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Registry No. I, 52594-52-2; II, 52594-55-5; III (R = Me), 88036-59-3; III (R = Et), 88036-60-6; III (R = I-Pr), 88036-61-7; III (R = H), 88036-62-8; III (R = H, X = PF_6), 88036-79-7; IIIa, 88036-68-4; IIIb, 88036-69-5; IIIc, 88036-70-8; IIId, 88036-76-4; IIIe, 88036-77-5; IIIf, 88036-78-6; IV (R = Me), 88036-63-9; IV (R = Et), 88036-64-0; IV (R = *i*-Pr), 88036-65-1; IV (R = H), 88036-66-2; IVa, 88036-71-9; IVb, 88036-72-0; VII, 88036-67-3; VIII, 88036-75-3; IX, 88036-74-2; $[PtMe_2(O\text{-}i\text{-}Pr)(OH)(phen)]$, 88036-73-1; $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$, 79870-64-7.

Mechanism of the Photochemical Oxidation of $Fe(CO)_5$ and $CpW(CO)_3Cl$ (Cp = η^5-C_5H_5) by Chlorocarbons

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The photochemical oxidation of $CpW(CO)_3Cl$ (Cp = η^5-C_5H_5) by carbon tetrachloride and other polychlorocarbons affords $CpW(CO)_2Cl_3$. The sole photoprocess is dissociation of CO from the complex to give $CpW(CO)_2Cl$. The major pathway of the oxidation involves the net transfer of two halogen atoms from one halocarbon molecule to the unsaturated metal complex. Pathways involving the formation of trichloromethyl radical were shown to be unimportant. In a related reaction, the photooxidation of $Fe(CO)_5$ in carbon tetrachloride gives $FeCl_2$, tetrachloroethylene, tar, and minor amounts of hexachloroethane. As in the $CpW(CO)_3Cl$ system, trichloromethyl radical is produced in, at most, only minor amounts. The reaction proceeds through an iron dichlorocarbene intermediate. Evidence for such an intermediate includes formation of isocyanides, phosgene, and thiophosgene when the oxidation is carried out in the presence of primary amines, dioxygen, and sulfur, respectively. In addition, tetrachloroethylene forms in neat carbon tetrachloride. Various alternative explanations for the above phenomena are considered and found unsatisfactory. The iron carbene species is proposed to arise via oxidative addition of carbon tetrachloride to photolytically generated $Fe(CO)_4$, followed by α-chlorine elimination. Degradation of the complex can then result in either dimerization or telomerization of the dichlorocarbene moiety. The $CpW(CO)_3Cl$ system is believed to follow an analogous pathway.

Introduction

We recently reported that $CpW(CO)_3Cl$ reacts photochemically with CCl_4 to give $CpW(CO)_2Cl_3$ (eq 1).[1] Because of our interest in the synthesis of high oxidation state organometallic complexes, we investigated the mechanism of this reaction. Mechanistic studies of halocarbon oxidations of organometallic complexes have been reported by several research groups.[2] Broadly speaking, three different fundamental mechanisms have been proposed.

$$CpW(CO)_3Cl \xrightarrow[CCl_4]{h\nu} CpW(CO)_2Cl_3 \qquad (1)$$

In the first type of mechanism, the initiating step is coordination of the halocarbon to the metal complex.[3] An example is the oxidation of $ReCl_3(RCN)(PPh_3)_2$ reported by Wilkinson[4] (eq 2). He suggested the mechanism shown in eq 3–5. The essence of this and related mechanisms is the coordination of RX to a vacant coordination site followed by R–X bond cleavage:

$$ReCl_3(RCN)(PPh_3)_2 + CCl_4 \rightarrow ReCl_4(PPh_3)_2 + RCN + {}^1/{}_2C_2Cl_6 \qquad (2)$$

$$ReCl_3(RCN)(PPh_3)_2 + CCl_4 \rightarrow ReCl_3(CCl_4)(PPh_3)_2 + RCN \qquad (3)$$

$$ReCl_3(CCl_4)(PPh_3)_2 \rightarrow ReCl_4(PPh_3)_2 + CCl_3 \qquad (4)$$

$$2CCl_3 \rightarrow C_2Cl_6 \qquad (5)$$

$$M \leftarrow X\text{–}R \rightarrow M\text{–}X + R \qquad (6)$$

A second type of pathway proposed in halocarbon oxidation mechanisms is the electron-transfer mechanism[5] invoked, for example, in the oxidation of $Mo(CO)_2(dmpe)_2$ (dmpe = $Me_2PCH_2CH_2PMe_2$) by CCl_4. Connor[6] has proposed that this reaction proceeds as shown in eq 7–10. The key feature of this and related reactions is the initial step in which the metal complex is oxidized by the alkyl halide.

$$Mo(CO)_2(dmpe)_2 + CCl_4 \rightarrow [Mo(CO)_2(dmpe)_2]^+ + CCl_4^- \qquad (7)$$

$$CCl_4^- \rightarrow Cl^- + CCl_3 \qquad (8)$$

$$[Mo(CO)_2(dmpe)_2]^+ + Cl^- \rightarrow [Mo(CO)_2(dmpe)_2]Cl \qquad (9)$$

$$[Mo(CO)_2(dmpe)_2]Cl + CCl_4 \rightarrow [MoCl(CO)_2(dmpe)_2]Cl + CCl_3 \qquad (10)$$

The third type of mechanism proposed in halocarbon oxidation reactions is the radical pathway, exemplified by the photochemical oxidation of $Mn_2(CO)_{10}$ in CCl_4 to form

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Table I. Relevant Spectroscopic Data

complex	infrared, ν(CO), cm^{-1} (ϵ, M^{-1} cm^{-1})	^{1}H NMR, δ(Cp)	electronic, λ_{max}, nm (ϵ, M^{-1} cm^{-1})
$CpW(CO)_3Cl$	2052 (3000), 1969 (5300), 1950 (2450)^{a} 2044 (2400), 1956 (3500)^{b}	5.980 (s)^{h}	460 (560), 315 (2400)^{b}
$(MeCp)W(CO)_3Cl$	2046 (2600), 1963 (4100), 1945 (2000)^{a}	5.696 (t, J(HH) = 2.1 Hz)^{i} 5.272 (t, J(HH) = 2.1 Hz), 2.022 (s)	455 (540), 318 (2000), 252 (8000)^{l}
$CpMo(CO)_3Cl$	2056, 1986, 1962^{a} 2052, 1977^{b}		470 (504), 320 (1980, sh)^{b,10}
$(MeCp)Mo(CO)_3Cl$	2051, 1981, 1957^{a}		
$[CpW(CO)_3]_2$	1952, 1903^{b}	5.47 (s)^{i,10}	484 (2500), 356 (21 000)^{f}
$[(MeCp)Mo(CO)_3]_2$	1954 (9000), 1913 (7000)^{a}		506 (2400), 390 (20 000)^{a}
$(MeCp)W(CO)_2Cl_3$	2091, 2040^{c}		
$CpW(CO)_2Cl_3$	2094 (900), 2044 (1400)^{d}	6.332 (s),^{h} 6.372^{j}	395 (240), 255 (3400, sh)^{l}
$CpW(CO)_2Br_3$	2084, 2036^{d}	6.417 (s)^{j}	
$CpW(CO)_2BrCl_2$	2089 (980), 2039 (1450)^{d}	6.393 (s)^{j}	
$CpW(CO)_2(PhCH_2)Cl_2$	2090, 2042^{e}	7.26 (s), 6.49 (s), 2.95 (s)^{k}	
$CpW(CO)_2(PPh_3)Cl$	1965, 1870^{f,10}		
$CpW(CO)_2(AsPh_3)Cl$	1962, 1870^{11}	5.39^{11}	
$CpW(CO)_2(THF)Cl$	1937, 1822^{g}		
CS_2	1522 (2200)^{a,m}		
Cl_2CS	1124 (900)^{a,m}		
Cl_2CO	1811 (950)^{a,m}		
BuNC	2145 (250)^{a,m}		

