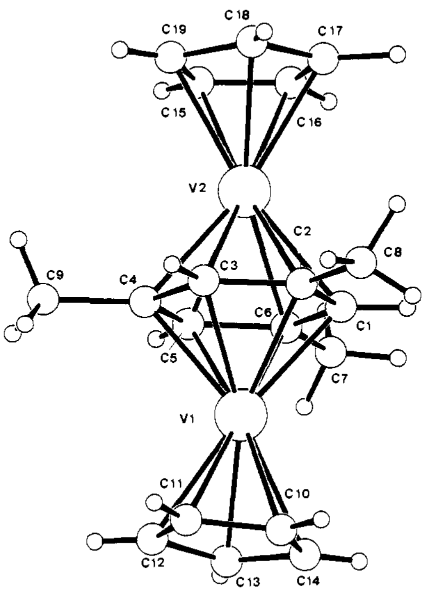


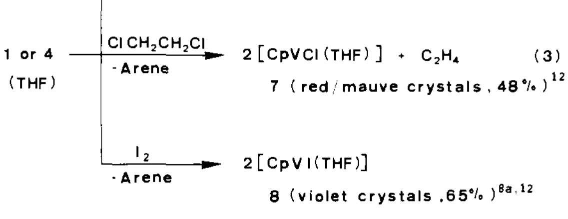
Figure 2. **4** crystallizes in the monoclinic space group $P2_1/a$, $Z = 4$. Cell dimensions are $a = 9.990$ (2) Å, $b = 16.032$ (3) Å, $c = 10.811$ (1) Å, $\beta = 92.81$ (1)°; R 0.045 (R_w 0.050) for 256 parameters and 3906 (2306 observed) reflections.

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 ($C-C_{av}$ 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).



$$\textbf{1}\text{ or }\textbf{4}\ (\text{THF}) \longrightarrow \begin{cases} \xrightarrow[\text{-Arene}]{2\,C_3H_5Cl} 2[\text{CpV}(C_3H_5)\text{Cl}(\text{THF})] & \textbf{6}\ (\text{red crystals, }56\%)^{12} \\ \xrightarrow[\text{-Arene}]{\text{ClCH}_2\text{CH}_2\text{Cl}} 2[\text{CpVCl}(\text{THF})] + C_2H_4 & \textbf{7}\ (\text{red/mauve crystals, }48\%)^{12} \\ \xrightarrow[\text{-Arene}]{I_2} 2[\text{CpVI}(\text{THF})] & \textbf{8}\ (\text{violet crystals, }65\%)^{8a,12} \end{cases} \qquad (3)$$

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).

$$\underset{\textbf{5}}{[\text{CpV}(C_6H_5\text{Pr})]} + I_2 \xrightarrow{\text{THF}} \underset{\textbf{9}\ (\text{dk. red crystals, }52\%)^{12}}{[\text{CpVI}_2(\text{THF})]} + C_6H_5\text{Pr} \qquad (4)$$

In contrast to the known species $(\text{CpVClPR}_3)_2$ and $\text{CpVCl}_2(\text{PR}_3)_2$,[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 $\text{CpCp}^{\text{Me}}\text{V}$ (**10**) in high yield (eq 5).[14]

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

Acknowledgment. Financial Support of the Deutsche Forschungsgemeinschaft is gratefully acknowledged (C.K. and H.-J.K.).

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; $\text{CpV}(C_3H_5)_2$, 86374-53-0; LiCpMe, 54061-45-9; C_3H_5Cl, 107-05-1; $\text{ClCH}_2\text{CH}_2\text{Cl}$, 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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[13] Nieman, J.; Scholtens, H.; Teuben, J. H. *J. Organomet. Chem.* **1980**, *186*, C12.

[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 $(\text{CpVH})_2C_6H_6$ (**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., $\text{Pd}_2(\text{Al}_2\text{Cl}_7)_2(C_6H_6)_2$ and $\text{Pd}_2(\text{AlCl}_4)_2(C_6H_6)_2$,[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 $[\text{Ru}_3(\text{CO})_6(\mu_3\text{-SBu}^+)\{\mu_3\text{-}(\eta^7\text{-}C_7H_7)\}]$[3] or $[\text{Ni}_3(\text{CO})_3(\text{CF}_3\text{C}_2\text{CF}_3)\{\mu_3\text{-}(\eta^8\text{-}C_8H_8)\}]$.[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 $\text{K}[\text{Cp}_2\text{V}]$,[6] a 1:1 adduct between

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[1] (a) Geibel, G.; Wilke, G.; Goddard, R.; Krüger, C.; Mynott, R. *J. Organomet. Chem.* **1978**, *160*, 139. (b) Werner, H. *Adv. Organomet. Chem.* **1981**, *19*, 155–182 and references cited therein.

[2] Allegra, G.; Immirzi, A.; Porri, L. *J. Am. Chem. Soc.* **1965**, *87*, 1394. Allegra, G.; Tettamanti Casagrande, G.; Immirzi, A.; Porri, L.; Vitulli, G. *Ibid.* **1970**, *92*, 289.

