limited to the preparation of such enolates as would be obtained by H removal from the methyl group of methyl ketones, it is a useful complement to our approach, which is not regioselective in the case of some methyl ketones (cf. **4a**). The preparation of Ti enolates from $TiCl_4$ and trimethylsilyl enol ethers,[14] from $(i\text{-PrO})_3TiCl$ and Li enolates,[15] or from $Cp_2TiMeCl$ and Li enolates[16] is limited by the selectivity with which the starting materials can be prepared.

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Supplementary Material Available: Table II, selected NMR data for Ti enolates, and the structures of **8**, **10**, and **12–14** (2 pages). Ordering information is given on any current masthead page.

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Bis(arene)vanadium Anions: A New Class of Organovanadium Complexes. X-ray Structural Characterization of Solvated $K[(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)_2V]$

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Summary: Reduction of bis(η^6-arene)vanadium(0) complexes with potassium gives the corresponding bis(η^6-arene)vanadium(−I) derivatives (arene = C_6H_6, 1,3,5-$C_6H_3Me_3$) as their K^+ salts. A single-crystal diffraction study of solvated $K[(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)_2V]$ shows that the anion presents two different rotameric configurations in the solid, though the sandwich structure is preserved, and that contact ion pairs are established with the K^+ cations, which also interact with THF and dioxane solvent molecules. Crystal data: monoclinic, space group $P2_1$, a = 10.213 (2) Å, b = 18.518 (3) Å, c = 13.402 (3) Å, β = 89.58 (1)°, V = 2534.6 Å^3, and Z = 4.

In 1975 it was reported that the EPR signal of $[V(C_6H_6)_2]$ (**1a**) disappears on contacting the latter with a potassium mirror in chelating solvents.[1] However, in spite of the theoretical and practical implications of this observation, organovanadium(−I) chemistry is still restricted to the hexacarbonylvanadate anion and its substituted derivatives.[2]

We now report that, when **1** is mixed with excess potassium sand in tetrahydrofuran, THF[3] at room temperature, dark exceedingly air-sensitive solutions result.[4]

$$\underset{\mathbf{1a,b}}{[\mathrm{V(arene)_2}]} + \mathrm{K} \xrightarrow{\mathrm{THF}} \underset{\mathbf{2a,b}}{\mathrm{K[V(arene)_2]}} \qquad (1)$$

a, arene = C_6H_6;
b, arene = 1,3,5-$C_6H_3Me_3$ (mesitylene)

After filtration of the unreacted potassium and addition of either diethyl ether or *n*-heptane, **2a** precipitates as a black microcrystalline solid.[5] On the other hand, dilution of a filtered THF solution of **2b** by either of the same solvents causes immediate and quantitative decomposition to **1b** and elemental potassium.[6]

On cooling a concentrated solution (0.22 M) to −40 °C, **2b** was isolated as a black microcrystalline product in low yield (ca. 20%). **2b** is even more air sensitive than **2a** and is decomposed into elemental potassium and **1b** when suspended in *n*-heptane.[7]

When **1b** and potassium sand were mixed in 1,4-dioxane, a burgundy-brown powder separated out. When it was redissolved by adding sufficient THF to the reaction mixture and cooling to −40 °C, black-brown crystals, **2c**, suitable for X-ray data collection, could be grown.[8]

The crystallographic study shows that the asymmetric unit contains two independent $[V(C_6H_3Me_3)_2]^-$ sandwiches and their respective K^+ cations and two THF, and one dioxane solvent molecules.[9] Despite the poor quality of

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(3) Vanadium concentrations were 0.03–0.1 M.

(4) In the case of benzene as the ligand, by careful filtration and titration of the unreacted potassium, the quantitative formation of a 1:1 K/V adduct was demonstrated.

(5) The composition $KV(C_6H_6)_2\cdot 1.25THF$ was established analytically after careful addition of water (alkalimetric titration for K; recovery of **1a**; GC for THF).

(6) On the basis of a titration of the potassium released during such a decomposition, a 70% yield could be evaluated for the formation of **2b** in reaction 1.

(7) From the titration of the released potassium, the approximate composition $KV(C_6H_3Me_3)_2\cdot 2THF$ was deduced (K: found, 8.0; calcd, 8.2).

(8) **Crystal data for $K[V(C_6H_3Me_3)_2]\cdot(C_4H_8O)\cdot{}^1/_2(C_4H_8O_2)$ (2c):** monoclinic, space group $P2_1$ from satisfactory refinement (see below); a = 10.213 (2) Å, b = 18.518 (3) Å, c = 13.402 (3) Å, β = 89.58 (1)°, V = 2534.6 Å^3, Z = 4, $F(000)$ = 952, D_{calcd} = 1.17 g/cm^3, Mo Kα radiation, λ = 0.71069 Å, μ(Mo Kα) = 5.56 cm^{-1}, $\omega-2\theta$ scan mode, θ range = 2.5–25°, R = 0.057, and R_w = 0.061 for 1181 independent reflections with $F_o > 5\sigma(F_o)$. The space group determination was not straightforward: initial attempts in the orthorhombic $P2_12_12_1$ (from systematic absences) were not successful; the monoclinic choice was adopted after a careful examination of the equivalence conditions.