^{a} CCl_4 solution. ^{b} Benzene solution. ^{c} Suspension in CCl_4. ^{d} Acetone solution. ^{e} Benzyl chloride solution. ^{f} Chloroform solution. ^{g} THF solution. ^{h} CCl_4 and acetone-d_6 solution. ^{i} $CDCl_3$ solution. ^{j} Acetone-d_6 solution. ^{k} Me_2SO-d_6 solution. ^{l} Dichloromethane solution. ^{m} ν(CX) (X = S, O, and N).

$Mn(CO)_5Cl$.[7] The pathway shown in eq 11 and 12 is proposed.

$$Mn_2(CO)_{10} \xrightarrow{h\nu} 2Mn(CO)_5 \qquad (11)$$

$$Mn(CO)_5 + CCl_4 \rightarrow Mn(CO)_5Cl + CCl_3 \qquad (12)$$

Note that both the coordination and electron-transfer pathways can involve the intermediate formation of metal complex radicals and/or organic radicals. The distinction between these pathways and the radical mechanism is that only in the latter does the halocarbon react initially with a metal-centered radical.

In our investigation of the mechanism of reaction 1 we soon discovered that none of the above pathways was operative, and we therefore undertook a thorough study of the mechanism. Because of certain ambiguities in the results, we also studied a "model" system, the CCl_4 oxidation of $Fe(CO)_5$[8] (eq 13). The results of our mechanistic study of the $Fe(CO)_5$ and $CpW(CO)_3Cl$ systems are reported in this paper.

$$Fe(CO)_5 + CCl_4 \rightarrow FeCl_2 + 5CO + \text{carbon-containing products} \qquad (13)$$

Results

$CpW(CO)_3Cl$. Irradiation (330 < λ < 550 nm) of $CpW(CO)_3Cl$ in CCl_4 forms $CpW(CO)_2Cl_3$ according to eq 1 in greater than 90% yield. The quantum yield (ϕ = 0.48, 366 nm, neat CCl_4) for the reaction is independent of radiation intensity (2.8×10^{-7}–39×10^{-7} einsteins/min) and it is also independent of the concentration of the $CpW(CO)_3Cl$ complex (2.5×10^{-3}–14×10^{-3} M). The reaction with CCl_4 is inhibited by excess CO; in 1.8 M CCl_4 in benzene the quantum yield (366 nm) drops from 0.31 under 1 atm argon to 0.21 under 1 atm CO. The quantum yield is not affected by the radical inhibitor galvinoxyl. When a solution of $CpW(CO)_3Cl$ (27 mM) and galvinoxyl (54 mM) in CCl_4 and acetone (2:3, v:v) is irradiated (λ > 470 nm),[9] reaction 1 proceeds at a rate no different than in the absence of galvinoxyl in an otherwise identical solution.

Irradiation (λ = 366 nm) of $CpW(CO)_3Cl$ (5×10^{-2} M) in THF solution at −78 °C caused the disappearance of the $CpW(CO)_3Cl$ absorption bands at 1954 and 2042 cm^{-1} and the appearance of two new absorption bands at 1937 and 1822 cm^{-1}, as monitored by infrared spectroscopy. The infrared spectrum of the product is typical of a $CpM(CO)_2(L)Cl$ species (see Table I), and we conclude that this photoreaction is described by eq 14. The $CpW(CO)_2(THF)Cl$ complex is stable as long as the reaction solution is kept at −78 °C. On warming the solution to room temperature, however, the $CpW(CO)_3Cl$ complex is regenerated. The addition in the dark of a THF solution of triphenylphosphine to a solution of $CpW(CO)_2(THF)Cl$ followed by warming to room temperature results in formation of $CpW(CO)_2(PPh_3)Cl$ as determined by infrared spectroscopy (Table I). Addition of 0.3 mL of CCl_4 in the dark to a $CpW(CO)_2(THF)Cl$ solution and subsequent warming to room temperature yielded $CpW(CO)_2Cl_3$ (and some $CpW(CO)_3Cl$) (eq 15).

$$CpW(CO)_3Cl \xrightarrow[-78\ ^\circ C]{h\nu,\text{THF}} CpW(CO)_2(THF)Cl + CO \qquad (14)$$

$$CpW(CO)_2(THF)Cl \xrightarrow[CCl_4]{\text{dark}} \xrightarrow{\text{warm to room temp}} CpW(CO)_2Cl_3 \qquad (15)$$

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Table II. Summary of Reactions, Conditions, and Products

reaction and conditions	metal-containing product	halocarbon products (yield)
Control Experiments		
$[(MeCp)Mo(CO)_3]_2$ (96 mM)/acetone:CCl_4 (3:1) (λ > 490 nm)	$(MeCp)Mo(CO)_3Cl$	C_2Cl_6 (70 ± 10%)
$[(MeCp)Mo(CO)_3]_2$ (96 mM)/acetone:CCl_4 (3:1); CO bubbled through during irradiation (λ > 490 nm)	$(MeCp)Mo(CO)_3Cl$	C_2Cl_6 (70 ± 10%)
$[(MeCp)Mo(CO)_3]_2$ (15 mM)/CCl_4 (λ > 490 nm)	$(MeCp)Mo(CO)_3Cl$	C_2Cl_6 (100 ± 10%)
$Mn_2(CO)_{10}$ (15 mM)/CCl_4 (λ > 350 nm)	$Mn(CO)_5Cl$	C_2Cl_6 (100 ± 10%)
$[(MeCp)Mo(CO)_3]_2$ (15 mM)/CCl_4 (λ > 545 nm)	$(MeCp)Mo(CO)_3Cl$	C_2Cl_6 (90 ± 10%)
$[(MeCp)Mo(CO)_3]_2$ (15 mM)/CCl_4 (λ > 560 nm)	$(MeCp)Mo(CO)_3Cl$	C_2Cl_6 (90 ± 10%)
$[(MeCp)Mo(CO)_3]_2$ (15 mM) + $Fe(CO)_5$ (0.1 M)/CCl_4 (λ > 560 nm)	$(MeCp)Mo(CO)_3Cl$	C_2Cl_6(80 ± 10%) C_2Cl_4 (1.4 mM)
$[(MeCp)Mo(CO)_3]_2$ (15 mM)/CCl_4; neutral density filter (OD = 1.0)[a] (λ > 560 nm)	$(MeCp)Mo(CO)_3Cl$	C_2Cl_6 (90 ± 10%)
$[(MeCp)Mo(CO)_3]_2$ (15 mM) + $Fe(CO)_5$ (20 mM)/CCl_4; neutral density filter (OD = 1.0) (λ > 560 nm)	$(MeCp)Mo(CO)_3Cl$	C_2Cl_6 (85 ± 10%) C_2Cl_4 (<0.4 mM)
Some Typical $CpW(CO)_3Cl$ and $Fe(CO)_5$ Oxidation Conditions		
$CpW(CO)_3Cl$ (0.135 M)/acetone:CCl_4 (3:1) (λ > 320 nm)	$CpW(CO)_2Cl_3$	C_2Cl_6 (<2%)
$CpW(CO)_3Cl$ (15 mM)/CCl_4 (λ > 400 nm)	$CpW(CO)_2Cl_3$	C_2Cl_6 (10%)
$Fe(CO)_5$ (0.1 M)/CCl_4 (λ > 350 nm)	$FeCl_2$	C_2Cl_4 (45 ± 5%) C_2Cl_6 (4 ± 1%)
$Fe(CO)_5$ (20 mM)/CCl_4 (λ > 350 nm)	$FeCl_2$	C_2Cl_4 (65 ± 5%) C_2Cl_6 (4 ± 1%)
$Fe(CO)_5$ (10 mM)/CCl_4 (λ > 370 nm)	$FeCl_2$	C_2Cl_4 (65 ± 5%) C_2Cl_6 (3 ± 1%)
$Fe(CO)_5$ (20 mM)/CCl_4; neutral density filter (OD = 1.0) (λ > 370 nm)	$FeCl_2$	C_2Cl_4 (50 ± 5%) C_2Cl_6 (4 ± 1%)

