synthesis[12] and point the way for further development using other asymmetric, nontrigonal carbon nucleophiles.[13] Results of further studies will be described in due course.

Acknowledgment. We thank the Research Corporation, the Faculty Research Committee and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of our programs. We are also grateful to Dr. Laszlo Tokes for his assistance in obtaining elemental analyses and high-resolution mass spectra.

Registry No. 1 (M = Li), 86272-31-3; **2**, 86272-32-4; **4**, 86272-33-5; (±)-**5a**, 86272-34-6; (±)-**5b**, 86272-35-7; (±)-**6a**, 52209-39-9; (±)-**6b**, 72457-70-6; (±)-**8**, 86272-36-8; (±)-**9**, 86272-37-9; (±)-**10**, 86272-38-0; (±)-**11**, 17015-46-2; (±)-R_2CuLi (R = *cis*-2-methoxycyclopropyl), 86272-25-5; (±)-$CH_3O(CH_3)_2CC_2CuR$ (R = *cis*-2-methoxycyclopropyl), 86272-27-7; (±)-PhSCuR (R = cis = 2-methoxycyclopropyl), 86272-28-8; (±)-PhSCuR (R = *cis*-2-methoxycyclopropyl), 86272-29-9; (±)-$C_3H_7C_2CuR$ (R = *cis*-2-methoxycyclopropyl), 86272-30-2; (±)-Bu_3PCuR (R = *cis*-2-methoxycyclopropyl), 86272-26-6; lithio-2-(2-methylpropyl)-1,3-dithiane, 86272-39-1; 2-cyclohexen-1-one, 930-68-7; dimethylcarbonate, 616-38-6.

Supplementary Material Available: A listing of purification and characterization data for all compounds (4 pages). Ordering information is given on any current masthead page.

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The First Triple-Decker Sandwich with a Bridging Benzene Ring

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Until now triple- and tetra-decker sandwich complexes have only been prepared with five-[1] or eight-membered[2] carbocyclic or heterocyclic[3] groups or group 5 element rings (P_3, As_3,[4] or As_5[5]) as the bridging ligands. Considering that many examples of mononuclear complexes with η^6-bound arenes are known,[6] it is indeed surprising that no reports of multiple deckers containing bridging arenes have yet appeared in the literature.

We wish to report the preparation and characterization of the first examples of arene-bridged, binuclear transition-metal compounds with triple-decker sandwich structures. In these novel complexes, two (cyclopentadienyl)vanadium moieties are linked by benzene, toluene, *n*-propylbenzene, or mesitylene. They are formally unsaturated 26-electron complexes, and as such violate the "30- and 34-electron rule" put forward by Hoffmann et al. for triple-decker sandwiches.[7] The parent complex **1**, with benzene as the central fragment, was prepared by reaction of $CpV(C_3H_5)_2$[8] with an excess of 1,3-cyclohexadiene in refluxing *n*-heptane (eq 1).

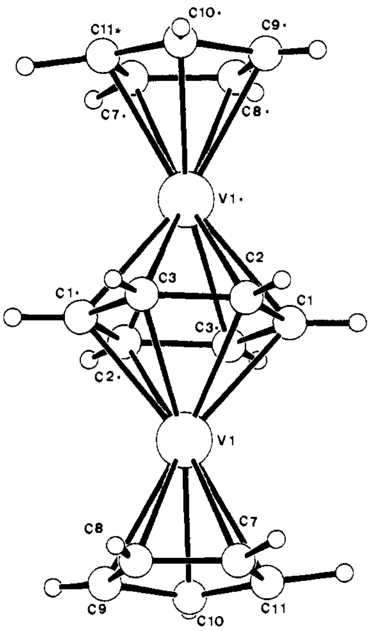


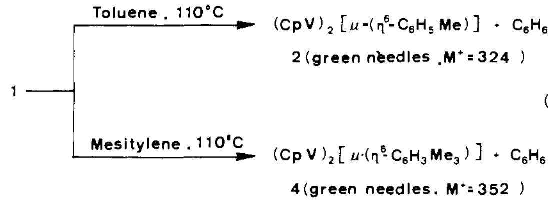
Figure 1. **1** crystallizes in the monoclinic space group $P2_1/n$ with $Z = 2$ and cell dimensions $a = 6.068$ (1) Å, $b = 7.928$ (1) Å, $c = 13.821$ (1) Å, $\beta = 96.94$ (1)°; center of inversion at the midpoint of the central benzene ring. R 0.051 (R_w 0.074) for 114 parameters and 2129 reflections (λ 0.71069, ϑ_{max} 30°) of which 1946 were considered observed (2σ).

