Inorg. Chem. **1987**, *26*, 1871-1875 **1871**

Contribution from the Chemistry Department, Columbia University, New York, New York 10027,
and Istituto di Strutturistica Chimica, Centro di Studio per la Strutturistica Diffrattometrica del CNR,
Università di Parma, 43100 Parma, Italy

Bis(indenyl)vanadium(II): Its Oxidation and Carbonylation of Its Cation

Jeffrey R. Bocarsly,[†] Carlo Floriani,*[†‡] Angiola Chiesi-Villa,[§] and Carlo Guastini[§]

Received July 30, 1986

The sandwich complex Ind_2V (Ind = η^5-C_9H_7) was synthesized, and the formation of its one-electron-ionization product and the carbonylation of its cation were studied. Ind_2V itself appears to have a structure analogous to that of other members of the bis(cyclopentadienyl)vanadium family. The oxidation of Ind_2V with iodine gave the corresponding vanadium(III) derivative, $Ind_2V(I)$, which is paramagnetic by two electrons ($\mu_{eff} = 2.67\ \mu_B$ at 294 K). $Ind_2V(I)$ may be carbonylated in the presence of a suitable anion to form the dicarbonyl cation $Ind_2V(CO)_2^+$. The structures of the monoiodo product and the dicarbonyl cation were determined by X-ray analysis. The indenyl ring in both cases exhibits slippage away from the "pure" η^5-configuration toward a η^3-arrangement, a phenomenon that has been observed in a variety of indenyl-containing complexes. Crystallographic details for $(\eta^5\text{-}C_9H_7)_2V(I)$: space group $P2_1/n$ (monoclinic), $a = 8.186$ (1) Å, $b = 12.494$ (2) Å, $c = 15.025$ (2) Å; $\beta = 95.48$ (1)°, $V = 1529.7$ (4) Å^3, $Z = 4$, $D_{calcd} = 1.772$ g cm^{-3}. The final R factor for 1940 observed reflections was 0.037. Crystallographic details for $[(\eta^5\text{-}C_9H_7)_2V(CO)_2^+][BPh_4^-]$: space group $P2_1/n$ (monoclinic), $a = 11.278$ (1) Å, $b = 16.146$ (2) Å, $c = 21.381$ (5) Å, $\beta = 102.46$ (1)°, $V = 3802$ (1) Å^3, $Z = 4$, $D_{calcd} = 1.273$ g cm^{-3}. The final R factor for 2100 observed reflections was 0.060.

Studies of substitution reactions on cyclopentadienyl containing inorganic complexes have led to the suggestion that, in cases where the mechanism is associative, the reaction proceeds through a $\eta^5 \rightarrow \eta^3$ shifted intermediate.[1a-d] The observation of such an unstable intermediate[1e] via matrix techniques in addition to the structural characterization of a η^3-C_5H_5-containing transition-metal complex[1f] has given futher support to the possibility of "ring slippage" as an integral part of the substitution mechanism. In addition, it has recently been shown that some η^5-bonded indenyl ($C_9H_7^-$ = Ind) ligands undergo a $\eta^5 \rightarrow \eta^3$ shift when complexes containing these cyclopentadienyl analogues react with the appropriate ligands.[2]

On another front, recent cyclopentadienyl chemistry has led to the observation that the more sterically hindered members of the cyclopentadienyl ligand family may exhibit a reactivity that is profoundly affected by the cyclopentadienyl substituents.[3] Since the primary mode of reaction of $(cp^*)_2V$ (cp^* = substituted cyclopentadienyl) involves the bending of the two cp^* ligands to form a cavity in the equatorial plane of the molecule, steric barriers to such bending may affect the reaction, especially in the case of a small ion like vanadium. The steric constraints placed upon bending by the cp^* ligands may force upon vanadium-bonded substituents (up to three may be accommodated) a proximity that would not otherwise occur.

Both of these factors, the coordinative flexibility of the indenyl ligand and the potential for sterically imposed proximity between substrates, suggested to us that the indenyl ligand may provide advantages beyond the realm of modeling mechanisms of associative substitution and within the realm of synthesis. This led us to attempt the synthesis of Ind_2V, its one-electron oxidation, and the formation of its carbonylated cation. Herein we report those syntheses and the structural characterization of the title compounds.

Experimental Section

All reactions were carried out under an atmosphere of purified nitrogen. Solvents were dried and purified by standard techniques. ^1H NMR spectra were recorded on a Bruker WM 300 NMR spectrometer. Infrared spectra were recorded on a Perkin-Elmer 983 spectrometer. Mass spectral analyses were performed on a Ribermag R10-10 mass spectrometer at 70 eV. Magnetic measurements were performed on solid samples by using a Faraday balance.

Synthesis of Bis(indenyl)vanadium(II) (1). A 10.2-mL aliquot of distilled indene (87.5 mmol) was added to 200 mL of distilled THF. A 135-mL aliquot of CH_3Li in ether solution was added over a 15-min period with vigorous stirring, at the end of which gas evolution had stopped. $[V_2Cl_3(THF)_6]_2[Zn_2Cl_6]$ (17.35 g, 10.7 mmol) formed by refluxing VCl_3 in THF and then reducing it with zinc dust[4] was then added at room temperature. The solution immediately turned a deep green brown. The solution was evaporated to dryness, and the residue was sublimed in an oil bath up to 180 °C for 2.5 h to give deep green crystals of $(Ind)_2V$ (5.56 g, 46%). Anal. Calcd for $C_{18}H_{14}V$: C, 76.87; H, 5.02; V, 18.11. Found: C, 75.96; H, 5.14; V, 16.19.

