup>18</sup>



**Figure 1.** Mass spectrum (GC-MS, 70 eV) of ethyl phenylacrylate (**2**) partially labeled with <sup>18</sup>O.

On the other hand, 2.2 equiv of the oxidant were also consumed in the reaction of carbene complex **1** with a CO<sub>2</sub>-free DMD solution performed under the above conditions.<sup>19</sup> When this reaction was carried out in N<sub>2</sub> atmosphere, only a 40% conversion of **1** into **2** was observed. However, a 70% yield (NMR analysis) of ester **2** was formed when N<sub>2</sub> was replaced by O<sub>2</sub>. In this case, an equimolar amount of CO<sub>2</sub> (determined by absorption into a Ba(OH)<sub>2</sub> solution) with respect to the starting carbene **1** was trapped.<sup>20</sup> Moreover, the Cr(III) present in the insoluble part of the crude reaction mixture accounted for 67% of the chromium present in **1**, which is a percentage comparable to the yield in ester **2**. These results indicated that (i) the dioxirane probably induced the oxidation of a CO ligand, (ii) part of the dioxirane could be involved in the further oxidation of the intermediate chromium carbonyl species, and (iii) yields in the reaction product depended also on the amount of O<sub>2</sub> present in the reaction medium.

Then, a series of experiments were carried out in the presence of labeled O<sub>2</sub> atmosphere to elucidate the role of O<sub>2</sub> in this decomplexation reaction. When an acetone solution of carbene complex **1** was allowed to stand in an <sup>18</sup>O<sub>2</sub> atmosphere for 7 h at –20 °C, no decomplexation was observed (GC analysis). However, when this assay was performed in the presence of the DMD solution in a solvent system which was previously degassed to ensure the absence of dissolved O<sub>2</sub>, a 25:75 mixture of compounds **1**:**2** was obtained and the GC-MS analysis of this mixture revealed the partial incorporation (approximately 50%) of <sup>18</sup>O in the carbonyl moiety of ester **2** (Figure 1). The presence of peaks at *m/z* 176 (M<sup>+</sup> + 2) and 131 (M<sup>+</sup> + 2 – OEt), accompanied by their non-labeled counterparts at *m/z* 174 and 129, supported this identification. This result confirmed the intervention of O<sub>2</sub> in the decomplexation process.

The unequivocal confirmation that the first step of the decomplexation process involved the dioxirane promoted oxidation of a CO ligand was obtained from the assays carried out using an <sup>18</sup>O-labeled reagent. The reports on

(11) Shen, J. K.; Shi, Y. L.; Gao, Y. C.; Shi, Q. Z.; Basolo, F. *J. Am. Chem. Soc.* **1988**, *110*, 2414–2418.

(12) Shen, J. K.; Gao, Y. C.; Shi, Q. Z.; Basolo, F. *Organometallics* **1989**, *8*, 2144–2147.

(13) For a review on the application of amine *N*-oxides to transition group organometallics, see: Albin, A. *Synthesis* **1993**, 263–277.

(14) Adam, W.; Haas, W.; Lohray, B. B. *J. Am. Chem. Soc.* **1991**, *113*, 6202–6208.

(15) Baumstark, A. L.; Harden, D. B. *J. Org. Chem.* **1993**, *58*, 7615–7618.

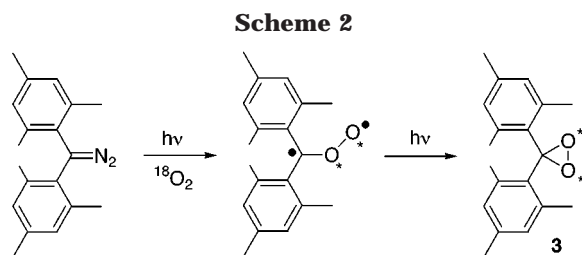
(16) Murray, R. W.; Gu, D. *J. Chem. Soc., Perkin Trans 2* **1993**, 2203–2207.

(17) Adam, W.; Curci, R.; D'Accolti, L.; Dinoi, A.; Fusco, C.; Gasparrini, F.; Kluge, R.; Paredes, R.; Schulz, M.; Smerz, A. K.; Angela Velosa, L.; Weinkötz, S.; Winde, R. *Chem. Eur. J.* **1997**, *3*, 105–109.

(18) In this context, it had been previously checked that the DMD solutions are stable in the presence of Cr(III) salts under the experimental conditions used.

