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THE REACTIVITY OF $Cp_2V_2(CO)_5$ TOWARDS ALKYNES

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Summary

The chemistry of $Cp_2V_2(CO)_5$ (I) with alkynes is reported. In non-coordinating solvents, I reacts with large, electron-poor alkynes to give the cyclobutadiene complexes $CpV(CO)_2(C_4R_4)$, which are not formed from photolysis of $CpV(CO)_4$ in the presence of alkyne. Smaller, more basic alkynes give simple monomeric adduct products of the type $CpV(CO)_2(RC{\equiv}CR)$. This latter product is the only one obtained if coordinating solvents are employed. It is demonstrated that coupling to form the cyclobutadiene ligand occurs on the dimer. The dimeric intermediate, produced at low temperature and observed at low temperature by IR and NMR, is believed to have the formula $Cp_2V_2(CO)_4(\mu\text{-}RC{\equiv}CR)$ (X).

$Cp_2V_2(CO)_5$ is active as a catalyst precursor in the photochemical hydrogenation of diphenyl acetylene to *cis*-stilbene. The mechanism appears to proceed through a $Cp_2V_2(CO)_4$(alkyne) intermediate.

Introduction

Recently we reported the mechanism of the photochemical synthesis of $Cp_2V_2(CO)_5$ (I) [1]. This molecule is unusual in several respects. Unlike the homologous series of cyclopentadienyl carbonyl dimers: $Cp_2Ni_2(CO)_2$, $Cp_2Co_2(CO)_3$, $Cp_2Fe_2(CO)_4$, $Cp_2Re_2(CO)_5$ and $Cp_2Cr_2(CO)_6$, it does not have the expected stoichiometry, $Cp_2V_2(CO)_7$. In addition, it adopts an asymmetric structure (Fig. 1) [2]. The molecule possesses a vanadium–vanadium double bond. V(2) has two terminal carbonyls, V(1) has a single terminal carbonyl (CO^*), and there are two semibridging carbonyls. It has been argued [3] that these semibridges may act as donors to some extent, not unlike the four electron donor carbonyl in $Mn_2dpm_2(CO)_5$ [4].

It has been shown [1] that strong nucleophiles are capable of directly attacking

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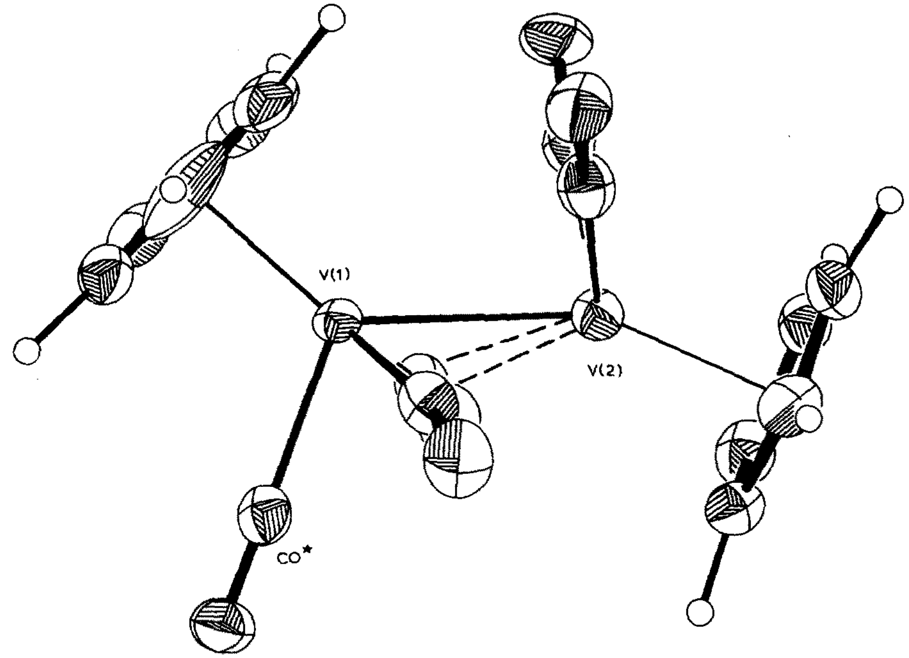
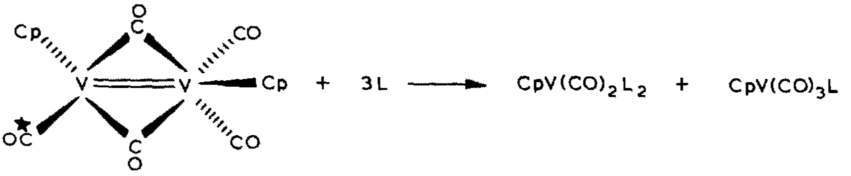


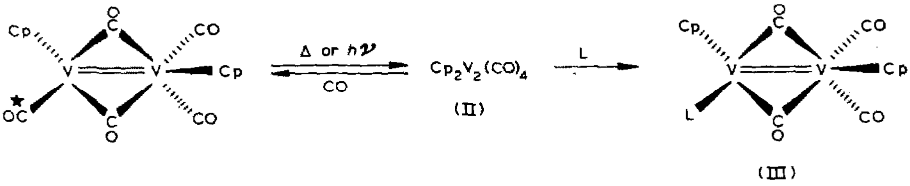
Fig. 1. Structure of $Cp_2V_2(CO)_5$ [3]. The weakly bonded terminal carbonyl on V(1) is referred to in this paper as CO *.

the vanadium–vanadium double bond to give monomeric products (eq. 1, L = PEt_2Ph).