Synthesis of Bis(indenyl)iodovanadium(III) (2). A 0.61-g sample of solid I_2 (2.40 mmol) was degassed and dissolved in distilled toluene. A 1.30-g sample of $(Ind)_2V$ (4.63 mmol) was added. A deep red-brown solution formed. The solution was heated just up to the boiling point of toluene to dissolve all solid material. The solution was then filtered to remove a small amount of solid and again stored at room temperature for 24 h, during which the crystalline produce formed. The product was filtered from solution; the mother liquor was stored for a few hours at −20 °C and then for several hours in dry ice. Additional crystalline product was filtered from the solution while cold. A total of 1.15 g of product was collected, representing a 61% yield. Anal. Calcd for $C_{18}H_{14}IV$: C, 52.97; H, 3.46; I, 31.09; V, 12.48. Found: C, 53.00; H, 3.21; I, 30.50; V, 11.75. The magnetic moment determined on a solid sample of **2** is 2.67 μ_B at 294 K.

Synthesis of $[Ind_2V(CO)_2][BPh_4]$ (3). $[(Ind)_2V(I)]$ was synthesized as above by using 0.73 g of I_2 (2.89 mmol) and 1.62 g of $(Ind)_2V$ (5.77 mmol) in THF. The solution was swirled under a CO atmosphere. No noticeable CO uptake occurred. A 1.99-g sample of $NaBPh_4$ (5.82 mmol) was degassed and added to the solution, which was then again swirled under CO. The solution was stored overnight at room temperature under a CO atmosphere. A total of 0.261 g of product (7%) was collected after 24 h at room temperature (vide infra). Anal. Calcd for $C_{48}H_{42}BO_3V$: C, 79.13; H, 5.81. Found: C, 78.85; H, 5.70.

X-ray Crystallography. The crystals selected for study were mounted in glass capillaries and sealed under nitrogen. Data were collected at room temperature on a single-crystal four-circle diffractometer. Crystal data and details of the parameters associated with data collection are given in Table I. The reduced cells quoted were obtained with use of TRACER.[5] For intensities and background the "three-point" technique

---

[†] Columbia University.

[‡] Present address: ICMA, Université de Lausanne, CH-1005 Lausanne, Switzerland.

[§] Università di Parma.

(1) (a) Rerek, M. E.; Basolo, F. *Organometallics* **1982**, *2*, 372–376. (b) Hart-Davis, A. J.; Mawby, R. J. *J. Chem. Soc. A* **1969**, 2403–2407. (c) Rest, A. J.; Whitwell, I.; Graham, W. A. G.; Hoyano, J. K.; McMaster, A. D. *J. Chem. Soc., Chem. Commun.* **1984**, 624–626. (d) Yang, G. K.; Bergman, R. G. *Organometallics* **1985**, *4*, 129–138. (e) Crichton, O.; Rest, A. J.; Taylor, D. J. *J. Chem. Soc., Dalton Trans* **1980**, 167–173. (f) Huttner, G.; Brintzinger, H. H.; Bell, L. G.; Friedrich, P.; Benjenke, V.; Neubauer, D. *J. Organomet. Chem.* **1978**, *145*, 329–333.

(2) (a) Merola, J. S.; Kacmarcek, R. T.; Van Engen, D. *J. Am. Chem. Soc.* **1986**, *108*, 329–331. (b) Kowaleski, R. M.; Rheingold, A. L.; Trogler, W. C.; Basolo, F. *J. Am. Chem. Soc.* **1986**, *108*, 2460–2462.

(3) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1984**, *23*, 1739–1747.

(4) Cotton, F. A.; Duraj, S. A.; Extine, M. W.; Lewis, G. E.; Roth, W. J.; Schmulbach, C. D.; Schwotzer, W. *J. Chem. Soc., Chem. Commun.* **1983**, 1377–1378.

(5) Lawton, S. L.; Jacobson, R. A. "TRACER", a cell reduction program; Ames Laboratory, Iowa State University of Science and Technology: Ames, IA, 1965.

0020-1669/87/1326-1871$01.50/0

Table I. Experimental Data for the X-ray Diffraction Studies on Crystalline Complexes **2** and **3**