[a] OD = optical density.

Analysis of the non-metal-containing products of reaction 1 revealed the formation of CO, some C_2Cl_6, and a tar. Measurements showed that 1 mol of CO was evolved/mol of $CpW(CO)_3Cl$ consumed. In a typical experiment 0.070 g (1.90×10^{-4} mol) of $CpW(CO)_3Cl$ was irradiated (λ > 330 nm) in 8 mL of acetone and 2 mL of CCl_4, and 4.4 mL of CO was collected in a gas-tight syringe at 25 °C. This volume corresponds to 1.8×10^{-4} mol of CO; i.e., the stoichiometry is 1:1 $CpW(CO)_3Cl$ (consumed):CO (evolved). That the gas evolved is indeed CO was confirmed by infrared spectroscopy.[12]

Gas chromatographic analysis of the reaction solution obtained from reaction 1 showed that C_2Cl_6 was formed in only 5–15% yield based on $CpW(CO)_3Cl$ disappearance. To check that the solvent/reaction system was not somehow decomposing C_2Cl_6 or reacting with trichloromethyl radicals from which it would presumably form, we generated CCl_3 by known methods in the same solvent system used in reaction 1. The reactions used to generate CCl_3 are shown in eq 16 and 17.[7] These control experiments were run under a wide variety of conditions (Table II), and a high yield of C_2Cl_6 was obtained in all cases. Thus, the low yield of C_2Cl_6 in reaction 1 cannot be attributed to CCl_3 radicals being intercepted by the solvent system before coupling can occur. ESR spin-trapping experiments confirm that only small amounts of CCl_3 radicals form in reaction 1. Irradiation of $CpW(CO)_3Cl$ (19 mM) in CCl_4 with nitrosodurene (40 mM) in the cavity of the ESR spectrometer produces a signal attributable to the CCl_3–nitrosodurene adduct[13] ($g = 2.007$, $a_N = 10.7$, $a_{Cl} = 1.3$). The signal was very weak, approximately 5% of the intensity of the signal obtained when 19 mM solutions of either $(MeCp)_2W_2(CO)_6$ or $Mn_2(CO)_{10}$ were irradiated in CCl_4 with nitrosodurene.

$$(MeCp)_2M_2(CO)_6 \xrightarrow[CCl_4]{h\nu} 2(MeCp)M(CO)_3Cl + 2CCl_3 \qquad (16)$$

$$M = Mo, W$$

$$Mn_2(CO)_{10} \xrightarrow[CCl_4]{h\nu} 2Mn(CO)_5Cl + 2CCl_3 \qquad (17)$$

Finally, regarding the low yield of C_2Cl_6, control experiments showed that C_2Cl_6 is not consumed under the conditions of reaction 1. When a CCl_4 solution of $CpW(CO)_3Cl$ (15 mM) and C_2Cl_6 (10 mM) was irradiated, the resulting small net production of C_2Cl_6 (≃1 mM) was no different than that from an otherwise identical solution to which no C_2Cl_6 had been added, as monitored by gas chromatography. It should also be noted that irradiation of $CpW(CO)_3Cl$, either in neat CCl_4 or in CCl_4 with added C_2Cl_6 (10 mM), does not result in the formation of C_2Cl_4, the expected product of C_2Cl_6 reduction. Irradiation of $CpW(CO)_3Cl$ (15 mM) in CCl_4 in the presence of C_2Cl_4 (10 mM) results in no change in the concentration of C_2Cl_4. Thus, C_2Cl_6 is not consumed at the concentrations in which it might be produced under the conditions of reaction 1.

For the sake of completeness the reactivity of $CpW(CO)_3Cl$ with a much higher concentration of C_2Cl_6 was investigated. When $CpW(CO)_3Cl$ (20 mM) in benzene (2.5 mL) and C_2Cl_6 (1.0 g) was irradiated (λ > 350 nm), C_2Cl_4 was produced in quantitative yield (19 ± 2 mM) based on eq 18. (The same result was obtained by using $Fe(CO)_5$ in place of $CpW(CO)_3Cl$.) It is noteworthy that photooxidation of $[(MeCp)Mo(CO)_3]_2$ in the same solvent system yields C_2Cl_4 in approximately 3 times stoichiometric yield based on eq 19. Specifically, irradiation (λ > 540 nm) of $[(MeCp)Mo(CO)_3]_2$ (20 mM) in benzene (2.5 mL) and C_2Cl_6 (1.0 g) results in formation of $(MeCp)Mo(CO)_3Cl$ (37

$$CpW(CO)_2Cl + C_2Cl_6 \xrightarrow{h\nu} CpW(CO)_2Cl_3 + C_2Cl_4 \qquad (18)$$

$$[(MeCp)Mo(CO)_3]_2 + C_2Cl_6 \xrightarrow{h\nu} 2(MeCp)Mo(CO)_3Cl + C_2Cl_4 \qquad (19)$$

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mM) as detected by infrared spectroscopy and C_2Cl_4 (58 ± 5 mM) as detected by gas chromatography.

$CpW(CO)_3Cl$ can be photooxidized by various other halocarbons as well as CCl_4; the quantum yield for the oxidation is dependent on the halocarbon. Disappearance quantum yields (436 nm, 2.0 M halocarbon in methylene chloride under 1 atm of CO[14]) decreased in the order Ph_2CCl_2 (0.22) > $PhCCl_3$ (0.16) > CCl_4 (0.13) > Ph_3CCl (0.12) > $PhCH_2Cl$ (0.09). The only metal-containing product of the reaction with $PhCCl_3$, Ph_2CCl_2, and CCl_4 is $CpW(CO)_2Cl_3$. In the reaction with benzyl chloride only a minor amount (<20%) of $CpW(CO)_2Cl_3$ formed and the major product was a violet, thermally unstable, oxygen-sensitive complex. This product had an infrared spectrum very similar to that of a $CpW(CO)_2X_3$ complex, but the color and solubilities were very different from those of the yellow-green $CpW(CO)_2Cl_3$. The NMR spectrum of the complex (Table I) suggests that it is $CpW(CO)_2Cl_2(CH_2Ph)$, i.e., a product of the oxidative addition of $PhCH_2Cl$ to the fragment $CpW(CO)_2Cl$.

