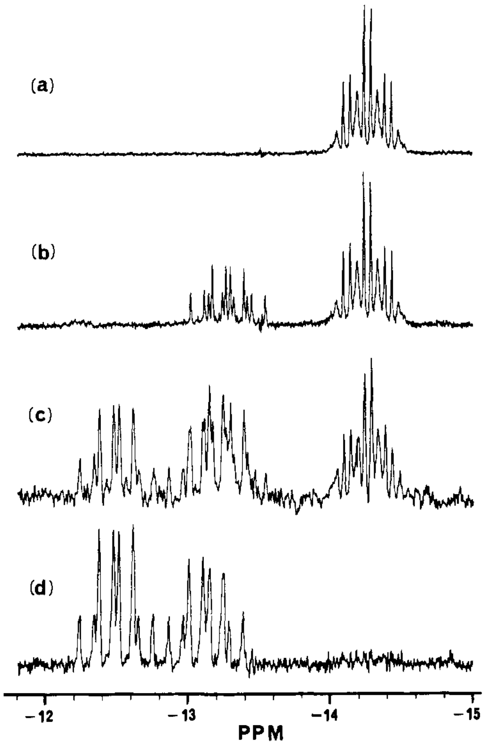
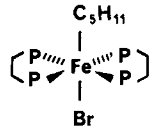


Figure 1. High-field (iron hydride) region of the ^1H NMR spectra (400 MHz, pentane solution, -50 °C): (a) *cis*-$Fe(DMPE)_2H_2$ (**2**); (b) solution of **2** after irradiation[9] in pentane for 70 min at -90 °C; (c) solution of **2** after irradiation[9] in pentane for 70 min at -30 °C; (d) mixture of (*E*)- and (*Z*)-1-pentenyl hydrides, **5a** and **5b**, obtained on irradiation of **2** in a solution (5%) of 1-pentene in pentane for 90 min at -80 °C.

Irradiation of **2** in cyclopentane (or other alkanes) at low temperature produced analogous but different alkyl metal hydrides.

When a solution containing **3** was allowed to react[12] with CH_2Br_2 at -78 °C and warmed to room temperature, *trans*-(1-pentyl)$Fe(DMPE)_2Br$ (**4**)[13] was formed. Treatment of a solution containing **3** with bromine in pentane at -78 °C resulted in formation of 1-bromopentane.[14] When a solution containing **3** was quenched at -78 °C with deuteriotrifluoroacetic acid, the ^2H NMR spectrum of pentane[14] which was recovered from the reaction mixture showed incorporation of deuterium at C1. There was no evidence for reaction of pentane at C2 or C3.



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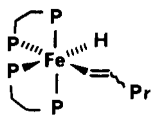
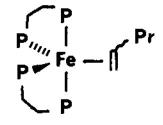


5a: E
5b: Z



5c

Irradiation of **2** in dilute pentane solution at higher temperatures (ca. -30 °C) produced 1-pentene[14] and a mixture containing the known[8] 1-pentenyl iron hydrides **5a** and **5b** and the π-complex **5c**, as well as **3** (Figure 1c). We have previously shown[8] that the complexes **5a–c** are formed when **2** is irradiated in the presence of 1-pentene (Figure 1d). We propose that on irradiation at -30 °C, the pentyl iron hydride **3** forms initially but is unstable at this temperature and decomposes by β-hydride elimination[15] to produce 1-pentene[16] and regenerate the starting dihydride **2** (Scheme II). While the scheme is cyclic, the 1-pentene formed is far more reactive than pentane and the reactive iron species **1** is trapped eventually by the alkene.

The major byproducts of the photolysis of **2** (in all solvents) showed resonances at ca. 62 and 10 ppm in the ^{31}P NMR spectrum, and these are close to those reported for the DMPE-bridged dimer, $Fe_2(DMPE)_5$.[7c] After short periods of irradiation, the resonances were reasonably sharp and showed some multiplicity; the resonances broadened significantly after prolonged irradiation. In more concentrated solutions, the byproducts formed in higher yield. These observations suggest that the byproducts are probably oligomeric or polymeric species arising via intermolecular attack of **1** on other iron complexes present in solution.

