Synthesis and Characterization of $[Cp_2V(\mu\text{-}\eta^2:\eta^4\text{-butadiyne})ZrCp'_2]$ Heterodimetallic Complexes ($Cp' = C_5H_4t\text{-Bu}, C_5H_4Me$). Formation Mechanism and Theoretical (ELF) Evidence for the Existence of Planar Tetracoordinate Carbon (ptC)

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Reaction of $(C_5H_4R)_2Zr(C{\equiv}CPh)_2$ (R = Me, *t*-Bu) with vanadocene Cp_2V yields the heterodimetallic complexes $Cp_2V(\mu\text{-}\eta^2:\eta^4\text{-butadiyne})Zr(C_5H_4R)_2$ (**4**, R = *t*-Bu; **5**, R = Me). Both compounds have been characterized by elemental analysis, Raman spectroscopy, and magnetic susceptibility. According to the X-ray structure of $Cp_2V(\mu\text{-}\eta^2:\eta^4\text{-butadiyne})Zr(C_5H_4t\text{-Bu})_2$ (**4**), the $[Cp_2V]$ and $[(C_5H_4t\text{-Bu})_2Zr]$ metallocene moieties are bonded to a butadiene framework through the two internal carbon atoms for $[Cp_2V]$ and through the two internal and the two external carbon atoms for $[(C_5H_4t\text{-Bu})_2Zr]$. The distances and angles observed around the internal carbon atoms of the butadiene framework indicate that both carbons are planar and tetracoordinate. These structural considerations are supported by a topological analysis of the electron localization function (ELF). The existence of the $(C_5H_4R)_2Zr(\eta^4\text{:1,2,3,4-}PhC{=}C{=}C{=}CPh)$ (R = H, $SiMe_3$, *t*-Bu, Me) zirconacyclocumulene species as a key intermediate in the formation of the $(Cp_2V(\mu\text{-}\eta^2:\eta^4\text{-butadiyne})Zr(C_5H_4R)_2$ heterodimetallic compounds is evidenced by NMR studies of either the formation of such zirconacyclocumulene species by addition to $(C_5H_4R)_2Zr(C{\equiv}CPh)_2$ of a catalytic amount of Cp_2V or of the formation of compounds **4** or **5** by addition of Cp_2V to $(C_5H_4R)_2Zr(\eta^4\text{:1,2,3,4-}PhC{=}C{=}C{=}CPh)$ (R = *t*-Bu, Me, respectively; synthesized from dialkynyl zirconocene complexes $(C_5H_4R)_2Zr(C{\equiv}CPh)_2$ via $h\nu$ daylight). The X-ray structure of the $(C_5H_4R)_2Zr(C{\equiv}CPh)_2$ (R = H (**6**), *t*-Bu (**7**), $SiMe_3$ (**8**)) dialkynyl zirconocene complexes is also reported.

Introduction

Heterodimetallic complexes associating two transition metals have recently attracted an increasing amount of attention because of their new chemical reaction behavior resulting from the synergistic combination of the properties of both metals which may be utilized in stoichiometric or catalytic reactions.[1] Quite often, an electron-poor metal (Ti, Zr) is associated with an electron-rich metal (Rh, Ru;[2] Ni;[3] Fe, Co, Ni, Cu, Ag[4]). The association in a single molecule of two electron-poor metals is more unusual, and indeed, a limited number of heterodimetallic compounds of group IV−V elements have been described.[5−9]

On the other hand, the organometallic chemical vapor deposition (OMCVD) of thin films of complex materials, i.e., materials containing several elements, requires the availability of appropriate organometallic molecular precursors containing the desired elements. For example, Fischer et al. have obtained Ni−In and Co−Ga thin films by using transition metal substituted indanes and gallanes.[10] One of the goals of our research is to provide heterodimetallic titanium−vanadium molecular

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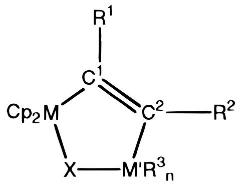
complexes for use as single precursors in the OMCVD of ceramic thin films containing titanium, vanadium, carbon, and nitrogen.[11,12] In the course of this research, the $Cp_2V(\mu\text{-}\eta^2{:}\eta^4\text{-butadiyne})TiCp_2$ (**1**), $Cp_2V(\mu\text{-}\eta^2{:}\eta^4\text{-butadiyne})ZrCp_2$ (**2**), and $Cp_2V(\mu\text{-}\eta^2{:}\eta^4\text{-butadiyne})Zr(C_5H_4SiMe_3)_2$ (**3**) heterodimetallic complexes were prepared, but only the structure of **3** could be fully resolved then.[13]

We report here the synthesis and characterization of two additional members of this series, namely, $Cp_2V(\mu\text{-}\eta^2{:}\eta^4\text{-butadiyne})Zr(C_5H_4\textit{t}\text{-Bu})_2$ (**4**) and $Cp_2V(\mu\text{-}\eta^2{:}\eta^4\text{-butadiyne})Zr(C_5H_4Me)_2$ (**5**), and the crystal structure of **4**. A catalytic mechanism of formation of complexes **1**−**5** based on the identification of the intermediate zirconacyclocumulene species $(C_5H_4R)_2Zr(\eta^4{:}1,2,3,4\text{-PhC}{=}C{=}C{=}CPh)$ (R = H, Me, *t*-Bu, $SiMe_3$) is also proposed in this work and extended to the formation of other related heterodimetallic complexes. The crystal structures of three $(C_5H_4R)_2Zr(C{\equiv}CPh)_2$ (R = H (**6**), *t*-Bu (**7**), $SiMe_3$ (**8**)) dialkynylzirconocene Zr^{IV} compounds, from which the corresponding zirconacyclocumulene species may be generated by irradiation or catalytic process, are also reported.