	complex **2**	complex **3**
formula	$C_{18}H_{14}IV$	$C_{44}H_{34}BO_2V \cdot C_4H_8O$
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
cell dimens at 295 K[a]		
a, Å	8.186 (1)	11.278 (1)
b, Å	12.494 (2)	16.146 (2)
c, Å	15.025 (2)	21.381 (5)
α, deg	90	90
β, deg	95.48 (1)	102.46 (1)
γ, deg	90	90
V, Å^3	1529.7 (4)	3802 (1)
Z	4	4
D_{calcd}, g cm^{-3}	1.772	1.273
mol wt	408.2	728.6
max cryst dimens, mm	0.32 × 0.45 × 0.50	0.15 × 0.25 × 0.45
linear abs coeff, cm^{-1}	26.1	2.92
diffractometer	Philips PW 1100	Philips PW 1100
diffraction geometry	equatorial	equatorial
scan type	$\omega/2\theta$	$\omega/2\theta$
scan speed deg/s	0.100	0.075
scan width, deg	1.20	1.20
radiation	*b*	*b*
2θ range, deg	6–52	6–47
reflcns measd	$\pm h,\pm k,l$	$\pm h,\pm k,l$
tot. no. of measd data	4737	8700
tot. no. of unique data	3061	5756
criterion for observn	$I > 3\sigma(I)$	$I > 3\sigma(I)$
no. of measd obsd data	3121	3552
no. of unique obsd data (NO)	1940	2100
agreement between equiv reflcns	0.034	0.050
no. of variables	181	430
overdetermination ratio	10.7	4.9
max shift/error on last cycle	0.1	0.1
$R = \sum\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\sum\lvert F_o\rvert$	0.037	0.060

[a] Unit cell parameters were obtained by least-squares analysis of the setting angles of 20 carefully centered reflections chosen from diverse regions of reciprocal space. [b] Graphite monochromated Mo Kα (λ = 0.7107 Å).

was used. The structure amplitudes were obtained after the usual Lorentz and polarization corrections,[6] and the absolute scale was established by the Wilson method.[7a] The crystal quality was tested by ψ scans showing that crystal absorption effects could be neglected for compound **3** but not for compound **2**. The data from compound **2** were corrected by a semiempirical method[7b] with maximum and minimum absorption coefficients of 1.166 and 1.003, respectively. The function minimized during the least-squares refinement for both complexes was $\sum_w|\Delta F|^2$. Unit weights were applied since these gave acceptable agreement analysis. Anomalous scattering corrections were included in all structure factor calculations.[8b] Scattering factors for neutral atoms were taken from ref 8a for V, O, C, B, and I, and from ref 9 for H. Among the low-angle reflections no correction for secondary extinction was deemed necessary.

The structures were solved by the heavy-atom method starting from a three-dimensional Patterson map. Refinement was performed first isotropically and then anisotropically for non-H atoms, by full-matrix least squares. Solution and refinement were based on the observed reflections [$E > 3\sigma(I)$]. Refinement was continued for both structures until no parameter shifted by more than 0.1 times its standard deviation. All the hydrogen atoms in both complexes except those associated with THF in compound **3** were located in difference maps and introduced in re-

Table II. Fractional Atomic Coordinates (×10^4) for Complex **2**

atom	x/a	y/b	z/c
I	3853 (1)	1785 (0)	632 (0)
V	2666 (1)	2599 (1)	−1038 (1)
C1	4088 (10)	2036 (7)	−2176 (5)
C2	2432 (11)	2164 (7)	−2512 (5)
C3	1490 (9)	1362 (6)	−2100 (4)
C4	−216 (10)	1105 (7)	−2219 (5)
C5	−743 (10)	278 (7)	−1746 (6)
C6	323 (12)	−309 (6)	−1137 (6)
C7	1947 (10)	−78 (5)	−1008 (5)
C8	2570 (9)	773 (5)	−1496 (4)
C9	4187 (9)	1221 (6)	−1526 (5)
C10	3161 (15)	4403 (7)	−1087 (10)
C11	1758 (15)	4172 (7)	−1674 (7)
C12	497 (10)	3833 (6)	−1165 (5)
C13	−1212 (12)	3528 (7)	−1382 (6)
C14	−2093 (11)	3237 (8)	−695 (8)
C15	−1430 (14)	3240 (8)	163 (8)
C16	125 (13)	3502 (6)	410 (5)
C17	1129 (9)	3814 (5)	−249 (5)
C18	2827 (11)	4147 (6)	−222 (7)

