

Aravamudan, Heijdenrijk & Schenk, 1990). The short Co—O(4) equatorial bond is probably due to steric reasons since the two inversion-related planes CoO(1)O(3)O(4) and Co'O(1')O(3')O(4') are nearly planar and bring about a crowding in the equatorial region. The Co—O(2) and Co—N(1) bonds are of covalent nature. That the Co—O(2) bond is longer may be attributed to the fact that O(1) and O(2) are bonded to C(1) with O(1) lying in the equatorial plane and O(2) in the apical position.

Each dithiodibenzoate ion links three Co atoms through its carboxylate O atoms making the structure polymeric. The polymerization is chain-like and extends along the *a* axis. The polymeric nature of the compound is depicted in Fig. 2. The chains are packed in layers nearly parallel to the *ac* plane. The bond parameters in the dithiodibenzoate group are normal when compared with those observed in bis(triethanolamine)nickel(II) dithiodibenzoate (Ramalingam, Aravamudan & Seshasayee, 1987).

The hexamethylenetetramine moiety is linked to Co through N(1) and occupies the apical position. The bond parameters in hexamethylenetetramine are normal and compare well with those observed by

Becka & Cruickshank (1963). Each hexamethylenetetramine moiety has a proton attached to it as confirmed by X-ray analysis.

#### References

- BECKA, L. N. & CRUICKSHANK, D. W. J. (1963). *Proc. R. Soc. London Ser. A*, **273**, 435–454.  
 CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.  
 CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.  
 GANESH, V., SESHASAYEE, M., ARAVAMUDAN, G., HEIJENRIJK, D. & SCHENK, H. (1990). *Acta Cryst.* **C46**, 949–951.  
 MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.  
 RADHA, A., SESHASAYEE, M., KUMAR, V. & ARAVAMUDAN, G. (1989). *Acta Cryst.* **C45**, 882–884.  
 RAMALINGAM, K., ARAVAMUDAN, G. & SESHASAYEE, M. (1987). *Z. Kristallogr.* **181**, 215–222.  
 SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.  
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.  
 SUBRAHMANYAN, T. (1982). PhD Thesis, Indian Institute of Technology, Madras, India.  
 VIOSSAT, B., KHODADAD, P. & RODIER, N. (1981). *Bull. Soc. Chim. Fr.* pp. 69–73.

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## Structure of $(\text{Cl})(\text{NO})_2\text{Cr}(\eta^5\text{-C}_5\text{H}_4)\text{C}(\text{O})(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)$

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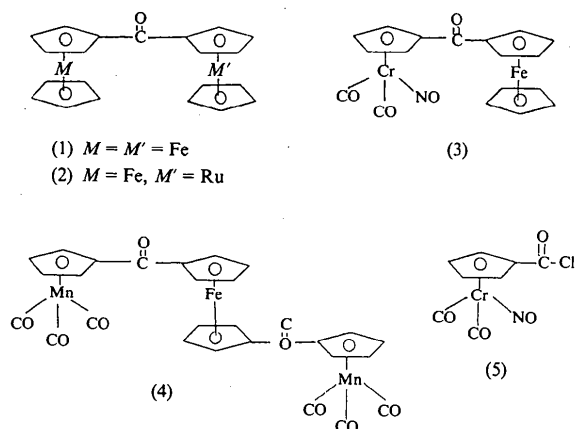
**Abstract.** Friedel–Crafts acylation of dicarbonyl[ $\eta^5$ -(ferrocenylcarbonylcyclopentadienyl)]nitrosylchromium (3) (hereafter called cynichrodenyl ferrocenyl ketone) with dicarbonyl[ $\eta^5$ -(chloroformyl)cyclopentadienyl]nitrosylchromium (5) led unexpectedly to chloro[ $\eta^5$ -(ferrocenylcarbonylcyclopentadienyl)]dinitrosylchromium (6),  $[\text{CrFe}(\text{C}_5\text{H}_5)(\text{C}_{11}\text{H}_8\text{O})\text{Cl}(\text{NO})_2]$ . The structure of (6) has been determined by an X-ray diffraction study: space group  $P2_1/c$ ,  $a = 10.938$  (2),  $b = 12.487$  (2),  $c = 12.460$  (2) Å,  $\beta = 111.43$  (1)°, and  $Z = 4$ . Compound (6) adopts a *transoid* conformation at the organic carbonyl carbon. The Cl atom of the  $(\eta^5\text{-C}_5\text{H}_4)\text{Cr}(\text{NO})_2\text{Cl}$  moiety is located at the site away from the exocyclic organic carbonyl carbon