In this paper, we have clearly demonstrated for the first time that iron species can be made that are sufficiently reactive to add intermolecularly to the C–H bonds of alkanes, even at −100 °C. We are currently investigating the application of iron complexes to the functionalization of alkanes and alkyl groups.

Acknowledgment. We gratefully acknowledge financial support from the Australian Research Grants Scheme and the Australian Government for a Commonwealth Postgraduate Award (M. V. B.).

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(12) In a typical experiment, 2–4 equiv of a solution of CH_2Br_2 0.2 M in pentane) was added to a photolysis mixture containing the iron hydride at -78 °C. The sample was warmed to room temperature, stripped of solvent under vacuum, and extracted into deuteriobenzene. After they were quenched, the mixtures always contained *trans*-$Br_2Fe(DMPE)_2$ in varying amounts.

(13) 4: $^{31}P\{^1H\}$ NMR spectrum (C_6D_6, 25 °C) δ 63.51. $^1H\{^{31}P\}$ NMR spectrum (C_6D_6, 25 °C) δ −1.672, $FeC\mathit{H}_2CH_2CH_2CH_2CH_3$; 0.488, $FeCH_2C\mathit{H}_2CH_2CH_2CH_3$; 0.902, $FeCH_2CH_2CH_2CH_2C\mathit{H}_3$; 1.118, $FeCH_2CH_2C\mathit{H}_2CH_2CH_3$; 1.278, $FeCH_2CH_2CH_2C\mathit{H}_2CH_3$; 1.102, 1.582, $P(C\mathit{H}_3)_2$; 1.545, 1.815, $PC\mathit{H}_2C\mathit{H}_2P$. This compound is also formed in the reaction of 1-pentylmagnesium bromide with *trans*-$Br_2Fe(DMPE)_2$ at 0 °C in THF.

(14) All quenching experiments were performed against appropriate (unirradiated) blanks. Formation of deuteriopentane was assayed by ^2H NMR spectroscopy of pentane recovered from the reaction mixture. Formation of 1-bromopentane was verified by ^1H NMR spectroscopy and GLC against an authentic sample. Formation of 1-pentene was verified by ^1H NMR spectroscopy and conversion to its dibromo derivative by reaction with Br_2.

(15) β-Elimination of the alkene from **3** would probably proceed with prior partial dissociation of one of the bidentate phosphine ligands to make available a coordination site on the metal. See, for example: (a) Jones, W. D.; Kosar, W. P. *J. Am. Chem. Soc.* **1986**, *108*, 5640–5641. (b) Jones, W. D.; Libertini, E. *Inorg. Chem.* **1986**, *108*, 1794–1800.

(16) Alkane dehydrogenation reactions have been reported previously in complexes of iridium and rhenium. See, for instance: (a) Crabtree, R. H.; Mihelcic, J. M.; Quirk, J. M. *J. Am. Chem. Soc.* **1979**, *101*, 7738. (b) Crabtree, R. H.; Mellea, M. F., Mihelcic, J. M.; Quirk, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 107. (c) Baudry, D.; Ephritikhine, M.; Felkin, H.; Zakrzewski, J. *Tetrahedron Lett.* **1984**, *25*, 1283. (d) Baudry, D.; Ephritikhine, M.; Felkin, H. *J. Chem. Soc., Chem. Common.* **1980**, 1243. (e) Baudry, D.; Ephritikhine, M.; Felkin, H.; Zakrzewski, J. *J. Chem. Soc., Chem. Commun.* **1982**, 1235.