(19) CO<sub>2</sub>-free DMD solutions are prepared by employing a phosphate solution instead of the sodium bicarbonate solution used to buffer the acetone–water–oxone reaction mixture (cf. ref 33).

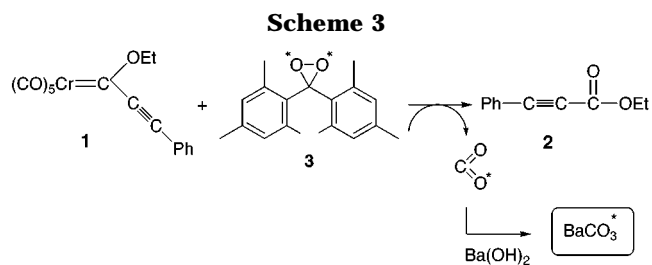
(20) A blank assay carried out in the absence of carbene **1** showed that the DMD concentration remained stable during 4 h.



the generation of  $^{18}\text{O}$ -labeled dioxiranes are scarce.<sup>21–25</sup> In a pioneering work, Edwards et al. used doubly labeled caroate  $^{-}\text{OSO}_2^{18}\text{O}^{18}\text{OH}$  to provide evidence for the involvement of dioxirane intermediates in the ketone-catalyzed decomposition of peroxomonosulfate.<sup>21</sup> However, to our knowledge there is no report on the isolation of an  $^{18}\text{O}$ -labeled dioxirane. In this context, the Sander group described the preparation of the first dioxirane stable in the solid state: dimesityldioxirane (**3**). This compound was obtained by photochemical reaction of the appropriate diazo precursor with oxygen to give the corresponding carbonyl oxide which upon irradiation rearranged into the dioxirane.<sup>26,27</sup> These authors described the generation of [ $^{18}\text{O}$ ]dimesityldioxirane in argon matrices and the registration of its IR spectrum, but there are no data on its isolation and reactivity applications. We deemed that if the above synthetic pathway could be conducted in solution in the presence of  $^{18}\text{O}_2$ , the expected [ $^{18}\text{O}$ ]dimesityldioxirane could be isolated. The ability of this less reactive dioxirane to attack carbene complex **1** as DMD does was, however, unpredictable.

Dimesityldioxirane was synthesized as described by Sander et al. (58% conversion yield,  $^1\text{H}$  NMR) (Scheme 2).<sup>27</sup> Minor modifications were then introduced to adapt the reaction conditions to the use of an  $^{18}\text{O}_2$  atmosphere. In a preliminary assay, a dichloromethane solution of the nonlabeled dioxirane **3** was allowed to react with the carbene complex **1** for 20 h at  $-20\text{ }^\circ\text{C}$ . An  $\text{O}_2$  flow was bubbled into the reaction medium and then through a  $\text{Ba}(\text{OH})_2$  solution to capture the  $\text{CO}_2$  eventually formed in the decomplexation reaction. The  $^1\text{H}$  NMR analysis of the crude reaction mixture showed the presence of ester **2** (15% yield) and unreacted carbene complex **1** as sole reaction products. Likewise, the formation of  $\text{BaCO}_3$  was also observed. These results confirmed that the dioxirane **3** was capable of inducing the oxidative decomplexation of the carbene complex, although the yield was considerably lower than that for the case of DMD.

The preparation of [ $^{18}\text{O}_2$ ]dimesityldioxirane took place in 34% conversion yield ( $^1\text{H}$  NMR).<sup>28</sup> The  $^1\text{H}$  and  $^{13}\text{C}$  NMR



spectra of this compound agreed with those reported by Sander et al. for the non-labeled derivative. Moreover, the GC-MS analysis of the crude reaction mixture showed the presence of dimesityl ketone and mesityl mesitoate, both labeled with  $^{18}\text{O}$ . The presence of this ester, a product from the rearrangement of the dioxirane under the analytical conditions used, confirmed the formation of the oxidation reagent.