with a twist angle of 137.9°. The organic carbonyl plane is turned away from the corresponding ring planes Cp<sup>1</sup>(Fe) and Cp(Cr) by 14.7 and 14.3°, respectively.

**Introduction.** Several metallocenyl ketones which contain two metalloaromatic substituents are known, for example, diferrocenyl ketone (1), ferrocenyl ruthenocenyl ketone (2) (Rausch, Fischer & Grubert, 1960), dicymantrenyl ketone, cymantrenyl ferrocenyl ketone (Cais & Feldkimmel, 1961) and cynichrodenyl ferrocenyl ketone (3) (Wang, Hwu & Wang, 1989). Compounds such as (1) and (3) have served as important precursors for the synthesis and structural elucidation of metallocenyl-stabilized carbonium ions (Cais, Dani, Herstein & Kapon, 1978; Cais &

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Eisenstadt, 1965; Wang & Hwu, 1990), and X-ray structural investigations of three ketones (1) (Trotter & MacDonald, 1966), (2) (Small & Trotter, 1964) and (3) (Wang, Hwu & Wang, 1989) have been undertaken.



Metallocenyl ketones which contain three metalloaromatic substituents are very few, for example, 1,1'-dicymantrenoylferrocene (4) (Cais & Feldkimmel, 1961). Since (3) has already been prepared (Wang, Hwu & Wang, 1989), it is of interest to synthesize a new trimetalloenyl ketone, namely, 1,1'-dicynichrodenoylferrocene (England & Reeves, 1987) by the Friedel-Crafts acylation of (3) with cynichrodenoyl chloride (5). Herein, we report the structure of chloro[η<sup>5</sup>-(ferrocenyl)Cp]dinitrosylchromium (6) (Cp = cyclopentadienyl), the unexpected product and a new dimetalloenyl ketone. This compound appeared to be the first example of a Cp functionally substituted derivative of (Cl)(Cp)(NO)<sub>2</sub>Cr.

**Experimental.** Light dark brown crystals were grown from a solution of methylene chloride/pentane (1/4). A crystal of approximate dimensions 0.31 × 0.35 × 0.70 mm was mounted on a Nicolet R3m/V diffractometer equipped with a graphite monochromator (Mo Kα radiation, λ = 0.71073 Å). Unit-cell constants were determined from a least-squares fit to the automatically centered settings for 26 reflections with 8.01 ≤ 2θ ≤ 28.44°. θ/2θ scan data were collected at room temperature (297 K) out to a 2θ limit of 50.0° (h 0 → 13, k 0 → 14, l -14 → 13) with a variable scan speed of 2.93–14.65° min<sup>-1</sup>. Three standard reflections were monitored every 50 reflections and showed no signs of crystal deterioration. The data were corrected for absorption, Lorentz and polarization effects. Corrections for absorption were on ψ scans of a few reflections. 3331 reflections were collected, 2797 unique, of which 2193 observed reflections with I ≥ 3.0σ(I) were used for refinement of the structure. The space group P2<sub>1</sub>/c was determined from the systematic absences: h0l, l = 2n + 1, and

0k0, k = 2n + 1. The structure was solved by direct methods using *SHELXTL-Plus* (Sheldrick, 1987) and refined by full-matrix least-squares methods based on *F* values. Neutral atom scattering form factors and anomalous-dispersion terms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The weights had the form  $w = [\sigma^2(F) + gF^2]^{-1}$  with  $g = 0.002$ . All of the non-H atoms were obtained from *E* maps and refined anisotropically. All of the H atoms were calculated and refined with a fixed *U* of 0.08 Å<sup>2</sup>. Final agreement factors are: *R* = 0.0357, *wR* = 0.0395, and GOF = 0.8. In the final difference Fourier map the deepest hole was 0.71 e Å<sup>-3</sup>, and the highest peak 0.50 e Å<sup>-3</sup>. All calculations were performed on a MicroVAX II-based Nicolet *SHELXTL Plus* system.