$$2\ CpV(C_3H_5)_2 \xrightarrow[\text{n-heptane, }100\,°C]{1,3\text{-}C_6H_8} (CpV)_2[\mu\text{-}(\eta^6\text{-}C_6H_6)] \quad (1)$$

1 (green/blue crystals, $M^+ = 310$)

Compound **1** was obtained in about 50% yield.[9] Hydrogen, propene, cyclohexene, 1,5-hexadiene, benzene, and *n*-propylbenzene are other products of the reaction. Two further organovanadium species were also isolated from the reaction mixture. They were identified by mass spectrometry as the *n*-propylbenzene analogue of **1**, $(CpV)_2C_6H_5Pr$ (**3**), and the mononuclear complex $CpV(C_6H_5Pr)$ (**5**). An attempt to isolate the parent compound, $CpV(C_6H_6)$, from the reaction mixture of $CpVCl_3$, C_3H_7MgCl, and 1,3-cyclohexadiene has been unsuccessful.[10]

It is interesting to note that **1** readily undergoes arene exchange reactions with retention of the triple-decker sandwich structure. Thus **1** may be converted to the toluene or mesitylene analogues, **2** or **4**, respectively, according to eq 2.[11] In contrast to **1**, both of these new triple-deckers are highly soluble in ethers, aliphatic and aromatic hydrocarbon solvents.



Complexes **1–4** have been characterized by mass spectrometry. Parent ions were observed in all cases. In addition, satisfactory elemental analyses have been obtained for **1**, **2**, and **4**.

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(9) Toluene was found to be the most suitable solvent for recrystallization, in spite of the low solubility (ca. 8 g/L at 110 °C) and loss due to the exchange reaction with toluene (see eq 2).

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(11) The formation of two further CpV organyls was observed. These were isolated as volatile (60 °C/10^{-4} mmHg) brown oils whose mass spectra corresponded to $CpV(C_6H_5Me)$ and $CpV(C_6H_3Me_3)$.

(12) Isolated yields were not optimized.

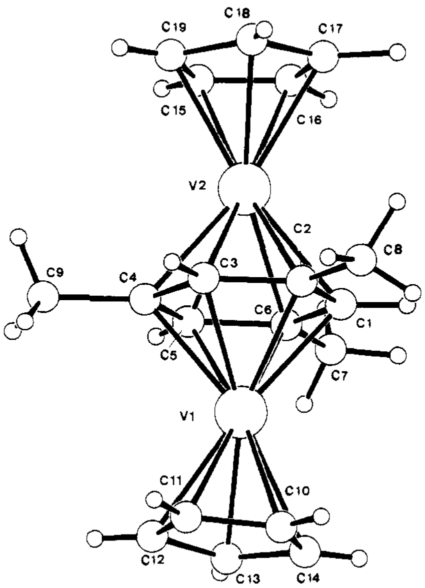


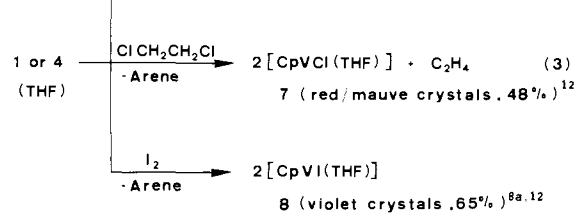
Figure 2. **4** crystallizes in the monoclinic space group $P2_1/a$, $Z = 4$. Cell dimensions are a = 9.990 (2) Å, b = 16.032 (3) Å, c = 10.811 (1) Å, β = 92.81 (1)°; R 0.045 (R_w 0.050) for 256 parameters and 3906 (2306 observed) reflections.

Compounds **1** and **4** have been investigated by X-ray crystallographic methods. As is evident from Figures 1 and 2, all cyclic fragments within both compounds are planar and essentially parallel to each other.

The intermetal distance V–V is slightly smaller in **4** (3.381 (1) Å) than in **1** (3.403 (1) Å, benzene–V distance 1.702 Å), indicating that additional electron density, supplied by the methyl groups of the mesitylene ring, may be released into a bonding orbital of the system. The smaller Cp–V distances in **4** (av 1.913 Å (**1**, 1.922 Å)) are in accordance with this explanation. The two Cp rings in each compound are in staggered conformation relative to one another. Whereas in **1** V–C distances to the benzene ring (C–C$_{\text{av}}$ 1.443 (5) Å **4**, 1.439 (8) Å) are approximately equal and average to 2.233 (2) Å, corresponding distances in **4** range from 2.193 (3) Å to 2.246 (4) Å, the shortest distance being to one of the unsubstituted carbon atoms of the ring. Both vanadium atoms in **4** tend toward the same carbon atom, C5, and as a result the whole molecule is slightly distorted so that the interplanar angle between both independent Cp rings is 174.4°.

