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PHOTOLYSIS OF $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$

II *. PHOTO-INDUCED FORMATION OF ETHANE *

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Summary

Photolysis of $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$ results in the formation of methane and ethane. The percentage of ethane detected in the evolved gas can vary from a trace to 70%. The percentage of ethane formed is dependent on the solvent, the concentration of $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$, time and temperature. The results of oxidation and reduction reactions involving $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$ are also presented.

Introduction

In a previous study we reported the photo-degeneration of $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$ [1]. In addition to the formation of methane, a significant quantity of ethane was also produced in the photo-degradation. This is in contrast to the photolysis of other Group VB metal methyl derivatives, $(\eta^5\text{-}C_5H_5)_2VCH_3$ [1], $(\eta^5\text{-}C_5H_5)_2Nb(CH_3)_2$ [1] and $(\eta^5\text{-}C_5H_5)_2Ta(CH_3)_2$ [2], as well as other early transition metal dimethylmetallocenes, $(\eta^5\text{-}C_5H_5)_2M(CH_3)_2$ (M = Ti, Zr, Hf) [3–6], in which at most only trace quantities of ethane are detected. We now report further photochemical, as well as non-photochemical, reactions of $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$.

Results and discussion

Ethane formation from the photolysis of $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$ is unique. The coupling of σ-bonded ligands is unprecedented as a major pathway in either the

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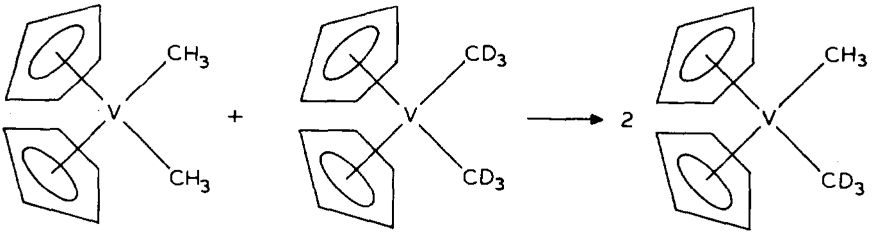
thermal [7–14] or photochemical [1,2] degradation of alkyl- or aryl-Group VB metallocene complexes. The ethane may arise from either the combination of methyl radicals [15] or by the reductive elimination of two methyl ligands [16].

Previous studies have shown that photolysis of $(\eta^5\text{-}C_5H_5)_2V(CD_3)_2$ in benzene produces only ethane-d_6 [1]. Hydrogen/deuterium exchange between the cyclopentadienyl rings and the methyl ligands, such as that observed in the thermolysis of $(\eta^5\text{-}C_5H_5)_2Ti(CH_3)_2$ [17], does not occur in the photo-degradation of $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$.

Analysis of the ethane produced from the photolysis of an equimolar mixture of $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$ and $(\eta^5\text{-}C_5H_5)_2V(CD_3)_2$ in hexane indicated only ethane-d_6 and ethane-d_0 were present. No ethane-d_3 was detected, indicating the components of ethane arise from the same metal center, i.e. reductive elimination of methyl ligands. Photo-induced reductive elimination has been observed in the photolysis of diaryl derivatives of titanocene and zirconocene [18–20]. However, analysis of the ethane formed in the photo-degradation of an equimolar mixture of $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$ and $(\eta^5\text{-}C_5H_5)_2V(CD_3)_2$ in benzene revealed a mixture of ethane-d_6, -d_3 and -d_0. The ratio of C_2D_6 to $C_2D_3H_3$ was 1/2, indicating a random scrambling of methyl ligands used in the formation of ethane. A control experiment indicated that $C_2D_3H_3$ was the result of non-photochemical scrambling of methyl ligands between molecules of dimethylvanadocene prior to reductive elimination. An equimolar mixture of $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$ and $(\eta^5\text{-}C_5H_5)_2V(CD_3)_2$ was stirred in the dark for 12 h at 15°C. Analysis of the resulting organometallic species by mass spectroscopy revealed a mixture of $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$, $(\eta^5\text{-}C_5H_5)_2V(CD_3)_2$ and $(\eta^5\text{-}C_5H_5)_2V(CH_3)$ (CD_3) (eq. 1). The implication of a radical combination of methyl units in the formation of ethane previously suggested [1] is invalid.