The existence of planar tetracoordinate carbon (ptC) in complexes **1**−**5**,[13,14] as well as in other transition metal containing organometallic compounds such as complexes **I** (Scheme 1),[15−17] has been postulated on simple structural considerations (in compounds **I**, for example, the sum of bond valence angles around C^2 is close to 360° and the $M{-}C^2$ bond length is within the bonding range). In complexes **I**, ptC atoms were also evidenced on the basis of quantum chemical calculations or electron density investigations. Calculations on model systems of complexes **I** with M = Zr and M′ = Al, B, or Zr show that the model containing ptC is much lower in energy (by 30−50 kcal/mol) than the structural alternative with ordinary three-coordinate sp^2 carbon atoms.[18,19] Extended Hückel orbital analyses show that structures with ptC are mainly stabilized by a strong $Zr(4d){-}C^2(2p)$ σ-bonding interaction visible in the HOMO-1, i.e., the orbital just below the HOMO.[19] The differential density map shows a local maximum that lies inside the $Zr{-}C^2{-}M'$ triangle that is outside the $Zr{-}C^2$ and $C^2{-}M'$ bond lines.[20] The latter observation suggests a multicentric arrangement.[17]

Scheme 1



M = Ti, Zr, Hf
M' = B, Al, Ga, Zr
X = H, Me, Cl, C≡CMe, C≡CPh, C≡C-*c*-Hex
R^1, R^2, R^3 = alkyl, aryl, $SiMe_3$

Recently Becke and Edgecombe[21] proposed an electron localization function (ELF) which provides a new description of the chemical bond.[22] The topological analysis of ELF appears to be very attractive to analyze the existence and nature of the bonding interactions between atoms in molecules and has been already successfully used to describe molecular systems and materials as well.[23,24] It will be used hereafter to discuss the existence of ptC in complexes **1**−**5**.

Experimental Section

General Procedures. All syntheses and subsequent manipulations were carried out under argon by conventional Schlenk tube techniques or using a drybox (Vacuum Atmosphere Dry-Lab) filled with argon. Liquids were transferred via syringe or cannula. All solvents were dried by conventional methods, distilled under argon, and degassed before use. Cp_2V,[25,26] $Cp_2Zr(C{\equiv}CPh)_2$,[27] $(C_5H_4SiMe_3)_2ZrCl_2$,[28] $(C_5H_4\textit{t}\text{-Bu})_2Zr(C{\equiv}CPh)_2$,[29,30] and $(C_5H_4Me)_2Zr(C{\equiv}CPh)_2$[30,31] were prepared according to previously reported procedures. We have reported

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the preparation of $(C_5H_4SiMe_3)_2Zr(C{\equiv}CPh)_2$, $Cp_2V(\mu\text{-}\eta^2{:}\eta^4\text{-butadiyne})TiCp_2$ (**1**), $Cp_2V(\mu\text{-}\eta^2{:}\eta^4\text{-butadiyne})ZrCp_2$ (**2**), and $Cp_2V(\mu\text{-}\eta^2{:}\eta^4\text{-butadiyne})Zr(C_5H_4SiMe_3)_2$ (**3**) in a previous paper.[13] Elemental analyses were performed at the laboratory (C, H). IR spectra were obtained in Nujol using a Perkin-Elmer, model 983G, spectrometer. Raman spectra were obtained using a XY-DILOR Raman spectrometer with a CCD-OMA4 detector and a Notch filter. Magnetic susceptibility measurements were carried out by Faraday's method. EPR spectra were obtained using a BRUKER ESP300E spectrometer. NMR spectra were recorded at room temperature on a Fourier transform NMR spectrometer BRUKER AC200 (at 200.13 MHz for ^1H, and 50.324 MHz for ^{13}C).

$(C_5H_5)_2V(\mu\text{-}\eta^2{:}\eta^4\text{-butadiyne})Zr(C_5H_4t\text{-}Bu)_2$ (4). A solution of $(C_5H_5)_2V$ (90 mg, 0.500 mmol) in toluene (8 mL) is added at room temperature to a solution of $(C_5H_4t\text{-}Bu)_2Zr(C{\equiv}CPh)_2$ (266 mg, 0.500 mmol) in toluene (5 mL) and stirred 3 h. After solvent evaporation under vacuum down to a nearly 6 mL volume of the reaction mixture, pentane (10 mL) is slowly added, resulting in a two-phase solution. After 3 days of slow diffusion, black crystals are filtered off, washed with pentane, and dried under vacuum. Yield: 210 mg (60%); $C_{44}H_{46}VZr$ (MW = 716.7 g mol^{-1}); calcd C 73.73, H 6.42; found C 73.17, H 6.16. IR (Raman) $\nu = 1550$ cm^{-1} (s; C=C).

$(C_5H_5)_2V(\mu\text{-}\eta^2{:}\eta^4\text{-butadiyne})Zr(C_5H_4Me)_2$ (5). A solution of $(C_5H_5)_2V$ (54 mg, 0.30 mmol) in toluene (5 mL) is added at room temperature to a solution of $(C_5H_4Me)_2Zr(C{\equiv}CPh)_2$ (135 mg, 0.30 mmol) in toluene (5 mL). The reaction mixture is left for 24 h. A black crystalline product precipitates, which is filtered off, washed with pentane, and dried under vacuum. Yield: 60 mg (32%); $C_{38}H_{34}VZr$ (MW = 632.6 g mol^{-1}); calcd C 72.14, H 5.42, found C 71.31, H 5.17. IR (Raman): $\nu = 1550$ cm^{-1} (s; C=C).

NMR Experiments. Generation of the Cyclocumulene Species $(C_5H_4R)_2Zr(\eta^4{:}1,2,3,4\text{-}PhC{=}C{=}C{=}CPh)$ (R = H, Me, *t*-Bu, SiMe$_3$). In a typical reaction, $(C_5H_4Me)_2Zr(C{\equiv}CPh)_2$ (52 mg, 0.115 mmol), Cp_2V (2 mg, 0.011 mmol), and 0.5 mL of deuterated benzene or toluene were introduced in an NMR tube wrapped with aluminum foil. The NMR tube was sealed and shaken during the entire experiment time and monitored from time to time by ^1H NMR spectroscopy.