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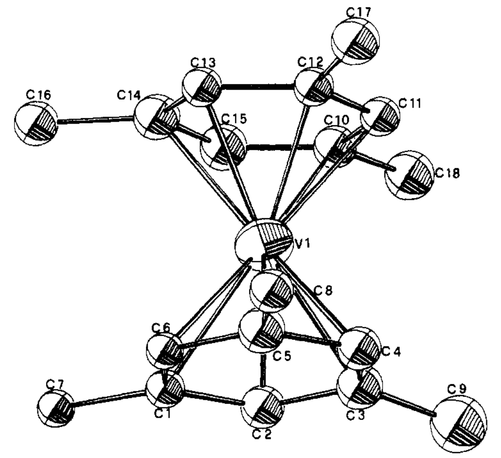

Figure 1. ORTEP diagram of one of the two independent $[(\eta^6\text{-}C_6H_3Me_3)_2V]^-$ anions in the asymmetric unit.

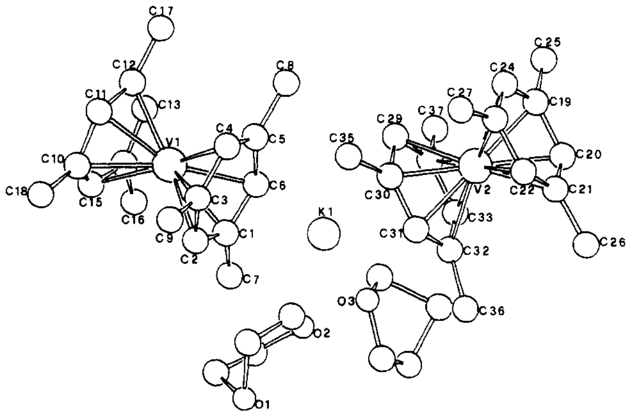

Figure 2. Schematic representation of the *pseudotetrahedral* coordination around one K^+ cation.

the X-ray data,[9] which allow only a description of the gross structural feature to be made, it has been possible to detect differences in the rotameric configurations of the mesitylene pairs sandwiching the vanadium atom. In fact, while the first anion [V(1), see Figure 1] shows a ca. 23° rotation of one mesitylene ligand with respect to the other one, thus almost leading to staggered aromatic rings, the second anion [V(2)] exhibits eclipsed rings.

Contrary to the out-of-plane distorsions sometimes observed in π-carbocyclic sandwich species,[10] the arene ligands in **2c** are planar and essentially parallel within each anion.

The average V–C distances are almost identical in the two anions [V(1)–C(1–6) = 2.18 (2), V(1)–C(10–15) = 2.21 (1) Å and V(2)–C(19–24) 2.19 (1), V(2)–C(28–33) = 2.19 (2) Å] and appear to be in agreement with the values reported for the triple-decker sandwich $[(C_5H_5V)_2(C_6H_3Me_3)]$ [V–C range = 2.193 (3) -2.246 (4) Å][11] containing the same arene.

Each K^+ cation interacts with one mesitylene ring from each anion [K(1)···C(1–6) = 3.17 (2), K(1)···C(28–33) = 3.21 (2), K(2)···C(10–15) = 3.22 (2), K(2)··C(19–24) = 3.23 (2) Å] establishing a quite complex packing pattern by simultaneously interacting with one THF molecule [K(1)···O(3) = 2.70 (2), K(2)···O(4) = 2.74(2) Å] and with one dioxane molecule (see Figure 2). The latter actually "bridges" two contiguous K^+ cations by using its oxygen extremities [K(1)···O(2) = 2.78 (1), K(2)···O(1) = 2.66 (1) Å]. The coordination geometry around each cation is approximately tetrahedral [V(1)–K(1)–V(2) = 136.5°, O(2)–K(1)–O(3) = 92.7° and V(1)–K(2)–V(2) = 136.0°, O(1)–K(2)–O(4) = 99.3°]. Similar contact ion pairs were also observed in the potassium salt of the carbocyclic $[Ce(C_8H_8)_2]^-$ system.[12]

The presence of solvent molecules in the coordination sphere of potassium in the crystal, together with the observed decomposition of **2b** when THF is diluted with noncoordinating solvents, reveals the role of solvation energy in the delicate thermodynamic balance for this system, as confronted with the ionization potential of the alkali metal. Consistent with this is the observation that sodium sand does not react with **1** even over prolonged reflux. The stability difference between **2a** and **2b** could be explained by different electron densities in **1a** and **1b**, the electron richer system being the more difficult to accept an *extra* electron, though also solid-state effects could be relevant.

The reducing properties of these systems as a function of the bonded arene are under investigation.

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Registry No. **1b**, 1272-71-5; **2c**, 111237-49-1.

Supplementary Material Available: Complete listings of positional and thermal parameters, crystal data bond distances, and bond angles and an unit-cell drawing for **2c** (32 pages); a listing of observed and calculated structure factors for **2c** (7 pages). Ordering information is given on any current masthead page.

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(9) **Experimental Data.** A single crystal was sealed in a Lindemann glass capillary and mounted on an Enraf-Nonius CAD4 diffractometer. Because no azimuthal scan reflections could be measured, an absorption correction was applied by the Walker and Stuart method[13] once the complete structural model was obtained and all atoms were refined isotropically. The structure was solved by combined use of Patterson and direct methods[14] which afforded the positions of the two V atoms. All other atoms were located from subsequent difference Fourier syntheses. The structure model was refined by least-squares calculations. Because of the poor quality of the X-ray data and the large number of structural parameters, only the V and K atoms were refined anisotropically. Geometrical constraints were applied to the mesitylene ligands, refining single values for both C(Ph)–C(Ph), [1.41 (2) Å] and C(Ph)–C(Me) [1.54 (2) Å] distances. H atoms were added in calculated positions and refined as riding on their C atoms. Residual electron density peaks were about 0.3 e Å^{-3}. All calculations were performed by using the SHELX76 package of crystallographic programs.[15] Very similar *R* values were found by refining an inverted set of coordinates for the absolute configuration test.

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