When a solution of [ $^{18}\text{O}_2$ ]dimesityldioxirane was reacted with Fischer carbene **1** under the conditions used for the assay with the non-labeled dioxirane (Scheme 3), the formation of  $\text{BaCO}_3$  was observed in the  $\text{Ba}(\text{OH})_2$  solution trap. The IRMS analysis of the  $\text{CO}_2$  present in this sample gave a  $\delta^{18}\text{O}_{\text{PDB}}$  value of  $-15.04$ , which compared to the value obtained from a blank  $\text{BaCO}_3$  sample ( $\delta^{18}\text{O}_{\text{PDB}} = -19.00$ ),<sup>29</sup> confirmed the incorporation of  $^{18}\text{O}$  into the  $\text{CO}_2$ . On the other hand, the  $^1\text{H}$  NMR of the crude reaction mixture showed the presence of a 30% of ester **2**. Moreover, the GC-MS analysis of the fractions obtained from the purification of this crude reaction mixture by column chromatography showed that ethyl phenylpropyl propyl ester was not labeled with  $^{18}\text{O}$ . These results indicated that the dioxirane oxidized a CO ligand of the Fischer carbene complex to give  $\text{CO}_2$  and that this reaction would originate an unstable species which reacted with  $\text{O}_2$  and not with labeled dioxirane **3** to give the non-labeled ester **2**.

At this point the detection of the intermediate chromium tetracarbonyl species was attempted. Foley et al. had described the characterization of tetracarbonyl species derived from tungsten Fischer carbene complexes. Thus, upon irradiation of  $[\text{W}(\text{CO})_5\text{C}(\text{OMe})\text{Ph}]$  in  $\text{CH}_3\text{CN}$  solution, the formation of the corresponding  $[\text{W}(\text{CO})_4(\text{CH}_3\text{CN})\text{C}(\text{OMe})\text{Ph}]$  complex was observed by IR, UV, and  $^1\text{H}$  NMR. The data obtained supported that the CO ligand replaced by the  $\text{CH}_3\text{CN}$  moiety was in the cis configuration.<sup>30</sup> In our case, the irradiation of a solution of the chromium complex **1** in  $\text{CH}_3\text{CN}$  led to the formation of a species with IR absorptions at 2023, 1946, 1905, and  $1841\text{ cm}^{-1}$ , consistent with the presence of the expected tetracarbonyl intermediate. When the reaction was assayed in THF solution, the above peaks appeared at 2059, 1978, 1938, and  $1895\text{ cm}^{-1}$ . In both cases, exposure of these solutions to the air atmosphere resulted in the formation of ester **2**.<sup>31</sup> To our knowledge this is the first detection of a tetracarbonyl species derived from a chromium Fischer carbene complex. However, when a solution of carbene complex **1** in  $\text{CH}_3\text{CN}$  was allowed to

(21) Edwards, J. O.; Pater, R. H.; Curci, R.; Di-Furia, F. *Photochem. Photobiol.* **1979**, *30*, 63–70.

(22) Armstrong, A.; Clarke, P. A.; Wood, A. *J. Chem. Soc., Chem. Commun.* **1996**, 849–850.

(23) Armstrong, A.; Barsanti, P. A.; Clarke, P. A.; Wood, A. *J. Chem. Soc., Perkin Trans. 1* **1996**, 1373–1380.

(24) Denmark, S. E.; Wu, Z. *J. Org. Chem.* **1997**, *62*, 8964–8965.

(25) Schulz, M.; Liebsch, S.; Kluge, R.; Adam, W. *J. Org. Chem.* **1997**, *62*, 188–193.

(26) Kirschfeld, A.; Muthusamy, S.; Sander, W. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2212–2214.

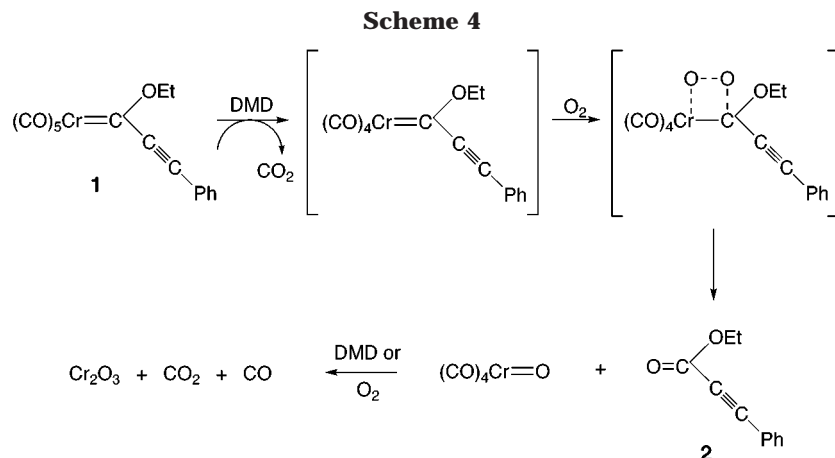
(27) Sander, W.; Schroeder, K.; Muthusamy, S.; Kirschfeld, A.; Kappert, W.; Boese, R.; Kraka, E.; Sosa, C.; Cremer, D. *J. Am. Chem. Soc.* **1997**, *119*, 7265–7270.