$Cp_2Zr(C{\equiv}CPh)_2$. ^1H NMR (C_6D_6): δ/ppm 7.49−6.90 (Ph), 6.14 (C_5H_5); (THF-d_8): δ/ppm 7.64−7.28 (Ph), 6.57 (C_5H_5). ^{13}C NMR (C_6D_6): δ/ppm 143.3(C(α)), 126.0(C(β)), 125.4(*i*-Ph), 131.9, 128.9, 127.8 (*o*-, *m*-, *p*-Ph), 114.7 (C_5H_5); $(C_5H_4CH_3)_2Zr(C{\equiv}CPh)_2$. ^1H NMR (C_6D_6): δ/ppm 7.49−6.90 (Ph), 6.20, 5.75 ($C_5H_4CH_3$), 2.34 ($C_5H_4CH_3$); ($C_6D_5CD_3$) δ/ppm 7.77−7.20 (Ph), 6.45, 5.99 ($C_5H_4CH_3$), 2.60 ($C_5H_4CH_3$).^{13}C NMR (C_6D_6): δ/ppm 144.6 (C(α)), 126.6 (C(β)), 126.2 (*i*-Ph), 132.0, 128.8, 127.7 (*o*-, *m*-, *p*-Ph), 122.8 ($C(CH_3)$), 114.2, 111.5 (C_5H_4), 16.6 (CH_3).

$(C_5H_4C(CH_3)_3)_2Zr(C{\equiv}CPh)_2$. ^1H NMR (C_6D_6): δ/ppm 7.50−6.90 (Ph), 6.39, 5.78 (C_5H_4), 1.48 ($C(CH_3)_3$); ($C_6D_5CD_3$) δ/ppm 7.67−70 (Ph), 6.60, 6.02 (C_5H_4), 1.71 ($C(CH_3)_3$); (THF-d_8) 7.40−7.0 (Ph), 6.62, 6.24 (C_5H_4), 1.58 ($C(CH_3)_3$). ^{13}C NMR (C_6D_6): δ/ppm 144.9 (C(α)), 142.4 ($CC(CH_3)_3$); (126.2 (C(β)), 124.6 (*i*-Ph), 131.5, 128.9, 127.7, (*o*-, *m*-, *p*-Ph), 111.7, 107.5 (C_5H_4), 33.5 ($C(CH_3)_3$), 32.2($C(CH_3)_3$).

$(C_5H_4Si(CH_3)_3)_2Zr(C{\equiv}CPh)_2$. ^1H NMR (C_6D_6): δ/ppm 7.52−6.90 (Ph), 6.66, 6.00 (C_5H_4), 0.43 ($Si(CH_3)_3$); ($C_6D_5CD_3$) δ/ppm 7.71−7.15 (Ph), 6.89, 6.23 (C_5H_4), 0.67 ($Si(CH_3)_3$). ^{13}C NMR (C_6D_6): δ/ppm 144.5 (C(α)), 126.2 (C(β)), 125.9 (*i*-Ph), 123.4 ($CSiMe_3$), 131.4, 128.9, 127.4, (*o*-, *m*-, *p*-Ph), 121.0, 112.4(C_5H_4), 1.20 ($Si(CH_3)_3$).

$(C_5H_5)_2Zr(\eta^4{:}1,2,3,4\text{-}PhC{=}C{=}C{=}CPh)$. ^1H NMR (C_6D_6): δ/ppm 8.12 (4H, *o*-Ph), 7.71 (4H, *m*-Ph), 7.40 (2H, *p*-Ph), 5.21 (10H, C_5H_5); (THF-d_8) δ/ppm 8.20 (4H, *o*-Ph), 7.50 (4H, *m*-Ph), 7.34 (2H, *p*-Ph), 5.56 (10H, C_5H_5); ^{13}C NMR(C_6D_6) δ/ppm 179.1 (C(α)), 111.7 (C(β)), 137.1 (*i*-Ph), 134.0, 129.4, 128.7 (*o*-, *m*-, *p*-Ph), 104.4 (C_5H_5).

$(C_5H_4CH_3)_2Zr(\eta^4{:}1,2,3,4\text{-}PhC{=}C{=}C{=}CPh)$. ^1H NMR (C_6D_6): δ/ppm 8.05 (4H, *o*-Ph), 7.34 (4H, *m*-Ph), 7.20 (2H, *p*-Ph), 5.40 (8H, C_5H_4), 0.80 (6H, CH_3); (THF-d_8) δ/ppm 8.11 (4H, *o*-Ph), 7.70 (4H, *m*-Ph), 7.40 (2H, *p*-Ph), 5.85, 5.55 (8H, C_5H_4), 1.03 (6H, CH_3). ^{13}C NMR (C_6D_6): δ/ppm 176.7 (C(α)), 114.5 (C(β)), 137.5 (*i*-Ph), 134.0, 129.5, 129.0 (*o*-, *m*-, *p*-Ph), 114.8 ($C(CH_3)$), 106.3, 100.5 (C_5H_4), 13.6 (CH_3).

$(C_5H_4C(CH_3)_3)_2Zr(\eta^4{:}1,2,3,4\text{-}PhC{=}C{=}C{=}CPh)$. ^1H NMR (C_6D_6): δ/ppm 8.10 (4H, *o*-Ph), 7.36 (4H, *m*-Ph), 7.09 (2H, *p*-Ph), 5.80, 5.56 (8H, C_5H_4), 0.62 (18H, CH_3); ($C_6D_5CD_3$) δ/ppm 8.20 (4H, *o*-Ph), 7.65 (4H, *m*-Ph), 7.42 (2H, *p*-Ph), 6.01, 5.80 (8H, C_5H_4), 0.85 (18H, CH_3). ^{13}C NMR ($C_6D_5CD_3$): δ/ppm 180.7 (C(α)), 115.5 (C(β)), 137.5 (*i*-Ph), 133.6, 129.0, 128.5, (*o*-, *m*-, *p*-Ph), 131.3 ($CC(CH_3)_3$) 103.5, 100.0 (C_5H_4), 32.5 ($C(CH_3)_3$), 30.4 ($C(CH_3)_3$).

$(C_5H_4Si(CH_3)_3)_2Zr(\eta^4{:}1,2,3,4\text{-}PhC{=}C{=}C{=}CPh)$. ^1H NMR (C_6D_6): δ/ppm 8.12 (4H, *o*-Ph), 7.34 (4H, *m*-Ph), 7.21 (2H, *p*-Ph), 6.15, 5.67(8H, C_5H_4), −0.25 (18H, CH_3); ($C_6D_5CD_3$) δ/ppm 8.33 (4H, *o*-Ph), 7.66 (4H, *m*-Ph), 7.43 (2H, *p*-Ph), 6.37, 5.91 (8H, C_5H_4), −0.02 (18H, CH_3). ^{13}C NMR (C_6D_6): δ/ppm 180.9 (C(α)), 112.6 (C(β)), 137.4 (*i*-Ph), 134.2, 129.4, 129.1, (*o*-, *m*-, *p*-Ph), 128.5 ($CSi(CH_3)3$) 113.9, 105.2 (C_5H_4), −0.5 ($Si(CH_3)_3$).