(1)

However, by a different mechanism, weaker nucleophiles react with $Cp_2V_2(CO)_4$, which is in equilibrium with I [1], to produce dimeric products (eq. 2).



(2)

Compound III, formed from reaction of intermediate II and a two electron donor, was observed by IR at low temperature following photolysis in THF (L = THF). Note that structurally CO* has a long V–C distance of 1.972(4) Å vs. the other two (average) terminal V–C distances of 1.916(12) Å [3]. It is also felt that this is responsible for the highest carbonyl stretching frequency band in the IR at 2000

cm^{-1} and thus it is believed that this carbonyl is the one that is dissociated in the equilibrium of eq. 2.

We report here the results of a study of the reactions of $Cp_2V_2(CO)_5$ with monoolefins, conjugated dienes, and alkynes, as well as an exploration of its capacity to stereoselectively catalyze alkyne hydrogenation. We show that I is more reactive than monomeric $CpV(CO)_4$, with a distinct thermal and photochemistry. Moreover, I exhibits a marked product selectivity in the reaction studied.

Experimental

General

All operations were carried out under an atmosphere of nitrogen by using either Schlenk techniques or a Vacuum Atmospheres glove box. $Cp_2V_2(CO)_5$ was prepared as reported previously [3]. Solvents, dried over purple NaK/benzophenone solutions, were degassed by vacuum transfer. Photochemical reactions generally were carried out in 17 mm OD Pyrex tubes capped with septa. Two syringe needles, one of which reached to the bottom of the tube, permitted a nitrogen purge (which expels CO) and served to agitate the solution. A medium pressure 550-W mercury lamp (Hanovia) was held vertically in a water-cooled immersion well. Both the immersion well and Pyrex tubes were held close together in a water-cooled bath (10–15°C). Low temperature IR measurements were carried out in a cell which was previously described [1]. Infrared measurements were made on a Perkin–Elmer Model 283 IR spectrometer using either the low temperature cell or 0.1 mm pathlength NaCl cell capped with air-tight septa. ^1H NMR were recorded on either Varian 220 MHz or on XL 100-A NMR spectrometers.

Due to the small amounts of reactants employed, i.e. mg scale, yields are not reported. Unless noted otherwise, reactions proceed to completion (judged by IR spectra) in the irradiation times noted to give homogeneous solutions. Products from the various acetylenes, $RC{\equiv}CR$, were identified by comparison to known ($R = Ph$) or analogous compounds, by internal comparison of ^1H NMR integrations of cyclopentadienyl to alkyne resonances, and by CO stretching frequencies. These criteria readily distinguish $CpV(CO)_2(RC_2R)$ from $CpVCO(RC_2R)_2$ and $[CpV(CO)_2]_2(RC_2R)$. The dicarbonyl complexes $CpV(CO)_2(RC_2R)$ and $CpV(CO)_2(\eta^4\text{-}C_4R_4)$ are distinguishable by the infrared spectra. For the alkynes employed here, the splitting of the two CO frequencies is larger (by about 20 cm^{-1}) for the acetylene complex, and this complex also has the higher absolute frequency. Finally, the $CpV(CO)_2(RC_2R)$ complexes are green, while all other species, including $CpV(CO)_2(\eta^4\text{-}C_4R_4)$, range from red to red-orange.

Reactions of $Cp_2V_2(CO)_5$ with unsaturated hydrocarbons

Reaction with olefins

There was no reaction between $Cp_2V_2(CO)_5$ (0.003 g, 0.01 mmol) and 1,4-cyclohexadiene (20 μl, 0.2 mmol) in 1 ml octane after 18 h 25°C. $Cp_2V_2(CO)_5$ (0.013 g, 0.03 mmol) reacted with 1,3-cyclohexadiene (10 μl, 0.1 mmol) in 5 ml of hexane for 48 h to quantitatively produce $CpV(CO)_2$(1,3-cyclohexadiene). IR (ν(CO)) at 1930, 1860 cm^{-1} in hexane [5]. There was no reaction between $Cp_2V_2(CO)_5$ and either 1 atm (excess) C_2H_4 or allene in hexane after 20 h at 25°C. Excess

2,5-norbornadiene similarly gave no reaction with I in hexane after 5 days at 25°C or by photolysis.

Reactions with PhC≡CPh

(a) Hexane reactions. $Cp_2V_2(CO)_5$ (0.04 g, 0.2 mmol) was reacted with either equimolar (0.04 g, 0.2 mmol) or excess diphenyl acetylene in ca. 5 ml hexane. A very slow reaction occurs at room temperature (ca. 20% conversion in 22 h) to produce the tetraphenylcyclobutadiene derivative, $CpV(CO)_2(C_4Ph_4)$ (see below). Photolysis (15 min) gives 100% conversion (> 90% yield when 4/1 alkyne/dimer is used) to the brown cyclobutadiene product. IR ν(CO) 1983s, 1927s cm^{-1} in hexane; ^1H NMR: (in C_6D_6) Cp resonance at δ 4.13, phenyl resonance at 8.04, 7.17 and 7.02 ppm [6].

(b) Reaction in THF. $Cp_2V_2(CO)_5$ (0.04 g, 0.1 mmol) and PhC≡CPh (0.04 g, 0.2 mmol) were combined in 10 ml of THF and photolyzed for 30 min. The solution was green after photolysis. The IR and ^1H NMR confirmed that the product was $CpV(CO)_2$(PhC≡CPh) (see below). When excess PhC≡CPh was used (> 4/1), photolysis produced a mixture of $CpV(CO)_2$(PhC≡CPh) and CpV(CO)$(PhC≡CPh)_2$.