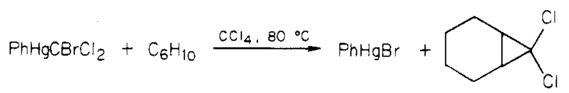
Irradiation of $CpW(CO)_3Cl$ in acetone and $CBrCl_3$ (1:1) proceeds according to eq 20.

$$CpW(CO)_3Cl \xrightarrow[CBrCl_3]{h\nu} CpW(CO)_2BrCl_2 \qquad (20)$$

The product $CpW(CO)_2BrCl_2$ was identified by IR (ν(CO) = 2039, 2089 cm^{-1} (acetone)), ^{1}H NMR (6.33 ppm (acetone-d_6)), and elemental analysis.

The tar formed in reaction 1 is a brown substance with no distinctive features in the infrared, electronic absorption, ^{1}H NMR, or ^{13}C NMR spectra. Studies using ^{14}C-labeled CCl_4 show that the tar contains 1.1 ± 0.2 ^{14}C-labeled mol of carbon/mol of $CpW(CO)_3Cl$ consumed. Attempts to obtain a satisfactory elemental analysis of this substance were unsuccessful as it contains substantial amounts of $CpW(CO)_2Cl_3$ from which the tar could not be separated.

Because C_2Cl_6 (and hence CCl_3) is not formed in any great amount in reaction 1, we felt dichlorocarbene might be the major organic species initially formed in reaction 1. However, all attempts to intercept :CCl_2 failed. For example, irradiation of $CpW(CO)_3Cl$ (15 mM) in a 10% volume solution of cyclohexene in CCl_4 did not afford 7,7-dichloronorcarane. Note that control experiments using the known dichlorocarbene precursor $PhHgCBrCl_2$[15] using mM), in the same solvent system, gave quantitative yields of dichloronorcarane (eq 21). Reaction 21 was carried out under various conditions mimicking those of reaction 1; under CO (1 atm) or in the presence of $CpW(CO)_3Cl$ (15 mM), the reaction proceeded no differently.



(21)

Because we were unable to get definitive results on the nature of the reduced organic product with the $CpW(CO)_3Cl$ system, we turned our attention to a simpler "model" system, the photoreaction of $Fe(CO)_5$ with CCl_4.

$Fe(CO)_5$. The photochemical reaction of $Fe(CO)_5$ with CCl_4 proceeds as in reaction 13.[8] Gas chromatographic analysis of the reaction solution, [$Fe(CO)_5$] = 10–150 mM, reveals C_2Cl_4 as the major organic product in yields of 35–70% and C_2Cl_6 in 3–5% yield. There was no clear dependence of the C_2Cl_4 yield on light intensity or $Fe(CO)_5$ concentration. ESR spin-trapping experiments with nitrosodurene gave no noticeable signal attributable to the CCl_3—nitrosodurene adduct or any other radical species. It can be shown that C_2Cl_6 is not being formed and then significantly consumed by irradiating $Fe(CO)_5$ (20 mM) in CCl_4 with added C_2Cl_6 (10 mM); only a slight increase in the concentration of C_2Cl_6 is observed by gas chromatography. Furthermore, the yield of C_2Cl_4, the expected reduction product of C_2Cl_6, is not increased by the addition of C_2Cl_6 to the reaction solution.

The following experiments also showed that C_2Cl_6 was not reacting to form C_2Cl_4 under the reaction conditions. Irradiation (λ > 350 nm) of $Fe(CO)_5$ (20 mM) in CCl_4 with added C_2Cl_5H (10 mM) followed by gas chromatographic analysis showed the following chlorocarbon species in solution: C_2Cl_4 (6.5 mM, 65% yield), C_2Cl_3H (0.4 mM), C_2Cl_6 (0.4 mM), and C_2Cl_5H ($\simeq$10 mM). It could be argued that the rate of reaction with C_2Cl_6 is much greater than with C_2Cl_5H and that even the small concentration of C_2Cl_6 present would suppress a reaction with C_2Cl_5H. However, this was shown not to be the case by irradiating (λ > 350 nm) $Fe(CO)_5$ (20 mM) in CCl_4 with both C_2Cl_6 (10 mM) and C_2Cl_5H (10 mM) present. The chlorocarbon product distribution as determined by gas chromatography was essentially unchanged from that above: C_2Cl_4 (6.5 mM), C_2Cl_3H (0.4 mM), C_2Cl_6 ($\simeq$10 mM), and C_2Cl_5H ($\simeq$10 mM). Thus we can conclude that the small concentrations of C_2Cl_6 produced in reaction 13 do not react significantly with $Fe(CO)_5$.

To test for the formation of free dichlorocarbene, reaction 13 was carried out in the presence of cyclohexene (1.0 M) resulting in a small yield ($\simeq$7%) of 7,7-dichloronorcarane but no C_2Cl_6 or C_2Cl_4.

As mentioned, C_2Cl_4 forms in reaction 13 in yields of 35–70%. The remaining carbon is found in a brown tar. ^{14}C studies reveal the presence of CCl_4-derived carbon in amounts corresponding to 1.1 ± 0.2 mol/mol of oxidized iron not accounted for by C_2Cl_4 or C_2Cl_6. The tar was separated from $FeCl_2$ by extracting it with H_2O. The resulting residue contained approximately 30% by weight labeled carbon as determined by ^{14}C counting, and in agreement with this it analyzed as $C_{1.0}H_{0.34}Cl_{0.54}O_{0.27}$.

Tests for the formation of a coordinated dichlorocarbene species were positive. Irradiation (λ > 350 nm) of $Fe(CO)_5$ (50 mM) with sulfur (0.5 mol L^{-1}) produced 13.5 mM carbon disulfide (as detected by infrared spectroscopy, Table I) and an approximately 2% yield of C_2Cl_4. The expected product of a $Fe{=}CCl_2$ species with S_8 would be $SCCl_2$,[16,18] but control experiments show that irradiation (λ > 350 nm) of the above reaction mixture with added $SCCl_2$ gives complete conversion of the $SCCl_2$ to CS_2. Metallodichlorocarbene complexes have been found to react with amines to form isocyanides (eq 22).[19] We employed this reaction as a test for such species. Irradiation (λ > 350 nm) of $Fe(CO)_5$ (20 mM) in CCl_4 with added $BuNH_2$ (0.12 M) at −20 °C gave BuNC (2 mM, 10% yield as determined by infrared spectroscopy, Table I):

$$Fe(TPP)(CCl_2) + 2RNH_2 \rightarrow Fe(TPP)(RNH_2)(CNR) \qquad (22)$$

TPP = tetraphenylphorphyrin

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[14] Quantum yields were measured under CO in order to maintain a rate of back-reaction with CO which was nearly constant and significantly competitive with the halocarbon oxidation reaction.

