

**PHOTO-DEGRADATION STUDIES ON
 DI- η^5 -CYCLOPENTADIENYLDIMETHYLVANADIUM,
 DI- η^5 -CYCLOPENTADIENYLMETHYLVANADIUM,
 DI- η^5 -CYCLOPENTADIENYLDIMETHYLNIOBIUM, AND SOME
 DEUTERATED ANALOGS**

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Summary

The photolysis of alkyl metallocene derivatives of vanadium and niobium in hydrocarbon solvents results in cleavage of the carbon–metal σ -bond. In the cases of $(\eta^5\text{-C}_5\text{H}_5)_2\text{VCH}_3$ and $(\eta^5\text{-C}_5\text{H}_5)_2\text{Nb}(\text{CH}_3)_2$, only methane (>99%) is produced photochemically. $(\eta^5\text{-C}_5\text{H}_5)_2\text{V}(\text{CH}_3)_2$, prepared on a convenient new synthesis from $(\eta^5\text{-C}_5\text{H}_5)_2\text{VCl}_2$ and methyllithium in toluene, degrades under photochemical conditions to yield both methane and ethane in a 2 : 1 ratio. The ethane arises from intra- and intermolecular methyl dimerization. Deuterium labeling studies have shown that the methyl group, the cyclopentadienyl ring, and the solvent are all sources of hydrogen in the formation of methane in these photolyses. The extent to which each source participates in the hydrogen abstraction process cannot be quantitatively determined because of the influence of an isotope effect. Chemical reactions with carbon monoxide during the photolyses give low yields of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_4$ from $(\eta^5\text{-C}_5\text{H}_5)_2\text{VCH}_3$ or $(\eta^5\text{-C}_5\text{H}_5)_2\text{V}(\text{CH}_3)_2$, and of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Nb}(\text{CO})\text{CH}_3$ from $(\eta^5\text{-C}_5\text{H}_5)_2\text{Nb}(\text{CH}_3)_2$.

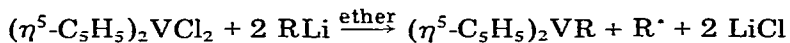
Introduction

Photo-induced reactions of dialkyl- and diaryl-metallocenes of titanium, zirconium and hafnium have attracted much attention in recent years [1–11]. In contrast, photochemical reactions of Group VB analogs such as $(\eta^5\text{-C}_5\text{H}_5)_2\text{V}(\text{CH}_3)_2$ (I) [12] and $(\eta^5\text{-C}_5\text{H}_5)_2\text{Nb}(\text{CH}_3)_2$ (II) [13] have not yet been investigated. In the present paper we describe a convenient new synthesis for I, as well as

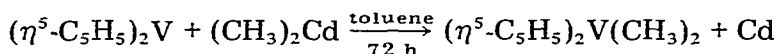
detailed studies of the photochemical degradations of I, II, $(\eta^5\text{-C}_5\text{H}_5)_2\text{VCH}_3$ (III) [14], and certain deuterated analogs.

Results and discussion

Organometallic compounds of the type $(\eta^5\text{-C}_5\text{H}_5)_2\text{VR}_2$ were originally thought to be thermally unstable, owing to steric factors associated with the relatively small size of vanadium [15–17]. Reactions of organolithium or Grignard reagents with $(\eta^5\text{-C}_5\text{H}_5)_2\text{VCl}_2$ in ether resulted in most cases on a reduction of the metal, and compounds of the type $(\eta^5\text{-C}_5\text{H}_5)_2\text{VR}$ were obtained [15–17].

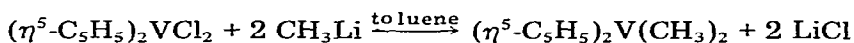


Subsequent studies involving the synthesis of metallacyclic derivatives of vanadocene, however, made this conclusion subject to question [18]. Still more recent findings have indicated that $(\eta^5\text{-C}_5\text{H}_5)_2\text{V}(\text{CH}_3)_2$ (I) can be isolated as a relatively thermally stable compound from the interaction of dimethylcadmium and vanadocene [12]. This reaction is reported to be a complicated process involving several steps [12].