Reaction of $CpV(CO)_4$ with PhC≡CPh

$CpV(CO)_4$ (0.2 g, 0.9 mmol) and PhC≡CPh (0.57 g, 0.32 mmol) were combined in 40 ml of hexane. The solution was photolyzed for 30 min. Removal of solvent, after photolysis, gave an orange oil. Trituration with hexane of the oil gave an orange solid and a green soluble fraction in hexane. The hexane solubles were chromatographed on silica/hexane. A green band eluted with hexane which was identified as $CpV(CO)_2$(PhC≡CPh) (0.1 g, 22% yield). IR ν(CO) 2000s, 1930s cm^{-1} in hexane; ^1H NMR (in C_6D_6) Cp resonance at δ 5.02, phenyl resonances at 7.43, 7.07 and 6.95 ppm [6]. The orange solid from above was identified as CpV(CO)$(PhC≡CPh)_2$. IR ν(CO) 1975 cm^{-1} in hexane; ^1H NMR (in C_6D_6) Cp resonance at δ 5.07, phenyl resonances at 7.40, 7.20 and 6.98 ppm [6]. No cyclobutadiene product is obtained by photolysis of $CpV(CO)_4$ with PhC≡CPh in either hexane or THF. CpV(CO)$(PhC≡CPh)_2$ dissolved in THF, reacted with 1 atm of CO in 24 h to give 100% conversion to $CpV(CO)_2$(PhC≡CPh). $CpV(CO)_2$(PhC≡CPh) when photolyzed in THF with excess PhC≡CPh gave CpV(CO)$(PhC≡CPh)_2$.

Reactions of $Cp_2V_2(CO)_5$ with PhC≡CMe

(a) THF reaction. $Cp_2V_2(CO)_5$ (0.12 g, 0.32 mmol) and PhC≡CMe (1 ml of a 0.32 *M* solution in THF) were combined in THF. After 24 h at room temperature, the solution had changed from green to dark orange. Two new IR bands, ν(CO) 1992s, 1910s cm^{-1} in hexane, which were shown to be due to $CpV(CO)_2$(PhC≡CMe), were observed.

(b) Hexane reaction. $Cp_2V_2(CO)_5$ (0.05 g, 0.13 mmol) and PhC≡CMe (1 ml of a 0.33 *M* solution in hexane) were combined in 12 ml of hexane and photolyzed for 30 min. A green solution was obtained along with a red precipitate. The green hexane soluble species was identified as $CpV(CO)_2$(PhC≡CMe) (see below). The IR and ^1H NMR for the red precipitate is consistent with it being the dimethyldiphenylcyclobutadiene derivative $CpV(CO)_2(C_4Me_2Ph_2)$; IR ν(CO) 1968s, 1911s cm^{-1} in hexane; ^1H NMR (in C_6D_6) Cp resonance at δ 4.08, methyl resonance at 1.79 and phenyl resonances at 7.82 and 7.16 ppm. Only one isomer was observed (about the cyclobutadiene ring).

Reaction of CpV(CO)$_4$ with PhC≡CMe

CpV(CO)$_4$ (0.075 g, 0.33 mmol) and PhC≡CMe (1 ml of a 0.33 *M* THF solution) were combined in 4 ml of THF, and photolyzed 30 min. The green CpV(CO)$_2$(PhC≡CMe) was produced. IR ν(CO) 1992s, 1910s cm^{-1} in hexane; ^{1}H NMR (in C_6D_6) Cp resonance at δ 5.05, methyl resonance at 3.05 and phenyl resonances at 7.30, 7.18 and 7.02 ppm.

Reaction of Cp$_2$V$_2$(CO)$_5$ with MeC≡CMe

Cp$_2$V$_2$(CO)$_5$ (0.09 g, 0.24 mmol) and MeC≡CMe (1 ml of a 0.51 *M* solution in hexane) were combined in 4 ml of hexane and photolyzed for 25 min. The only observed product was CpV(CO)$_2$(MeC≡CMe) (see below), IR and ^{1}H NMR analysis.

Reaction of CpV(CO)$_4$ with MeC≡CMe

CpV(CO)$_4$ and excess MeC≡CMe were combined in hexane and photolyzed for 30 min. The green compound CpV(CO)$_2$(MeC≡CMe) was produced in this reaction. IR ν(CO) 1980s, 1900s cm^{-1} in hexane; ^{1}H NMR (in C_6D_6), Cp resonance at δ 5.00, methyl resonance at 2.65 ppm.

Reaction of Cp$_2$V$_2$(CO)$_5$ with HC≡CH

A saturated THF solution of I was placed in a septum capped Pyrex tube. Acetylene was bubbled through the solution by means of a long syringe needle which reached to the bottom of the tube; a second short syringe needle was connected to a one-way bubbler. This solution was photolyzed for 10 min. The resulting green solution was shown to contain mostly CpV(CO)$_2$(HC≡CH) (see below). In a like manner, Cp$_2$V$_2$(CO)$_5$ (0.03 g, 0.08 mmol) was dissolved in 7 ml of pentane and photolyzed under a purge of acetylene for 10 min. IR and ^{1}H NMR confirmed the presence of CpV(CO)$_2$(HC≡CH).

Reaction of CpV(CO)$_4$ with HC≡CH

CpV(CO)$_4$ was dissolved in 5 ml of THF (saturated solution) and photolyzed under a C_2H_2 flow for 3 min. The solution changed color from orange to green. CpV(CO)$_2$(HC≡CH) was identified as the only product. IR ν(CO) 1995s, 1916s cm^{-1} in hexane; ^{1}H NMR (in C_6D_6) Cp resonance at δ 4.92, HC≡ at 10.80 ppm [7].