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$$Fe(CO)_5 + BuNH_2 \xrightarrow[-20\ °C,\ CCl_4]{h\nu} CNBu \qquad (23)$$

Carrying out reaction 13 ([$Fe(CO)_5$] = 3.0 mM, $\lambda > 350$ nm) in CCl_4 saturated with dry air ([O_2] = 2.6 mM)[20] resulted in the formation of phosgene (1.5 mM), as detected by infrared spectroscopy (Table I). The yield of phosgene was 50% based on oxidation of a metallodichlorocarbene species. As it is known[21] that trichloromethyl can react with dioxygen to yield phosgene and hexachloroethane, control experiments were run to determine if trichloromethyl would be oxidized under the reaction conditions. Irradiation ($\lambda > 560$ nm) of $[(MeCp)Mo(CO)_3]_2$ (3.0 mM) afforded quantitative $(MeCp)Mo(CO)_3Cl$ (6.0 mM) and hexachloroethane (2.8 ± 0.2 mM), as determined by infrared spectroscopy (Table I) and gas chromatography, respectively, and no significant amounts of phosgene (<0.2 mM). Experiments in our laboratory show that the oxidation of trichloromethyl radical does not significantly compete with dimerization under the steady-state concentrations that would result from the conditions of reaction 13 in the case of a radical mechanism.[22]

Finally, we added "activated" olefins[17] (vinyl ethyl ether, dimethyl maleate) to the $Fe(CO)_5/CCl_4$ reaction solution. A multitude of carbon-containing products was formed as detected by gas chromatography, but no dichlorocyclopropane species were among the various products.

Noteworthy is the fact that the results of similar experiments to detect metallodichlorocarbene species with the $CpW(CO)_3Cl/CCl_4$ system were mostly negative. In the presence of *n*-butylamine (0.12 M), irradiation ($\lambda >$ 400 nm) of $CpW(CO)_3Cl$ in CCl_4 failed to yield either $CpW(CO)_2Cl_3$ or *n*-butyl isocyanide. In nondegassed CCl_4, irradiation ($\lambda > 400$ nm) of $CpW(CO)_3Cl$ (3.0 mM) afforded a small amount of $CpW(CO)_2Cl_3$ ($\simeq$0.5 mM) and a small yield of phosgene ($\simeq$0.5 mM). Independent experiments showed that $CpW(CO)_2Cl_3$ is destroyed by both *n*-butylamine and oxygen, and it is thus undetermined whether the complex ever actually formed in these experiments. In the presence of sulfur (0.5 mol L^{-1}) irradiation of $CpW(CO)_3Cl$ failed to yield $CpW(CO)_2Cl_3$, and neither thiophosgene nor carbon disulfide were observed. $CpW(CO)_2Cl_3$ was found to be stable in the presence of sulfur; thus sulfur in some way inhibited reaction 1.

Discussion

The low-temperature photoreaction of $CpW(CO)_3Cl$ in THF to form the complex $CpW(CO)_2(THF)Cl$ indicates that the primary photoprocess of reaction 1 is dissociation of a CO molecule from the complex. This is not unexpected in view of the extensive substitution chemistry of $CpW(CO)_3Cl$ and related complexes.[10] The reactivity of the $CpW(CO)_2(THF)Cl$ complex with CCl_4 can be attributed to cleavage of the very weak W–THF bond when the solution is warmed; the coordinatively unsaturated $CpW(CO)_2Cl$ species thus generated then reacts with CCl_4. The resulting formation of $CpW(CO)_2Cl_3$ in the dark shows that the reaction of CCl_4 with $CpW(CO)_2Cl$ is thermal and not photochemical. Thus, the only effect of the photon in reaction 1 is to create a vacant coordination site on the tungsten complex. Presumably reaction 13 is initiated analogously, by the photodissociation of CO from $Fe(CO)_5$ to form the unsaturated species $Fe(CO)_4$.[23]

Scheme I

$$Fe(CO)_5 \xrightarrow{h\nu} Fe(CO)_4 + CO$$

$$Fe(CO)_4 + CCl_4 \longrightarrow Fe(CO)_4(CCl_3)Cl$$

I

$$Fe(CO)_4(CCl_3)Cl \longrightarrow Fe(CO)_3(CCl_3)Cl + CO$$

II

α-elimination

$$Fe(CO)_3(CCl_3)Cl \longrightarrow Fe(CO)_3(CCl_2)Cl_2$$

III

$$2Fe(CO)_3(CCl_2)Cl_2 \longrightarrow 2FeCl_2 + C_2Cl_4 + 6CO$$

The unsaturated intermediates produced by photolysis might react with CCl_4 in any of several ways. Radical mechanisms are commonly implicated in oxidations of transition-metal carbonyls and related species,[2-7,24] but our results clearly demonstrate that CCl_3 radicals are not formed in reactions 1 and 13. Control experiments show that CCl_3, under the conditions of reactions 1 and 13, inevitably dimerizes to give C_2Cl_6. The production of C_2Cl_6 in amounts much less than stoichiometric based on reactions 1 or 13 (<15% for eq 1, <5% for eq 13) is indicative of, at most, an only secondary radical pathway.

It has been proposed that reactions similar to reactions 1 and 13 (for example the thermal oxidation of $Fe(CO)_5$ in Ph_2CCl_2) afford radicals that dimerize forming vicinal dihalides.[25] These saturated species then undergo 1,2 dehalogenation to yield olefins. This possibility was considered for reactions 1 and 13; i.e., there is a possibility that C_2Cl_6 is formed but subsequently consumed. However, as the final values of C_2Cl_6 concentration were typically 1–2 mM, this would imply that the rate constant for C_2Cl_6 reduction be on the order of 1000 times that for CCl_4 reduction. This was clearly shown not to be the case by the competition experiments discussed above. These experiments demonstrated that C_2Cl_6 is not consumed at the concentrations in which it would be produced in either reaction 1 or 13.

ESR experiments confirm the conclusion that reactions 1 and 13 involve at most only secondary radical pathways. The small signal intensities due to CCl_3 from reactions 1 and 13, relative to those from reactions known to follow radical pathways, compare nicely with the typical small C_2Cl_6 yields.

An alternative to the radical mechanisms discussed above is a pathway involving oxidative addition. There are numerous precedents for the oxidative addition of alkyl halides to $Fe(CO)_5$.[25,26] For example, $Fe(CO)_5$ is known to react with perfluoroalkyl halides to afford complexes of the type $R_FFe(CO)_4I$.[27] The unusual stability of (perfluoroalkyl)metal complexes is believed to be due to d_π–σ^* back-donation from the metal to the haloalkyl ligand, resulting from the high electronegativity of fluorine.[28] In another example, irradiation of pentane solutions of allyl halides and $Fe(CO)_5$ gives (π-allyl)iron tricarbonyl hal-

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ides.[29] The stability of these species compared to that of corresponding alkylmetal complexes is clearly due to the multiple bonding of the allyl ligand. Thus, oxidative addition of halocarbons to $Fe(CO)_4$ and related unsaturated complexes is probably a quite general reaction; however, the resulting adduct is probably usually thermodynamically and kinetically less stable than the examples above.

We propose a non-radical mechanism for the photooxidation of $Fe(CO)_5$ by CCl_4 as shown in Scheme I.

The phenomena accounted for by this mechanism are as follows: (a) the reaction is initiated by dissociation of CO from $Fe(CO)_5$; (b) different reactivity is displayed by monohalocarbons, i.e., the reaction stops after the oxidative addition step because α-elimination is not possible; (c) no free $:CCl_2$ or CCl_3 intermediates are formed; (d) the intermediacy of a metallodichlorocarbene is indicated. This latter point will now be discussed.