(1)

Other examples of organometallic alkyl transfer have been described [21–29]. Methyl transfer has also been observed between various alkyl derivatives of vanadocene [30]. These reactions are also dependent on the solvent.

Another dependence on solvent was observed in the photo-generation of ethane from $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$. The photolysis of 1.50×10^{-2} M solutions of dimethylvanadocene for 10 h at 15°C in benzene, hexane, cumene or cyclohexene resulted in a variation in the percentage of ethane in the evolved gas (Table 1). Those solvents containing hydrogens more easily abstracted by methyl radicals [31] show lower percentages of ethane, i.e. higher percentages of methane. Methyl ligands can abstract hydrogen from the solvent, the cyclopentadienyl ring or another methyl group and form methane [1] or couple together to form ethane. Reducing the radical-abstractability of solvent hydrogens favors the coupling of methyl ligands and the formation of ethane.

The percentage of ethane in the evolved gas resulting from the photolysis of $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$ is also dependent upon the concentration of $(\eta^5\text{-}$

TABLE 1

EFFECT OF SOLVENT ON THE FORMATION OF ETHANE FROM THE PHOTOLYSIS OF $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$ [a]

Solvent	Ethane in evolved gas [b]
Benzene	58
Hexane	40
Cumene	34
Cyclohexene	21

[a] Photolyses performed on 1.50×10^{-2} *M* solutions of $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$ in Pyrex Schlenkware at 15°C for 10 h with a 450 W Hanovia lamp. [b] Mol ethane/(mol ethane + mol methane), ±3%.

TABLE 2

EFFECT OF CONCENTRATION ON THE FORMATION OF ETHANE FROM THE PHOTOLYSIS OF $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$ IN BENZENE, HEXANE, CUMENE AND CYCLOHEXENE [a]

Concentration of $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$ (*M*)	Ethane in evolved gas (%) [b]			
	Benzene	Hexane	Cumene	Cyclohexene
5.73×10^{-2}	–	67	–	18
3.44×10^{-2}	–	53	38	23
1.50×10^{-2}	58	40	34	21
9.0×10^{-3}	–	–	–	10
7.8×10^{-3}	64	6	26	–
4.3×10^{-3}	59	<1	17	5
2.0×10^{-3}	47	–	–	–
8.4×10^{-4}	14	–	–	<1
5.7×10^{-4}	<1	–	–	–
4.3×10^{-4}	–	–	<1	–

[a] Photolyses performed in Pyrex Schlenkware at 15°C for 10 h with a 450 W Hanovia lamp. [b] ±3%.

TABLE 3

EFFECT OF TIME ON THE FORMATION OF ETHANE FROM THE PHOTOLYSIS OF $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$ IN BENZENE [a]

Time (h, min)	Ethane in evolved gas (%) [b]
9	7
23	22
47	41
1, 08	43
2, 22	46
4, 12	48
8, 09	54
10, 10	58
12, 04	60
21, 36	24

[a] Photolysis performed on a 1.50×10^{-2} *M* solution of $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$ in Pyrex Schlenkware at 15°C with a 450 W Hanovia lamp. [b] ±3%.

TABLE 4

EFFECT OF TIME ON THE FORMATION OF ETHANE FROM THE PHOTOLYSIS OF (η^5-$C_5H_5)_2V(CH_3)_2$ IN HEXANE [a]

Time (h, min)	Ethane in evolved gas (%) [b]
5	<1
1, 00	26
2, 10	41
4, 10	46
10, 00	49
19, 40	14
24, 30	13

[a] Photolysis performed on a 1.50×10^{-2} *M* solution of $(\eta^5$-$C_5H_5)_2V(CH_3)_2$ in Pyrex Schlenkware at 15°C with a 450 W Hanovia lamp. [b] ±3%.

$C_5H_5)_2V(CH_3)_2$ (Table 2). With low concentrations of dimethylvanadocene, the evolved gas is greater than 99% methane. As the concentration of $(\eta^5$-$C_5H_5)_2V(CH_3)_2$ was increased, the percentage of ethane, resulting from the photolysis, increased. Apparently, the formation of ethane is more than unimolecular in $(\eta^5$-$C_5H_5)_2V(CH_3)_2$.