**Discussion.** The molecular structure of compound (6) is shown in Fig. 1. The view of part of (6) along the normal of Cp(Cr) and Cr is given in Fig. 2(a) and along the normal of Cp<sup>1</sup>(Fe) and Cp<sup>2</sup>(Fe) in Fig. 2(b). The atomic coordinates of the non-H atoms are listed in Table 1.\* Selected bond distances and angles are given in Table 2.

Compound (6) adopts a *transoid* conformation at the organic carbon. The Cl atom of the (η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>)Cr(NO)<sub>2</sub>Cl moiety is located at the site away from the exocyclic organic carbonyl carbon with twist angle 137.9°. The twist angle is defined as the torsional angle between the Cl atom, the Cr atom, the Cp ring center and the ring C atom bearing the exocyclic carbon.

Both Cr—N distances in compound (6), 1.714 (4) and 1.718 (3) Å, are considerably shorter than the

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53170 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

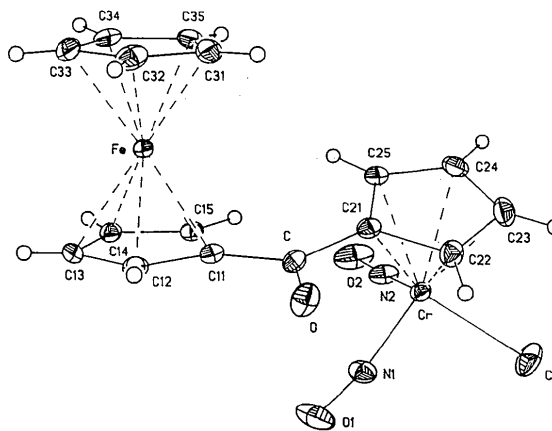


Fig. 1. Molecular configuration of (6).

predicted values (Carter, McPhail & Sim, 1966) and there must be appreciable electron donation from the metal  $d\pi$  orbitals to the  $\pi^*$  orbitals of the nitrosyl groups. The Cr—N length agrees well with the reported values of 1.711 Å in  $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{NO})_2\text{Cl}$  and 1.72 (1) Å in  $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{NO})_2(\text{NCO})$ . The Cr—Cl distance of 2.310 (1) Å is comparable with the 2.311 Å found in  $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{NO})_2\text{Cl}$ .

The Cr—N—O angles of 169.2 (3) and 169.8 (3)° are not significantly different from those of 169° in  $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{NO})\text{Cl}$  (Carter, McPhail & Sim, 1966) and  $[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{NO})\text{NMe}_2]_2$  (Bush & Sim, 1970), 170° in  $[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{NO})\text{SPh}]_2$  (McPhail & Sim, 1968) and 171° in  $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{NO})_2(\text{NCO})$  (Bush, Sim, Knox, Ahmad & Robertson, 1969).

The Cr—centroid [Cp(Cr)] distance of 1.859 Å agrees with 1.844 Å in  $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_2\text{NO}$  and 1.884 Å in  $(\eta^5\text{-C}_{13}\text{H}_6)\text{Cr}(\text{CO})_2(\text{NO})$  (Atwood, Shakir, Malito, Herberhold, Kremnitz, Bernhagen & Alt, 1979). The average C—C distance in the ring [Cp(Cr)] is 1.420 Å. The mean angle in the ring is 108°.