(1)

We have found that comparable yields (64%) of I may be obtained in a much more convenient manner. The slow addition of a stoichiometric quantity of ethereal methyllithium to $(\eta^5\text{-C}_5\text{H}_5)_2\text{VCl}_2$ during a period of 2 hours yields I if the solvent is toluene rather than ether. It is possible that the increased solubility of $(\eta^5\text{-C}_5\text{H}_5)_2\text{VCl}_2$ in toluene enables a more facile reaction with the alkylating agent, preventing the reduction of vanadium by the unreacted metal alkyl. Purification by vacuum sublimation yields I in high purity*.



(1)

The ESR spectrum of I produced in this manner is consistent with the product being a d^1 compound ($g = 1.9934$). In toluene solution at room temperature, the spectrum consists of an eight-line pattern ($A_V = 63.89 \text{ G}$), together with super-hyperfine interaction with the six methyl protons ($a_H = 4.74 \text{ G}$). These results are also consistent with earlier ESR data for I [12]. The mass spectrum of I indicates a weak molecular ion at $m/e = 211$, together with stepwise loss of the two methyl groups at $m/e = 196$ and 181 , respectively.

When a hexane solution of I is subjected to photolysis under polychromatic conditions ($\lambda > 300 \text{ nm}$), cleavage of the vanadium–methyl σ -bond occurs. Gas chromatographic analysis of the gas above the reaction solution indicates the presence of methane and ethane in a 2 : 1 ratio, along with traces of ethylene

* Compound I may also be prepared in 7% yield by the reaction of $(\eta^5\text{-C}_5\text{H}_5)_2\text{V}$ and $(\text{CH}_3)_2\text{Zn}$ in toluene at room temperature for 3 days [19].

TABLE 1

GAS COMPOSITIONS DERIVED FROM THE PHOTOLYSIS OR THERMOLYSIS OF $(\eta^5\text{-C}_5\text{H}_5)_2\text{VCH}_3$, $(\eta^5\text{-C}_5\text{H}_5)_2\text{V}(\text{CH}_3)_2$, AND $(\eta^5\text{-C}_5\text{H}_5)_2\text{Nb}(\text{CH}_3)_2$

Compound	Mode of decomposition	Percentage of gases			
		CH ₄	C ₂ H ₆	C ₂ H ₄	Ref.
$(\eta^5\text{-C}_5\text{H}_5)_2\text{VCH}_3$	$h\nu$	>99	trace	trace	this work ^a
$(\eta^5\text{-C}_5\text{H}_5)_2\text{VCH}_3$	thermal	100	—	—	20
$(\eta^5\text{-C}_5\text{H}_5)_2\text{V}(\text{CH}_3)_2$	$h\nu$	64	36	trace	this work ^{a, b}
$(\eta^5\text{-C}_5\text{H}_5)_2\text{V}(\text{CH}_3)_2$	thermal	100	—	—	20
$(\eta^5\text{-C}_5\text{H}_5)_2\text{Nb}(\text{CH}_3)_2$	$h\nu$	>99	trace	trace	this work ^a
$(\eta^5\text{-C}_5\text{H}_5)_2\text{Nb}(\text{CH}_3)_2$	thermal	96–98	—	1–2	13

^a Gas chromatographic analyses; flame ionization detector; Porapak Q column. ^b Gas percentages $\pm 3\%$.

(Table 1). This result is in contrast to that observed in thermal studies of I [20,21] which reveal that only methane is produced upon thermal degradation. The photo-degradation of I also differs from that of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CH}_3)_2$ [5]. Upon photolysis under similar conditions, the latter yields almost exclusively methane (>99%), with only traces of ethane and ethylene.