These cyclocumulene zirconocene species can be also generated in the same experimental conditions in the presence of daylight and in the absence of Cp_2V.

Generation of 3 and 4 from $(C_5H_4R)_2Zr(\eta^4{:}1,2,3,4\text{-}PhC{=}C{=}C{=}CPh)$ (R = Me, *t*-Bu) and Cp_2V. In a typical experiment, Cp_2V (17 mg, 93 mmol) was added to a toluene solution of $(C_5H_4C(CH_3)_3)_2Zr(\eta^4{:}1,2,3,4\text{-}PhC{=}C{=}C{=}CPh)$ generated from the above experiment made in daylight starting with **7** (50 mg, 93 mmol). After workup, **4** was isolated as a powder and characterized by IR and EPR.

EPR Experiments. In a typical experiment, **4** (11 mg, 15.36 mmol) was dissolved in 0.470 mL of THF, and an aliquot of the solution was introduced into a standardized capillary tube for EPR measurements (**3**: 15 mg, 20 mmol; THF: 0.225 mL). The EPR spectrum was then compared to that of a standardized solution of a sample of $V(NMe_2)_4$, recorded with the same acquisition parameters. Two experiments, at least, were made for **3** and **4** at nearly the same concentration.

Crystallographic Details for $(C_5H_4R)_2Zr(C{\equiv}CPh)_2$ (R = H (6), *t*-Bu (7), SiMe$_3$ (8)) and $Cp_2V(\mu\text{-}\eta^2{:}\eta^4\text{-butadiyne})Zr(C_5H_4t\text{-}Bu)_2$ (4). Crystals of compounds **6**, **7**, **8**, and **4**, sensitive to air and humidity, were obtained by slow diffusion of pentane into a toluene solution of freshly synthesized $(C_5H_4R)_2Zr(C{\equiv}CPh)_2$ or of compound **4**. The selected crystal of each compound was protected in vaseline oil and put into a capillary. Diffraction data were collected on a STOE IPDS diffractometer. Relevant crystal data and data collection parameters are summarized in Table 1. Final unit cell parameters were obtained by least-squares refinement of a set of 5000 reflections per image. Any fluctuations of the intensities were observed over the course of the data collection. A numerical absorption[32] was applied on the diffracted intensities for **4** and **8**.

The structures were determined by using direct methods (SIR92)[33] and refined by standard full-matrix least-squares and Fourier techniques using the SHELXL-97 program package.[34] All hydrogen atoms were located on the final difference

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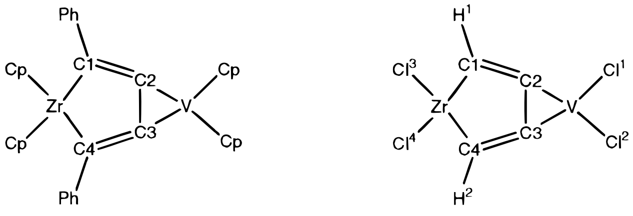
Table 1. Crystallographic Data for Complexes 6, 7, 8, and 4

	6	7	8	4
chemical formula	$C_{26}H_{20}Zr$	$C_{34}H_{36}Zr$	$C_{32}H_{36}Si_2Zr$	$C_{44}H_{46}Zr$
formula weight	423.64	535.85	568.01	716.7
cryst syst	orthorhombic	orthorhombic	orthorhombic	orthorhombic
space group	*Pnma*	*Pna*2_1	*Ccc*2	$P\bar{1}$
Z	4	4	4	4
a, Å	12.559(3)	11.4943(6)	18.078(3)	10.998(2)
b, Å	17.019(3)	18.844(3)	18.908(3)	18.153(4)
c, Å	9.663(2)	12.956(2)	8.5840(12)	18.670(3)
α, deg				80.10(2)
β, deg				86.06(2)
γ, deg				83.72(2)
vol, Å^3	2065.4(7)	2806.2(7)	2934(8)	3646(1)
temp, K	160	160	160	150
goodness of fit on F_2	0.908	1.039	1.051	1.069
R1 [$I > 2\sigma(I)$]	0.0211	0.0304	0.0266	0.0336
wR2	0.0522	0.0633	0.0651	0.0784

Scheme 2



Model **3a** Model **3b**

Fourier maps and refined as a riding model with a fixed isotropic thermal parameter at 20% higher than those of the carbon atoms to which they were connected. All non hydrogen atoms were anisotropically refined. Drawing of the molecules was performed with the program ZORTEP[35] with a 50% probability displacement ellipsoids for non hydrogen atoms.

Attempted X-ray Study of Cp$_2$V(μ-η^2:η^4-butadiyne)Zr(C$_5$H$_4$Me)$_2$ (5). Selected crystals of **5**, sensitive to air and humidity, were protected in vaseline oil and put into capillaries. Diffraction data were collected on a STOE IPDS diffractometer at 180 K. Examination of the profiles of the Bragg reflections indicated that all crystals were of poor quality. A set of diffraction intensities was nevertheless collected, but no quantitative data could be drawn from this study.

