

## Synthesis, Structure, and Reactivity of ( $\eta^5$ -Indenyl)tetracarbonylvandium(I)

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The compound ( $\eta^5$ -C<sub>9</sub>H<sub>7</sub>)V(CO)<sub>4</sub> was prepared for the first time and its structure determined by X-ray crystallography. The structure closely resembles that of ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)V(CO)<sub>4</sub>, with the V(CO)<sub>4</sub> moiety forming a square pyramid, and a planar indenyl group coordinating to the vanadium through the five-membered ring. The compound crystallizes in the space group *Pna*2<sub>1</sub> with *a* = 22.722 (6) Å, *b* = 6.814 (1) Å, *c* = 7.449 (2) Å, and *Z* = 4. The reaction of ( $\eta^5$ -C<sub>9</sub>H<sub>7</sub>)V(CO)<sub>4</sub> with P(*n*-Bu)<sub>3</sub> and with P(OEt)<sub>3</sub> to form ( $\eta^5$ -C<sub>9</sub>H<sub>7</sub>)V(CO)<sub>3</sub>PR<sub>3</sub> takes place by a dissociative (S<sub>N</sub>1) process with kinetic parameters of *k*(100 °C) = 3.7 × 10<sup>-4</sup> s<sup>-1</sup>, Δ*H*<sup>‡</sup> = 31.9 ± 0.3 kcal/mol, and Δ*S*<sup>‡</sup> = 10.5 ± 0.9 cal/(mol K). Again the indenyl effect on dissociative reactions is shown to be much smaller than on associative reactions when compared with the effect for corresponding cyclopentadienyl compounds.

### Introduction

Recent kinetic studies<sup>2</sup> in our group have established a remarkable rate enhancement (10<sup>8</sup> times) in the associative substitution reactions of ( $\eta^5$ -C<sub>9</sub>H<sub>7</sub>)Rh(CO)<sub>2</sub> when compared with the much slower substitution in ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Rh(CO)<sub>2</sub>. This "indenyl ligand effect"<sup>3-5</sup> for reactions occurring by associative pathways was first observed by Mawby and Hart-Davis, and is believed to arise from the enhanced ability of the indenyl ligand to accept an electron pair from the metal, thus causing the ring to assume an  $\eta^3$ -coordination and creating a vacant site for nucleophilic attack at the metal.

The indenyl ligand has been shown to enhance ligand dissociative (S<sub>N</sub>1) processes as well, although the effects are not as dramatic as for reactions proceeding by associative mechanisms. Replacement of the cyclopentadienyl ring in ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Mo(CO)<sub>3</sub>I with indenyl increases the rate of the dissociative pathway by 6600 times and allows an associative pathway for CO substitution not observed for ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Mo(CO)<sub>3</sub>I.<sup>4</sup> A comparison of ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>I and ( $\eta^5$ -C<sub>9</sub>H<sub>7</sub>)Fe(CO)<sub>2</sub>I shows rate enhancements of 575 times, with both reactions proceeding by dissociative pathways.<sup>6</sup>

Our interest in the indenyl effect led us to determine if similar rate enhancements could be observed in ( $\eta^5$ -C<sub>9</sub>H<sub>7</sub>)V(CO)<sub>4</sub>, whose synthesis and structure we now report. Kinetic studies on the analogous ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)V(CO)<sub>4</sub> indicate CO substitution occurs slowly by a dissociative pathway.<sup>7,8</sup>

### Experimental Section

**General Procedures.** All manipulations were carried out under an atmosphere of purified nitrogen. Decalin, hexane, tetrahydrofuran, and toluene were distilled under nitrogen from Na. Chlorobenzene was washed with H<sub>2</sub>SO<sub>4</sub> and distilled. Deionized water used in the synthesis was degassed by three freeze-pump-thaw cycles and saturated with nitrogen. The compound [Na(diglyme)<sub>2</sub>][V(CO)<sub>6</sub>] was purchased from Strem Chemicals. Both P(*n*-Bu)<sub>3</sub> and P(OEt)<sub>3</sub> were obtained from Aldrich Chemicals and distilled over Na. Indene (Aldrich) was distilled prior to use. The compound (C<sub>9</sub>H<sub>7</sub>)HgCl was synthesized by a literature procedure.<sup>9</sup>