Table III. Fractional Atomic Coordinates (×10^4) for Complex **3**

atom	x/a	y/b	z/c
V	3914 (1)	2753 (1)	1799 (1)
O1	3449 (7)	1366 (5)	2720 (4)
C19	3618 (9)	1875 (6)	2375 (5)
O2	1705 (6)	1979 (4)	847 (4)
C20	2518 (9)	2252 (6)	1180 (5)
C1	3515 (11)	3437 (7)	2648 (5)
C2	4275 (9)	3948 (6)	2390 (5)
C3	3608 (7)	4232 (5)	1773 (5)
C4	3899 (9)	4804 (6)	1338 (6)
C5	3051 (12)	4976 (6)	795 (6)
C6	1928 (10)	4570 (7)	647 (5)
C7	1606 (8)	3998 (6)	1053 (5)
C8	2462 (8)	3831 (5)	1636 (4)
C9	2405 (8)	3304 (5)	2178 (5)
C10	5728 (8)	2150 (7)	2046 (5)
C11	5930 (8)	2950 (6)	1848 (5)
C12	5420 (7)	3014 (5)	1180 (5)
C13	5432 (8)	3654 (6)	721 (5)
C14	4894 (11)	3510 (8)	103 (5)
C15	4312 (10)	2745 (9)	−104 (5)
C16	4265 (9)	2111 (7)	307 (5)
C17	4821 (7)	2245 (6)	969 (4)
C18	5002 (8)	1721 (5)	1524 (5)
B	4019 (9)	898 (6)	−2061 (5)
C21	3591 (5)	287 (3)	−2725 (2)
C22	4309 (5)	291 (3)	−3181 (2)
C23	4006 (5)	−214 (3)	−3721 (2)
C24	2985 (5)	−724 (3)	−3806 (2)
C25	2266 (5)	−729 (3)	−3350 (2)
C26	2569 (5)	−224 (3)	−2809 (2)
C31	2902 (4)	962 (4)	−1660 (3)
C32	2491 (4)	247 (4)	−1408 (3)
C33	1573 (4)	299 (4)	−1063 (3)
C34	1067 (4)	1066 (4)	−971 (3)
C35	1477 (4)	1781 (4)	−1224 (3)
C36	2395 (4)	1729 (4)	−1568 (3)
C41	4430 (5)	1857 (3)	−2264 (3)
C42	5255 (5)	2316 (3)	−1815 (3)
C43	5594 (5)	3109 (3)	−1969 (3)
C44	5108 (5)	3442 (3)	−2573 (3)
C45	4284 (5)	2983 (3)	−3022 (3)
C46	3944 (5)	2191 (3)	−2868 (3)
C51	5284 (4)	509 (3)	−1558 (3)
C52	6278 (4)	270 (3)	−1806 (3)
C53	7347 (4)	6 (3)	−1395 (3)
C54	7422 (4)	−18 (3)	−735 (3)
C55	6427 (4)	221 (3)	−486 (3)
C56	5358 (4)	485 (3)	−897 (3)
O1S	4011 (11)	1499 (7)	4997 (6)
C1S	4084 (20)	1992 (13)	4494 (9)
C2S	3422 (23)	2718 (16)	4410 (12)
C3S	2840 (17)	2623 (10)	4985 (11)
C4S	3403 (18)	1959 (12)	5353 (8)

---

(6) Data reduction, structure solution, and refinement were carried out on a GOULD SEL 32/77 computer, using the SHELX-76 system of crystallographic computer programs: Sheldrick, G. "Shelx-76"; University of Cambridge: Cambridge, England, 1976.

(7) (a) Wilson, A. J. C. *Nature (London)* **1942**, *150*, 151–152. (b) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr. Sect. A: Cryst. Phys., Diffr. Theor. Gen. Crystallogr.* **1968**, *A24*, 351–359.

(8) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol IV: (a) p 99; (b) p 149.

(9) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175–3187.

Table IV. Bond Distances (Å) and Angles (deg) for **2**[a]

V–I	2.794 (1)		
V–C1	2.270 (8)	C4–C5	1.348 (12)
V–C2	2.271 (8)	C5–C6	1.409 (12)
V–C3	2.360 (7)	C6–C7	1.356 (13)
V–C8	2.382 (6)	C7–C8	1.414 (10)
V–C9	2.286 (8)	C8–C9	1.442 (10)
V–C10	2.293 (9)	C10–C11	1.410 (17)
V–C11	2.279 (9)	C10–C18	1.391 (18)
V–C12	2.346 (8)	C11–C12	1.407 (15)
V–C17	2.362 (7)	C12–C13	1.457 (13)
V–C18	2.287 (9)	C12–C17	1.424 (10)
C1–C2	1.410 (12)	C13–C14	1.364 (15)
C1–C9	1.408 (11)	C14–C15	1.350 (16)
C2–C3	1.440 (11)	C15–C16	1.332 (15)
C3–C4	1.428 (11)	C16–C17	1.401 (12)
C3–C8	1.412 (9)	C17–C18	1.448 (12)
V–Ind(1)	1.973 (8)	V–Ind(2)	1.976 (9)
C17–V–C18	36.3 (3)	C8–V–C9	35.9 (3)
C12–V–C17	35.2 (3)	C3–V–C8	34.7 (2)
C11–V–C12	35.4 (4)	C2–V–C3	36.2 (3)
C10–V–C18	35.4 (4)	C1–V–C9	36.0 (3)
C10–V–C11	35.9 (4)	C1–V–C2	36.2 (3)
C2–C1–C9	108.7 (7)	C11–C10–C18	108.5 (10)
C1–C2–C3	107.7 (7)	C10–C11–C12	108.5 (10)
C2–C3–C8	108.1 (7)	C11–C12–C17	108.2 (8)
C2–C3–C4	131.3 (7)	C11–C12–C13	134.1 (8)
C4–C3–C8	120.6 (7)	C13–C12–C17	117.7 (7)
C3–C4–C5	117.7 (7)	C12–C13–C14	117.8 (9)
C4–C5–C6	122.1 (8)	C13–C14–C15	121.9 (9)
C5–C6–C7	121.3 (7)	C14–C15–C16	123.6 (10)
C6–C7–C8	118.9 (7)	C15–C16–C17	118.7 (9)
C3–C8–C7	119.4 (7)	C12–C17–C16	120.3 (7)
C7–C8–C9	133.3 (6)	C16–C17–C18	133.4 (8)
C3–C8–C9	107.3 (6)	C12–C17–C18	106.4 (7)
C1–C9–C8	108.1 (7)	C10–C18–C17	108.3 (9)
Ind(1)–V–Ind(2)	142.2 (3)	I–V–Ind(2)	108.7 (2)
I–V–Ind(1)	109.1 (3)		

[a] Ind(1) and Ind(2) refer to the centroids of the rings containing C1, C2, C3, C8, and C9 and C10, C11, C12, C17, and C18, respectively.

finement as fixed contributors with isotropic *U*'s fixed at 0.10 Å^2. During refinement, the phenyl rings of the BPh_4^- anion were treated as regular hexagons. The molecule of crystallization in **3** (THF) exhibits high thermal motion, which is typical. The intensities of the maximum residual electron density peaks were 0.5 Å^{-3} for **2** and 0.3 Å^{-3} for **3**. Final atomic co-ordinates for structures **2** and **3** are found in Tables II and III, respectively.