The generation of ethane from the photolysis of $(\eta^5$-$C_5H_5)_2V(CH_3)_2$ showed a dependence on time (Tables 3–6). Ethane was not detected during the early stages of photolysis; only methane was formed. Further into the reaction, significant quantities of ethane were found. After 10 h of irradiation the percentage of ethane in the evolved gas reached a maximum. Further photolysis resulted in a decrease in the percentage of ethane, apparently due to increased quantities of photo-generated methane. These results are characteristic of a product formed in a secondary, multimolecular process.

The percentage of ethane in the evolved gas is also affected by the temperature of the reaction. The photolysis of 1.50×10^{-2} *M* solutions of $(\eta^5$-$C_5H_5)_2V(CH_3)_2$ in benzene for 2¼ h resulted in greater percentages of ethane at lower temperatures than at higher temperatures (Table 7).

When $(\eta^5$-$C_5H_5)_2V(CH_3)_2$ was photolyzed in the presence of a radical scavenger,

TABLE 5

EFFECT OF TIME ON THE FORMATION OF ETHANE FROM THE PHOTOLYSIS OF (η^5-$C_5H_5)_2V(CH_3)_2$ IN CUMENE [a]

Time (h, min)	Ethane in evolved gas (%) [b]
20	<1
1, 20	17
2, 25	22
4, 25	25
10, 20	34
19, 45	29
24, 30	23

[a] Photolysis performed on a 1.50×10^{-2} *M* solution of $(\eta^5$-$C_5H_5)_2V(CH_3)_2$ in Pyrex Schlenkware at 15°C with a 450 W Hanovia lamp. [b] ±3%.

TABLE 6

EFFECT OF TIME ON THE FORMATION OF ETHANE FROM THE PHOTOLYSIS OF $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$ IN CYCLOHEXENE [a]

Time (h, min)	Ethane in evolved gas (%) [b]
15	6
43	12
1, 03	17
1, 37	18
2, 12	23
4, 04	26
7, 23	27
10, 05	26
12, 01	30
21, 30	15

[a] Photolysis performed on a 1.50×10^{-2} *M* solution of $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$ in Pyrex Schlenkware at 15°C with a 450 W Hanovia lamp. [b] ±3%.

triphenylmethane, the percentage of ethane in the evolved gas (45%) was nearly the same as the photolysis in the absence of the scavenger (40%). This demonstrates that ethane is not the result of the coupling of free methyl radicals. The percentage of methane in the evolved gas was also not affected by the scavenger.

The results of photolyzing $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$ in bulk vinylmonomers are summarized in Table 8. While the photolysis of a number of early transition alkylmetal derivatives in the presence of vinyl monomers results in the polymerization of the monomers [5,20,32–35], the photolysis of dimethylvanadocene is not an effective means of initiating the polymerization of styrene or methyl methacrylate.

Interestingly, $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$ initiated the polymerization of methyl methacrylate in the dark. Although this reaction was performed at 35°C, dimethylvanadocene is reported not to decompose until 122°C [8]. The polymerization of methyl methacrylate may be the result of $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$ undergoing methyl scrambling in the dark (eq. 1).

Gas chromatographic analysis of the liquid portion of the reaction mixture resulting from the photolysis of a 1.50×10^{-2} *M* solution of $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$ in benzene revealed partial loss of the metallocene structure of the organometallic species; cyclopentadiene (4%) was detected in the photo-mixture. Toluene (< 1%) was also detected.

TABLE 7

EFFECT OF TEMPERATURE ON THE FORMATION OF ETHANE FROM THE PHOTOLYSIS OF $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$ IN BENZENE [a]

Temperature (°C)	Ethane in evolved gas [b]
< −15	69
12	60
23	54
35	49

[a] Photolyses performed on 1.50×10^{-2}*M* solutions of $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$ in Pyrex Schlenkware for $2\frac{1}{4}$ h with a 450 W Hanovia lamp. [b] ±3%.