Computational Details. The calculations were performed at the DFT level using Gaussian94[36] on model compounds of complex **3** presented in Scheme 2. Model **3a** was obtained from the crystallographic structure (vide infra) by substituting hydrogen atoms for SiMe$_3$ groups. The even simpler model **3b** was derived from the same X-ray diffraction structure by substituting hydrogen atoms for phenyl groups and chlorine atoms for Cp ligands, as it was successfully done in other studies without affecting the essential electronic features of the system under consideration.[37]

Model **3c** was obtained by geometry optimization of model **3b** under C_{2v} symmetry constraint at the ROB3LYP level using a 6-31G* basis except for V and Zr, for which the DGauss DZVP2 and DZVP polarized DFT orbitals basis sets[38] were respectively used. Single-point energy calculations were carried out at the same level on model **3a** and **3b**. ELF calculations and topological analysis were carried out with TopMoD.[39] Visualization of ELF isosurfaces and basins was done with the freeware SciAn.[40]

Topological Analysis of ELF. The bonding in molecules may be investigated by different techniques. The topological methods investigate well-defined local functions. In the theory "atoms in molecules" of Bader,[41] criteria are proposed in order to determine the existence and nature of the bonds from the electron density analysis. Two atoms are bound if a bond path may be found between them. The value of the Laplacian of the charge density at bond critical points allows one to discriminate between closed shell and electron-shared (covalent) interactions. In the latter case, however, it is not possible to distinguish between the formation of an electron pair of opposite spin and the sharing of only one electron. The same type of analysis may be performed using the electron localization function (ELF),[22] but it will additionally allow the measurement of the pairing of the electrons. ELF is defined as ELF $= 1/[1 + (D_\sigma/D_\sigma^0)^2]$, in which D_σ and D_σ^0 are the excess local kinetic energy due to the Pauli repulsion (the difference of the kinetic energy of the actual fermionic system with respect to that of the bosonic system having the same density) for the actual system and for a homogeneous electron gas of the same density, respectively. ELF takes values between 0 and 1. When electrons are alone or form pairs of opposite spin, the Pauli principle has little influence, and ELF is therefore close to 1. However, when parallel spin electrons are close to one another, ELF comes close to 0. The topological analysis of the ELF gradient field yields a partition of the molecular space in basins and attractors (i.e., the local maxima of ELF). The basins are classified into core, valence bonding, and nonbonding basins. A core basin contains a nuclei X (except a proton) and will be referred to as C(X). A bonding basin lies between two or more core basins. Valence bonding basins are further distinguished depending on their connectivity to the core basins. The topological analysis of the gradient field of ELF assigns a region of space—the basin—to each attractors, providing a partition of the molecular space analogous to that made in hydrography to define river basins and watersheds.

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complexes 6, 7, and 8

compound	*d* (Zr−C1) *d*(Zr−C3)	*d*(C1−C2) *d*(C3−C4)	*d*(C2−C5) *d*(C4−C11)	Zr−C1−C2 Zr−C3−C4	Cp−Zr−Cp[a]	C1−Zr−C3	C1−C2−C5 C3−C4−Cl1
6	2.233(2)	1.206(3)	1.434(3)	179.9(2)	134.77	104.53(9)	175.4(3)
	2.251(2)	1.211(3)	1.441(3)	172.8(2)			179.9(3)
7	2.239(5)	1.212(6)	1.421(6)	171.6(4)	132.63	102.64(15)	178.9(4)
	2.250(4)	1.203(5)	1.448(5)	176.8(3)			178.3(4)
8	2.231(3)	1.217(4)	1.440(5)	166.6(3)	130.85	100.16(17)	175.8(5)
$(C_5H_4Me)_2Zr(CCPh)_2$[29]	2.249(3)	1.206(4)	1.462(5)	177.0(3)	132.6	103.6(1)	179.4(4)

[a] Cp is the centroid of the cyclopentadienyl ring (C_5H_4R).

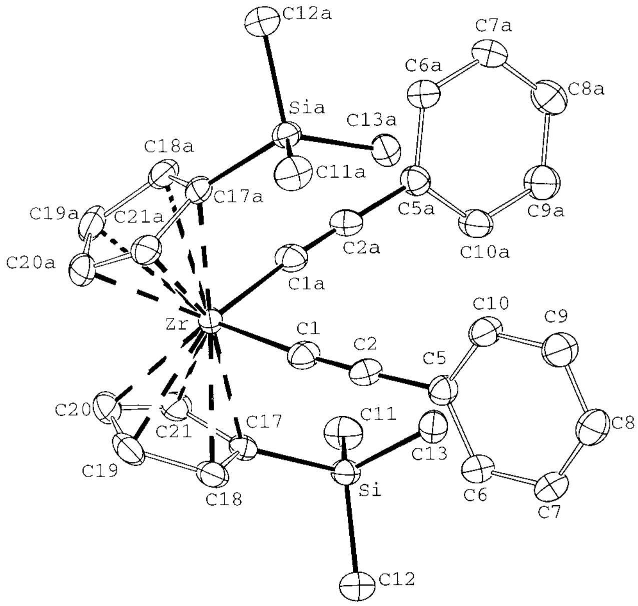

Figure 1. Molecular structure and atom-numbering scheme for $(C_5H_4SiMe_3)_2Zr(C{\equiv}CPh)_2$ (**8**).

Each valence basin is characterized by its synaptic order, which is the number of core basins with which it shares a common boundary. Therefore, the monosynaptic basins correspond to nonbonded pairs (referred to as V(X)), whereas the di- and polysynaptic ones are related to bi- or multicentric bonds (referred to as $V(X_1,X_2,X_3, ...)$). A localization domain is a space region limited by an isoELF surface. It has been shown that ELF performs partitions of the molecular space that are consistent with the Lewis description and with the VSEPR model.

Results and Discussion

Crystal Structure of $(C_5H_4R)_2Zr(C{\equiv}CPh)_2$ (R = H (6), *t*-Bu (7), $SiMe_3$ (8)). The crystal structure of some members of the $Cp_2Zr(C{\equiv}CR)_2$ series (R = Me, *n*-Bu); $Cp_2{}^*Zr(C{\equiv}CPh)_2$) have already been reported.[29] The molecular structure of the additional members **6**, **7**, and **8** were determined by X-ray diffraction methods. Selected bond lengths and angles are listed in Table 2. No significant difference in the structural parameters of **6**, **7**, and **8** is observed. As an example, the molecular structure of **8** is shown in Figure 1.

The Zr−C1, Zr−C3 distances are in the range of Zr−C bond lengths in other organometallic zirconium compounds (for example, 2.27 Å in Cp_2ZrMe_2[42]), which indicates that no significant π-conjugation between the 16-electron Zr center and the π-system of the alkyne ligand takes place. The Cp(centroid)−Zr−Cp(centroid) angles are typical of group 4 metallocene complexes.[43] The C(1)−C(2)−C(5)/C(3)−C(4)−C(11) angles make the carbon skeleton of the phenylethynyl ligand almost linear. The C(2)−C(5)/C(4)−C(11) distances correspond to that of a C(sp)−C(sp^2) single bond. The C(1)−C(2)/C(3)−C(4) distances are close to that of a C≡C bond (1.21 Å in acetylene[44]).