Results and Discussion

The synthesis of bis(indenyl)vanadium(II) (**1**) was pursued by a route based on that used to synthesize bis(pentamethylcyclopentadienyl)vanadium(II)[10a] and is similar to one recently used by Basolo, Trogler, et al., to synthesize the same molecule.[2b,10b] The synthesis is straightforward: reaction of lithium indenide with $[V_2Cl_3THF_6]_2[Zn_2Cl_6]$ in THF at room temperature affords $(Ind)_2V$ in moderate yields (ca. 45%). A significant amount of organic byproducts, including the apparent coupling product of the carbocyclic ligand,[11] also form. Product **1** is thermally stable and can be sublimed up to 200 °C. $(Ind)_2V$ may be recrystallized from toluene or THF as deep green air-sensitive crystals.

$(Ind)_2V$ exhibits a magnetic moment of 3.97 μ_B at 294.3 K, which is consistent with three unpaired spins. This value agrees with those obtained for analogous sandwich-type structures.[3,12] Its mass spectrum exhibits peaks at the parent mass as well as at masses for the expected major fragments.[13] There is no reason to expect that the structure of **1** deviates from the sandwich arrangement of the parent compound.[14a]

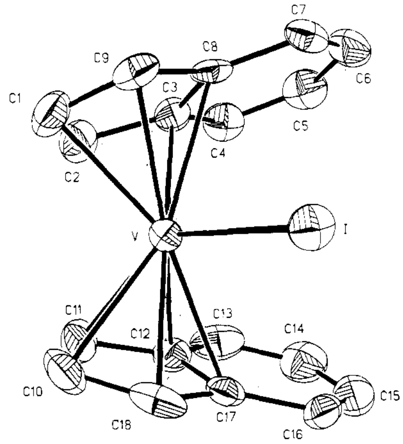


Figure 1. ORTEP view of complex **2** (30% probability ellipsoids).

Table V. Bond Distances (Å) and Angles (deg) for **3**[a]

V–C1	2.252 (12)	C1–C2	1.387 (16)
V–C2	2.294 (10)	C1–C9	1.442 (14)
V–C3	2.412 (8)	C2–C3	1.445 (13)
V–C8	2.364 (9)	C3–C4	1.399 (15)
V–C9	2.223 (10)	C3–C8	1.419 (12)
V–C10	2.224 (9)	C4–C5	1.364 (16)
V–C11	2.276 (9)	C5–C6	1.400 (17)
V–C12	2.405 (10)	C6–C7	1.369 (16)
V–C17	2.377 (9)	C7–C8	1.428 (12)
V–C18	2.222 (9)	C8–C9	1.450 (13)
V–C19	1.953 (11)	C10–C11	1.393 (15)
V–C20	1.996 (9)	C10–C18	1.415 (13)
O1–C19	1.147 (14)	C11–C12	1.424 (14)
O2–C20	1.123 (11)	C12–C13	1.427 (14)
		C12–C17	1.439 (12)
V–Ind(1)	1.964 (11)	C13–C14	1.350 (14)
V–Ind(2)	1.960 (10)	C14–C15	1.424 (18)
		C15–C16	1.358 (17)
		C16–C17	1.435 (13)
		C17–C18	1.436 (13)
C17–V–C18	36.2 (3)	C8–V–C9	36.7 (3)
C12–V–C17	35.0 (3)	C3–V–C8	34.5 (3)
C11–V–C12	35.3 (3)	C2–V–C3	35.7 (3)
C10–V–C18	37.1 (4)	C1–V–C9	37.6 (4)
C10–V–C11	36.1 (4)	C1–V–C2	35.5 (4)
C2–C1–C9	109.2 (10)	C11–C10–C18	108.6 (9)
C1–C2–C3	107.9 (9)	C10–C11–C12	108.4 (9)
C2–C3–C8	108.4 (8)	C11–C12–C17	108.2 (8)
C2–C3–C4	131.7 (9)	C11–C12–C13	132.9 (9)
C4–C3–C8	119.9 (9)	C13–C12–C17	118.9 (9)
C3–C4–C5	118.6 (10)	C12–C13–C14	118.7 (10)
C4–C5–C6	122.1 (10)	C13–C14–C15	122.2 (10)
C5–C6–C7	121.6 (10)	C14–C15–C16	122.2 (10)
C6–C7–C8	117.3 (9)	C15–C16–C17	117.1 (10)
C3–C8–C7	120.6 (8)	C12–C17–C16	121.0 (9)
C7–C8–C9	132.1 (8)	C16–C17–C18	132.9 (9)
C3–C8–C9	107.4 (8)	C12–C17–C18	106.0 (8)
C1–C9–C8	106.7 (8)	C10–C18–C17	108.6 (8)
C19–V–Ind(1)	104.0 (4)	Ind(1)–V–Ind(2)	138.5 (4)
C19–V–Ind(2)	105.4 (4)	C19–V–C20	84.6 (4)
C20–V–Ind(1)	105.2 (4)	V–C19–O1	179.1 (9)
C20–V–Ind(2)	106.2 (4)	V–C20–O2	177.4 (9)

[a] Ind(1) and Ind(2) refer to the centroids of the rings containing C1, C2, C3, C8, and C9 and C10, C11, C12, C17, and C18, respectively.