[3] Howard, J. A. K.; Kennedy, F. G.; Knox, S. A. R. *J. Chem. Soc., Chem. Commun.* **1979**, 839.

[4] Davidson, J. L.; Green, M.; Stone, F. G. A.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1979**, 506.

[5] Jonas, K.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 520–537. Jonas, K. *Adv. Organomet. Chem.* **1981**, *19*, 97–122.

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

0002-7863/83/1505-5480$01.50/0

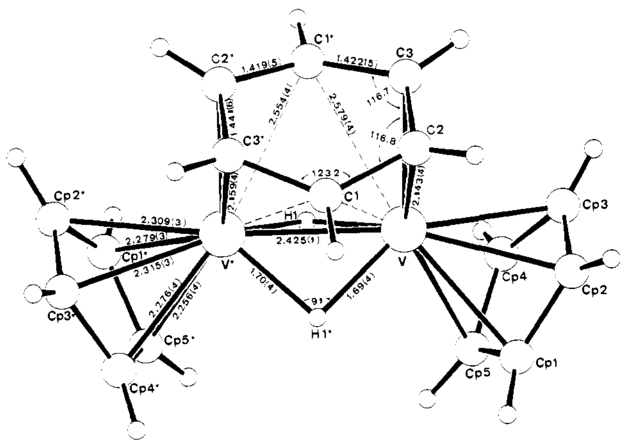

Figure 1.

a metallocene and an alkali metal.[7] Reaction of this deep red compound with 1,3-cyclohexadiene in tetrahydrofuran (THF) yields diamagnetic **1** (dark brown plates, 40%; $M^+ = 312$, ν_{VH_2V} (KBr) 1795, 1701, and 1611 cm^{-1}).

$$2K[Cp_2V] + 1,3\text{-}C_6H_8 \xrightarrow[-78\,°C \to +20\,°C]{THF} \underset{\mathbf{1}}{(CpVH)_2C_6H_6} + 2KCp \qquad (1)$$

The structure of **1** has been determined by a single-crystal X-ray analysis[8] and is shown in Figure 1. Two Cp-V units are bridged by a nonplanar benzene ring as well as two hydrogen atoms in such a way that a 2-fold axis passes through the center of the six-membered ring and the middle of the V-V* link. All hydrogen atoms were located on a difference Fourier synthesis and have been included in the structural refinement. The vanadium distance of 2.425 (1) Å compares favorably with that found in accurate studies of $Cp_2V_2(CO)_5$[9] (2.459 (3) Å) and its triphenylphosphine derivative $Cp_2V_2(CO)_4PPh_3$ (2.466 (1) Å).[10] These compounds contain semibridging carbonyl groups, and the metal-metal bonds have been assigned multiple bonding character. A formal triple bond between two bridged vanadium atoms has been assigned for a metal-metal distance of 2.200 (2) Å in $V_2(2,6\text{-}(MeO)_2Ph)_4\cdot$THF.[11a] Assignment of bond orders to metal-metal bonds, however, seems only to be unambiguous when no bridging groups are linking the metal-metal unit.[11b,12]

There is a noncrystallographic mirror in the plane of C1, C1*, H1, and H1* and a dihedral angle between both planar Cp rings of 69.7°. The interplanar angle in the folded benzene moiety is 19.8°. Whereas all C-C distances within this unit are equal within 3σ (av 1.427 (10) Å), the metal-carbon distances (V-C2 2.143 (4), V-C3 2.159 (4) Å) as well as the angles within the ring (C1-C2-C3 116.8 (3)°, C2-C3-C1* 116.7 (3)°, C2-C1-C3* 123.2 (3)°) are slightly different. The distances to the bridging carbon atoms are 2.554 (4) Å for V-C1 and 2.579 (4) Å for V-C1*. The hydrogen atom attached to this carbon atom is bent by 0.12 Å toward the midpoint between the vanadium atoms. The bridging hydrogen atoms are arranged symmetrically (V-H 1.70 (4), V*-H 1.69 (4) Å, V-H-V* 91 (2)°) and show a nonbonding H-H separation of 1.97 (5) Å.

1 is a fluxional molecule in solution. At −115 °C the ^{1}H NMR spectrum (400 MHz) of a THF-d_8 solution shows four resonances: δ 4.49 (4 H), 2.99 (2 H), 5.49 (10 H, Cp), −2.74 (2 H, bridging hydrogens). Coalescence of the first two resonances into one signal at δ 3.99 occurs at −90 °C. The chemical shift of the vanadium-bound hydrogen remains unaffected between −115 °C and room temperature although the half-width of the signal increases. The ^{13}C NMR spectrum (25.2 MHz) at room temperature shows only two signals (δ 97.9 ($^1J_{CH} = 173 \pm 1$ Hz, Cp), 76.2 ($^1J_{CH} = 169 \pm 1$ Hz, C_6H_6)). On lowering the temperature to −120 °C the signal for the C_6H_6 ring is slightly broadened ($\Delta\nu_{1/2} \approx 20$ Hz), but full coalescence is not achieved. We interpret these results as a rotation of the C_6H_6 ring about its midpoint.