Low temperature reactions of Cp$_2$V$_2$(CO)$_5$ with PhC≡CMe

(a) NMR experiment. Cp$_2$V$_2$(CO)$_5$ (0.03 g, 0.08 mmol) and PhC≡CMe (10 μl, 0.8 mmol) were combined in toluene-d_8 in a sealed NMR tube. The tube was photolyzed at −42°C for 30 min. The ^{1}H NMR (100 MHz) at −30°C revealed the presence of CpV(CO)$_2$(PhC≡CMe), unreacted I, free PhC≡CMe and new resonances at δ 4.63 and 2.78 ppm (3.33/1.0 integrated intensities). Upon warming to room temperature (in the dark), the new resonance decreased in intensity as did the resonances due to PhC≡CMe. CpV(CO)$_2$(C$_4$Me$_2$Ph$_2$) grew in intensity while CpV(CO)$_2$(PhC≡CMe) remained unchanged.

(b) Control experiment. Cp$_2$V$_2$(CO)$_5$ (0.03 g, 0.08 mmol) and PhC≡CMe (10 μl, 0.08 mmol) were combined in 5 ml of toluene at 25°C and photolyzed for 30 min. The IR confirmed the formation of CpV(CO)$_2$(C$_4$Me$_2$Ph$_2$) as the major product and CpV(CO)$_2$(PhC≡CMe) as a minor product.

(c) Infrared experiment. $Cp_2V_2(CO)_5$ (0.05 g, 0.08 mmol) and PhC≡CMe (0.25 ml of a 0.33 *M* solution in THF) were combined in 4 ml of THF. A portion of this solution was added to the low temperature IR cell. The cell was cooled to −42°C and the solution photolyzed for 35 min through the cell windows. The green solution (−37°C) following photolysis revealed four new peaks in the IR, ν(CO) 1970s, 1920m, 1900s, 1842m. Upon warming, these peaks decayed and peaks due to $CpV(CO)_2(C_4Me_2Ph_2)$ grew in.

Catalytic hydrogenation of PhC≡CPh

(a) Photochemical hydrogenation. $Cp_2V_2(CO)_5$ (0.1 g, 0.27 mmol) and PhC≡CPh (0.48 g, 2.7 mmol) were combined in 5 ml of THF in a 100 ml Pyrex reactor equipped with a stir bar. The reactor was charged with 1 atm (4 mmol) of H_2 and photolyzed at ca. 40°C for 45 min with stirring. The solvent was removed under vacuum after irradiation and the solid residue completely taken up in C_6D_6. ^1H NMR confirmed that 85% conversion of PhC≡CPh to stilbene (95% *cis*, 5% *trans*) had occurred. The major organometallic species present was $CpV(CO)_2(C_4Ph_4)$ [10] with traces of $CpV(CO)_2$(PhC≡CPh).

Solvent was again removed following a repetition of the above experiment. THF was reintroduced along with 0.5 g PhC≡CPh. The reactor was given a fresh charge of H_2 (1 atm) and photolysis was continued for another 40 min. ^1H NMR analysis revealed that no further conversion of PhC≡CPh to stilbene had occurred.

It was possible to distinguish the *cis*- and *trans*-stilbenes from each other and from diphenyl acetylene by ^1H NMR at 220 MHz employing C_6D_6 solvent. It should be emphasized that C_6D_6 alone permits differentiating mixtures of *cis*- and *trans*-stilbenes and diphenyl acetylene by ^1H NMR. The ^1H NMR of these three compounds follows. PhC≡CPh has two multiplets at δ 7.43 and 6.90 ppm of relative intensity 2/3. *trans*-Stilbene has two multiplets at δ 7.27 and 7.11 and a singlet at 6.94 ppm *cis*-Stilbene has two multiplets at δ 7.16 and 6.95 and a singlet at 6.42 ppm. In mixtures of the three compounds diphenylacetylene is identified by its most downfield multiplet at δ 7.43 ppm, *trans*-stilbene is identified by its most downfield multiplet at 7.27 ppm and *cis*-stilbene has a characteristic resonance, a singlet at δ 6.42 ppm.

$Cp_2V_2(CO)_5$ (0.05 g, 0.13 mmol) and PhC≡CPh (2.39 g, 13 mmol), or a 1/100 mole ratio of I to alkyne, were combined in the 100 ml reactor in 13 ml of THF. The reactor was charged with H_2 at −196°C (16 mmol), warmed to 25°C and photolyzed for 45 min. A 4% conversion to stilbene (*cis* only) was noted.

A THF solution containing a 10/1 PhC≡CPh to $Cp_2V_2(CO)_5$ mole ratio as above was divided into two portions. One part was charged with H_2 (4 mmol, 1 atm) and photolyzed for 5 min. Immediately following photolysis and further reaction was quenched by pumping away both H_2 and solvent. The other portion was likewise charged with H_2 and photolyzed for 5 min. The solution was then stirred an additional 40 min in the dark. This latter solution revealed, upon NMR analysis, a 5% conversion to stilbene had occurred whereas the former solution revealed only 1% conversion to stilbene.

(b) Control experiment. PhC≡CPh (0.48 g, 2.7 mmol) was dissolved in 5 ml of THF in the 100 ml Pyrex reactor as above and charged with 1 atm of H_2 (4 mmol). Irradiation with stirring for 45 min produced no stilbene.

(c) Thermal hydrogenation. A 5/1 mole ratio of PhC≡CPh and I were combined

in C_6D_6 and charged with H_2 as above. The solution was stirred for 18 h at 25°C in the dark. ^{1}H NMR revealed 33% conversion to stilbene had occurred (*cis/trans* 3/1). Also present were small amounts of $CpV(CO)_2(PhC{\equiv}CPh)$ and $CpV(CO)(PhC{\equiv}CPh)_2$.