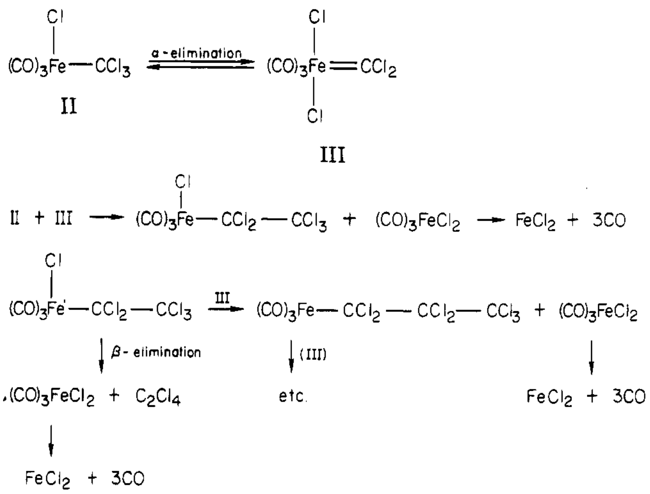
Several metallodichlorocarbene complexes are known, especially for metals in the +2 oxidation state. Mansuy and co-workers have prepared numerous complexes of the type Fe^{II}(porphyrin)(CRR′) (R, R′ = F, Cl, Br).[30] They found that at high temperatures $Fe(TPP)CCl_2$ decomposes to give C_2Cl_4.[31] The formation of olefins is a general decomposition pathway of metallocarbenes, and the mechanism for this process is usually considered not to involve free (uncoordinated) carbenes.[17] Only in special cases does metallocarbene degradation in the presence of olefins lead to cyclopropanation.[17,32] Thus we can explain the formation of C_2Cl_4 in reaction 13 along with the poor yields of cyclopropanation products. Mansuy also found that the reaction of the stable $Fe(TPP)(CCl_2)$ with primary amines, RNH_2 (R = alkyl, aryl), results in production of isocyanides, RNC.[19] Reaction 13 in the presence of $BuNH_2$ affords small yields of BuNC. In view of the short lifetime of intermediate III and competing reactions of $Fe(CO)_5$ with amines[33] it is not surprising that reaction 23 was not quantitative.

Reaction of metallocarbenes, M(CRR′), with S_8 has been found to yield thioketones, SCRR′.[16-18] We find that reaction 13 in the presence of S_8 affords CS_2. Control experiments show that under the same conditions, $SCCl_2$ is quantitatively consumed and converted to CS_2. Similarly, reaction of metallocarbenes with O_2 yields the corresponding ketone, RR′CO. Thus we find that reaction 13 in the presence of O_2 affords phosgene.

Roper has synthesized a stable osmium dichlorocarbene complex $Os(CO)(PPh_3)_2(CCl_2)Cl_2$ (IV).[34] This species is isoelectronic with intermediate III in Scheme I. The greater stability of the osmium complex compared to intermediate III may be due to greater π-back-bonding from the more electron-rich phosphine-disubstituted third-row metal atom. Increased π-back-bonding would be expected to stabilize the electron-deficient dichlorocarbene ligand as well as the metal–CO bond. It is noteworthy that IV is derived from a complex, $Os(Cl)(CCl_3)(CO)(PPh_3)_2$, isoelectronic with the proposed intermediate II.

In other work relevant to metallodichlorocarbene complexes, Rudler and co-workers have suggested the existence of the intermediate $W(CO)_3Cl_2(CCl_2)$ to account for the metathesis of olefins by irradiated solutions of $W(CO)_6$ in CCl_4.[35] However, unlike intermediate III in Scheme I, the $W(CO)_3Cl_2(CCl_2)$ complex was proposed to arise via a pathway involving both free dichlorocarbene and trichloromethyl radical.

Scheme II



^{14}C analysis of the brown tar formed in reaction 13 revealed the presence of the remainder of the reduced carbon (based on the stoichiometry in Scheme II) that is not found as C_2Cl_4 or C_2Cl_6. Although attempts at isolation and characterization were unsuccessful, elemental analyses show that the tar is a chlorocarbon. As its formation does not result from the consumption of uncoordinated C_2Cl_4 or C_2Cl_6, we propose that it is formed by the decomposition of III, perhaps initiated by reaction with II, as shown in Scheme II.

$CpW(CO)_3Cl$. There is a lack of direct evidence for an intermediate analogous to III (i.e., $CpW(CO)Cl_3(CCl_2)$) in the chlorocarbon oxidation of $CpW(CO)_3Cl$ (eq 1). However, we believe there is sufficient negative evidence eliminating the possibility of other, a priori, reasonable mechanisms. As in reaction 13 no major amounts of free $:CCl_2$ or CCl_3 are formed, nor is C_2Cl_6 produced in significant yield. Circumstantial evidence indicates that reaction 1 proceeds by a pathway analogous to that of reaction 13. All the reduced carbon of reaction 1 (1.1 ± 0.2 mol/mol of $CpW(CO)_3Cl$ consumed is found, as detected by ^{14}C studies, in a brown tar with solubility properties similar to those of the tar formed in reaction 13. The tar is highly soluble in acetone, moderately soluble in diethyl ether, benzene, and chloroform, and very slightly soluble in carbon tetrachloride and light petroleum ether.

Several experiments taken together form a firm basis on which to propose that reaction 1 involves a net transfer of two halogen atoms from one halocarbon molecule.[36] (a) The reaction of $CpW(CO)_3Cl$ with $CBrCl_3$ gives $CpW(CO)_2BrCl_2$. Since bromine–carbon bonds are weaker than chlorine–carbon bonds by about 15 kcal/mol,[37] a mechanism involving the transfer of only one halogen atom from each of two halocarbon molecules would be expected to yield $CpW(CO)_2Br_2Cl$. (b) Irradiation of $CpW(CO)_3Cl$ in

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[35] Garnier, F.; Krausz, P.; Rudler, H. *J. Organomet. Chem.* **1980**, *186*, 77–83.

[36] A reviewer has suggested that only an isotope/crossover-type experiment will unambiguously establish that formation of $CpW(CO)_2Cl_3$ involves obtaining two Cl atoms from the same halocarbon molecule. While technically correct, it is difficult to imagine any such alternative mechanism that does not involve the formation of CCl_3—a species that we have shown does not quantitatively form in this reaction system.

[37] "Handbook of Chemistry and Physics", 62nd ed.; Weast, R. C., Ed.; CRC Press: Cleveland, OH, 1981; pp F191–F195.