The two cyclopentadienyl rings of the ferrocene moiety exhibit an average twist angle of 0.8° (Trotter & MacDonald, 1966; Palenik, 1970). The two Cp rings of the ferrocene moiety are separated by 3.31 Å

Table 1. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{Å}^2 \times 10^3$ )

	x	y	z	$U_{eq}^*$
Fe	7531 (1)	5788 (1)	1087 (1)	26 (1)
Cr	12491 (1)	6076 (1)	4403 (1)	30 (1)
Cl	14493 (1)	6507 (1)	5802 (1)	75 (1)
O	9799 (3)	8174 (2)	2615 (3)	50 (1)
O(1)	10747 (4)	6954 (3)	5396 (3)	84 (2)
O(2)	12030 (5)	3899 (3)	4879 (3)	85 (2)
N(1)	11535 (3)	6622 (3)	5088 (3)	45 (1)
N(2)	12315 (3)	4779 (3)	4785 (3)	47 (1)
C	9855 (3)	7193 (3)	2628 (3)	32 (1)
C(11)	8700 (3)	6548 (3)	2545 (3)	32 (1)
C(12)	7422 (3)	7000 (3)	2156 (3)	36 (1)
C(13)	6512 (3)	6170 (3)	2144 (3)	38 (1)
C(14)	7246 (3)	5208 (3)	2528 (3)	35 (1)
C(15)	8584 (3)	5421 (3)	2759 (3)	32 (1)
C(21)	11140 (3)	6699 (3)	2751 (3)	32 (1)
C(22)	12305 (4)	7337 (3)	3103 (3)	40 (1)
C(23)	13364 (4)	6659 (4)	3128 (3)	50 (2)
C(24)	12857 (4)	5610 (3)	2813 (3)	45 (1)
C(25)	11506 (3)	5634 (3)	2586 (3)	35 (1)
C(31)	8324 (5)	5987 (4)	-141 (4)	55 (2)
C(32)	7069 (5)	6422 (3)	-529 (3)	48 (2)
C(33)	6173 (4)	5594 (3)	-552 (3)	41 (1)
C(34)	6907 (4)	4649 (3)	-183 (3)	40 (1)
C(35)	8235 (4)	4885 (4)	76 (3)	49 (2)

\* Equivalent isotropic  $U$  defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

Table 2. Selected bond distances (Å) and angles (°) of (6)

Fe—C(11)	2.035 (3)	Fe—C(12)	2.049 (4)
Fe—C(13)	2.068 (4)	Fe—C(14)	2.063 (4)
Fe—C(15)	2.031 (3)	Fe—C(31)	2.031 (5)
Fe—C(32)	2.047 (4)	Fe—C(33)	2.053 (3)
Fe—C(34)	2.050 (3)	Fe—C(35)	2.039 (5)
Cr—C(21)	2.192 (3)	Cr—C(22)	2.215 (4)
Cr—C(23)	2.253 (5)	Cr—C(24)	2.236 (5)
Cr—C(25)	2.193 (3)		
Cr—N(1)	1.714 (4)	Cr—N(2)	1.718 (3)
Cr—Cl	2.310 (1)	N(1)—O(1)	1.142 (6)
N(2)—O(2)	1.160 (5)	C—C(11)	1.470 (5)
C—C(21)	1.490 (5)	C—O	1.226 (4)
Cr—Cp	1.859	Cr...C	3.239
Fe...C	3.108	O(1)...Cl	3.981
[Cp <sup>1</sup> (Fe)]...[Cp <sup>2</sup> (Fe)]	3.309		
H(C15)...H(C25)	2.060	O(2)...Cl	4.114
N(1)—Cr—Cl	96.5 (1)	N(1)—Cr—N(2)	95.0 (2)
C(11)—C—C(21)	122.3 (3)	N(2)—Cr—Cl	100.5 (1)
Cr—N(2)—O(2)	169.2 (3)	Cr—N(1)—O(1)	169.8 (3)
C—C(11)—C(15)	130.6 (3)	C—C(11)—C(12)	121.3 (3)
C—C(21)—C(25)	132.5 (3)	C—C(21)—C(22)	120.2 (3)
C(21)—C—O	117.1 (3)	C(11)—C—O	120.6 (3)
cen—Cr—N(1)	122.3	Cp—Cr—Cl	118.0
		Cp—Cr—N(2)	119.4

#### Dihedral angles between planes

N(1), Cr, N(2) and Cr, N(1), O(1)	93.7
N(1), Cr, N(2) and Cr, N(2), O(2)	92.2
N(1), Cr, Cl and Cr, N(1), O(1)	7.5
N(2), Cr, Cl and Cr, N(2), O(2)	9.8

Cp is the center of a cyclopentadiene ring.