An X-ray study on a single crystal of **1** was attempted. The crystal data suggest that the molecules of **1** pack into the crystal lattice in two separate orientations, which differ from one another by a 180° rotation about the centroid–V–centroid axis. The

---

(10) (a) Robbins, J. L.; Edelstein, N.; Spencer, B.; Smart, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 1882-1893. (b) Basolo, F. private communication.

(11) As observed by mass spectrometry: M^+ 230.

(12) Fisher, E. O.; Hafner, W. *Z. Naturforsch.* **1954**, *96*, 503.

(13) M^+ 281; (M^+ − 115) 166; (M^+ − 115 − 51) 115.

(14) (a) Antipin, M. Yu.; Lobkovskii, E. B.; Semenenko, K. N.; Soloveichik, G. L.; Struchkov, Yu. T. *J. Struct. Chem.* (*Engl. Trans.*) **1979**, *20*, 810-811. (b) Crystallographic data: unit cell parameters *a* = 6.258 (2) Å, *b* = 9.584 (3) Å, *c* = 11.287 (4) Å and β = 92.47 (2)°; space group $P2_1/n$; *Z* = 4 for the formula C_9H_7V.

Table VI. Slip Parameters[a] for $(Ind)_2V(I)$ and Similar Complexes

complex	$\Delta = \lvert S \rvert$, Å	σ, deg	ψ, deg	$\overline{\Delta(M-C)}$, Å	ref
$(Ind)_2V(I)$					
ring 1	0.122	9.9	3.5	0.10	*b*
ring 2	0.079	5.0	2.3	0.07	*b*
$(Ind)_2V(CO)_2^+$					
ring 1	0.192	27.9	5.6	0.13	*b*
ring 2	0.197	17.7	5.8	0.15	*b*
$(Ind)_2V(CO)_2$					
η^5-Ind	0.157	0.0	4.6	0.13	2b
η^3-Ind	0.798	1.5	20.9	0.56	2b
$(Ind)_2Ti(CH_3)_2$	0.189	16.0	5.1	0.14	15a

[a] Parameters are defined in ref 15a,b. Calculations were performed by projecting the positions of the apex carbon atom, the ring centroid, and the vanadium atom onto the least-squares plane determined by the five ring carbons. The coordinates of the projections were then used to find Δ, σ, and ψ. [b] This work.

population of each orientation is 50%, resulting in a calculated structure consisting of the superimposition of one orientation on the other. Thus, the calculated structure contains two vanadium atoms and two indenyl rings with a pseudocenter of symmetry between the vanadium positions. Due to this problem, a satisfactory structure has not been obtained at present.[14b] In spite of the difficulties encountered, however, the crystal data tend to confirm the expected sandwich configuration.

The synthesis of bis(indenyl)iodovanadium(III) (**2**) was achieved by oxidation of **1** according to the following reaction 1.

$$\underset{\mathbf{1}}{(Ind)_2V} + {}^1/_2 I_2 \rightarrow \underset{\mathbf{2}}{(Ind)_2V(I)} \qquad (1)$$

Reaction 1 was performed in toluene solution. The product is a crystalline solid whose structure was determined by an X-ray study on a single crystal. The molecular structure and numbering scheme are presented in Figure 1; bond distances and angles for compound **2** appear in Table IV. The carbocyclic ligands are η^5-bonded to the vanadium center through the five-membered rings. The V–C distances range from 2.270 (8) to 2.382 (6) Å. Both of the rings exhibit slippage away from a pure η^5-configuration toward a η^3-arrangement, which is typical for indenyl complexes,[15] as can be seen from the vanadium–carbon distances (Table IV). The average V–C bond lengths for the two carbons common to both rings in each carbocycle (the "long" V–C distances) are 2.371 (8) [Ind(1)] and 2.354 (9) Å [Ind(2)]. The average V–C bond distances for the remaining three carbons in each cyclopentadienyl ring (the "short" V–C lengths) are 2.275 (10) [Ind(1)] and 2.286 (10) Å [Ind(2)]. This is reflected in the slip parameters for **2**, which are compared to those for related indenyl complexes in Table VI.[15] The values obtained for both rings are in the range reported for η^5-indenyl complexes ($\Delta < 0.3$).[15a] We note that, from the slip parameters, it appears that Ind(1) deviates more toward a η^3-configuration than Ind(2) does. However, it must be pointed out that this apparent η^3-distortion for Ind(1) is not supported by a comparison of the average V–C bond distances mentioned above. That is, the difference between the averages of the two "long" V–C bond lengths for both rings is not significant and neither is the difference between the averages of the three "short" V–C lengths. In other words, the difference between the Δ(M–C) values (Table VI) for Ind(1) and Ind(2) is not significant. On the other hand, the pattern of C–C bond distances in Ind(1) suggests that an allyl–ene resonance hybrid may contribute to the structure. Such a distortion is similar to that found in the η^3-bonded ring of $(Ind)_2V(CO)_2$[2b] (although the Ind(1) distortion in **2** is, not unexpectedly, less pronounced). This is seen in the C1–C2 and the C1–C9 lengths, which are quite similar [1.410 (12) and 1.408 (11) Å], and in the C2-C3 and C8–C9 distances [1.440 (11) and 1.442 (10) Å], which also are close, as well as in the contracted C3-C8 length [1.412 (9) Å].