Synthesis and Characterization of Complexes 1−5. Oxidative addition of a diyne on a ligand-stabilized metallocene of a group 4 element or reaction of an alkyne compound of a group 4 element with a Lewis metal complex was proven suitable for obtaining dimetallic complexes.[45−48] Different situations may be encountered depending on the nature of the metal, the substituents on the diyne or alkyne, and the stoichiometry, the simplest situation being the formation of the homodimetallic complex such as $[Cp_2M(\mu\text{-}C{\equiv}CPh)]_2$.[45] Moreover, compounds such as $Cp_2Ti(Me_3SiC{\equiv}CSiMe_3)$, $Cp_2Zr(THF)(Me_3SiC{\equiv}CSiMe_3)$,[49] and $Cp_2Zr(butadiene)$[9] were identified as convenient sources of transient "Cp_2-Ti" and "Cp_2Zr" metallocene species, which can react with alkynes and dialkynes and self-organize to afford [Ti,Ti] and [Zr,Zr] homodimetallic as well as heterodimetallic [Ti,Zr] complexes.[9,16,29,49] The subsequent reaction of these "Cp_2M" species with other metal alkyne systems leads to the formation of new homo- and heterodimetallic complexes with various structural configurations, such as those in which the second metal is a group 11 element[4,48] or Hf.[9] These results showed the way toward heterodimetallic [Ti,V] or [Zr,V] complexes involving the use of acetylenic titanium or zirconium compounds. Moreover, the synthesis of the

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$[Cp_2V(\eta^2\text{-}R^1C_2R^2]$ compound[50] indicated that the oxidative addition of vanadocene Cp_2V to $R^1C{\equiv}CR^2$ alkynes was possible.[51]

Indeed, when reacting the appropriate $(C_5H_4R)_2M(C{\equiv}CPh)_2$ alkyne compound with vanadocene, heterodimetallic complexes were obtained, which were characterized (vide infra) as $[Cp_2V(\mu\text{-}\eta^2\text{:}\eta^4\text{-butadiyne})MCp'_2]$ [**1**: M = Ti, R = H; **2**: M = Zr, R = H; **3**: M = Zr, R = $SiMe_3$; **4**: M = Zr, R = *t*-Bu; **5**: M = Zr, R = Me]. Complexes **1** and **2** are insoluble and **5** is only slightly soluble in common solvents, but **3** and **4** are soluble in THF, toluene, and benzene. Physicochemical characterization of **1**−**3**,[13] **4**, and **5** gave similar indications. Elemental analyses are consistent with the formula corresponding to a 1:1 adduct of the two starting components. The band corresponding to the alkynyl C≡C bonds observed at ≈2065 cm^{-1} in the infrared absorption spectrum of the starting M^{IV} alkyne compound,[4a,52] or at lower frequencies in the range 1960−1850 cm^{-1} when alkynyl groups interact with another metal,[4b,48,53] is not observed in the spectrum of the adduct, but an intense ν(C=C) band at nearly 1600 cm^{-1} appears in the Raman spectra of the adduct. The measured magnetic moments (≈1.73 μB) show that the formal oxidation state of vanadium has been increased from II to IV. The EPR spectrum of **3** in C_6D_6 and of **4** in THF show, as expected, eight lines due to the hyperfine coupling of a single electron with the 7/2 nuclear spin of vanadium ($a(^{51}V) = 42.8$ G).

All these data are clearly indicative of a reaction of vanadocene with both (C≡CPh) alkynyl groups of the starting M^{IV} alkyne compound, leading in all considered cases to heterodimetallic systems containing vanadium^{IV} and zirconium atoms and C=C double bonds. We noted, however, that when the substituent on the alkyne is the $SiMe_3$ group, no reaction was observed with vanadocene.[11] This confirms that the reactivity of M^{IV} alkyne compounds does depend on the nature of the substituents carried by the alkyne.[4b,54]

Crystal Structures of Complexes 2−4. The easiness of solving the crystal structure of the complexes of the series of compounds **1**−**5** seems to be very much dependent on the nature and size of the different substituents on the cyclopentadienyl groups of the metal alkyne compound, let alone the stability and crystal quality. No suitable crystals of **1** could be obtained, mainly because of its insolubility. In the case of the Zr−V complexes **2**[13] and **5**, with substituent H and Me on the Zr cyclopentadienyl groups, respectively, severe difficulties due to statistical disorders in distinguishing between the two metal centers were encountered throughout the refinements. Nevertheless, in both cases, an overall arrangement similar to that observed in the fully resolved structure of **3**[13] and **4** (vide infra) was found.

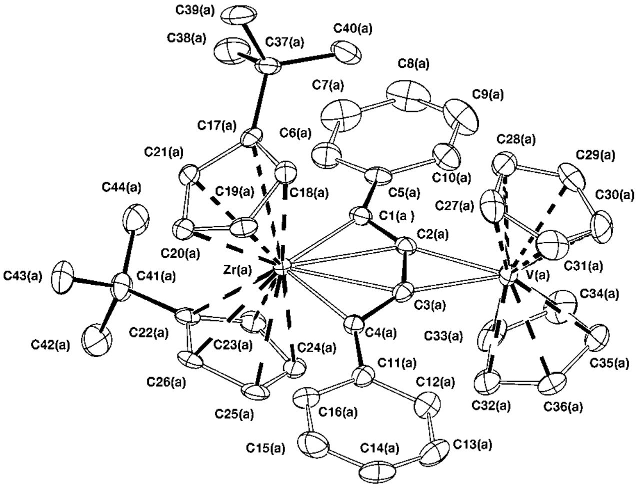

Figure 2. Molecular structure and atom-numbering scheme for the independent molecule (a) of $Cp_2V(\mu\text{-}\eta^2\text{:}\eta^4\text{-butadiyne})Zr(C_5H_4t\text{-Bu})_2$ (**4**).