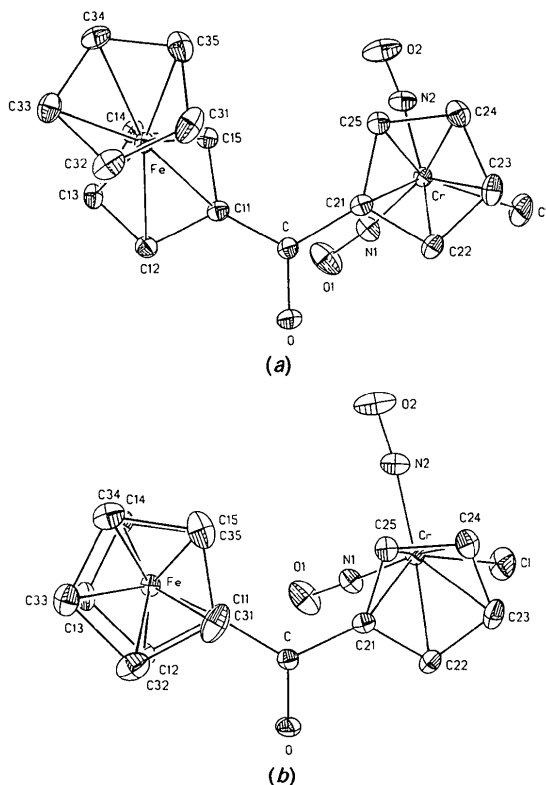


Fig. 2. View of part of (6) along the normal (a) of Cp(Cr) and Cr; (b) to planes of rings Cp<sup>1</sup>(Fe) and Cp<sup>2</sup>(Fe).

(Krukonis, Silverman & Yannoni, 1972). The average C—C distances in the rings are C—C [Cp<sup>1</sup>(Fe)] 1.43 Å, C—C [Cp<sup>2</sup>(Fe)] 1.41 Å. The exocyclic C—C bond is 1.470 (5) [C—C(11)], 1.490 (5) Å [C—C(21)] and the mean angle in the rings is 108°.

The exocyclic carbon (C) is bent toward Fe and away from Cr, with angles of 0.89 and -0.64° respectively, the angle is defined as the angle between the exocyclic C—C bond and the Cp ring with positive angle toward metal. The carbonyl plane [C(11), C, O, C(21)] is turned away from the corresponding ring Cp<sup>1</sup>(Fe) and Cp(Cr) by 14.7 and 14.3°, respectively. These rotations might be the result of intramolecular steric interference between atoms H[C(15)] and H[C(25)]. This is supported by the enlargement of bond angles C(15)—C(11)—C and C(25)—C(21)—C to 130.6 (3) and 132.5 (3)°, respectively.

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#### References

ATWOOD, J. L., SHAKIR, R., MALITO, J. T., HERBERHOLD, M., KREMNITZ, W., BERNHAGEN, W. P. E. & ALT, H. G. (1979). *J. Organomet. Chem.* **165**, 65–78.