Selective deuteration of the solvent, the methyl groups and the cyclopentadienyl rings illustrates that the hydrogen which is incorporated into the methane produced in the photolysis of I arises from all three possible sources. These results again differ from those in the photolysis of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CH}_3)_2$ [5] and the thermolysis of I [20], in which the solvent does not participate in the methane formation. Results of these photolytic studies involving deuterium-labeled systems are summarized in Table 2.

TABLE 2

DEUTERIUM CONTENT OF METHANE DERIVED FROM THE PHOTOLYSIS OF $(\eta^5\text{-C}_5\text{H}_5)_2\text{VCH}_3$, $(\eta^5\text{-C}_5\text{H}_5)_2\text{V}(\text{CH}_3)_2$, $(\eta^5\text{-C}_5\text{H}_5)_2\text{Nb}(\text{CH}_3)_2$, AND SPECIFICALLY DEUTERATED DERIVATIVES ^a

Compound	Solvent	Deuterium content, ratio ^b			
		CH ₄	CDH ₃	CD ₃ H	CD ₄
$(\eta^5\text{-C}_5\text{H}_5)_2\text{VCH}_3$	C ₆ D ₆	0.85	0.15	—	—
$(\eta^5\text{-C}_5\text{H}_5)_2\text{VCD}_3$	C ₆ H ₆	—	—	0.96	0.04
$(\eta^5\text{-C}_5\text{D}_5)_2\text{VCH}_3$	C ₆ H ₆	0.93	0.07	—	—
$(\eta^5\text{-C}_5\text{D}_5)_2\text{VCD}_3$	C ₆ H ₆	—	—	0.91	0.09
$(\eta^5\text{-C}_5\text{D}_5)_2\text{VCH}_3 +$ $(\eta^5\text{-C}_5\text{H}_5)_2\text{VCD}_3$ ^c	C ₆ H ₆	—	—	0.92	0.08
$(\eta^5\text{-C}_5\text{H}_5)_2\text{V}(\text{CH}_3)_2$	C ₆ D ₆	0.93	0.07	—	—
$(\eta^5\text{-C}_5\text{H}_5)_2\text{V}(\text{CD}_3)_2$	C ₆ H ₆	—	—	0.92	0.08
$(\eta^5\text{-C}_5\text{D}_5)_2\text{V}(\text{CH}_3)_2$	C ₆ H ₆	0.94	0.06	—	—
$(\eta^5\text{-C}_5\text{D}_5)_2\text{V}(\text{CH}_3)_2 +$ $(\eta^5\text{-C}_5\text{H}_5)_2\text{V}(\text{CD}_3)_2$ ^c	C ₆ H ₆	—	—	0.96	0.04
$(\eta^5\text{-C}_5\text{H}_5)_2\text{Nb}(\text{CH}_3)_2$	C ₆ D ₆	0.86	0.14	—	—
$(\eta^5\text{-C}_5\text{H}_5)_2\text{Nb}(\text{CD}_3)_2$	C ₆ H ₆	—	—	0.55	0.45
$(\eta^5\text{-C}_5\text{D}_5)_2\text{Nb}(\text{CH}_3)_2$	C ₆ H ₆	0.53	0.47	—	—
$(\eta^5\text{-C}_5\text{D}_5)_2\text{Nb}(\text{CD}_3)_2$	C ₆ H ₆	—	—	0.25	0.75

^a Deuterium content of benzene was 99.5%, methyl groups 99%, and cyclopentadienyl rings 96–97%.

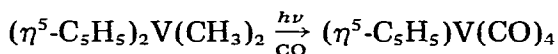
^b Deuterium content of gases generated was determined by GC/MS at 18 eV, $\pm 3\%$. ^c Equimolar mixture.

The photolysis of an equimolar mixture of $(\eta^5\text{-C}_5\text{D}_5)_2\text{V}(\text{CH}_3)_2$ (IV) and $(\eta^5\text{-C}_5\text{H}_5)_2\text{V}(\text{CD}_3)_2$ (V) in benzene reveals intermolecular hydrogen abstraction from the cyclopentadienyl rings is not occurring, since there is no significant increase in the amount of CD_4 generated relative to the photolysis of V alone in benzene. This result is also in contrast to thermal degradation studies involving I [20].