(28) Actually a 62% of the corresponding ketone derivative was present in the crude reaction mixture. It has been described that this ketone is mostly originated from the carbonyl oxide intermediate (cf. ref 27).

(29) The  $\text{BaCO}_3$  formed in the preliminary reaction carried out in the presence of non-labeled dioxirane **3** was used as a blank probe for the IRMS measurements.

(30) Foley, H. C.; Strubinger, L. M.; Targos, T. S.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1983**, *105*, 3064–3073.

(31) All attempts to identify the above species by  $^{13}\text{C}$  NMR were unsuccessful and only the presence of ester **2** was detected in the NMR tube. This result could be due to the long times needed for the accumulation of the corresponding spectra.



react with 1 equiv of a  $\text{CCl}_4$  solution of DMD at  $0^\circ\text{C}$  in the absence of oxygen, the IR spectrum of the crude reaction mixture showed the presence of ester **2** and no evidence of the above tetracarbonyl species was observed. This result suggested that DMD might oxidize a CO ligand different from that removed under the above photochemical conditions and that the generated chromium tetracarbonyl intermediate would be highly unstable.

In conclusion, we propose that the dioxirane promoted decomplexation of Fischer carbene complexes follows the reaction course shown in Scheme 4. Thus, the dioxirane would oxidize a CO ligand to  $\text{CO}_2$  with the concomitant formation of an unstable chromium tetracarbonyl species. This species would react with  $\text{O}_2$  to give the final ester product and chromium(III) oxide. Therefore, the metal coordination sphere, and not the carbene moiety, is the target for the initial attack of the dioxirane. On the other hand, the generated chromium tetracarbonyl intermediate, a species with an electron configuration capable of promoting mono-electron-transfer processes, would be the responsible for the first step of the reaction with  $\text{O}_2$ . This reaction might involve a dioxetane-like intermediate which would lead to the formation of ester **2** and a chromium tetracarbonyloxo species, and ultimately to chromium(III) oxide by further oxidation. The proposed mechanism is also consistent with our observations about the DMD excesses required for driving the decomplexation of compound **1** to completion, the fact that only a 50% label was incorporated into ester **2** when the decomplexation of **1** was carried out in  $^{18}\text{O}_2$  atmosphere and that in the absence of oxygen atmosphere the reaction does take place although with lower conversion yields. It is known that reducing species such as superoxide or iodide anions are capable to catalytically induce an efficient decomposition of DMD with the concomitant release of oxygen.<sup>32</sup> In the present case, it is conceivable that the intermediate chromium species generated during the decomplexation could act as electron-transfer agents in front of DMD and promote its decomposition.

### Experimental Section

**General.** The IR spectra were recorded in with a Bomen model MB120 apparatus. The NMR spectra ( $^1\text{H}$  NMR, 300 MHz;  $^{13}\text{C}$  NMR, 75 MHz) were recorded with a Varian model Unity 300 apparatus: the spectra were performed in freshly

neutralized  $\text{CDCl}_3$  solutions, and chemical shifts are given in ppm downfield from  $\text{Si}(\text{CH}_3)_4$  for  $^1\text{H}$  and  $\text{CDCl}_3$  for  $^{13}\text{C}$ . All spectra were registered from solutions where Fischer carbene complexes could be present that were previously filtered through Millipore Millex-HV<sub>13</sub> cartridges. For the quantitative measures carried out by  $^1\text{H}$  NMR using 1,1,2,2-tetrachloroethane as internal standard, 19 s per scan were fixed for ensuring the same response for all hydrogen atoms. The gas chromatography–mass spectrometry (GC–MS) analyses were performed with the electron ionization mode using a 30 m HP-5 capillary column (0.25 mm i.d.). The HPLC analyzes were performed with a modular system formed by two Waters 510 pumps and an Model 783 Applied Biosystems detector–gradient controller (UV detection). The HPLC column used was a Spherisorb ODS-2 (5  $\mu\text{m}$ ) and  $\text{CH}_3\text{CN}-\text{H}_2\text{O}$  mixtures at 1 mL/min were employed as mobile phase. Unless indicated otherwise, photochemical experiments were carried out by employing a Rayonet photochemical reactor (Middletown, CT, USA). The  $^{18}\text{O}_2$  cylinder (98.1 atom %) was from SDS, Peypin, France. The Isotopic Ratio Mass Spectrometry (IRMS) determinations were carried out with a Delta S (Finnigan Mat) apparatus at the University of Barcelona.