TABLE 8

PHOTOCHEMICAL AND DARK REACTIONS OF $(\eta^5\text{-C}_5\text{H}_5)_2\text{V(CH}_3)_2$ IN METHYL METHACRYLATE AND STYRENE

Reaction mixture	Grams Polymer	
	Photochemical [a]	Dark [b]
$(\eta^5\text{-C}_5\text{H}_5)_2\text{V(CH}_3)_2$ + methyl methacrylate [c]	1.83	1.95
Methyl methacrylate [d]	0.21	0.00
$(\eta^5\text{-C}_5\text{H}_5)_2\text{V(CH}_3)_2$ + styrene [c]	0.23	< 0.01
Styrene [d]	0.15	< 0.01

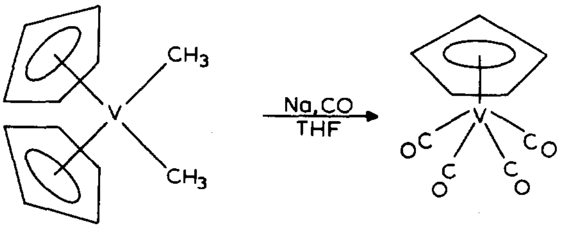
[a] Photolyzed with a 450 W Hanovia lamp for 1 h at 35°C in Pyrex Schlenkware. [b] Stirred 1 h at 35°C. [c] 1.50×10^{-2} *M* $(\eta^5\text{-C}_5\text{H}_5)_2\text{V(CH}_3)_2$ in 20.0 ml of monomer. [d] 20.0 ml of monomer.

The loss of the metallocene structure was evident when dimethylvanadocene was photolyzed in pentane. The resulting photo-residue was not vanadocene nor methylvanadocene. Degradation of this product with HCl gave a mixture of $(\eta^5\text{-C}_5\text{H}_5)_2\text{VCl}_2$ and $(\eta^5\text{-C}_5\text{H}_5)\text{VCl}_3$ (eq. 2).

$$(\eta^5\text{-C}_5\text{H}_5)_2\text{V(CH}_3)_2 \xrightarrow[\text{pentane}]{h\nu} \underset{\text{residue}}{\text{insoluble}} \xrightarrow{\text{HCl}} (\eta^5\text{-C}_5\text{H}_5)_2\text{VCl}_2 + (\eta^5\text{-C}_5\text{H}_5)\text{VCl}_3 \quad (2)$$

Degradation of vanadocene with HCl would give $(\eta^5\text{-C}_5\text{H}_5)_2\text{VCl}$ and hydrogen [11] while the degradation of methylvanadocene with HCl would yield $(\eta^5\text{-C}_5\text{H}_5)_2\text{VCl}$ and methane [36]. When the solution of $(\eta^5\text{-C}_5\text{H}_5)\text{VCl}_3$ was exposed to the air, $(\eta^5\text{-C}_5\text{H}_5)\text{VOCl}_2$ immediately formed [37].

While cleavage of one of the cyclopentadienyl rings is not observed in the thermolysis of σ-bonded alkyl- and aryl-vanadocene derivatives [7,8,11,13,14], it has precedent in other reactions of dicyclopentadienyl derivatives of vanadium [37–48]. The photolysis of $(\eta^5\text{-C}_5\text{H}_5)_2\text{V(CH}_3)_2$ in the presence of carbon monoxide also results in the loss of a cyclopentadienyl ring as demonstrated by the isolation of $(\eta^5\text{-C}_5\text{H}_5)\text{V(CO)}_4$ [1]. The conversion of $(\eta^5\text{-C}_5\text{H}_5)_2\text{V(CH}_3)_2$ to $(\eta^5\text{-C}_5\text{H}_5)\text{V(CO)}_4$ involves the reduction of vanadium from an oxidation state of +4 to +1. Cyclopentadienyltetracarbonylvanadium was also obtained by a non-photochemical process involving dimethylvanadocene: mixing a solution of $(\eta^5\text{-C}_5\text{H}_5)_2\text{V(CH}_3)_2$ and sodium with carbon monoxide in the dark resulted in formation of $(\eta^5\text{-C}_5\text{H}_5)\text{V(CO)}_4$ (13% yield) (eq. 3).



(3)

Stirring a mixture of $(\eta^5\text{-C}_5\text{H}_5)_2\text{V(CH}_3)_2$ and sodium resulted in the decomposition of $(\eta^5\text{-C}_5\text{H}_5)_2\text{V(CH}_3)_2$ and the formation of methane.