**( $\eta^5$ -Indenyl)tetracarbonylvandium(I) (( $\eta^5$ -C<sub>9</sub>H<sub>7</sub>)V(CO)<sub>4</sub>).** The synthesis used is based on the method for the preparation of ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)V(CO)<sub>4</sub> from (C<sub>5</sub>H<sub>5</sub>)HgCl and [V(CO)<sub>6</sub>]<sup>-</sup>.<sup>10</sup> A solution of 2.26 g of

Table I. Crystal Data for ( $\eta^5$ -C<sub>9</sub>H<sub>7</sub>)V(CO)<sub>4</sub>

formula	C <sub>13</sub> H <sub>7</sub> O <sub>4</sub> V
fw	278.1
cryst size, mm	0.42 × 0.06 × 0.04
space group	<i>Pna</i> 2 <sub>1</sub>
cryst system	orthorhombic
<i>a</i> , Å	22.722 (6)
<i>b</i> , Å	6.814 (1)
<i>c</i> , Å	7.449 (2)
<i>V</i> , Å <sup>3</sup>	1153.3 (5)
<i>Z</i>	4
<i>d</i> <sub>calcd</sub> , g/cm <sup>3</sup>	1.602
<i>T</i> , K	130
λ(Mo Kα), Å	0.710 73
μ(Mo Kα), cm <sup>-1</sup>	13.3
2θ range, deg	2 < 2θ < 55
scan speed range, deg/min	1.03-2.35
scan mode	ω/2θ
scan width, deg	ω = 0.7 + 0.35 tan θ
reflens measd	± <i>h</i> , ± <i>k</i> , ± <i>l</i>
no. of reflens colld	1424
no. of unique reflens with <i>I</i> > 2σ( <i>I</i> )	749
no. of params	138
transmission factors	0.943-0.966
<i>R</i> , <i>R</i> <sub>w</sub> <sup>a</sup>	0.0715, 0.0826
weighting scheme	w = 1/σ <sup>2</sup> ( <i>F</i> <sub>o</sub> )

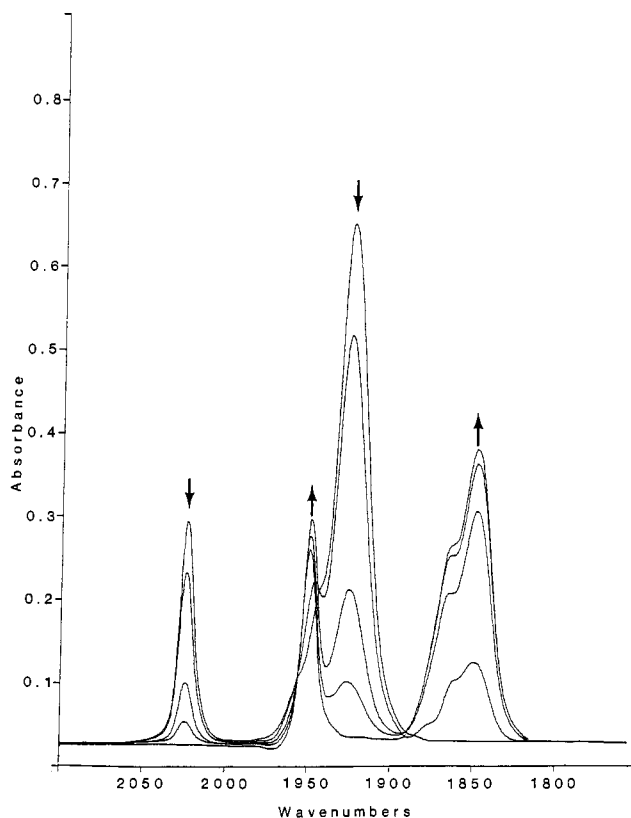
$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|; R_w = \sum w(|F_o| - |F_c|)^2 / \sum |F_o|^2.$$