The DMD solutions (80 mM in acetone) were prepared as described elsewhere<sup>33</sup> and dried over 4 Å molecular sieves. For the experiments carried out to measure the evolution of  $\text{CO}_2$ , the DMD was generated in a phosphate buffer solution at pH 7.8. The TFMD solutions (0.5–0.6 M) were prepared as described elsewhere.<sup>34</sup> Unless otherwise stated, organic solutions obtained from the workup of crude reaction mixtures were dried over  $\text{MgSO}_4$  and the purification procedures were carried out by flash chromatography on silica gel.

**Pentacarbonyl(ethoxy)phenylethynylcarbenechromium(0) (1a).** This complex was prepared according to the procedure described by Fischer and Kreissl<sup>35</sup> with slight modifications. Butyllithium (12 mmol, 1.5 M in hexane) was added to a solution of phenylacetylene (1.3 mL, 12 mmol) in anhydrous THF (70 mL) at  $-78^\circ\text{C}$  under argon atmosphere. The reaction mixture was stirred for 30 min at that temperature and 1 h at  $-30^\circ\text{C}$ ; then 100 mL of anhydrous THF and hexacarbonylchromium(0) (2.6 g, 12 mmol) were added to the crude reaction mixture, and the stirring was prolonged at the same temperature for 2 h. Triethyloxonium tetrafluoroborate (5 g, 26 mmol) was added to the mixture, and after 5 min the reaction was quenched by addition of saturated  $\text{NaHCO}_3$  solution (25 mL). The crude reaction mixture was extracted with hexane, and the organic fractions were washed with brine and dried. The residue obtained from the elimination of solvents was purified by chromatography on silica gel eluting with a 95:5 hexane– $\text{CH}_2\text{Cl}_2$  mixture to give 3.50 g (83% yield)

(33) Adam, W.; Bialas, J.; Hadjarapoglou, L. *Chem. Ber.* **1991**, *124*, 2377.

(34) Mello, R.; Fiorentino, M.; Fusco, C.; Curci, R. *J. Am. Chem. Soc.* **1989**, *111*, 6749–6757.

(35) Fischer, E. O.; Kreissl, F. R. *J. Organomet. Chem.* **1972**, *35*, C47–C51.

(32) Adam, W.; Asensio, G.; Curci, R.; Gonzalez, N. M. E.; Mello, R. *J. Am. Chem. Soc.* **1992**, *114*, 8345–9.

of the pure carbene complex. For **1a**: IR (CH<sub>3</sub>CN) 2156, 2061, 1988, 1951; <sup>1</sup>H NMR  $\delta$  7.45–7.60 (5 H), 4.76 (q, 2 H,  $J = 7.1$  Hz), 1.59 (t, 3 H,  $J = 7.1$  Hz); <sup>13</sup>C NMR  $\delta$  313.8, 225.7, 216.3, 135.6, 132.7, 131.6, 128.9, 121.0, 91.8, 75.8, 15.0.

**Decomplexation of the Fischer Carbene Complex 1 with DMD.** A solution of complex **1** (0.099 g, 0.28 mmol) in acetone (10 mL), previously filtered over Celite and protected from light, was treated with the DMD solution (two dropwise additions of 6.8 mL, 0.56 mmol overall, during 4 h at  $-20$  °C). When the reaction was completed (TLC monitoring), the excess of reagent was eliminated by evaporation under vacuum (25 °C, 20 Torr). The residue was resuspended in CH<sub>2</sub>Cl<sub>2</sub> and filtered through Celite to remove the chromium oxides. The evaporation of the solvent afforded pure ethyl phenylpropiolate (**2**) (0.044 g, 90% yield).

**Determination of the CO<sub>2</sub> Generated during the Reaction of the Fischer Carbene Complex 1 with DMD.** A solution of **1** (0.140 g, 0.40 mmol) in acetone (20 mL) was treated with DMD (19 mL, 0.9 mmol, generated in phosphate buffer and added in two aliquots within 4 h). The volatile compounds formed were flushed with an O<sub>2</sub> stream and bubbled through a known volume of a 0.9 M Ba(OH)<sub>2</sub> solution. Titration of the nonreacted Ba(OH)<sub>2</sub> permitted the determination of the CO<sub>2</sub> evolved (0.4 mmol). On the other hand, the <sup>1</sup>H NMR analysis of the crude reaction mixture showed the presence of ethyl phenylpropiolate (**2**) (70% conversion yield).