(d) Test: $CpV(CO)_2(PhC{\equiv}CPh)$ for catalytic activity. $Cp_2V_2(CO)_5$ (0.04 g, 0.1 mmol) and $PhC{\equiv}CPh$ (0.04 g, 0.2 mmol) were combined in the 100 ml reactor in 5 ml of THF and photolyzed for 30 min. The green solution contained (> 95%) $CpV(CO)_2(PhC{\equiv}CPh)$ (IR analysis). To this solution was added $PhC{\equiv}CPh$ (0.35 g, 2 mmol). The reactor was charged with 1 atm H_2 and photolyzed for 40 min. ^{1}H NMR revealed only a trace of *cis*-stilbene with mostly unreacted $PhC{\equiv}CPh$.

(e) Test: $CpV(CO)_2(C_4Ph_4)$ for catalytic activity. $Cp_2V_2(CO)_5$ (0.04 g, 0.1 mmol) was combined with (> 3 fold excess) $PhC{\equiv}CPh$ in hexanes and the solution was photolyzed for 30 min. The hexanes were removed under vacuum. $CpV(CO)_2(C_4Ph_4)$ produced (confirmed by IR and NMR) was dissolved in THF. $PhC{\equiv}CPh$ was added to establish an alkyne to vanadium ratio of ca. 10/1 (^{1}H NMR analysis). The THF solution was added to the 100 ml reactor. The reactor was charged with 1 atm of H_2 and photolyzed for 45 min with stirring. ^{1}H NMR revealed only a trace of *cis*-stilbene to be present and the unreacted $PhC{\equiv}CPh$.

Results and discussion

Reaction with unsaturated hydrocarbons

$Cp_2V_2(CO)_5$ is unreactive under both thermal (25°C) and photochemical conditions towards ethylene, allene, 1,4-cyclohexadiene, 1-hexene and 2,5-norbornadiene. The thermal reaction with 1,3-cyclohexadiene yields $CpV(CO)_2$(1,3-cyclohexadiene); $Cp_2V_2(CO)_5$ is thus selective for conjugated chelating (cf. allene) dienes, and is ineffective at isomerization of the non-conjugated cyclohexadiene to the 1,3-isomer.

Photochemistry of I with alkynes

There is enhanced reactivity toward alkynes, however. In what follows, photochemical rather than thermal reactions are discussed. This is primarily due to the slow rate of the thermal reactions. For example, in the reaction between $Cp_2V_2(CO)_5$

TABLE 1

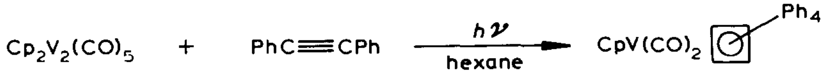
PRODUCTS OF THE PHOTOCHEMICAL REACTIONS OF $Cp_2V_2(CO)_5$ (I) WITH ALKYNES, RC_2R' AT 25°C

R,R'	Solvent	
	Hexane	THF
H,H	$CpV(CO)_2(HC{\equiv}CH)$	$CpV(CO)_2(HC{\equiv}CH)$
Me,Me	$CpV(CO)_2(MeC{\equiv}CMe)$ (IX)	Not studied
Ph,Me [a]	$CpV(CO)_2(MeC{\equiv}CPh)$ (VIII) and $CpV(CO)_2(C_4Me_2Ph_2)$ (VII)	$CpV(CO)_2(MeC{\equiv}CPh)$ (VIII)
Ph,Ph	$CpV(CO)_2(C_2Ph_4)$ (IV)	$CpV(CO)_2(PhC{\equiv}CPh)$ (V) and $CpV(CO)(PhC{\equiv}CPh)_2$ (VI)

[a] Same results in toluene.

and diphenyl acetylene discussed below, after 22 h only 20% conversion to products occurs vs. nearly 100% conversion after 15 min following irradiation.

Table 1 gives the products from the photochemical reaction between $Cp_2V_2(CO)_5$ and $RC{\equiv}CR'$ in either the coordinating solvent THF or the non-coordinating solvent hexane. The most important new result is the production of the cyclobutadiene product $CpV(CO)_2(Ph_4C_4)$ (eq. 3).



(3)

(IV)

The significance of this result is immediately evident upon comparing to the result of irradiating $CpV(CO)_4$ in the presence of $PhC{\equiv}CPh$ in hexane (eq. 4).

$$\begin{aligned} &CpV(CO)_4 + PhC{\equiv}CPh \xrightarrow[\substack{\text{hexane}\\ \text{(a)}}]{h\nu} \underset{\text{(V)}}{CpV(CO)_2(PhC{\equiv}CPh)} \\ &CpV(CO)_2(PhC{\equiv}CPh) + PhC{\equiv}CPh \underset{\substack{CO\\ \text{(b)}}}{\overset{h\nu}{\rightleftharpoons}} \underset{\text{(VI)}}{CpV(CO)(PhC{\equiv}CPh)_2} \end{aligned} \tag{4}$$

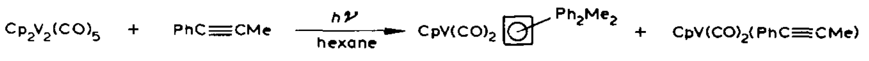
Note that compound IV is not produced from this reaction. Indeed, a recent review [11] has cited $CpV(CO)_2(RCCR)$ as exemplifying the inertness of early transition metal alkyne complexes to cyclization. That eq. 4(b) is reversible upon addition of CO is convincing evidence that compound VI is not a cyclobutadiene compound (like IV) but a bis-diphenyl acetylene complex. Comparison of eqs. 3 and 4 provides the strongest evidence that eq. 3 involves alkyne cyclization on a dimeric intermediate. If reaction 3 proceeded through any monomeric fragments, then products V or VI would be observed from eq. 3.