The ethane produced appears to be the result of the dimerization of methyl moieties from the same or from different molecules. While the photolysis of IV in benzene yields only C_2H_6 and the photolysis of V in benzene produces only C_2D_6 , photolysis of an equimolar mixture of IV and V gives $\text{C}_2\text{D}_3\text{H}_3$ in addition to C_2H_6 and C_2D_6 .

It was initially anticipated that the organometallic species produced in the photolysis of I might be $(\eta^5\text{-C}_5\text{H}_5)_2\text{V}$ or $(\eta^5\text{-C}_5\text{H}_5)\text{VCH}_3$ (III). However, sublimation of the material remaining after photolysis yielded no volatile products. Further studies to elucidate the nature of the organometallic photolysis products are under investigation.

When I is photolyzed under an atmosphere of carbon monoxide, small amounts of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_4$ [22] can be isolated following sublimation. This suggests that partial cleavage of the $(\eta^5\text{-C}_5\text{H}_5)_2\text{V}$ moiety occurs under these photolytic conditions.



Photolysis of $(\eta^5\text{-C}_5\text{H}_5)_2\text{VCH}_3$ in benzene gives only methane (>99%) (Table 1). Specific deuterium labeling of the solvent, methyl group, and cyclopentadienyl rings demonstrates that the hydrogen required to form methane again comes from all three sources (Table 2). The extent to which each source contributes to the abstraction process cannot be exactly determined, because of differences in reactivities of the isotopes of hydrogen (i.e., an isotope effect). Thus, photolysis of III in benzene- d_6 resulted in 15% deuterium incorporation in the resulting methane, while photolysis of $(\eta^5\text{-C}_5\text{D}_5)_2\text{VCD}_3$ in benzene resulted in 91% CD_3H *.

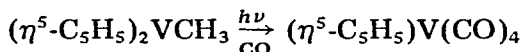
Thermal decomposition studies on III show production of only methane, with hydrogen abstraction from the cyclopentadienyl rings and the methyl group, but no attack on the solvent [20]. The organometallic products resulting from thermal degradation of III were reported to be vanadocene and substituted vanadocene [20]. In our studies, as with the photo-degradation of I, no vanadocene or substituted vanadocenes can be isolated following degradation of III under photochemical conditions.

When an equimolar mixture of $(\eta^5\text{-C}_5\text{D}_5)_2\text{VCH}_3$ (VI) and $(\eta^5\text{-C}_5\text{H}_5)_2\text{VCD}_3$ (VII) is photolyzed in benzene, the amount of CD_4 shows no significant increase compared to the photolysis of VII alone in benzene. This result likewise con-

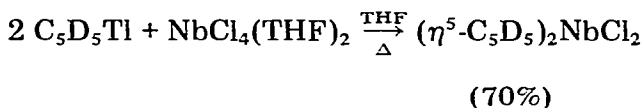
* Photolysis of $(\eta^5\text{-C}_5\text{H}_5)\text{Pt}(\text{CH}_3)_3$ results in the generation of methyl radicals which abstract hydrogen from the solvent, other methyl groups, and the cyclopentadienyl ring to form methane (90%). Isotopic selectivity is evoked in explaining the results of deuteration studies [23]. An isotope effect is also presumed to occur in the photolysis of deuterated derivatives of $(\eta^5\text{-C}_5\text{H}_5)_2\text{-Ti}(\text{CH}_3)_2$ [5].

trasts with thermal degradation studies of III, which indicate intermolecular cyclopentadienyl ring hydrogen abstraction [20].

Photolysis of II with carbon monoxide results in the production of $(\eta^5\text{-C}_5\text{H}_5)\text{-V}(\text{CO})_4$ in low yield, again indicating partial cleavage of the $(\eta^5\text{-C}_5\text{H}_5)_2\text{V}$ unit under these conditions.