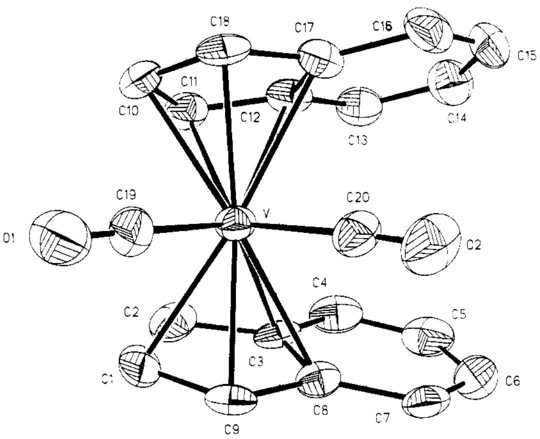


Figure 2. ORTEP view of complex **3** (30% probability ellipsoids).

The apparent allyl–ene distortion of Ind(1), in addition to the suggestion of greater slippage by some of its slip parameters, supports the interpretation that Ind(1) is closer to a η^3-configuration than Ind(2) is.

Both indenyl rings deviate only slightly from planarity. The maximum deviation from the least-squares plane of Ind(1) is 0.042 (8) Å (C1). The analogous value for Ind(2) is 0.038 (9) Å (C10). C1 and C10 are "unique" indenyl carbons (i.e. they lie on the twofold axes of the indenyl rings); these "apex" deviations suggest envelope conformations for both five-membered rings. A clearer illustration of this structural features derives from the least-squares planes of each ring calculated by excluding C1 and C10, respectively. C1 is 0.056 (6) Å out of the C2···C9 least-squares plane; C10 is 0.051 (3) Å out of the C11···C18 plane. In both rings, the apex carbon is displaced from the ring plane away from the vanadium center.

The centroid–V–centroid angle in **2** is 142.2 (3)°, which is comparable to the cp–V–cp angle in $(cp)_2V(Cl)$ of 139.5 (3)°.[16] The wider angle of **2** vs. that found in $(cp)_2V(Cl)$ in spite of the large iodine in the equatorial cavity of the molecule is attributable to steric interaction between the indenyl rings. The vanadium–centroid lengths of 1.973 (8) [Ind(1)] and 1.976 (9) Å [Ind(2)] are in the range (1.92–2.00 Å) for $(cp)_2{}^*V(X)$ complexes[3,16] and are similar to the V–Ind length in $(Ind)V(CO)_4$ [1.935 (1) Å].[17] The iodine sits in the equatorial cavity formed by the bent Ind–V–Ind unit at a distance of 2.794 (1) Å from the vanadium center. There are no interactions between the I ligand and either six-membered ring, or between the rings themselves, other than normal van der Waals interactions.

The structure of **2** is confirmed by its mass spectrum, which exhibits a parent peak at M^+ 408 as well as major fragment peaks corresponding to free indenyl ligand (*m/e* 115), the monoindenylvanadium fragment (*m/e* 166) and loss of iodine (*m/e* 281).

Complex **2** exhibits a magnetic moment of 2.67 μ_B at 294 K, consistent with two unpaired spins. All other reported $(cp)_2{}^*V(X)$ (X = Cl, I) are also paramagnetic by two electrons.[16,18] While the $1a_1$ and b_2 energy levels of the bent $(cp)_2M$ fragment are calculated to be nondegenerate,[19] the pairing energy in the $(cp)_2{}^*V(X)$ systems apparently exceeds the orbital separation, resulting in the observed paramagnetism.

The synthesis of $(Ind)_2V(CO)_2{}^+BPh_4{}^-$ (**3**) was performed in THF according to the reaction 2. The yield of **3** is low; the

$$\underset{\mathbf{2}}{(Ind)_2V(I)} + CO + NaBPh_4 \rightarrow \underset{\mathbf{3}}{(Ind)_2V(CO)_2{}^+BPh_4{}^-} \quad (2)$$

---

(15) (a) Faller, J. W.; Crabtree, R. H.; Habib, A. *Organometallics* **1985**, *4*, 929–935. (b) Honan, M. B.; Atwood, J. L.; Bernal, I.; Herrmann, W. A. *J. Organomet. Chem.* **1979**, *179*, 403–410.

(16) Fieselmann, B. F.; Stucky, G. D. *J. Organomet. Chem.* **1977**, *137*, 43–54.

(17) Kowaleski, R. M.; Kipp, D. O.; Stauffer, K. J.; Swepston, P. N.; Basolo, F. *Inorg. Chem.* **1985**, *24*, 3750–3752.

(18) Curtis, C. J.; Smart, J. C.; Robbins, J. L. *Organometallics* **1985**, *4*, 1283–1286.