(C<sub>9</sub>H<sub>7</sub>)HgCl in 15 mL of tetrahydrofuran was added dropwise to a solution of 2.25 g of [Na(C<sub>6</sub>H<sub>14</sub>O<sub>3</sub>)<sub>2</sub>][V(CO)<sub>6</sub>] in 25 mL of tetrahydrofuran at room temperature. Gas evolution was visible for 10 min, and the reaction mixture was stirred overnight under N<sub>2</sub>. The solvent was removed under vacuum, and the remaining mixture was washed with three 10-mL portions of water that were cannulated off of the solid containing primarily ( $\eta^5$ -C<sub>9</sub>H<sub>7</sub>)V(CO)<sub>4</sub> and Hg. Toluene (30 mL) was added, and the ( $\eta^5$ -C<sub>9</sub>H<sub>7</sub>)V(CO)<sub>4</sub> solution was cannulated off of the Hg residue through a short column of alumina to remove small amounts of impurities. The orange solution was washed through the column with additional toluene, which was then removed under vacuum, leaving an orange-red oily solid. The solid was sublimed onto a water-cooled probe by using an oil bath or infrared heat lamp (100 °C; 0.05 mm), yielding 0.5 g of ( $\eta^5$ -C<sub>9</sub>H<sub>7</sub>)V(CO)<sub>4</sub> (40%) as an orange-red crystalline solid. IR: (Decalin) 2022 (m), 1953 (sh), 1932 (s) cm<sup>-1</sup>; (Nujol mull) 2022 (m), 1955 (sh), 1930 (s) cm<sup>-1</sup>. Mass spectrum: parent ion at *m/e* 278 with successive loss of 4 CO's.

**Phosphine Derivatives.** The substituted compounds ( $\eta^5$ -C<sub>9</sub>H<sub>7</sub>)V(CO)<sub>3</sub>P(*n*-Bu)<sub>3</sub> and ( $\eta^5$ -C<sub>9</sub>H<sub>7</sub>)V(CO)<sub>3</sub>P(OEt)<sub>3</sub> were identified by their IR carbonyl stretching frequencies, which occurred at frequencies analogous to those of the phosphine-substituted ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)V(CO)<sub>4</sub> derivatives.<sup>8</sup> IR ( $\eta^5$ -C<sub>9</sub>H<sub>7</sub>)V(CO)<sub>3</sub>P(*n*-Bu)<sub>3</sub> (Decalin): 1951 (s), 1875 (m), 1851 (s) cm<sup>-1</sup>. IR ( $\eta^5$ -C<sub>9</sub>H<sub>7</sub>)V(CO)<sub>3</sub>P(OEt)<sub>3</sub> (Decalin): 1968 (s), 1895 (m), 1865 (s) cm<sup>-1</sup>.

**Instrumentation.** A Perkin-Elmer 283 or Nicolet FTIR spectrophotometer was used to record IR spectra with either 0.2-mm KBr or 0.1-mm CaF<sub>2</sub> solution cells. Compounds were stored in a Vacuum Atmospheres glovebox, and solutions were prepared by ampule transfer. The mass spectrum was obtained by Dr. D. Hung of the Northwestern University Analytical Services Laboratory on a HP5985A spectrometer using 70-eV ionization.

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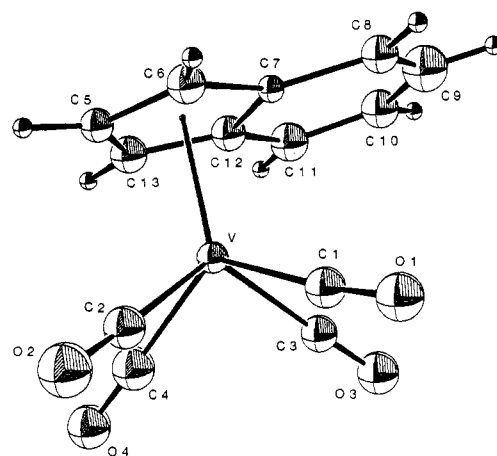


**Figure 1.** Infrared spectral changes for the reaction between  $(\eta^5\text{-C}_9\text{H}_7)\text{V}(\text{CO})_4$  and  $\text{P}(n\text{-Bu})_3$  in chlorobenzene at  $100^\circ\text{C}$ .

**Kinetic Measurements.** Reaction rates were determined by monitoring the decrease in the low-frequency IR carbonyl stretching absorption of  $(\eta^5\text{-C}_9\text{H}_7)\text{V}(\text{CO})_4$  at  $1932\text{ cm}^{-1}$  (Figure 1). Solutions were ca.  $1.8 \times 10^{-3}\text{ M}$  in metal complex, with at least a 50-fold excess of phosphine. Reaction tubes were immersed in a thermostated bath and stirred in the absence of light. Samples were withdrawn periodically by syringe, and spectra were recorded immediately in IR cells previously purged with  $\text{N}_2$ . Plots of  $-\ln(A - A_\infty)$  vs. time were linear (correlation coefficients  $>0.995$ ) for at least 3 half-lives, and  $k_{\text{obsd}}$  was determined from the slope of this line by least-squares methods.