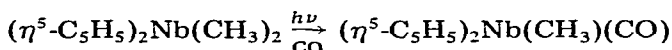


$(\eta^5\text{-C}_5\text{H}_5)_2\text{Nb}(\text{CH}_3)_2$ (II) in hexane results in the formation of only methane (>99%) (Table 1) *. The hydrogen incorporated into the photo-generated methane originates from the solvent, the methyl groups and the cyclopentadienyl rings, as determined by specific deuteration (Table 2). Pyrolysis of II yields 96–98% methane and 1–2% ethylene [13]. No deuterium-labeling studies were reported in the thermolysis study. An aid in the formation of deuterated derivatives of III was the synthesis of $(\eta^5\text{-C}_5\text{D}_5)_2\text{NbCl}_2$ from the reaction of $\text{C}_5\text{D}_5\text{Ti}$ [25] and $\text{NbCl}_4(\text{THF})_2$ [13] in refluxing THF.



As with the photolysis of III, II, when photo-degraded, undergoes some isotopic selectivity. Thus, II, when photolyzed in benzene- d_6 , yields 14% CDH_3 , whereas $(\eta^5\text{-C}_5\text{D}_5)_2\text{Nb}(\text{CD}_3)_2$, when photolyzed in benzene, gives 25% CD_3H .

II is known to undergo photolysis in the presence of CS_2 to give $(\eta^5\text{-C}_5\text{H}_5)_2\text{Nb}(\text{CH}_3)(\eta^2\text{-CS}_2)$. We find that photolysis of II in the presence of carbon monoxide likewise produces $(\eta^5\text{-C}_5\text{H}_5)_2\text{Nb}(\text{CH}_3)(\text{CO})$ [27] in low yield **.



Conclusions

The use of toluene rather than ether in the methylation of $(\eta^5\text{-C}_5\text{H}_5)_2\text{VCl}_2$ enables formation of $(\eta^5\text{-C}_5\text{H}_5)_2\text{V}(\text{CH}_3)_2$ in 64% yield. Photolysis of methyl metallocene derivatives of Groups IVB and VB metals results in degradation pathways other than those achieved under thermolysis conditions. The nature of this decomposition is dependent on the metal triad, the particular metal within a triad, and a given methyl derivative of a specific metallocene. $(\eta^5\text{-C}_5\text{H}_5)_2\text{VCH}_3$, $(\eta^5\text{-C}_5\text{H}_5)_2\text{V}(\text{CH}_3)_2$, and $(\eta^5\text{-C}_5\text{H}_5)_2\text{Nb}(\text{CH}_3)_2$, when photolyzed in hydrocarbon solvents, result in hydrogen abstraction from the solvent to form methane, while $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CH}_3)_2$, as previously studied, does not result in solvent attack under similar conditions. When photolyzed in the presence of carbon monoxide, $(\eta^5\text{-C}_5\text{H}_5)_2\text{VCH}_3$ and $(\eta^5\text{-C}_5\text{H}_5)_2\text{V}(\text{CH}_3)_2$ produce $(\eta^5\text{-C}_5\text{H}_5)\text{-V}(\text{CO})_4$

* The other members of this series of alkyl derivatives of Group VB metallocenes, $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ta}(\text{CH}_3)_2$, when photolyzed in hexane likewise yields >99% methane and only traces of ethane and ethylene [24].

** No reaction was observed with $(\eta^5\text{-C}_5\text{H}_5)_2\text{Nb}(\text{CH}_3)_2$ and olefins during photolysis [28].

$V(CO)_4$ in low yields, whereas $(\eta^5-C_5H_5)_2Nb(CH_3)_2$ produces a low yield of $(\eta^5-C_5H_5)_2Nb(CH_3)(CO)$ under these conditions. $(\eta^5-C_5H_5)_2V(CH_3)_2$ photochemically degrades to form both methane and ethane, whereas the photo-degradations of $(\eta^5-C_5H_5)_2VCH_3$ and $(\eta^5-C_5H_5)_2Nb(CH_3)_2$ under similar conditions afford only methane. Selective deuteration studies have shown that all possible hydrogen sources, the methyl group, the cyclopentadienyl ring, and the solvent, are utilized to form methane during the photo-degradations.