Scheme III

$$CpW(CO)_3Cl \xrightarrow{h\nu} CpW(CO)_2Cl + CO \tag{24}$$

$$CpW(CO)_2Cl \xrightarrow{CCl_4} CpW(CO)_2Cl_2(CCl_3) \tag{25}$$

$$CpW(CO)_2Cl_2(CCl_3) \xrightarrow{-CO} CpW(CO)Cl_3(CCl_2) \tag{26}$$

$$n CpW(CO)Cl_3(CCl_2) \xrightarrow{CO} n CpW(CO)_2Cl_3 + [CCl_2]_n \tag{27}$$

halocarbons of the series Ph_nCCl_{4-n} (n = 0–3) reveals an anomalously low disappearance quantum yield in the case of Ph_3CCl. Similar results have been reported by Coffey who found that $Fe(CO)_5$ reacted thermally (in refluxing benzene) with CCl_4 and Ph_2CCl_2 but not with Ph_3CCl.[38] Coffey attempted to react $Fe(CO)_5$ with a wide variety of organic halides. For a reaction to occur it appeared to be a necessary, though not sufficient, condition that the molecule have at least two halogen atoms on the same carbon atom. The only exception was found to be 1,2-dichloro-1,1,2,2-tetraphenylethane. (c) Irradiation of $CpW(CO)_3Cl$ in benzyl chloride results in formation of what appears to be the unstable complex $CpW(CO)_2(PhCH_2)Cl_2$. The oxidative addition of benzyl chloride may represent what is only the first step in the reaction of $CpW(CO)_2Cl$ with polyhalocarbons.

In summary, it is reasonable to suggest that reaction 1 proceeds according to Scheme III.

Failure to detect reactions with dioxygen, n-butylamine, and sulfur, which might be expected of a metallodichlorocarbene complex, may be due to the conditions of these experiments preventing the formation of such a species. For example, the $CpW(CO)_2Cl$ complex might react with any or all of the above reagents. An alternative explanation is that reaction of the metallocarbene intermediate with the above reagents is not competitive with reaction 27.

Reaction with C_2Cl_6. As reported above, the reactions of $(MeCp)W(CO)_3Cl$ or $Fe(CO)_5$ with C_2Cl_6 are stoichiometric, yielding 1.0 mol of C_2Cl_4/mol of $(MeCp)W(CO)_2Cl_3$ or $FeCl_2$, respectively. In contrast, under the same reaction conditions, the photooxidation of $[(MeCp)W(CO)_3]_2$ by C_2Cl_6 yields C_2Cl_4 in approximately 3 times the stoichiometric yield. The latter yield can be explained on the basis of a chain reaction scheme advanced by Wilkinson (eq 28–30).[4] ($(MeCp)W(CO)_3$ is generated by photochemical homolytic cleavage of the W–W bond.) Wilkinson reported that the C_2Cl_6 oxidation of $ReCl_3(RCN)(PPh_3)_2$ to $ReCl_4(PPh_3)_2$ resulted in formation of greater than 1 mol of C_2Cl_4/mol of $ReCl_4(PPh_3)_2$ (0.5 mol of C_2Cl_4 = stoichiometric yield). Thus the stoichiometric yield of C_2Cl_4 resulting from the photoreactions of $(MeCp)W(CO)_3Cl$ and $Fe(CO)_5$ with C_2Cl_6 is strongly indicative of a non-radical pathway. Note that $(MeCp)W(CO)_3Cl$ is the product of the oxidation reaction of $[(MeCp)W(CO)_3]_2$, and therefore the former complex could not in some way be inhibiting a radical chain in reaction 1.

$$(MeCp)W(CO)_3 + C_2Cl_6 \rightarrow (MeCp)W(CO)_3Cl + C_2Cl_5 \tag{28}$$

$$C_2Cl_5 \rightarrow C_2Cl_4 + Cl \tag{29}$$

$$Cl + C_2Cl_6 \rightarrow Cl_2 + C_2Cl_5 \tag{30}$$

Experimental Section

Materials and Supplies. $CpW(CO)_3Cl$,[39] $CpMo(CO)_3Cl$,[39] $(MeCp)_2Mo_2(CO)_6$,[40] and $(MeCp)_2W_2(CO)_6$[40] were prepared by literature methods. The complex $(MeCp)W(CO)_3Cl$ was prepared from Na(MeCp) by the same method used to prepare $CpW(CO)_3Cl$. $Fe(CO)_5$ and $Mn_2(CO)_{10}$ were purchased from Strem Chemical Co. and used as received.

All solvents and halocarbons used in this study were stored under nitrogen or argon. CCl_4 was obtained from Fisher and distilled from P_2O_5 under nitrogen. Benzene was distilled under nitrogen from $LiAlH_4$. The following chemicals were obtained from Aldrich: benzyl chloride, Ph_2CCl_2, Ph_3CCl, $PhCCl_3$, $BrCCl_3$, C_2Cl_6, C_2Cl_5H, C_2Cl_3H, cyclohexene, vinyl ethyl ether, dimethyl maleate, tetramethylethylene, galvinoxyl, and thiophosgene. Benzyl chloride was distilled from $CaSO_4$ under nitrogen. Ph_2CCl_2 and $PhCCl_3$ were distilled from $CaSO_4$ in vacuo. Ph_3CCl was recrystallized from benzene and petroleum ether. $BrCCl_3$ was distilled under nitrogen from P_2O_5. C_2Cl_6 was recrystallized from ethanol. Cyclohexene was distilled from CaH_2 under nitrogen. All others mentioned above were used as received. $PhHgCBrCl_2$ was obtained from Alfa and used as received. ^{14}C-labeled CCl_4 (20 μCi/g) was a generous gift from Professor S. J. Lippard.

Nitrosodurene[41] and dichloronorcarane[42] were synthesized by literature methods.

Instruments and Techniques. All infrared spectra were obtained by using a Perkin-Elmer 621 or 425 spectrophotometer. Electronic spectra were recorded by using a Cary 17 spectrophotometer. ^1H NMR and ^{13}C NMR spectra were obtained with a Bruker Model WP80 or Varian XL-200 FT spectrometer. EPR spectra were obtained with a Varian E line Century Series spectrometer. Hewlett-Packard 5750 and Varian Series 1400 gas chromatographs with a Spectra-Physics Autolab Minigrator were used for gas chromatographic analyses. The stationary phases used were TCEP, SE-30, or Carbowax 20M.

Concentrations were determined by comparison of peak areas and/or heights with those of authentic samples of known concentrations approximately equal to that of the sample being analyzed. Several runs were performed for each determination, and the uncertainty was calculated statistically.

Photochemical reactions were carried out under argon in Schlenk flasks or septum-stoppered test tubes. The light source was a 200-W Oriel high-pressure mercury lamp. Corning filters were used for broad-band irradiations (CS 0-52, >350 nm; CS 3-74, >400 nm; CS 3-71, >470 nm; CS 3-66, >540 nm). The 366-nm band was isolated with a Corning CS 7-83 filter.

Quantum yield measurements were made by monitoring the ca. 1960 and 2040 cm^{-1} bands of $CpW(CO)_3Cl$. The technique has been described previously.[1] Lamp intensities were measured by ferrioxolate actinometry[43] or Reinecke's salt actinometry.[44]

Microanalyses were performed by Galbraith Laboratories, Knoxville, TN.

The techniques for performing low-temperature photolyses and obtaining infrared spectra at low temperature have been described previously.[45]

$^{14}CCl_4$ Experiments. $Fe(CO)_5$ (0.54 mL, 4.0 mmol) in ^{14}C-labeled CCl_4 (3.16 μCi/in 40 mL) was irradiated until complete disappearance of the $Fe(CO)_5$ was observed by IR, and the resulting solution was filtered to yield a precipitate that was dried in vacuo to constant weight (0.50 g). The precipitate that contained $FeCl_2$ and tar was dissolved in acetone (20 mg/5.0 mL). One milliliter of the resulting solution was then added to 9.0 mL of scintillation cocktail ("Bray's solution"). To account for absorption by the tar and the $FeCl_2$, a chemically identical sample was prepared for calibration purposes by the photoreaction of $Fe(CO)_5$ with unlabeled CCl_4. Various amounts of $^{14}CCl_4$ were added to the calibration sample scintillation cocktail in order to

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construct a calibration curve. Additionally, in some experiments $^{14}CCl_4$ was added to the labeled samples as an internal calibration. Other ^{14}C analyses were calibrated by using similar techniques.