TABLE 9

EFFECT OF CONCENTRATION ON THE FORMATION OF ETHANE FROM THE REACTION OF $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$ AND AgCl IN THF [a]

Concentration of $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$ (M)	Ethane in evolved gas (%) [b]
4.7×10^{-1}	32
4.7×10^{-2}	18
4.7×10^{-3}	<1

[a] Performed in the dark for 4½ h at 15°C, AgCl in a 15-fold mol-excess. [b] ±3%.

TABLE 10

EFFECT OF TIME ON THE FORMATION OF ETHANE FROM THE REACTION OF $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$ AND AgCl IN THF [a]

Time (h, min)	Ethane in evolved gas (%) [b]
20	4
25	8
41	11
1, 20	13
2, 19	16
3, 30	14
4, 28	18
7, 07	18
9, 53	20
23, 06	15
31, 55	11
46, 28	14

[a] Performed in the dark on a 4.7×10^{-2} M solution of $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$ at 15°C, AgCl in a 15-fold mol-excess. [b] ±3%.

TABLE 11

EFFECT OF TIME ON THE FORMATION OF ETHANE FROM THE REACTION OF $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$ AND AgCl IN BENZENE [a]

Time (h, min)	Ethane in evolved gas (%) [b]
22	<1
40	<1
1, 15	3
2, 14	9
3, 27	9
4, 23	13
7, 07	15
9, 52	13
23, 01	16
31, 52	17
46, 22	17

[a] Performed in the dark on a 4.7×10^{-2} M solution of $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$ at 15°C, AgCl in a 15-fold mol-excess. [b] ±3%.

Oxidation of $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$ with a mild oxidant, AgCl, resulted in formation of ethane, ethylene and methane. The percentage of ethane in the evolved gas was dependent on the concentration of $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$ (Table 9). A unimolecular mechanism such as the simple reductive elimination of methyl ligands does not account for the formation of ethane in the oxidation of $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$.

The dependence of time on the percentage of ethane in the gas evolved from the oxidation of $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$ is shown in Tables 10 and 11. Methane was the predominant species in the evolved gas at the outset of the oxidation. The percentage of ethane in the evolved gas increased with time, reached a plateau and then decreased (when THF was the solvent). A similar pattern was observed in the photolysis of $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$ (Tables 3–6).

Conclusions

Photo-induced reactions of $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$ result in methane and ethane. Ethane formation is the result of reductive elimination of methyl ligands rather than the combination of methyl radicals. A variety of factors including concentration, time, temperature and solvent influence the extent of ethane formation. A complex mechanism, more than unimolecular in $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$, undoubtedly accounts for ethane formation. The decomposition of $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$ via oxidation to form ethane may be a pathway in the photo-decomposition. Reduction of $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$ could account for the loss of the metallocene framework observed in the photolysis of dimethylvanadocene. Further studies are warranted in order to reveal the exact mechanism by which ethane is formed in the photolysis of $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$.

Experimental

All reactions and manipulations were conducted under an argon atmosphere. The argon was dried with P_2O_5 and H_2SO_4, and trace oxygen was removed using BTS catalyst (BASF). Benzene, cumene, cyclohexene, hexane, pentane and toluene were dried over CaH_2 and freshly distilled under argon. THF was predried with potassium hydroxide, then with sodium, and finally distilled under argon from sodium/benzophenone. Methyl methacrylate and styrene were washed with 5% aqueous NaOH, dried over anhydrous magnesium sulfate, vacuum distilled, and stored under argon in the dark at −20°C. Alfa-Ventron neutral alumina was predried in a 60°C oven overnight, and then heated with a heat gun while mixing on a rotary evaporator attached to a vacuum pump for 1 h. The alumina was subsequently deactivated with argon-saturated distilled water (5% by weight). $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$ and $(\eta^5\text{-}C_5H_5)_2V(CD_3)_2$ were prepared according to literature procedures [1]. Gas chromatographic analysis was performed on a Varian 2400 gas chromatograph equipped with a flame ionization detector. A 6′ × 1/8″ Porapak Q column was used to separate gaseous components and a 5′ × 1/8″ column of 1.5% OV-101 on Chromosorb was used to separate liquid components. Mass spectra were obtained on a Hitachi–Perkin–Elmer RMU 6L mass spectrometer by Mr. E. Guzik. Visible spectra were recorded on a Perkin–Elmer 202 ultraviolet-visible spectrophotometer. Photolyses were conducted in Pyrex Schlenkware with a 450 W Hanovia photochemical lamp located in a water-cooled immersion well. Low temperature reactions were cooled with a FTS Flexi-Cool unit. Microanalyses were performed by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts, Amherst, Massachusetts.