Experimental

All operations were conducted under argon using Pyrex Schlenk tubes. Argon, solvents and alumina were purified as described previously [5]. Photolyses were conducted with a 450 W Hanovia photochemical lamp located in a Pyrex, water-cooled immersion well. This unit was placed 1–2 cm from a water-jacketed Schlenk tube containing the solution to be photolyzed.

Gas chromatographic analyses were performed on a Varian Series 2400 gas chromatograph equipped with a flame ionization detector. Analyses were made on a 6-ft Porapak Q column. The compositions of various samples were identified by means of a Perkin-Elmer-Hitachi RMU-6L mass spectrometer interfaced with a Perkin-Elmer 990 gas chromatograph. The gaseous products were separated on a 6-ft Porapak Q column, and the mass spectrum was obtained for each component in the sample. IR spectra were obtained on a Beckman IR-10 or a Perkin-Elmer 237-B infrared spectrophotometer. ESR spectra were recorded on a Varian E-12 spectrometer. Proton NMR spectra were obtained on a Varian A-60 spectrometer.

$(\eta^5-C_5H_5)_2Nb(CH_3)_2$ [13] and $(\eta^5-C_5H_5)_2VCl$ [30] were prepared by literature procedures. $(\eta^5-C_5H_5)_2VCl_2$ [31] was synthesized quantitatively by bubbling gaseous HCl and air through a methylene chloride solution of $(\eta^5-C_5H_5)_2VCl$. C_5D_5Ti (96.5% deuterated) was obtained by a literature method [25]. Deuterated benzene was put through three freeze-thaw cycles, after which no gas evolved on melting. Commercial methyllithium was standardized by a published procedure [29].

Preparation of $(\eta^5-C_5H_5)_2V(CH_3)_2$ (I)

$(\eta^5-C_5H_5)_2VCl_2$ (2.14 g, 8.49 mmol) was suspended in 125 ml of toluene at 0°C. Freshly standardized ethereal methyllithium (16.8 mmol) was added during 2 h. The mixture was then allowed to warm to room temperature, and was stirred for an additional 1 h. The black solution was filtered and the residue washed with toluene until the washings were nearly colorless. The black filtrate was evaporated to dryness by vacuum. The resulting solid residue was sublimed at 65–100°C at 10^{-3} Torr, yielding black crystals of $(\eta^5-C_5H_5)_2V(CH_3)_2$ (1.14 g, 64%). Found: C, 67.57; H, 7.72; V, 24.2. $C_{12}H_{16}V$ calcd.: C, 68.24; H, 7.64; V, 24.12%.

The mass spectrum of I exhibited the following major peaks: m/e 211 (1, M^+), 196 (7, $M - CH_3^+$), 181 (100, $M - 2 CH_3^+$), 115 (53, $C_5H_4V^+$), 66 ($C_5H_6^+$), and 51 (26, V^+). ESR spectrum (toluene, room temperature): $g = 1.9934$, $A_v = 63.89$ G, $a_H = 4.74$ G.

Preparation of $(\eta^5\text{-C}_5\text{H}_5)_2\text{VCH}_3$ (III)

$(\eta^5\text{-C}_5\text{H}_5)_2\text{VCl}$ (3.30 g, 15.2 mmol) was dissolved in 100 ml of ethyl ether and cooled to 0°C, and standardized methyl lithium in ether (15.4 mmol) was added dropwise. The color changed from blue to black, with formation of a precipitate. After the addition was complete, the mixture was allowed to warm to room temperature and stirred for 2 h. The solvent was removed by vacuum and the black residue was sublimed at 40–60°C at 10^{-3} Torr, yielding black crystals of $(\eta^5\text{-C}_5\text{H}_5)_2\text{VCH}_3$ (1.33 g, 44%).