There is a marked solvent dependence in the photochemical reaction between I and $PhC{\equiv}CPh$. Thus unlike eq. 3, photolysis in THF (eq. 5) gives only the monomeric products V and VI. Compound VI was shown independently to be the

$$Cp_2V_2(CO)_5 + PhC{\equiv}CPh \xrightarrow[\text{THF}]{h\nu} \underset{\text{(V)}}{CpV(CO)_2(PhC{\equiv}CPh)} + \underset{\text{(VI)}}{CpV(CO)(PhC{\equiv}CPh)_2} \tag{5}$$

product of a simple photosubstitution of CO in V by $PhC{\equiv}CPh$. THF acts to inhibit alkyne cyclization, a result which suggests that THF accelerates bond scission in I, to produce monomeric fragments, which then go on to add alkyne.

In addition to a solvent effect, there is an effect due to the basicity and size of the alkyne. Thus substituting one electron donating methyl group for a relatively electron withdrawing phenyl group, $PhC{\equiv}CMe$, results in both cyclized (VII) product and simple adducts (VIII) (eq. 6) in hexane.



(6)

(VII) (VIII)

Smaller and more basic butyne, $MeC{\equiv}CMe$ leads to only the adduct product (IX) in eq. 7.

$$\mathrm{Cp_2V_2(CO)_5 + MeC{\equiv}CMe \xrightarrow[\text{hexane}]{h\nu} \underset{(IX)}{CpV(CO)_2(MeC{\equiv}CMe)}} \qquad (7)$$

Acetylene itself, HC≡CH, behaves like MeC≡CMe.

Since previous work [1] had revealed $Cp_2V_2(CO)_4$ as the primary photoproduct from irradiation of I, and since this work (eq. 4) shows monomers do not promote alkyne cyclization, we sought evidence for a V_2/alkyne intermediate. Low temperature (−42°C) photolysis of $Cp_2V_2(CO)_5$ in THF in the presence of PhC≡CMe (chosen to enhance product solubility) yields a compound, X, with four carbonyl stretching absorptions, the lowest of which is at 1842 cm^{-1}. Upon warming to 25°C, these absorptions decay, concomitant with the growth of bands due to $CpV(CO)_2(C_4Me_2Ph_2)$ (VII) (eq. 8) [12]. In a complementary experiment, equimolar $Cp_2V_2(CO)_5$ and PhC≡CMe were irradiated at −42°C in toluene-d_8 (a solvent

$$\mathrm{Cp_2V_2(CO)_5 + PhC{\equiv}CMe \xrightarrow[\text{THF}]{h\nu,\,-42^\circ C} X \xrightarrow{25^\circ C} VII} \qquad (8)$$

which, at 25°C, gives a product distribution identical to that in hexane, see eq. 6). The ^1H NMR at −30°C (the tube was not permitted to warm up above this temperature) revealed $CpV(CO)_2(PhC{\equiv}CMe)$ and the new species X. Species X exhibited resonances at δ 4.63 (C_5H_5) and 2.78 ppm (CH_3) in an intensity ratio of 10/3. Warming the NMR tube caused conversion of X into $CpV(CO)_2(C_4Me_2Ph_2)$. Taken together, these spectral results are consistent with $Cp_2V_2(CO)_4(PhC{\equiv}CMe)$ as the identity of X; a plausible structure is shown in Fig. 2, the low ν(CO) value suggesting the presence of a carbonyl semibridge. Only one C_5H_5 resonance is observed in the analogous species $Cp_2Mo_2(CO)_4(EtC{\equiv}CEt)$ [13].

This study reveals that the reactions of I with alkynes, as with phosphines [1], are subject to a subtle influence of steric and electronic ("basicity") effects. Steric effects are aggravated by the congestion inherent in a dimer aggregate (Fig. 3). The influence of a coordinating solvent is consistent with THF competing with alkynes for coordination at vanadium. $Cp_2V_2(CO)_4(THF)$ subsequently undergoes V/V bond scission upon attack by alkyne (Scheme 1). It follows from results reported here that alkyne coupling to give cyclized products IV or VII must occur on the dimer X. Compound XI, analogous to a dichromium species with coupled alkynes [14] is a plausible intermediate. Coupling of alkynes on Mo_2 centers has also been reported [15].