**X-ray Crystal Structure of  $(\eta^5\text{-C}_9\text{H}_7)\text{V}(\text{CO})_4$ .** An orange-red needle crystal of  $(\eta^5\text{-C}_9\text{H}_7)\text{V}(\text{CO})_4$  obtained by heat-lamp sublimation was mounted on a fiber and placed in a  $\text{N}_2$  cold stream ( $130\text{ K}$ ) on an Enraf-Nonius CAD4 diffractometer. Crystal structure data are collected in Table I. All crystallographic computations were performed on a VAX11/730 computer, using the SDP crystallographic software package.<sup>11</sup> Data were corrected for Lorentz and polarization effects. A numerical absorption correction was applied based on a Gaussian integration formula.<sup>12</sup> Atomic scattering and anomalous dispersion factors for the non-hydrogen atoms were taken from Cromer and Waber.<sup>13</sup>

Lattice parameters were determined by using 20 well-centered reflections ( $23.38 < 2\theta < 36.58$ ) measured with graphite-monochromated  $\text{Mo K}\alpha$  radiation. The data set was collected by using the parameters shown in Table I. The intensities of six standard reflections were measured every 100 min and showed insignificant variations in intensity. The initial coordinates of the vanadium atom were determined from an interpretation of the Patterson function; the remaining non-hydrogen positions were located with DIRDIF-strengthened Fourier techniques.<sup>14</sup> Hydrogen atoms of the indenyl ligand were fixed at idealized positions and were not refined. The systematic extinctions were characteristic of the two space groups  $Pnma$  and  $Pna2_1$ . Solution of the structure in the centro symmetric space group  $Pnma$  proved impossible. A solution containing one molecule in these asymmetric unit was obtained in the



**Figure 2.** ORTEP drawing of  $(\eta^5\text{-C}_9\text{H}_7)\text{V}(\text{CO})_4$  showing the atomic numbering scheme.

**Table II.** Bond Lengths ( $\text{\AA}$ ) and Angles (deg) for  $(\eta^5\text{-C}_9\text{H}_7)\text{V}(\text{CO})_4$

Bond Lengths			
V-C <sub>1</sub>	1.94 (1)	C <sub>4</sub> -O <sub>4</sub>	1.13 (2)
V-C <sub>2</sub>	1.92 (1)	C <sub>5</sub> -C <sub>6</sub>	1.41 (2)
V-C <sub>3</sub>	1.95 (2)	C <sub>6</sub> -C <sub>7</sub>	1.51 (2)
V-C <sub>4</sub>	1.94 (2)	C <sub>7</sub> -C <sub>12</sub>	1.38 (2)
V-C <sub>5</sub>	2.23 (2)	C <sub>12</sub> -C <sub>13</sub>	1.38 (2)
V-C <sub>6</sub>	2.26 (1)	C <sub>13</sub> -C <sub>5</sub>	1.46 (2)
V-C <sub>7</sub>	2.33 (1)	C <sub>7</sub> -C <sub>8</sub>	1.47 (2)
V-C <sub>12</sub>	2.31 (1)	C <sub>8</sub> -C <sub>9</sub>	1.27 (2)
V-C <sub>13</sub>	2.29 (1)	C <sub>9</sub> -C <sub>10</sub>	1.46 (2)
C <sub>1</sub> -O <sub>1</sub>	1.15 (1)	C <sub>10</sub> -C <sub>11</sub>	1.37 (2)
C <sub>2</sub> -O <sub>2</sub>	1.18 (1)	C <sub>11</sub> -C <sub>12</sub>	1.47 (2)
C <sub>3</sub> -O <sub>3</sub>	1.14 (2)		
Bond Angles			
C <sub>1</sub> -V-C <sub>2</sub>	78.4 (5)	C <sub>12</sub> -C <sub>13</sub> -C <sub>5</sub>	107 (1)
C <sub>1</sub> -V-C <sub>3</sub>	74.6 (8)	C <sub>13</sub> -C <sub>5</sub> -C <sub>6</sub>	110 (1)
C <sub>2</sub> -V-C <sub>4</sub>	72.1 (7)	C <sub>12</sub> -C <sub>7</sub> -C <sub>8</sub>	122 (1)
C <sub>3</sub> -V-C <sub>4</sub>	79.2 (7)	C <sub>7</sub> -C <sub>8</sub> -C <sub>9</sub>	117 (2)
V-C <sub>1</sub> -O <sub>1</sub>	174 (2)	C <sub>8</sub> -C <sub>9</sub> -C <sub>10</sub>	125 (2)
V-C <sub>2</sub> -O <sub>2</sub>	176 (2)	C <sub>9</sub> -C <sub>10</sub> -C <sub>11</sub>	119 (1)
V-C <sub>3</sub> -O <sub>3</sub>	178 (1)	C <sub>10</sub> -C <sub>11</sub> -C <sub>12</sub>	119 (1)
V-C <sub>4</sub> -O <sub>4</sub>	176 (2)	C <sub>11</sub> -C <sub>12</sub> -C <sub>7</sub>	118 (1)
C <sub>5</sub> -C <sub>6</sub> -C <sub>7</sub>	104 (1)	C <sub>6</sub> -C <sub>7</sub> -C <sub>8</sub>	130 (1)
C <sub>6</sub> -C <sub>7</sub> -C <sub>12</sub>	108 (1)	C <sub>11</sub> -C <sub>12</sub> -C <sub>13</sub>	131 (1)
C <sub>7</sub> -C <sub>12</sub> -C <sub>13</sub>	111 (1)		