The mass spectrum of III exhibited the following major peaks: 196 (1, M^+), 181 (100, $M - \text{CH}_3^+$), 115 (76, $\text{C}_5\text{H}_4\text{V}^+$), 66 (96, C_5H_6^+), 65 (69, C_5H_5^+), 51 (27, V^+).

Preparation of $(\eta^5\text{-C}_5\text{D}_5)_2\text{VCl}$

$(\eta^5\text{-C}_5\text{D}_5)_2\text{VCl}$ was prepared as described for $(\eta^5\text{-C}_5\text{H}_5)_2\text{VCl}$ [30] using $\text{C}_5\text{D}_5\text{Tl}$ in place of $\text{C}_5\text{H}_5\text{Tl}$. Mass spectral analysis indicated 96–97% deuteration of the product.

Preparation of $(\eta^5\text{-C}_5\text{D}_5)_2\text{VCl}_2$

$(\eta^5\text{-C}_5\text{D}_5)_2\text{VCl}_2$ was prepared by the procedure used for $(\eta^5\text{-C}_5\text{H}_5)_2\text{VCl}_2$ [31] using $(\eta^5\text{-C}_5\text{H}_5)_2\text{VCl}$ in place of $(\eta^5\text{-C}_5\text{H}_5)_2\text{VCl}$. The compound was found to have 96–97% deuterated cyclopentadienyl rings by mass spectral analysis.

Preparation of $(\eta^5\text{-C}_5\text{D}_5)_2\text{NbCl}_2$

$\text{NbCl}_4(\text{THF})_2$ [13] (5.30 g, 14.3 mmol) and 7.88 g (28.7 mmol) of $\text{C}_5\text{D}_5\text{Tl}$ were slurried in 200 ml of THF. The mixture was heated to reflux for 2 h, to give a dark brown solution with a fine white precipitate. The solvent was removed by vacuum and the residue sublimed at 250°C and 10^{-3} Torr, resulting in 3.10 g (71%) of black-brown $(\eta^5\text{-C}_5\text{D}_5)_2\text{NbCl}_2$.

Preparation of other deuterated analogs

$(\eta^5\text{-C}_5\text{H}_5)_2\text{VCD}_3$, $(\eta^5\text{-C}_5\text{H}_5)_2\text{V}(\text{CD}_3)_2$, $(\eta^5\text{-C}_5\text{H}_5)_2\text{Nb}(\text{CD}_3)_2$, $(\eta^5\text{-C}_5\text{D}_5)_2\text{VCD}_3$ and $(\eta^5\text{-C}_5\text{D}_5)_2\text{Nb}(\text{CD}_3)_2$ were prepared by the methods used for the non-deuterated methyl derivatives, utilizing the appropriate metallocene chloride and LiCD_3 *. $(\eta^5\text{-C}_5\text{D}_5)_2\text{VCH}_3$, $(\eta^5\text{-C}_5\text{D}_5)_2\text{V}(\text{CH}_3)_2$, and $(\eta^5\text{-C}_5\text{D}_5)_2\text{Nb}(\text{CH}_3)_2$ were prepared from the appropriate deuterated metallocene chloride and methyl lithium.

Photolysis of $(\eta^5\text{-C}_5\text{H}_5)_2\text{V}(\text{CH}_3)_2$ in hexane

In a typical run, 0.59 g (2.8 mmol) of I was dissolved in 250 ml of hexane. The black solution was irradiated in a water-jacketed Schlenk tube equipped with a magnetic stirrer and a mercury overpressure valve. Gas chromatographic analysis of the space above the reaction mixture after 24 h of photolysis showed that the gas was composed of methane (64%) and ethane (36%) **. A dark

* CD_3Li was prepared from CD_3I and 2 equivalents of lithium wire (1% Na) in ethyl ether. CD_3MgI , made from magnesium turnings and CD_3I in ethyl ether, works equally well for the preparation of the deuterated derivatives.