Oxidative Addition of Carbon Dioxide, Epoxides, and Related Molecules to $WCl_2(PMePh_2)_4$ Yielding Tungsten(IV) Oxo, Imido, and Sulfido Complexes. Crystal and Molecular Structure of $W(O)Cl_2(CO)(PMePh_2)_2$

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We have recently reported the first examples of complexes with both terminal oxo ligands and carbonyl or olefin groups: $W(O)Cl_2(L)(PMePh_2)_2$, L = CO (**2**), $CH_2{=}CH_2$ (**3**), $CH_2{=}CHMe$ (**4**), $CNCMe_3$ (**5**), etc.[2] We proposed that compounds **2–4** might be models for intermediates in olefin or carbon monoxide oxidation by metal oxides. These compounds do not, however, rearrange to epoxides, carbon dioxide, or other products of ligand oxidation. Ligand oxidation was suggested to be

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(1) (a) University of Washington. (b) University of Delaware.

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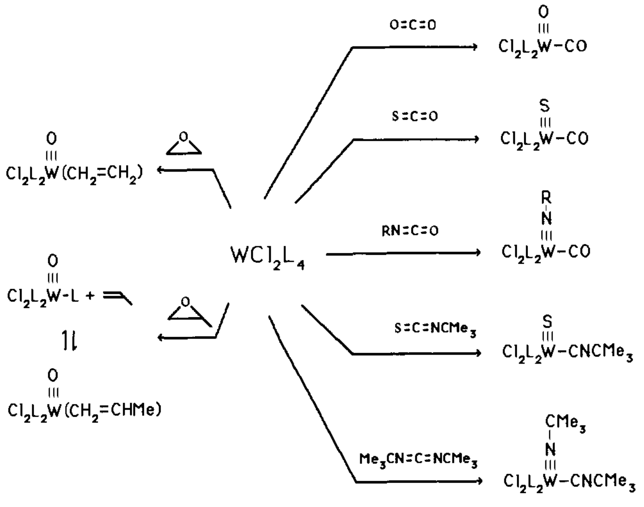
0002-7863/87/1509-2826$01.50/0

Scheme I. Reactions of WCl_2L_4:
L = $PMePh_2$; R = CMe_3, $SiMe_3$, *p*-Tolyl



thermodynamically unfavorable because of the strength of the tungsten–oxygen multiple bond. We now report that **2**–**4** can be prepared by the reverse reaction, oxidative addition of CO_2 and epoxides to $WCl_2(PMePh_2)_4$ (**1**).

A benzene solution of the tungsten(II) complex $WCl_2(PMePh_2)_4$ (**1**)[3] reacts with carbon dioxide at 1 atm of pressure and ambient temperatures to form the tungsten(IV) oxo-carbonyl complex **2** and $PMePh_2$ in >95% yields (by NMR, eq 1, Scheme I). This

$$\underset{\mathbf{1}}{WCl_2(PMePh_2)_4} + CO_2 \rightarrow \underset{\mathbf{2}}{W(O)Cl_2(CO)(PMePh_2)_2} + 2PMePh_2 \quad (1)$$

is an unprecedented reaction of carbon dioxide, involving insertion of a metal into the carbon–oxygen double bond. CO_2 is usually considered difficult to activate with transition-metal complexes, although there are examples of reactions that form carbonyl or in a few cases oxo complexes.[4]

Complex **2** has been fully characterized by an X-ray crystal structure (Figure 1).[5] The cis-chloride/trans-phosphine configuration and the bond lengths are similar to those found for the oxo-ethylene complex **3**.[2] The short tungsten–oxygen multiple bond length of 1.689 (6) Å and the tungsten–carbon distance of 2.029 (9) Å are within the ranges previously observed for these bonds.[2,6,7] These data, together with the linear W–C–O linkage (177.0 (7)°) and the separation between the oxo and carbonyl ligands (O(1)···C(2) = 2.63 Å), show that there is little if any contribution from a possible η^2-carbon dioxide resonance form. There may, however, be significant direct orbital overlap between the strongly π-donating oxo group and the π-accepting carbonyl ligand.[8] Complex **2** adopts a very distorted octahedral geometry, with all three "trans" angles below 167° and "cis" angles ranging from 75.5 (3) to 103.4 (2)°; in **3** the distortions primarily involve the phosphine ligands (cf. the P–W–P angle of 154.7 (1)°). The distortions may occur not only for steric reasons but also to maximize π-bonding between the tungsten center and the oxo and carbonyl ligands.[8a] The large O(1)–W–Cl(2) angle in **2** (103.4 (2)°) and the long W–Cl bond trans to the oxo ligand (W–Cl(1) = 2.504 (2) Å, W–Cl(2) = 2.411 (3) Å) are typical of metal oxo complexes.[2,6,9]