acentric space group  $Pna2_1$  after much effort.

Determination of the polar direction for the chosen crystal was made after full refinement of the original model and a model obtained by reversing the signs of all the coordinates. The correct model was chosen by examining the Friedel pairs of reflections showing the largest differences between  $F_o(hkl)$  and  $F_o(\bar{h}\bar{k}\bar{l})$  for both models.<sup>15</sup>

In spite of all experimental efforts to obtain the best data set possible (slow, low-temperature data collection; numerical absorption correction) the small size of the crystal and consequent paucity of observed data prevented the refinement of all non-hydrogen atoms anisotropically. The final cycle of full-matrix least-squares refinement involved 138 variables and 749 unique reflections with  $I > 2\sigma(I)$ . The function minimized was  $\sum w(|F_o| - |F_c|)^2$ , where  $w = 1/\sigma^2(|F_o|)$ . The final residuals are  $R(F_o) = 0.0715$  and  $R_w(F_o) = 0.0826$ , and an error in an observation of unit weight is 1.54. The final difference map showed a maximum peak height of  $0.664\text{ e}/\text{\AA}^3$ .

## Results and Discussion

**X-ray Diffraction Studies.** An ORTEP drawing of the molecule is shown in Figure 2, and bond distances and angles and positional parameters are given in Tables II and III.

The indenyl ligand is approximately planar and lies above the square pyramid defined by the vanadium and carbonyl groups. Mean plane calculations on the nine carbons in the indenyl ring show that the carbon atoms deviate less than  $0.05\text{ \AA}$  from the

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**Table III.** Positional Parameters and Their Estimated Standard Deviations

atom	x	y	z
V	0.15603 (9)	0.0534 (3)	0.779 (2)
O <sub>1</sub>	0.2168 (4)	0.459 (1)	0.797 (2)
O <sub>2</sub>	0.2876 (4)	-0.065 (2)	0.755 (2)
O <sub>3</sub>	0.0933 (5)	0.296 (2)	0.484 (2)
O <sub>4</sub>	0.1641 (4)	-0.231 (2)	0.461 (2)
C <sub>1</sub>	0.1952 (5)	0.307 (2)	0.781 (2)
C <sub>2</sub> <sup>a</sup>	0.2372 (6)	-0.022 (2)	0.758 (3)
C <sub>3</sub> <sup>a</sup>	0.1176 (7)	0.207 (2)	0.591 (2)
C <sub>4</sub>	0.1629 (7)	-0.124 (3)	0.576 (3)
C <sub>5</sub> <sup>a</sup>	0.1475 (6)	-0.157 (2)	1.007 (2)
C <sub>6</sub>	0.1510 (7)	0.033 (2)	1.080 (2)
C <sub>7</sub>	0.0949 (6)	0.131 (2)	1.018 (2)
C <sub>8</sub>	0.0725 (6)	0.330 (2)	1.056 (2)
C <sub>9</sub>	0.0233 (7)	0.377 (2)	0.986 (3)
C <sub>10</sub> <sup>a</sup>	-0.0131 (7)	0.247 (3)	0.877 (2)
C <sub>11</sub>	0.0081 (7)	0.065 (3)	0.834 (2)
C <sub>12</sub>	0.0650 (6)	0.001 (2)	0.909 (2)
C <sub>13</sub> <sup>a</sup>	0.0943 (6)	-0.176 (2)	0.899 (2)
H <sub>C5</sub>	0.1754	-0.2636	1.0305
H <sub>C6</sub>	0.1831	0.0398	1.1517
H <sub>C8</sub>	0.0936	0.4240	1.1266
H <sub>C9</sub>	0.0069	0.5070	1.0118
H <sub>C10</sub>	-0.0516	0.2875	0.8349
H <sub>C11</sub>	-0.0134	-0.0278	0.7566
H <sub>C13</sub>	0.0798	-0.2914	0.8320