** Photolysis with a 275W GE sun lamp or in aromatic solvents gave identical results.

air-sensitive precipitate was formed during the reaction and elemental analysis indicated carbon, hydrogen and vanadium to be present. Evaporation of the solvent by vacuum produced a dark solid, which did not yield $(\eta^5\text{-C}_5\text{H}_5)_2\text{V}$ upon sublimation.

Photolysis of $(\eta^5\text{-C}_5\text{H}_5)_2\text{VCH}_3$ in benzene

In a typical run, 0.64 g (3.0 mmol) of III was dissolved in 250 ml of benzene in a water-jacketed Schlenk tube. The black solution was photolyzed for 24 h. Analysis of the evolved gas by GLC indicated that methane (>99%), ethane and ethylene (<1%) were present.

Photolysis of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Nb}(\text{CH}_3)_2$ in hexane

In a typical run, 0.45 g (3.6 mmol) of II was dissolved in 250 ml of hexane and photolyzed for 24 h in a water-jacketed Schlenk tube. The red-brown solution changed to a blue color within the first hour of photolysis. Gas chromatographic analysis of the evolved gas indicated methane (>99%), ethane and ethylene (<1%).

Photolysis of $(\eta^5\text{-C}_5\text{H}_5)_2\text{VCH}_3$, $(\eta^5\text{-C}_5\text{H}_5)_2\text{V}(\text{CH}_3)_2$, and $(\eta^5\text{-C}_5\text{H}_5)_2\text{Nb}(\text{CH}_3)_2$ and deuterated analogs in benzene and benzene d_6

Approximately 100 mg of the appropriate methyl metallocene derivative was dissolved in 10 ml of benzene in a 30 ml Schlenk tube. The samples were photolyzed in a water bath as previously described [5]. Gas samples were analyzed by interfaced GC/MS at 18 eV utilizing a 6-ft Porapak Q column to separate the gases. The results are summarized in Table 2.

Photolysis of $(\eta^5\text{-C}_5\text{H}_5)_2\text{V}(\text{CH}_3)_2$ with carbon monoxide

I (0.55 g, 2.6 mmol) was dissolved in 250 ml of hexane in a water-jacketed Schlenk tube and photolyzed for 19 h while the atmosphere above the mixture was constantly swept with carbon monoxide. The solvent was then removed by vacuum. The dark residue was chromatographed on silica gel (100–200 mesh). Hexane eluted a yellow band. Removal of the solvent from this band produced a yellow solid which upon sublimation at room temperature and 10^{-3} Torr produced 20 mg (3%) of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_4$ [22]. IR (hexane): 2030, 1934, 1904 cm^{-1} ; NMR (C_6D_6): τ 5.77 (s); Mass spectrum: M^+ m/e 228.

Photolysis of $(\eta^5\text{-C}_5\text{H}_5)_2\text{VCH}_3$ with carbon monoxide

III (0.62 g, 3.2 mmol) was photolyzed for 6 h in 250 ml of benzene as described for I. Workup gave $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_4$ in low yield.

Photolysis of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Nb}(\text{CH}_3)_2$ with carbon monoxide

II (0.98 g, 3.9 mmol) was dissolved in 250 ml of pentane in a water-jacketed Schlenk tube. The red-brown solution was photolyzed for 2 h while a slow stream of carbon monoxide was bubbled through the solution. The resulting green solution was evaporated by vacuum. The residue was sublimed at 80°C and 10^{-3} Torr. An air-sensitive green solid, $(\eta^5\text{-C}_5\text{H}_5)_2\text{Nb}(\text{CH}_3)(\text{CO})$ (50 mg, 5%) was identified by comparisons of its spectra with literature data [27]. NMR (C_6D_6): τ 5.45 (s, 10 H), 10.52 (s, 3 H); IR (THF): 1890 cm^{-1} .

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