A. Photolysis of $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$*: ethane analysis*

1. Solvent dependence. Solutions of $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$ (1.50×10^{-2} *M*) in either benzene, hexane, cumene or cyclohexene were photolyzed for 10 h in a 15°C water bath. The resulting gases were analyzed by gas chromatography. The results are summarized in Table 1.

2. Concentration dependence. Solutions of $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$ ranging in concentration from 5.73×10^{-2} *M* to 4.3×10^{-4} *M* in either benzene, hexane, cumene or cyclohexene were photolyzed for 10 h in a 15°C water bath. The gases above the reaction mixtures were analyzed by gas chromatography. The results are summarized in Table 2.

3. Time dependence. Solutions of $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$ (1.50×10^{-2} *M*) in either benzene, hexane, cumene or cyclohexene were photolyzed in a 15°C water bath for 24 h. Periodically during the photolyses, gas samples were removed from the reaction vessels and analyzed by gas chromatography. The results are summarized in Tables 3–6.

4. Temperature dependence. Mixtures of $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$ (1.50×10^{-2} *M*) in benzene were photolyzed for $2\frac{1}{4}$ h at either 35, 23, 12 or < -15°C. The gas above the reaction mixtures was analyzed by gas chromatography. The results are summarized in Table 7.

5. Radical scavengers. A 1.50×10^{-2} *M* solution of $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$ (45.6 mg, 0.216 mmol) in hexane (14.4 ml) was photolyzed in the presence of a ten-fold mol-excess of triphenylmethane (0.53 g, 2.2 mmol) in a water-jacketed Schlenk tube for 10 h. The gas above the reaction mixture was found by gas chromatographic analysis to contain 45% ethane and 55% methane.

6. Methyl scrambling. A mixture of 0.10 g (0.46 mmol) of $(\eta^5\text{-}C_5H_5)_2V(CD_3)_2$ and 0.09 g (0.4 mmol) of $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$ in 16 ml of hexane was photolyzed for 12 h in a water-jacketed Schlenk tube. The ethane produced was analyzed by GC/MS and was found to contain C_2D_6 and C_2H_6; no $C_2D_3H_3$ was detected.

A solution of 91 mg (0.42 mmol) of $(\eta^5\text{-}C_5H_5)_2V(CD_3)_2$ and 85 mg (0.40 mmol) $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$ in 14.7 ml of benzene was photolyzed for 12 h in a water-jacketed Schlenk tube. The ethane produced was analyzed by GC/MS and was found to consist of a mixture of C_2H_6, $C_2D_3H_3$ and C_2D_6. The ratio of C_2D_6 to $C_2D_3H_3$ was 1/2.

In a related experiment, a mixture of 75 mg (0.35 mmol) of $(\eta^5\text{-}C_5H_5)_2V(CD_3)_2$ and 77 mg (0.36 mmol) of $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$ in 12.7 ml of benzene was photolyzed for 1 h in a water-jacketed Schlenk tube. The solvent was then removed by vacuum and the residue analyzed by mass spectrometry. The analysis indicated a mixture $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$, $(\eta^5\text{-}C_5H_5)_2V(CD_3)_2$ and $(\eta^5\text{-}C_5H_5)_2V(CH_3)(CD_3)$.

A control experiment was run by dissolving 94 mg (0.43 mmol) of $(\eta^5\text{-}C_5H_5)_2V(CD_3)_2$ and 106 mg (0.488 mmol) of $(\eta^5\text{-}C_5H_5)_2V(CD_3)_2$ in 16.6 ml of benzene. The solution was stirred for 12 h in the dark at 15°C and then the solvent was removed under reduced pressure. The residue was analyzed by mass spectrometry and was found to consist of a mixture of $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$, $(\eta^5\text{-}C_5H_5)_2V(CD_3)_2$ and $(\eta^5\text{-}C_5H_5)_2V(CH_3)(CD_3)$.

B. Photolysis of $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$ in the presence of vinyl monomers

A 1.50×10^{-2} *M* solution of $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$ in 20.0 ml of either methyl methacrylate or styrene was photolyzed for 1 h at 35°C. The photo-mixtures were added to 225 ml of methanol containing 5 ml of concentrated HCl. The mixture was stirred overnight and the precipitated polymer collected by filtration. Following washing with methanol, the white residue was dried in a vacuum oven at 50°C.