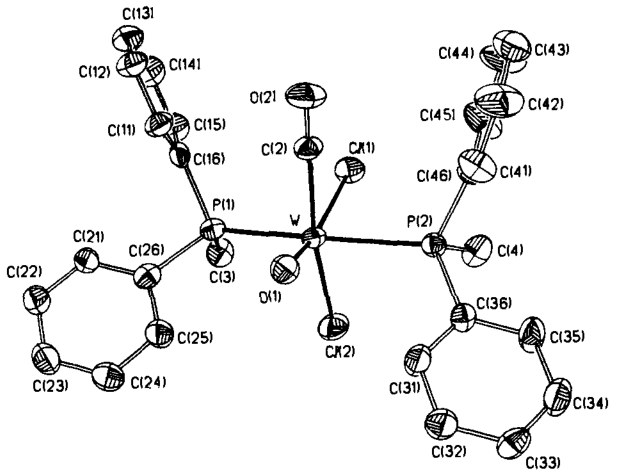


Figure 1. ORTEP drawing of $W(O)Cl_2(CO)(PMePh_2)_2$ with 50% probability thermal ellipsoids. Selected bond distances (Å) and angles (deg) not mentioned in the text: W–P(1) = 2.538 (2), W–P(2) = 2.539 (2), C(2)–O(2) = 1.142 (11), O(1)–W–C(2) = 89.6 (3), O(1)–W–P(1) = 98.3 (2), O(1)–W–P(2) = 97.4 (2), O(1)–W–Cl(1) = 165.1 (2), P(1)–W–P(2) = 163.2 (1), C(2)–W–Cl(2) = 166.8 (3), C(2)–W–Cl(1) = 75.5 (3), Cl(1)–W–Cl(2) = 91.6 (1), C(2)–W–P(1) = 93.9 (2), C(2)–W–P(2) = 92.0 (2).

Epoxides also react rapidly with **1**: 1 equiv of ethylene oxide gives a high yield of the oxo-ethylene complex **3** (eq 2). The

$$\underset{\mathbf{1}}{WCl_2(PMePh_2)_4} + \overline{CH_2CH_2O} \rightarrow \underset{\mathbf{3}}{W(O)Cl_2(CH_2{=}CH_2)(PMePh_2)_2} + 2PMePh_2 \quad (2)$$

reaction of propylene oxide yields an equilibrium mixture of **4**, $W(O)Cl_2(PMePh_2)_3$ (**6**), propylene, and $PMePh_2$ (Scheme I). Epoxides have previously been observed to react as oxygen atom donors,[10] but this is the first case in which both the oxygen and olefin remain bound to a metal center.

The facile reaction with CO_2 suggests that a variety of multiply bonded substrates will add to **1**. We have found that carbonyl sulfide, isocyanates, thioisocyanates, and carbodiimides react with **1** under mild conditions to form sulfido-carbonyl, imido-carbonyl, sulfido-isonitrile, and imido-isonitrile complexes (Scheme I).[11] NMR spectra indicate that in all cases only one tungsten product is formed, in other words that one C=X bond is selectively cleaved. The imido-carbonyl complex $W(NCMe_3)Cl_2(CO)(PMePh_2)_2$ and the previously prepared isomeric oxo-isonitrile complex **5**[2] do not interconvert at 80 °C. The reaction of **1** with carbon disulfide forms $SPMePh_2$[12] and paramagnetic tungsten product(s); sulfur dioxide gives $SPMePh_2$, **6**, and insoluble materials. Triphenyl-