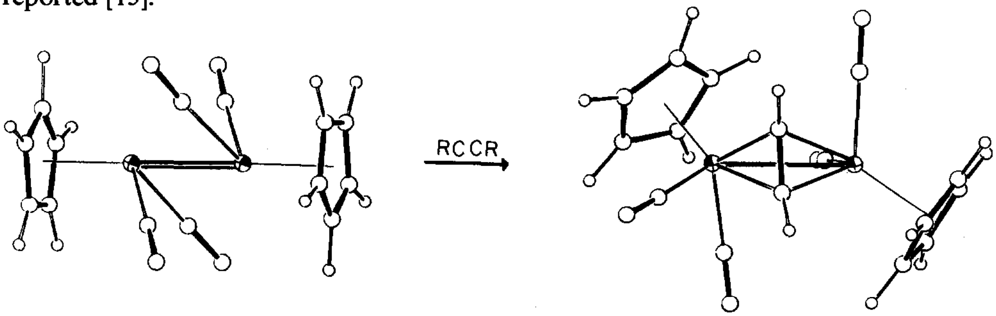
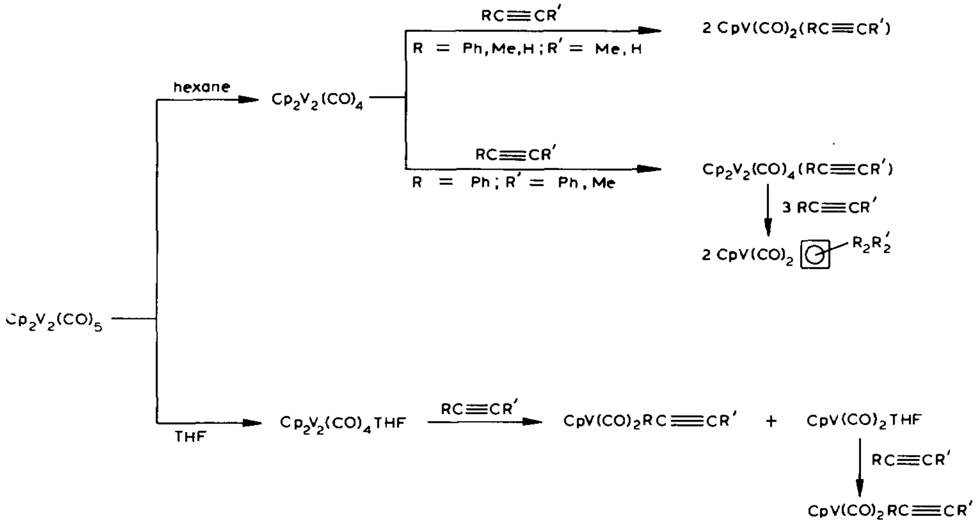
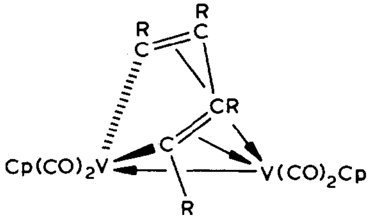


Fig. 2. Proposed structures of $Cp_2V_2(CO)_4$ (drawn from the coordinates of $Cp_2Mo_2(CO)_4$, R.J. Klingler, W.M. Butler and M.D. Curtis, J. Am. Chem. Soc., 100 (1978) 5034) and $Cp_2V_2(CO)_4(\mu\text{-}RC{\equiv}CR)$ (after $Cp_2Mo_2(CO)_4HC{\equiv}CH$ [13]).



SCHEME 1



(XI)

Catalytic hydrogenation of PhC≡CPh

Diphenyl acetylene was hydrogenated to *cis*-stilbene (stereoselectively) with one atmosphere of H_2 in THF using $Cp_2V_2(CO)_5$ as the catalyst (actually catalyst precursor). While slow catalytic reaction can be shown to occur thermally, irradiation for 45 min, employing a 10/1 substrate to catalyst ratio, yields 85% conversion of PhC≡CPh to stilbene with a *cis/trans* ratio of 95/5. Any thermal catalysis of this hydrogenation is negligible. Irradiation was shown to be essential for continued hydrogenation; short preliminary photolysis (5 min) produces a solution where hydrogenation occurs only at the slow thermal rate. The soluble material present following a hydrogenation experiment was inactive as a catalyst when a new charge of diphenyl acetylene and H_2 were added. These results demonstrate that the reaction is not photocatalytic i.e., catalytic in photons, since only the slow thermal reaction occurs in the dark following a short irradiation. The reaction is best described as being photoassisted [16] and catalytic in vanadium.

The monomeric compounds $CpV(CO)_2(PhC\equiv CPh)$ and $CpV(CO)_2(C_4Ph_4)$ were inactive as catalysts, under similar conditions, for hydrogenation of PhC≡CPh. Thus catalysis via a dimer (e.g. $Cp_2V_2(CO)_4(RC\equiv CR)$) is indicated [17]. This is further supported by the fact that, in an attempted repetition of the photoassisted hydrogenation with a substrate/catalyst (I) ratio of 100/1, only low (4%) conversion to stilbene occurred. At such high alkyne concentration (relative to H_2), X is siphoned off in monomer-producing reactions not involved in hydrogenation i.e., production of IV, V and VI. Note that the turnover number for the 100/1 reaction is only a factor of two less than the "efficient" catalysis where PhC≡CPh to I ratio was 10/1.

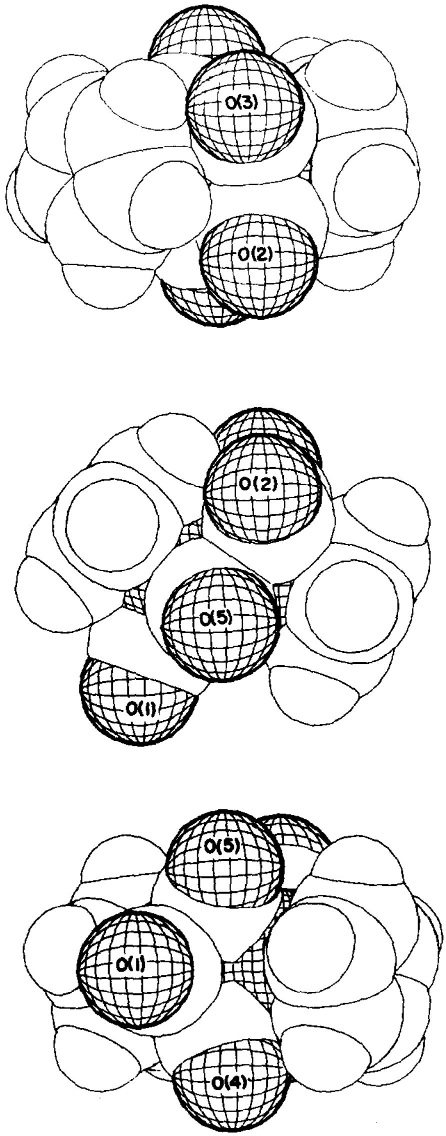


Fig. 3. Space Filling Models [3] (3 views) of $Cp_2V_2(CO)_5$. In each case V(1) is at the left. Oxygens of carbonyls are labeled. End-to-end Cp/OC contacts result in a nearly complete shielding of the vanadium atoms from attack by reagent molecules.