As a control experiment, the procedure was repeated for each monomer, this time in the dark. Both the light and dark experiments were repeated without the organometallic species present. The results of the light and dark experiments are summarized in Table 8.

C. Photolysis of $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$ in benzene; analysis of liquid products

A solution containing 10.0 ml of toluene-free benzene, 0.010 ml of mesitylene (internal standard) and 15 mmol of $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$ was photolyzed for 24 h in a 15°C water bath. The liquid portion of the photo-mixture was analyzed by gas chromatography. Cyclopentadiene (4%) and toluene ($< 1\%$) were detected. No methylcyclopentadiene, dicyclopentadiene, bis(methylcyclopentadiene) or biphenyl were detected in the photo-mixture.

D. Photolysis of $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$ in pentane: analysis of the insoluble products

A solution of 0.29 g (1.4 mol) of $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$ in 30 ml of pentane was filtered into a water-jacketed Schlenk tube. The solution was photolyzed for 48 h. The resulting grey-black precipitate was isolated by filtration and washed with pentane. The residue was then vacuum dried. Anal. Found: C, 61.68; H, 6.33; V, 31.9%.

To the residue was added 10 ml of HCl-saturated toluene. The solution turned purple $[(\eta^5\text{-}C_5H_5)VCl_3]$ and a green precipitate formed. A small amount of methane was detected in the evolved gas by gas chromatography. The solution was filtered and the green residue washed with pentane. Mass spectral analysis indicated that the solid was $(\eta^5\text{-}C_5H_5)_2VCl_2$.

The purple filtrate was exposed to the air and immediately turned royal blue. The solvent was removed by vacuum, leaving blue $(\eta^5\text{-}C_5H_5)VOCl_2$. The visible spectrum of $(\eta^5\text{-}C_5H_5)VOCl_2$ in cyclohexane exhibited a maximum at 544 nm [37].

E. Reduction of $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$

A mixture of 0.30 g (1.4 mmol) of $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$ and 0.20 g (8.7 mmol) of sodium sand was stirred for 10 h in 40 ml of THF. The dark green solution turned brown with the formation of a brown precipitate. Gas chromatographic analysis indicated only methane was evolved from the mixture. A similar reaction in benzene gave the same results.

A mixture of 0.59 g (2.8 mmol) of $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$ and 1.45 g (63.0 mmol) of sodium sand was stirred in 200 ml of THF while carbon monoxide was bubbled through the solution. After being stirred overnight the dark green solution had turned deep yellow in color. The solution was filtered through a 3 × 3 cm plug of alumina and then the plug was washed with THF. The filtrate was taken to dryness by vacuum. The dark yellow residue was sublimed at 55°C and 10^{-2} Torr, yielding 85 mg (13%) of orange $(\eta^5\text{-}C_5H_5)V(CO)_4$ [49].

F. Oxidation of $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$: ethane analysis

1. Solvent dependence. Solutions of $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$ (4.7×10^{-2} *M*) in either THF or benzene were stirred for $4\frac{1}{2}$ h in the dark at 15°C with a fifteen-fold molar excess of AgCl. By gas chromatographic analysis, the evolved gas was found to consist of methane, ethane and ethylene. The evolved gas was found to contain 18% ethane when THF was the solvent and 13% ethane when benzene was the solvent.

2. Concentration dependence. Three mixtures of $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$, AgCl and THF were stirred for $4\frac{1}{2}$ h at 15°C in the dark. The concentrations of $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$ in the three mixtures were 4.7×10^{-1} *M*, 4.7×10^{-2} *M* and 4.7×10^{-3} *M*, respectively. Silver chloride was present in a fifteen-fold molar excess in comparison to the vanadium species. The evolved gas was analyzed by gas chromatography and the results are summarized in Table 9.

3. Time dependence. Two 4.7×10^{-2} *M* solutions of $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$, one in THF, the other in benzene, were stirred in the dark with a fifteen-fold molar excess of AgCl for 2 days at 15°C. Gas samples were periodically taken from the reaction mixtures and analyzed by gas chromatography. The results are summarized in Tables 10 and 11.

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