The filtrate from the above separation was also analyzed. The solvent and volatile halocarbons (CCl_4, C_2Cl_4, C_2Cl_6) were removed by vacuum distillation, and the resulting residue was checked for ^{14}C content. Also analyzed for labeled carbon was the tar from the precipitate above after being washed free of $FeCl_2$ with water.

The resulting labeled carbon content was in agreement with the carbon content obtained from elemental analysis.

The $CpW(CO)_3Cl/CCl_4$ system was analyzed similarly although the carbon-containing tar was never isolated.

$CpW(CO)_2BrCl_2$. Irradiation ($\lambda > 400$ nm) of $CpW(CO)_3Cl$ (0.37 g, 1.0 mmol) in $CBrCl_3$ (6.0 mL) and acetone (6.0 mL) for 5 h resulted in disappearance of ca. 90% of the $CpW(CO)_3Cl$, as monitored by IR, and the production of an orange-yellow crystalline product. More product crystallized by keeping the reaction vessel at −20 °C for 12 h. The solution was filtered, and the resulting crystals (0.21 g) were washed with benzene and dried in vacuo. The product analyzed for $CpW(CO)_2BrCl_2$. Calcd for $C_7H_5BrCl_2W$: C, 18.45; H, 1.11; W, 40.34; Cl, 15.56; Br, 17.53; O, 7.02. Found: C, 18.18; H, 1.11; W, 39.95; Cl, 15.47; Br, 23.31; O, 1.99 (by difference). Repeated elemental analyses always gave variable amounts of Br but excellent C, H, W, and Cl values. The infrared spectrum of the product has bands at 2039 and 2089 cm^{-1} (acetone), a spectrum typical for $CpW(CO)_2X_3$-type complexes. Extinction coefficients (2039 (1450), 2089 cm^{-1} (980 M^{-1} cm^{-1})) calculated on the basis of 100% $CpW(CO)_2BrCl_2$ are also typical [$CpW(CO)_2Cl_3$ (acetone) 2044 (1400), 2094 cm^{-1} (900 M^{-1} cm^{-1})].

Reaction of $CpW(CO)_3Cl$ with Benzyl Chloride. Irradiation ($\lambda > 330$ nm) of $CpW(CO)_3Cl$ (0.6 g, 1.6 mmol) in $PhCH_2Cl$ (30 mL) under a CO atmosphere (the reaction was faster under Ar but yields were slightly lower) for approximately 20 h followed by filtration gave a dark blue solution, the infrared spectrum of which had bands at 2042 and 2092 cm^{-1}. The addition of 200 mL of petroleum ether formed a fluffy precipitate. Filtration followed by repeated washings with petroleum ether and then CCl_4 gave a dark blue solid (0.32 g) with bands in the infrared spectrum at 2030 and 2090 cm^{-1} (Nujol mull).

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Registry No. $CpW(CO)_3Cl$, 12128-24-4; $CpW(CO)_2(PPh_3)Cl$, 12115-03-6; $CpW(CO)_2(THF)Cl$, 87937-33-5; $CpW(CO)_2Cl_3$, 12107-08-3; $[(MeCp)Mo(CO)_3]_2$, 33056-03-0; $Mn_2(CO)_{10}$, 10170-69-1; $(MeCp)Mo(CO)_3Cl$, 87937-34-6; $CpMo(CO)_3Cl$, 12128-23-3; $[CpW(CO)_3]_2$, 12091-65-5; $(MeCp)W(CO)_2Cl_3$, 87937-35-7; $[(MeCp)W(CO)_3]_2$, 68111-11-5; $CpW(CO)_2Br_3$, 12107-03-8; $CpW(CO)_2BrCl_2$, 87937-36-8; $CpW(CO)_2(PhCH_2)Cl_2$, 87937-37-9; $CpW(CO)_2(AsPh_3)Cl$, 12114-95-3; $Fe(CO)_5$, 13463-40-6; $Mn(CO)_5Cl$, 14100-30-2; $FeCl_2$, 7758-94-3; $(MeCp)W(CO)_3Cl$, 87937-38-0; CCl_4, 56-23-5; Ph_2CCl_2, 2051-90-3; $PhCCl_3$, 98-07-7; Ph_3CCl, 76-83-5; $PhCH_2Cl$, 100-44-7; $CBrCl_3$, 75-62-7; $:CCl_2$, 1605-72-7.

The Carbene-like Behavior of Terminal Phosphinidene Complexes toward Olefins. A New Access to the Phosphirane Ring

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In the presence of copper(I) chloride, (7-R-7-phosphanorbornadiene)P–$M(CO)_5$ complexes (M = Cr, W) decompose around 55 °C to give the corresponding terminal phosphinidene complexes $RP{=}M(CO)_5$. These transient phosphinidene complexes react in situ with olefins to give phosphirane complexes. The stereochemistry of the starting olefin is retained in the phosphirane ring, thus suggesting a concerted process. The reaction with 1,3-dienes yields 2-vinylphosphirane complexes that rearrange around 100 °C to the corresponding phospholenes. On the contrary, the reaction with α,β-unsaturated ketones gives directly the 1,2-oxaphospholene complexes, but the formation of an intermediate 2-acylphosphirane cannot be excluded. With methyl methacrylate, the 2-(methoxycarbonyl)phosphirane is formed and is apparently stable. With ethyl vinyl ether, the 2-ethoxyphosphirane transiently obtained is so reactive that neutral water cleaves the P–C(OEt) bond of the ring to give a secondary α-phosphinoacetaldehyde that is stabilized as its P–$W(CO)_5$ complex. An excess of vinyl ether also reacts with the 2-ethoxyphosphirane to give a 2,4-diethoxyphospholane. In all its reactions, $PhP{=}W(CO)_5$ apparently behaves as a singlet electrophilic carbene.

Introduction

Numerous six-electron species including carbenes, silylenes, nitrenes, etc. are known to react easily with olefins to give three-membered rings. On the contrary, it has never been possible up to now to condense a phosphinidene, RP, or a phosphinidene derivative, $RP{=}Y$ (Y = O, S, ...), with an olefin to form a phosphirane.[1]

Recently, we have described[2-4] a new system based on the 7-phosphanorbornadiene skeleton (e.g., 1) which generates terminal phosphinidene complexes, $R{-}P{=}M(CO)_5$ (M = Cr, Mo, W), around 150 °C. The reactions of these complexes with conjugated dienes and acetylenes form P–C rings much more efficiently and selectively than the corresponding reactions of phosphinidenes (eq 1) (these phosphinidenes are generated by thermal depolymerization of cyclopolyphosphines[1]). Thus, it was very tempting for us to study the reaction of these phosphinidene complexes with olefins: indeed, a significant extension of the scope of phosphinidene chemistry seemed to be at hand.

Results and Discussion

Reaction of Terminal Phosphinidene Complexes with Nonfunctional Olefins. Our preliminary attempts to react complex 1 with monoolefins around 150 °C pro-

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