In the case of complexes **3** and **4**, in which the two metal centers are strongly differentiated by the substituents on their respective cyclopentadienyl groups (H for V, and $SiMe_3$ and *t*-Bu for Zr, respectively), the crystal structure could be fully resolved. The molecular structure of **4** involves two independent (*a*, *b*) but very similar molecules in the unit cell, and Figure 2 is a ZORTEP perspective view of one single molecule (*a*). Selected bond lengths and angles of both molecules are listed in Table 3.

The vanadium atom adopts a metallacyclopropane environment. The V−C2 and V−C3 bond lengths (mean value = 2.12 ± 0.02 Å) are those expected for a V−C σ-bond.[55] The C2−C3 distance, 1.432(5) Å, is characteristic of a single C−C bond in a conjugated system. Thus, the metallacyclopropane vanadium core observed in both motifs of **4** (and also in **3**[13]) is quite different from a metallacyclopropene in which the corresponding C=C bond length is typically 1.25−1.28 Å.[50,55]

On the other hand, the C2−C1−C5 and C3−C4−C11 bond angles (mean value = 127.3 ± 1.2°) are out of the range observed for the corresponding angles (134−148°) in systems containing π-bonded alkynyl C≡C triple bonds.[56] The environment around the zirconium atom could be regarded as a η^4-diene (or η^4-diyne) zirconium structure.[57] Indeed, the C1−C2 and C3−C4 distances (mean value = 1.337 ± 0.002 Å) are in the range of a C=C double bond linkage and similar to the C=C bond length observed in the zirconacyclopropene complex $Cp_2Zr(RC{\equiv}CR')(PMe_3)$ (R = H, R′ = Bu; R = R′ = Ph).[58] The distances of Zr to C1 and C4 (mean value = 2.23 ± 0.02 Å) are as expected for a Zr−C σ-bond (2.27 Å in Cp_2ZrMe_2[42]). The distances from Zr to C2 and C3 (mean

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Table 3. Selected Bond Lengths (a) and Angles (deg) for Complex 4

	molecule *a*	molecule *b*
V−C2	2.133(3)	2.127(3)
V−C3	2.110(3)	2.113(3)
Zr−C1	2.240(3)	2.243(3)
Zr−C2	2.462(3)	2.455(3)
Zr−C3	2.462(3)	2.459(3)
Zr−C4	2.266(3)	2.211(3)
C1−C2	1.334(5)	1.334(5)
C2−C3	1.432(5)	1.436(5)
C3−C4	1.342(5)	1.331(5)
C1−C5	1.465(5)	1.460(5)
C4−C11	1.450(5)	1.458(5)
C2−V−C3	39.45(12)	39.60(12)
C1−Zr−C4	99.04(12)	99.10(12)
C1−Zr−C2	32.53(11)	32.60(11)
C3−Zr−C4	32.78(12)	32.58(12)
C2−Zr−C3	33.82(11)	33.98(11)
C2−C1−C5	126.2(3)	126.5(3)
C2−C1−Zr	82.9(2)	82.5(2)
C5−C1−Zr	150.6(2)	150.7(2)
C1−C2−C3	137.6(3)	138.0(3)
C1−C2−V	152.7(3)	152.1(3)
C3−C2−V	69.38(18)	69.65(18)
C1−C2−Zr	64.55(19)	64.90(18)
C3−C2−Zr	73.10(18)	73.17(17)
V−C2−Zr	142.42(16)	142.80(16)
C4−C2−C2	136.9(3)	136.2(3)
C4−C3−V	151.6(3)	152.9(3)
C2−C3−V	71.17(18)	70.75(17)
C4−C3−Zr	63.92(18)	63.42(18)
C2−C3−Zr	73.08(18)	72.85(17)
V−C3−Zr	144.19(16)	143.59(16)
C3−C4−C11	128.2(3)	128.5(3)
C3−C4−Zr	83.3(2)	84.0(2)
C11−C4−Zr	148.3(2)	147.5(2)

value = 2.462 ± 0.002 Å) are smaller than those of Zr−C(Cp) (mean value = 2.55 Å), but close to the sum of the corresponding van der Waals radii (2.42 Å). This indicates that the Zr atom is coordinated in an olefinic σ-plane fashion to both internal carbon atoms of the butadiene skeleton.[16,18] Thus, the interatomic distances between C2 and C3 to their four neighboring atoms (Zr, V, C1, C3 and Zr, V, C2, C4, respectively) and the 360° value for the sum of the angles around C2, as well as around C3, indicate that these carbon atoms are planar. The environment of the zirconium atom looks as if this atom was connected symmetrically to a four-carbon chain which can be described as a butadiene (or butadiyne) fragment. For comparison, the bonding of the Zr atom to the diene in $Cp_2Zr(\eta^4$-s-*cis*-2,3-dimethylbutadiene) corresponds to similar Zr−C distances (2.300 and 2.597 Å).[59]

The same striking structural features were also observed in the previously reported structure of **3**.[13] Thus, as we did for **3**, we may postulate the presence of planar tetracoordinate carbons (ptC) in the crystal structure of **4** and most probably in that of **1**, **2**, and **5** also and propose that these complexes be designated as $Cp_2V(\mu\text{-}\eta^2{:}\eta^4$-butadiyne)$M(C_5H_4R)_2$.[13,14]

The objection may be raised that the central carbon atoms of the butadiyne (or butadiene) fragment could also be considered as unsaturated, and in that case, their planar tetracoordination could have been expected. Thus, one might alternately consider that the interaction between Zr and these central carbon atoms may be just enforced by the butadiene framework. The question as to whether there is an actual shared-electron interaction between the Zr atom and the central carbon atoms of the butadiyne (or butadiene) fragment will be addressed below using a topological analysis of the electron localization function (ELF).