Compound **1** reacts with carbon monoxide according to eq 2.

$$\underset{\mathbf{1}}{(CpVH)_2C_6H_6} + 8CO \rightarrow 2CpV(CO)_4 + 0.75C_6H_8 + 0.25C_6H_6 + 0.25H_2 \qquad (2)$$

Both benzene and 1,3-cyclohexadiene are observed in the condensate of the reaction mixture. Cyclohexadiene is formed as a result of transfer of the metal-bound hydrogen to the C_6H_6 ring, while displacement of the C_6H_6 ring as benzene is accompanied by the evolution of an equimolar amount of hydrogen. Quantitative liberation of benzene and hydrogen was effected by treating **1** with iodine (eq 3). A new vanadium(II) halide is formed, which

$$\underset{\mathbf{1}}{(CpVH)_2C_6H_6} + I_2 \xrightarrow{THF} \underset{\mathbf{2}}{2[CpVI(THF)]} + C_6H_6 + H_2 \qquad (3)$$

may be isolated directly as [CpVI(THF)] (**2**) or as adducts of tertiary phosphines or acetonitrile, e.g., $CpVIP_2$ [$P_2 = 2P(CH_3)_3$, diphos, or $CyPC_2H_4PCy_2$ ($Cy = C_6H_{11}$)] or $CpVICH_3CN$.

Acknowledgment. We thank Drs. Benn and Mynott for carrying out and interpreting the NMR experiments.

Registry No. 1, 86421-59-2; **2**, 86374-51-8; $CpVI(P(CH_3)_3)_2$, 86436-05-7; CpVIdiphos, 86421-61-6; $CpVICy_2PC_2H_4PCy_2$, 86421-62-7; $CpVICH_3CN$, 86421-63-8; K[Cp_2V], 86421-60-5; CO, 630-08-0; I_2, 7553-56-2; 1,3-cyclohexadiene, 592-57-4.

Supplementary Material Available: Atomic coordinates and thermal parameters for **1**, a table of selected interatomic distances and interbond angles, and a list of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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[7] We previously reported 1:1 adducts between alkali metals and metallocenes and between alkali metals and half-sandwich compounds, e.g., $[M(THF)_x][(C_5H_5)_2Co]$ and $[M(THF)_x][C_5H_5CoCOD]$[5] (M = Li or K, COD = 1,5-cyclooctadiene).

[8] **1** crystallizes in the orthorhombic space group *Fdd*2 (No. 43). Cell dimensions: $a = 16.905$ (2) Å, $b = 20.977$ (2) Å, $c = 7.699$ (1) Å, $Z = 8$, $d_{calcd} = 1.52$ g cm^{-3}, $R = 0.028$ ($R_w = 0.036$), 117 parameters refined with 1764 reflections, of which 342 were considered unobserved (2σ).

[9] Fischer, E. O.; Schneider, R. J. *Chem. Ber.* **1970**, *103*, 3648. Cotton, F. A.; Frenz, B. A.; Kruczynski, L. *J. Am. Chem. Soc.* **1973**, *95*, 951. Cotton, F. A.; Kruczynski, L.; Frenz, B. A. *J. Organomet. Chem.* **1978**, *160*, 93.

[10] Huffmann, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1980**, *19*, 2755.

[11] (a) Seidel, W.; Kreisel, G.; Mennenga, H. *Z. Chem.* **1976**, *16*, 492. (b) Cotton, F. A.; Millar, M. *J. Am. Chem. Soc.* **1977**, *99*, 7886.

[12] (a) Cotton, F. A.; Walton. In "Multiple Bonds in Metal Atoms"; Wiley: New York, 1982. (b) Goddard, R.; Krüger, C. In "The Electron Distribution and the Chemical Bond"; Plenum Press: New York, 1982.

Carbene Chemistry of Cations: The Chemistry of :C_3H^+ in the Gas Phase

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Much attention has been directed over the years toward the chemistry of neutral carbenes as reactive intermediates. Here we suggest and explore the notion that carbene character may be associated also with ions. We have chosen the alkynylcarbene cation, :C_3H^+, as our exemplary species.[1] Cationic and carbene character is indicated for this ion by the linear resonance structure (1), which has been shown by molecular orbital theory to be the

$$H\text{-}\overset{+}{C}{=}C{=}C{:} \leftrightarrow H\text{-}C{\equiv}C\text{-}C{:}^+ \qquad (1)$$

most stable form of C_3H^+.[2] In addition to these properties, the

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[1] :C_3H^+ may be regarded as the carbene cation derivative (by hydride abstraction) of vinylidene carbene, $H_2C{=}C{=}C{:}$, or propargylene, $HC{\equiv}C{-}\ddot{C}H$. Alternatively :C_3H^+ may be derived from the protonation at a terminal carbon of the dicarbene, :C=C=C:, which is the process upon which the nomenclature of this species is based.