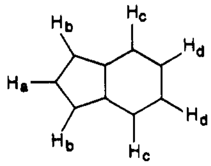
(19) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729–1742.

starting material, **2**, appears to undergo a dominant side reaction in THF that may involve loss of the indenyl rings and formation of a vanadium–iodide–THF complex. This reaction occurs in the absence of CO and may be a thermal decomposition. The nature of the product and the reaction path are under investigation. The structure of **3** was determined by an X-ray study on a single crystal. The molecular structure and numbering scheme of the cation are shown in Figure 2; bond angles and distances are found in Table V. The unit cell contains the bis(indenyl)dicarbonylvanadium(III) cation, the tetraphenylborate anion, and one molecule of THF. Both indenyl ligands are η^5-bonded to the vanadium center, as indicated by the range of V–C bond lengths (2.222 (9)–2.412 (8) Å), as expected for an 18-e complex. However, as indicated by the slip parameters listed in Table VI, both rings are slipped significantly with respect to the pure η^5-arrangement. Unlike complex **2**, there is no suggestion of any allyl–ene distortion even though both rings in **3** are slipped by roughly the same amount that ring 1 in **2** is.

The planarity of the carbocyclic rings is lower in the cation than in the neutral complex **2**. The maximum deviation from the least-squares plane of C1⋯C9 [Ind(1)] is 0.08 (1) Å; the maximum deviation for Ind(2) (C10⋯C18) is 0.07 (1) Å. The total deviation of all carbons from the least-squares planes is higher for both rings in **3** as compared with the rings in **2**. Both five-membered rings in **3** have an envelope conformation as do the rings in **2**. The apex carbons are canted away from vanadium as they are in **2** also.

The vanadium–centroid distances [1.964 (11) Å, V–Ind(1); 1.960 (10) Å, V–Ind(2)] are comparable to those in **2**. They are slightly longer than the V–centroid distance in $(Ind)V(CO)_4$[17] and the average V–centroid length in $[cp_2V(CO)_2^+][BPh_4^-]$, 1.92 Å.[20a] The Ind(1)–V–Ind(2) bond angle is 138.5 (4)°, which is narrower by 4° than the same angle in **2**. This is comparable to the analogous angle in $[(cp)_2V(CO)_2]^+$ [137.9 (7)°][20a] and in $(cp)_2Ti(CO)_2$ [138.6°].[20b] The C19–V–C20 bond angle of 84.6 (4)° is comparable to that found in $(Ind)_2V(CO)_2$[2b] [85.8 (1)°] and to the average bond angle found for $(cp)_2V(CO)_2]^+$ [84°].[20a] The V–C(carbonyl) distances for **3** are 1.953 (11) (V–C19) and 1.996 (9) Å [V–C20]. These are in the same range as those in $[(cp)_2V(CO)_2]^+$ (average, 1.97 Å)[20a] and in $(Ind)_2V(CO)_2$ (average, 1.95 Å)[20c] and are significantly shorter than the V–C(carbonyl) distances in $(cp)_2Ti(CO)_2$ [2.030 (11) Å].[20b] The V–C–O groups in **3** are almost linear [V–C19–O1, 179.1 (9)°; V–C20–O2, 177.4 (9)°] as are those in $(Ind)_2V(CO)_2$ (average, 178°).[20c] As in **2**, there are no ligand–ring or ring–ring interactions other than the usual van der Waals type. The plane formed by the ring centroids is orthogonal [89.9 (5)°] so that formed by the vanadium and the carbonyl carbons (V, C19, C20).

The IR spectrum of **3** exhibits two strong bands at 2041 and 2001 cm^{-1} and two weaker bands at 2025 and 1977 cm^{-1} in the solid phase (Nujol mull). The two weak bands are apparently due to a solid state effect. The IR spectrum of **3** in acetone solution is consistent with this explanation, exhibiting only two bands, at 2047 and 2000 cm^{-1}. The proton NMR of **3** supports the proposed structure. The spectrum exhibits four resonances in addition to the tetraphenylborate and the THF resonances: two multiplets at δ 7.58 and 7.42, a doublet at δ 6.49 and a triplet at δ 5.44. The triplet and the doublet integrate to one and two protons, respectively; proton-decoupling experiments demonstrate that they are coupled (J_{H-H} = 3.2 Hz). The triplet is assigned as H_a while the doublet corresponds to H_b. The multiplets centered at 7.42 and 7.58 integrate to two protons each and are also coupled. The peak shape of the multiplets suggests an AA′BB′ splitting pattern. One of the two resonances is assigned to H_c and the other to H_d.



Supplementary Material Available: Tables of hydrogen atom coordinates (Table SI) and thermal parameters (Table SII) for complex **2**, analogous tables for complex **3** (Tables SIII and SIV), and a table of nonessential bond lengths for complex **3** (Table SV) (5 pages); tables of calculated and observed structure factors for both structure determinations (23 pages). Ordering information is given on any current masthead page.

---

[20] (a) Atwood, J. L.; Rogers, R. D.; Hunter, W. D.; Floriani, C.; Fachinetti, G.; Chiesi-Villa, A. *Inorg. Chem.* **1980**, *19*, 3812–3817. (b) Atwood, J. L.; Stone, K. E.; Alt, H. G.; Hrncir, D. C.; Rausch, M. D. *J. Organomet. Chem.* **1977**, *132*, 367–375. (c) Basolo, F., private communication.