Preliminary results of a detailed investigation of the electronic deformation density in **1** by X–X and X–N methods indicate approximately octahedral distribution of electron density about the vanadium atoms.

Reaction of **1** or **4** with allylchloride, dichloroethane, or iodine, quantitatively liberates the arene ligand (followed by GC analyses) and affords the respective organovanadium halides **6–8** (eq 3).



$$\text{1 or 4 (THF)} \xrightarrow[\text{-Arene}]{2\,C_3H_5Cl} 2[CpV(C_3H_5)Cl(THF)]\ \text{6 (red crystals, 56\%)}^{12}$$

$$\text{1 or 4 (THF)} \xrightarrow[\text{-Arene}]{ClCH_2CH_2Cl} 2[CpVCl(THF)] + C_2H_4\ \text{7 (red/mauve crystals, 48\%)}^{12} \qquad (3)$$

$$\text{1 or 4 (THF)} \xrightarrow[\text{-Arene}]{I_2} 2[CpVI(THF)]\ \text{8 (violet crystals, 65\%)}^{8a,12}$$

Further treatment of the vanadium(II) halide **8** with iodine led to monomeric **9** (cryoscopy in benzene: found 448, calcd 442). By analogy, complex **5** was also characterized chemically by reaction with iodine (eq 4).

$$\underset{\mathbf{5}}{[CpV(C_6H_5Pr)]} + I_2 \xrightarrow{THF} \underset{\text{9 (dk. red crystals, 52\%)}^{12}}{[CpVI_2(THF)]} \cdot C_6H_5Pr \qquad (4)$$

In contrast to the known species $(CpVClPR_3)_2$ and $CpVCl_2(PR_3)_2$,[13] compounds **6** to **9** are phosphine free and represent useful precursors for the preparation of further (monocyclopentadienyl)vanadium organyls. Treatment of **7** with LiCp^{Me} for example leads to the new mixed metallocene CpCp^{Me}V (**10**) in high yield (eq 5).[14]

$$[CpVCl \cdot THF] + LiCp^{Me} \xrightarrow{THF} \underset{\text{10 (red crystals, } M^+ = 251\text{)}}{CpCp^{Me}V} + LiCl \qquad (5)$$

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Registry No. **1**, 86409-35-0; **2**, 86374-47-2; **3**, 86374-54-1; **4**, 86374-48-3; **5**, 86392-31-6; **6**, 86374-49-4; **7**, 86374-50-7; **8**, 86374-51-8; **9**, 86374-52-9; **10**, 32876-14-5; CpV$(C_3H_5)_2$, 86374-53-0; LiCpMe, 54061-45-9; C_3H_5Cl, 107-05-1; $ClCH_2CH_2Cl$, 107-06-2; I_2, 7553-56-2; 1,3-C_6H_8, 592-57-4.

Supplementary Material Available: Atomic coordinates and thermal parameters, a table of selected interatomic distances and angles, as well as a list of observed and calculated structure factors have been deposited for **1** and **4** (26 pages). Ordering information is given on any current masthead page.

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(14) The abbreviation Cp^{Me} refers to the 1,2,3,4,5-pentamethylcyclopentadienyl ligand.

Metal-Bridging Benzene in a Binuclear Hydridovanadium Complex

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Herein we report the synthesis, molecular structure, and chemical properties of $(CpVH)_2C_6H_6$ (**1**) (Cp = η-C_5H_5). **1** is the first example of a binuclear metal complex that has two metal centers bonded to one face of a η^6-bonded C_6H_6 ring.

Bridging C_nH_n-ring ligands coordinated to metal-metal-bonded M_2 units are known for n = 5, 6, 7, or 8,[1] but in the only reported examples for n = 6, viz., $Pd_2(Al_2Cl_7)_2(C_6H_6)_2$ and $Pd_2(AlCl_4)_2(C_6H_6)_2$,[2] the benzene rings are bound as conjugated dienes (η^4-bonded benzene). The seven- or eight-membered carbocycles have, in addition, been observed to bridge three metal centers as in $[Ru_3(CO)_6(\mu_3\text{-}SBu^+)\{\mu_3\text{-}(\eta^7\text{-}C_7H_7)\}]$[3] or $[Ni_3(CO)_3(CF_3C_2CF_3)\{\mu_3\text{-}(\eta^8\text{-}C_8H_8)\}]$.[4]

As an extension of our work on the reductive elimination of Cp ligands from metallocenes using alkali metals,[5,6] we have succeeded in isolating the novel K[Cp$_2$V],[6] a 1:1 adduct between

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(6) Jonas, K.; Wiskamp, V. *Z. Naturforsch.*, submitted for publication. Wiskamp, V. Dissertation University Bochum, 1981.

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