<sup>a</sup> Refined isotropically.

best-fit least-squares plane. The distance from the vanadium to this plane is 1.935 (1) Å, and the vanadium was found to lie less than 0.1 Å off center of the η<sup>5</sup> ring. All bond distances and angles between vanadium and the carbonyls or η<sup>5</sup> ring are not significantly different from those determined for (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)V(CO)<sub>4</sub>,<sup>16</sup> whose structure determination was hampered by disorder of the cyclopentadienyl ring. No disorder was encountered in the structure determination of (η<sup>5</sup>-C<sub>9</sub>H<sub>7</sub>)V(CO)<sub>4</sub>.

A view of the molecule from the plane defined by the indenyl ligand shows that one carbonyl group (C<sub>4</sub>-O<sub>4</sub>) passes almost directly beneath a carbon atom in the η<sup>5</sup>-ring, and another (C<sub>3</sub>-O<sub>3</sub>) lies beneath the six-membered ring. The metal-carbonyl bond distances and angles between carbonyls do not differ significantly from those observed in (η<sup>5</sup>-C<sub>9</sub>H<sub>7</sub>)Mo(CO)<sub>3</sub>I.<sup>17</sup> Although the vanadium-η<sup>5</sup>-ring-carbon distances do not differ significantly from their mean, two of these distances are slightly longer and indicate that the plane of the indenyl ligand is slightly tilted away from the plane defined by the carbonyl groups. Similar slight lengthening of two of the metal-η<sup>5</sup>-carbon bonds was observed in (η<sup>5</sup>-C<sub>9</sub>H<sub>7</sub>)<sub>2</sub>Ru<sup>18</sup> and (η<sup>5</sup>-C<sub>9</sub>H<sub>7</sub>)Mo(CO)<sub>3</sub>I.<sup>17</sup>

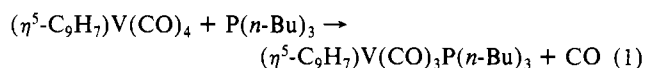
All crystallographic evidence indicates that the indenyl ligand is bound through the η<sup>5</sup> ring to the vanadium in a manner very similar to that in (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)V(CO)<sub>4</sub>. The similarities between (η<sup>5</sup>-C<sub>9</sub>H<sub>7</sub>)V(CO)<sub>4</sub> and (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)V(CO)<sub>4</sub> are also illustrated in their IR spectra in the CO region. In (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)V(CO)<sub>4</sub>, bands assigned to the a<sub>1</sub> and e modes occur at 2030 and 1933 cm<sup>-1</sup>, respectively, and in (η<sup>5</sup>-C<sub>9</sub>H<sub>7</sub>)V(CO)<sub>4</sub>, bands occur at 2022 cm<sup>-1</sup> (a<sub>1</sub>) and 1955 (sh) and 1930 cm<sup>-1</sup> (e). The splitting in the e mode is caused by the reduction from C<sub>4v</sub> symmetry of the V(CO)<sub>4</sub> fragment.<sup>19</sup>