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(5) Crystal data for $W(O)Cl_2(CO)(PMePh_2)_2$: monoclinic, $P2_1/c$; a = 17.551 (4), b = 6.866 (2), c = 22.806 (5) Å; β = 91.55 (2)°, V = 2747 (1) Å^3, Z = 4, D_c = 1.54 g cm^{-3}, 23 °C. A Nicolet R3 diffractometer was used to collect 5914 data ($4° \le 2\theta \le 50°$) of which 3541 data with $F_o > 5\sigma(F_o)$ were used in the solution and refinement. An empirical absorption correction was applied to all data (μ(Mo Kα) = 46.6 cm^{-1}). The structure was solved by heavy-atom methods. All remaining non-hydrogen atoms were located on subsequent difference Fourier syntheses. Methyl and phenyl hydrogens were calculated and fixed at 0.96 Å from carbon; the phenyl rings were refined as rigid hexagons (d(C–C) = 1.395 Å). Structure refined to R_F = 3.42% and R_{wF} = 3.87%; GOF = 1.046, highest final difference peak, 1.19 e/Å^3 (near W).

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(11) Full spectroscopic and analytical data are given in the supplementary material. Selected IR data (cm^{-1}): for $W(S)Cl_2(CO)L_2$, ν(CO) = 1986; for $W(NR)Cl_2(CO)L_2$ ν(WNC) = 1098, 1122, 1099 and ν(CO) = 1966, 1976, 1964 (R = CMe_3, $SiMe_3$, *p*-tolyl); for $W(S)Cl_2(CNCMe_3)L_2$ ν(CN) = 2127; for $W(NCMe_3)Cl_2(CNCMe_3)L_2$, ν(WNC) = 1100, ν(CN) = 2090.

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phosphine oxide, however, is not readily deoxygenated by **1**, although it does appear to coordinate to the tungsten(II) center.

The reactions shown in Scheme I are a novel type of oxidative addition process. Classical oxidative addition reactions, such as the addition of H_2, involve cleavage of a single bond and formation of two monovalent ligands.[13] In the reactions reported here a formal double bond is cleaved to form a divalent and a neutral ligand. Furthermore, very strong bonds are broken in the reactions: removal of an oxygen atom from CO_2 requires 127 kcal/mol.[14] In the reactions of heterocumulenes, the weaker C=X bond appears to be cleaved, which may reflect the formation of an η^2-cumulene intermediate.[4] Oxidative addition of epoxides may proceed via an oxametallacyclobutane intermediate,[15] as suggested for the reverse reaction, the formation of epoxides from metal oxo complexes.[16] Alternative mechanisms resembling inner-sphere electron-transfer processes[17] can also be imagined, such as direct oxygen atom transfer from an epoxide or from CO_2 to tungsten. These questions will be discussed in detail in a future publication.

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Supplementary Material Available: Spectroscopic data, analytical data, and crystallographic data—tables of atomic coordinates, bond distances and angles, anisotropic temperature factors, and hydrogen atom coordinates (8 pages); table of observed and calculated structure factors (21 pages). Ordering information is given on any current masthead page.

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10-Hydroperoxy-8,12-octadecadienoic Acid: A Diagnostic Probe of Alkoxyl Radical Generation in Metal-Hydroperoxide Reactions