BUSH, M. A. & SIM, G. A. (1970). *J. Chem. Soc.* pp. 605–611.  
 BUSH, M. A., SIM, G. A., KNOX, G. R., AHMAD, A. & ROBERTSON, C. G. (1969). *Chem. Commun.* pp. 74–75.  
 CAIS, M., DANI, S., HERBSTEN, F. H. & KAPON, M. (1978). *J. Am. Chem. Soc.* **100**, 5554–5558.  
 CAIS, M. & EISENSTADT, A. (1965). *J. Org. Chem.* **30**, 1148–1154.  
 CAIS, M. & FELDKIMEL, M. (1961). *Tetrahedron Lett.* pp. 440–443.  
 CARTER, O. L., MCPHAIL, A. T. & SIM, G. A. (1966). *J. Chem. Soc.* pp. 1095–1103.  
 ENGLAND, K. & REEVES, P. C. (1987). *J. Organomet. Chem.* **319**, 355–360.  
 KRUKONIS, A. P., SILVERMAN, J. & YANNONI, N. F. (1972). *Acta Cryst.* **B28**, 987–990.  
 MCPHAIL, A. T. & SIM, G. A. (1968). *J. Chem. Soc.* pp. 1858–1865.  
 PALENIK, G. J. (1970). *Inorg. Chem.* **9**, 2424–2430.  
 RAUSCH, M. D., FISCHER, E. O. & GRUBERT, H. (1960). *J. Am. Chem. Soc.* **82**, 76–82.  
 SHELDRIK, G. M. (1987). *SHELXTL Plus*. Release 3.4 for Nicolet R3m/V crystallographic system. Nicolet Instrument Corporation, Madison, Wisconsin, USA.  
 SMALL, G. J. & TROTTER, J. (1964). *Can. J. Chem.* **42**, 1746–1748.  
 TROTTER, J. & MACDONALD, A. (1966). *Acta Cryst.* **21**, 359–366.  
 WANG, Y.-P. & HWU, J.-M. (1990). *J. Organomet. Chem.* **385**, 61–70.  
 WANG, Y.-P., HWU, J.-M. & WANG, S.-L. (1989). *J. Organomet. Chem.* **371**, 71–79.

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## Bis(arene)vanadium Complexes. A Structural Study

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**Abstract.** Bis(η<sup>6</sup>-mesitylene)vanadium(0), (1): [V(C<sub>9</sub>H<sub>12</sub>)<sub>2</sub>], *M*<sub>r</sub> = 291.3, orthorhombic, *Ccca*, *a* = 19.529 (1), *b* = 29.559 (2), *c* = 16.446 (4) Å, *V* = 9493 (3) Å<sup>3</sup>, *Z* = 24, *D*<sub>x</sub> = 1.23 g cm<sup>-3</sup>, graphite-monochromated Mo *K*α radiation, λ = 0.71069 Å, μ = 5.64 cm<sup>-1</sup>, *F*(000) = 3720, *T* = 293 K, *R* = 0.058 for 1522 independent reflections. Potassium bis(η<sup>6</sup>-mesitylene)vanadate dioxane/tetrahydrofuran (0.5/1) solvate, (2): K[V(C<sub>9</sub>H<sub>12</sub>)<sub>2</sub>].C<sub>4</sub>H<sub>8</sub>O.½C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>, monoclinic, *P2<sub>1</sub>/n* (the space group assignment was not unambiguous), *a* = 10.213 (2), *b* = 18.518 (3), *c* = 13.402 (3) Å, β = 89.58 (1)°, *V* = 2535 (1) Å<sup>3</sup>, *Z* = 4, *D*<sub>x</sub> = 1.17 g cm<sup>-3</sup>, Mo *K*α radiation, λ = 0.71069 Å, μ = 5.56 cm<sup>-1</sup>, *F*(000) = 952, *T* = 293 K, *R* = 0.073 for 1211 independent reflections. The asymmetric unit of (1) contains one eclipsed sandwich molecule in a general position and half a molecule lying around a crystallographic *C*<sub>2</sub> axis. The

ionic species (2) retains the sandwich structure and establishes contact ion pairs with the K<sup>+</sup> cations, which also interact with tetrahydrofuran and dioxane solvent molecules in a complex packing pattern.

**Introduction.** Despite the richness of the organometallic chemistry of Group V elements, the structural data available in the literature on bis(arene) complexes of vanadium are very scarce (Fischer, Fritz, Manchot, Priebe & Schneider, 1963; Radonovich, Zuerner, Efner & Klabunde, 1976). Bis(arene)vanadium anions are extremely air sensitive and require great care in both their synthesis and solid-state characterization. In a preliminary report (Fochi, Braga & Sabatino, 1988) we showed that reduction of bis(arene)vanadium(0) complexes with potassium in coordinating ethereal solvents gives solutions of the corresponding bis(arene)vanadium(-1) derivatives (arene = benzene, mesitylene). Solvated potassium salts were isolated in yields depending on the

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