The selectivity toward alkene over alkane [18] products is consistent with the observed lack of reactivity of $Cp_2V_2(CO)_5$ with olefins. Since monomeric fragments

$CpV(CO)_n$ ($n \le 3$) readily bind olefins, this observation further supports the premise that the active catalyst is a dimer.

In summary, it has been shown that $Cp_2V_2(CO)_5$ can react with alkynes in a selective manner i.e., via two different pathways. Partitioning of pathways depends both on the basicity and/or size of the alkyne and donor ability of the solvent. Simple adduct formation occurs by alkyne attack at the V=V double bond in photochemically produced $Cp_2V_2(CO)_4$, by an associative mechanism. More basic alkynes are more efficient at bond scission than less basic alkynes. This mechanism can be slowed at low temperature so that the dimeric intermediate $Cp_2V_2(CO)_4(R\text{-}C{\equiv}CR)$ can form. This intermediate reacts below 25°C with further alkyne to yield products which contain the cyclized ligand, cyclobutadiene. This represents a marked increase in reactivity as compared to the reaction of $Cp_2Mo_2(CO)_4(RCCR)$ with alkyne, which may be a consequence of the V=V double bond in X (Fig. 2). Non-coordinating solvents favor the formation of X for less basic and more bulky alkynes;.coordinating solvents tend to result in the dimer bond scission pathway being followed. The intermediate X is believed to be the active catalyst in the hydrogenation of $PhC{\equiv}CPh$.

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References

1 L.N. Lewis and K.G. Caulton, Inorg. Chem., 19 (1980) 1840.

2 F.A. Cotton, B.A. Frenz and L. Kruczynski, J. Am. Chem. Soc., 95 (1973) 951; J. Organometal. Chem., 160 (1978) 93.

3 J.C. Huffman, L.N. Lewis and K.G. Caulton, Inorg. Chem., 19 (1980) 2755.

4 R. Colton, C.J. Commons and B.F. Hoskins, Chem. Comm., (1975) 363.

5 E.O. Fischer, H.P. Kogler and P. Kuzel, Chem. Ber., 93 (1960) 3006.

6 A.N. Nesmeyanov, K.N. Anisimov, N.E. Kolobova and A.A. Pasynskii, Adad. Nauk. S.S.S.R. Proc. Chem. Sec., 182 (1968) 789.

7 Note that the reported [8] ^1H NMR chemical shift for the alkyne hydrogen does not agree with our value. We believe our value is consistent with the reported [9] correlation of chemical shift to number of electrons donated by the alkyne. $HC{\equiv}CH$ in $CpV(CO)_2(HC{\equiv}CH)$ is a 4 electron donor and is expected to have a downfield chemical shift.

8 R. Tsumara and N. Hagihara, Bull. Chem. Soc. Japan, 38 (1965) 1901.

9 J.W. McDonald, J.L. Corbin and W.E. Newton, J. Am. Chem. Soc., 97 (1975) 1970.

10 The conditions of this experiment somewhat resemble those for which the synthesis of $CpV(CO)_2(C_4Ph_4)$ were reported [6]. In this synthesis $PhC{\equiv}CPh$ and $CpV(CO)_2(PhC{\equiv}CPh)$ were reacted in a melt to yield $CpV(CO)_2(C_4Ph_4)$.

11 S. Otsuka and A. Nakamura, Adv. Organomet. Chem., 14 (1976) 245.

12 This indicates that temperature can influence the occurrence of alkyne cyclization (compare eq. 5), vis a vis dimer scission to VIII.

13 In the related molybdenum systems, $Cp_2Mo_2(CO)_4(RC{\equiv}CR)$, the IR spectrum contains three or four carbonyl stretches, including a low stretch at about 1850 cm^{-1}. R.J. Klingler, W. Butler and M.D. Curtis, J. Am. Chem. Soc., 97 (1975) 3535; W.I. Bailey, M.H. Chisholm, F.A. Cotton and L.A. Rankel, J. Am. Chem. Soc., 100 (1978) 5764.

14 S.A.R. Knox, R.F.D. Stansfield, F.G.A. Stone, M.J. Winter and P. Woodward, Chem. Comm., (1978) 221; S.A.R. Knox, R.F.D. Stansfield, F.G.A. Stone, M.J. Winter and P. Woodward, J. Chem. Soc. Dalton Trans., (1982) 173.

15 A.M. Boileau, A.G. Orpen, R.F.D. Stansfield and P. Woodward, J. Chem. Soc., Dalton Trans., (1982) 187. J.A. Beck, S.A.R. Knox, R.F.D. Stansfield, F.G.A. Stone, M.J. Winter and P. Woodward, J. Chem. Soc., Dalton Trans., (1982) 195.

16 R.A. Faltynek, Inorg. Chem., 20 (1981) 1357.

17 A similar thermal catalysis of alkynes to alkenes has been shown for $Cp_2Mo_2(CO)_4(\mu\text{-}RC{\equiv}CR)$ systems, but only above 100°C. S. Slater and E.L. Muetterties, Inorg. Chem., 19 (1980) 3337.

18 E.L. Muetterties, Inorg. Chim. Acta, 50 (1981) 1.