**Dimesityldioxirane.** This compound was prepared according to the procedure described previously by Kirschfeld et al.<sup>26</sup> with slight modifications. An oxygen-saturated solution of dimesityldiazomethane in CFCl<sub>3</sub>, maintained at  $-78$  °C, was irradiated with a white lamp (50 W, high-temperature halogen), filtered through a solution of CuCl<sub>2</sub> (7.2 g), and concentrated HCl (5 mL) in 100 mL of H<sub>2</sub>O (2 cm optical path). When the reaction was completed (3 h, HPLC control), the analysis of the crude reaction mixture by <sup>1</sup>H NMR revealed the presence of 58% of dimesityldioxirane and 32% of dimesityl ketone. For dimesityldioxirane: <sup>1</sup>H NMR  $\delta$  6.82 (s, 4 H), 2.26 (s, 6 H), 2.21 (s, 12 H); <sup>13</sup>C NMR  $\delta$  138.9, 137.7, 130.8, 103.1, 21.5, 21.3. When the decomposition of the diazo compound was carried out in <sup>18</sup>O<sub>2</sub> atmosphere, a mixture of dimesityl ketone (62%) and dimesityldioxirane (34%) was obtained. The GC-MS analysis of this mixture revealed the presence of the ketone and mesityl mesitoate both labeled with <sup>18</sup>O.

**Decomplexation of Carbene Complex 1b with Dimesityldioxirane.** A three-necked flask containing 5.3 mg (15.1  $\mu$ mol) of complex **1** was purged with dry and CO<sub>2</sub>-free oxygen gas; then CH<sub>2</sub>Cl<sub>2</sub> (4 mL) was added to the flask, and the solution was purged for an additional 20 min. The reaction flask was immersed in an ice bath, and one outlet was connected to a 30 mM Ba(OH)<sub>2</sub> solution. A solution of the <sup>18</sup>O-

labeled dimesityldioxirane (1 mL) was added to the reaction flask in two portions at 30 min intervals, and the mixture was allowed to react for 20 h maintaining the O<sub>2</sub> flow to pull the evolved CO<sub>2</sub> into the Ba(OH)<sub>2</sub> solution trap. The BaCO<sub>3</sub> precipitate was isolated by centrifugation, dried (15 h, 60 °C), and analyzed by isotopic ratio mass spectrometry (IRMS). For this purpose, the precipitate was treated with H<sub>3</sub>PO<sub>4</sub> for 2 h at 50 °C and the CO<sub>2</sub> released was extracted and purified in a vacuum line by means of appropriate cryogenic traps. The BaCO<sub>3</sub> formed in the preliminary reaction carried out in the presence of non labeled dioxirane **3** was used as a blank probe for the IRMS measurements. On the other hand, the <sup>1</sup>H NMR analysis of the crude reaction mixture revealed the presence of a 30% of ethyl phenylpropiolate, and the GC-MS analysis of the collected fractions from the purification of the crude reaction mixture by column chromatography (elution with 4:1 hexane-CH<sub>2</sub>Cl<sub>2</sub>), showed only the presence of non-labeled ethyl phenylpropiolate.

**Irradiation of Fischer Carbene Complex 1.** Following a procedure described by Foley et al.,<sup>30</sup> a solution of **1** (25 mg, 0.07 mmol) in anhydrous AcCN (4 mL) was irradiated with UV light at 350 nm under inert atmosphere until reaction was completed (1 h, IR monitoring). The IR analysis (CH<sub>3</sub>CN) of the crude reaction mixture showed the presence of absorption peaks (2154, 2023, 1946, 1905, 1841) that were assigned to a tetracarbonyl ((ethoxy)phenylethynylcarbene) chromium(0) derivative.

**Acknowledgment.** Financial support from CICYT-Generalitat de Catalunya (grant QFN 95-4717) and fellowships from the Generalitat de Catalunya (M.G.) and the Ministerio de Educación y Ciencia (A.L.) are acknowledged. We are indebted to Prof. W. Sander and Mrs. Kerstin Schroeder (der Ruhr-Universität, Germany) for their valuable advise on the preparation of dimesityldioxirane. We thank Prof. J. L. Burdelande (Universitat Autònoma de Barcelona) for helpful discussions and suggestions on the photochemical aspects of this work and Dr. Pilar Teixidó (University of Barcelona) for the IRMS determinations.

**Supporting Information Available:** Experimental procedures, including synthesis and characterization data of all new compounds, and decomplexation experiments with dioxiranes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JO982065E