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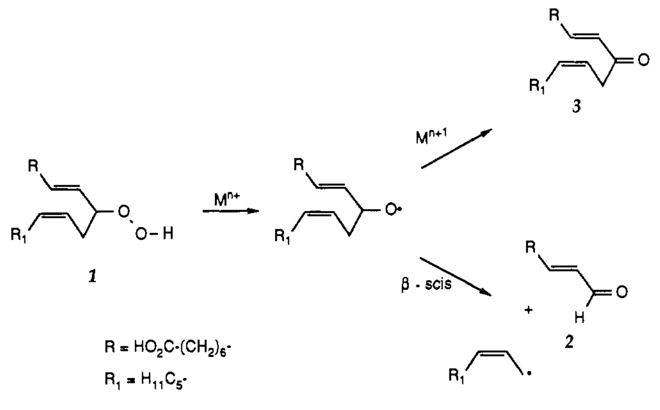
Alkyl hydroperoxides undergo heterolytic or homolytic cleavage when they react with metals and metalloproteins.[1] Homolytic cleavage generates alkoxyl radicals that oxidize cell constituents when the radicals are formed in plant and animal tissue.[2] One-electron reduction of hydroperoxides in chemical or biochemical systems is difficult to quantitate because alkoxyl radicals possess short half-lives and give rise to a wide variety of products. Recent reports that hydroperoxides contribute to the initiation, promotion, and progression phases of carcinogenesis have focused attention on the possible role of free radicals in these pathological events.[3] The paucity of quantitative information on metal-catalyzed homolysis of hydroperoxides to alkoxyl radicals prompted us to develop chemical probes for this reaction suitable for use in chemical, biochemical, and biological systems. We report here the results of experiments that indicate 10-hydroperoxy-8,12-octadecadienoic acid (**1**) is an ideal molecule for quantitating the reductive pathways available to hydroperoxides.

Scheme I



1

2

3

R = HO_2C-$(CH_2)_6$-

R_1 = $H_{11}C_5$-

Table I. Metabolism of 10-Hydroperoxy-8,12-octadecadienoic Acid by Metal Complexes

catalyst[a]	**2**,[b] %	**3**, %	**4**, %
$FeSO_4$ (1:1)	84	12	4
$FeCl_3$–cysteine (1:400:100)	92	8	ND[c]
hematin (1:100)	59	35	6
ferrihemoglobin (1:1.3)	65	15	20
PGH synthase (1:100)	4	1	95

[a] Conditions for each experiment were as follow: 3.2 mM $FeSO_4$, 3.2 mM **1** in methanol/water 4/1; 0.05 mM $FeCl_3$, 12.8 mM cysteine, 3.2 mM **1** in methanol/water 4/1; 0.5 μM hematin, 50 μM **1** in 0.1 M $NaPO_4$ (pH 7.8), 200 μM Tween 20; 300 μM ferrihemoglobin (1.2 mM heme), 1.6 mM **1** in 0.1 M $NaPO_4$ (pH 7.8), 200 μM Tween 20; 1 μM PGH synthase, 500 μM phenol, 100 μM **1** in 0.1 M $NaPO_4$ (pH 7.8), 200 μM Tween 20. [b] Values are reported as percent conversion based on recovered **1**. The percentages of **1** recovered were 2, 0, 44, 6, and 6, respectively, in the five experiments. [c] ND: not detected.

β-Scission is a well-established reaction of many alkoxyl radicals.[4] The extent to which β-scission occurs is determined by a number of factors, one of which is the stability of the organic radical generated.[5] Reaction of **1**[6] with ferric chloride–cysteine produced in 92% yield 10-oxo-8-decenoic acid (**2**),[7] a β-scission

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[6] [1-^{14}C]-**1** (21.2 μCi/mmol) was prepared by photosensitized oxygenation of [1-^{14}C]linoleic acid (90 mM, 23.6 μCi) in the presence of methylene blue (0.4 mM) in methanol. The solution was cooled to 0 °C and exposed to a 1000-W high-pressure sodium lamp, filtered to remove UV light. The solution was bubbled with oxygen during irradiation. Monohydroperoxides were purified on a silicilic acid column and then applied to a Whatman Magnum 9 10-μm silica column. Elution was performed with hexane/2-propanol/acetic acid (988/12/1 v/v) at a flow rate of 3.5 mL/min. The identity of **1** was verified by GC-MS of the methyl ester–trimethylsilyl ether of the alcohol reduction product (**4**).

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