**Table IV.** Rate Constants for the Substitution Reaction (Eq 1) of (η<sup>5</sup>-C<sub>9</sub>H<sub>7</sub>)V(CO)<sub>4</sub><sup>a</sup>

ligand	[L], M	T, °C	10 <sup>5</sup> k <sub>obsd</sub> , s <sup>-1</sup>
P( <i>n</i> -Bu) <sub>3</sub>	0.18	70.8	0.790
P( <i>n</i> -Bu) <sub>3</sub>	0.18	80.6	2.91
P( <i>n</i> -Bu) <sub>3</sub>	0.18	90.5	10.6
P( <i>n</i> -Bu) <sub>3</sub>	0.18	96.4	21.1
P( <i>n</i> -Bu) <sub>3</sub>	0.34	100.6	36.3
P( <i>n</i> -Bu) <sub>3</sub>	0.088	100.6	37.8
P( <i>n</i> -Bu) <sub>3</sub>	0.15	100.4	43.6 <sup>b</sup>
P(OEt) <sub>3</sub>	0.19	100.6	37.5

<sup>a</sup> ΔH<sup>‡</sup> = 31.9 ± 0.3 kcal/mol, ΔS<sup>‡</sup> = 10.5 ± 0.9 cal/(mol K) for V(η<sup>5</sup>-C<sub>9</sub>H<sub>7</sub>)(CO)<sub>4</sub> + P(*n*-Bu)<sub>3</sub> → V(η<sup>5</sup>-C<sub>9</sub>H<sub>7</sub>)(CO)<sub>3</sub>(P(*n*-Bu)<sub>3</sub>) + CO in Decalin. <sup>b</sup> In chlorobenzene; all other runs in Decalin.

**Kinetic Studies.** The compound (η<sup>5</sup>-C<sub>9</sub>H<sub>7</sub>)V(CO)<sub>4</sub> reacts with phosphines in decalin according to the reaction shown by eq 1.



The reaction is first order in metal complex and is independent of phosphine. The activation parameters (ΔH<sup>‡</sup> = 31.9 ± 0.3 kcal/mol, ΔS<sup>‡</sup> = 10.5 ± 0.9 cal/(mol K)) support a CO dissociative (S<sub>N</sub>1) mechanism. Comparison with (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)V(CO)<sub>4</sub><sup>20</sup> (ΔH<sup>‡</sup> = 35.3 kcal/mol, ΔS<sup>‡</sup> = 14.6 cal/(mol K)) indicates the rate increases by 13 times at 100 °C for the replacement of the cyclopentadienyl ring with indenyl. This rate enhancement is relatively small compared to the rate increases of 10<sup>2</sup>–10<sup>3</sup> times observed by other workers for similar dissociative reactions of (η<sup>5</sup>-C<sub>9</sub>H<sub>7</sub>)Fe(CO)<sub>2</sub>I<sup>6</sup> and (η<sup>5</sup>-C<sub>9</sub>H<sub>7</sub>)Mo(CO)<sub>3</sub>I<sup>4</sup> when compared to those of their cyclopentadienyl analogues, and the effect is quite small compared to the increases of up to 10<sup>8</sup> times observed for systems reacting by an associative pathway.<sup>2</sup>

It has been suggested that the rate increase in the dissociative reactions may imply stabilization of the transition state by interaction of the six-membered aromatic ring of the indenyl ligand with the metal center, thus compensating for the loss of M–CO bonding.<sup>4,6</sup> This suggestion is supported by the fact that hydrogenation of the six-membered ring results in a decreased rate of CO substitution in (η<sup>5</sup>-C<sub>9</sub>H<sub>11</sub>)Fe(CO)<sub>2</sub>I compared to that in (η<sup>5</sup>-C<sub>9</sub>H<sub>7</sub>)Fe(CO)<sub>2</sub>I.<sup>6</sup>

It is not clear why the rate enhancement is small for replacing the cyclopentadienyl ring in (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)V(CO)<sub>4</sub> with the indenyl ligand, compared to the larger increases in other systems that also react by dissociative mechanisms. Both (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)- and (η<sup>5</sup>-C<sub>9</sub>H<sub>7</sub>)V(CO)<sub>4</sub> react more slowly than the (η<sup>5</sup>-ring)Mo(CO)<sub>3</sub>I and (η<sup>5</sup>-ring)Fe(CO)<sub>2</sub>I systems, and the greater vanadium-carbonyl bond strength is reflected in the lower CO stretching frequencies and larger enthalpies of activation for the vanadium systems.

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**Supplementary Material Available:** Tables of bond distances and angles, positional and thermal parameters, least-squares planes, and observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.

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