Theoretical Evidence of ptC in Complex 3. Hypothetical planar methane would be the simpler molecule containing ptC. Orbital models may be used to describe its bonding features. The sp^2 hybridization of the carbon atom yields the σ-bond system where six electrons form the four bonds to hydrogen atoms while the remaining p orbital perpendicular to the bonding plane is occupied by two electrons. This picture by Hoffman et al.[60] suggests that multicentric bonds are required in the σ-plane and allow the design of ways of stabilization of ptC. The planar geometry may be obtained by incorporation of the carbon atom into sterically rigid systems such as small rings or polycyclic systems.[17] Another approach consists of stabilizing the unfavorable coordination by increasing the electron density in the σ-bond system and decreasing it in the π-system. The latter can be achieved either by delocalization into suitable empty orbitals of substituents or by incorporation into a conjugated π-system. Another possibility is to use suitable σ-donor/π-acceptor substituents such as transition metals. V_2(2,6-dimethoxyphenyl)$_4$·THF was the first compound in which the existence of a ptC could be postulated.[15] A number of other supposedly ptC-containing compounds have been subsequently prepared, often incidentally.[16,17] Most of the ptC-containing transition metal complexes reported to date are group 4 homodimetallic[18,61,62] and group 4 and 10 or 13 heterodimetallic complexes.[3,17] For example, in the heterodimetallic complexes **I** depicted in Eiker et al. Scheme 1, the planarity of the $MC^1C^2M'X$ cycle and the sum of the valence angles around C^2 close to 360° led these authors to postulate that this C^2 atom may be a ptC.[17] This was further evidenced from theoretical analysis as already mentioned.[18,19] Ab initio and extended Hückel calculations led these authors to interpret the stabilization of ptC in complex **Ia** (M = Zr, M′ = Al in Scheme 1) in terms of the presence of a σ-acceptor substituent, i.e., the d^0 zirconocene moiety. Moreover, these calculations showed that the π-electron delocalization plays essentially no role in the stabilization of ptC.[18,19] Similar conclusions were reached by Poumbga et al.[20c] for the ptC in V_2(2,6-dimethoxyphenyl)$_4$·THF.[15] On the other hand, in the case of dinuclear cobalt complexes of the general formula $(CpCo)_2(\mu\text{-}CR_2BCR'R'')$, Hyla-Kryspin et al.[20d] showed that the stabilization of ptC follows the strategy proposed by Hoffman et al.,[60] consisting in the accumulation of σ-electron density at the ptC.

The C2 and C3 carbon atoms of the *cis*-butadiene-like bridging ligand in complexes **3**[13] and **4** (Figure 2) exhibit the same structural features as C^2 in complexes **I** and may therefore be recognized as ptC. ELF analyses

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Table 4. Average Populations (*N*) of Selected Basins Obtained from the Topological Analysis of ELF for Models 3a, 3b (see Scheme 2), and 3c, Complex Ib (with M = M′ = Zr, $R^1 = R^2 = CH_3$, R^3 = Cl, the Cp ligands of M Being Substituted by Cl Atoms and *n* = 2; See Scheme 1), and *cis*-Butadiene

basin	model **3a**	model **3b**	model **3c**	complex **Ib**	*cis*-butadiene
V(Zr,C4)	2.0	2.3	2.0		
V(Zr,C1)	1.9	2.3	2.0	V(Zr,C^1) = 2.3	
V(Zr,C2,C3)	2.2	2.2	2.1	V(Zr,C^2,Zr) = 2.6	V(C2,C3) = 2.2
V(Zr,C1,C2)	3.2	3.2	1.7	V(C^1,C^2) = 2.9	V(C1,C2) = 3.4
			1.7		
V(V,C2)	1.5	1.5	1.6		
V(Zr,C3,C4)	3.2	3.2	1.7		V(C3,C4) = 3.4
			1.7		
V(C3,V)	1.5	1.5	1.6		

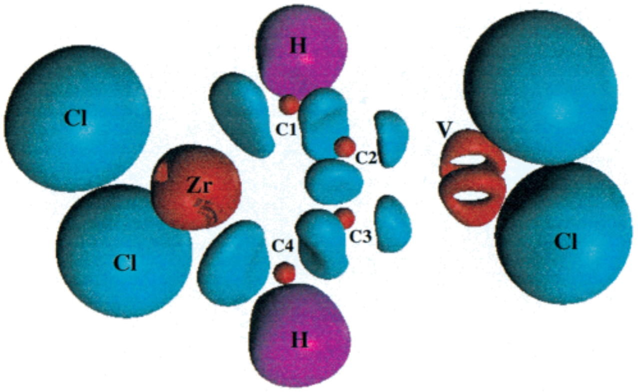


Figure 3. Localization domains corresponding to ELF = 0.8 for model **3b**.

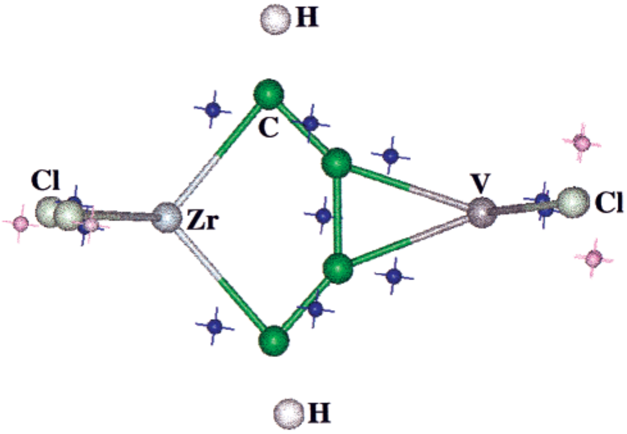


Figure 4. Map of the attractors in model **3b**. Core attractors are connected by sticks. Valence attractors are in blue, and nonbonding attractors are in violet.

of model complex **Ib** (with M = M′ = Zr, $R^1 = R^2 = CH_3$, R^3 = Cl, the Cp ligands of M being substituted by Cl atoms, and *n* = 2; see Scheme 1)[18] and **3** were therefore performed in order to establish this point on a theoretical basis.

The localization domains corresponding to ELF = 0.8 are shown for model **3b** (see Scheme 2) in Figure 3, and the corresponding map of the attractors is shown in Figure 4. Figures 3 and 4 show a clear shared-electron interaction between V and the supposedly planar tetracoordinate carbon atoms C2 and C3 on one hand and between Zr and the carbon atoms C1 and C4 on the other hand. However, no clear evidence of a shared-electron interaction between Zr and the central carbon atoms C2 and C3 is observed. The bridging butadiyne ligand is structurally very close to *cis*-butadiene, as shown by very comparable bond lengths and basin populations as well (Table 4). The valence Zr−C1−C2 angle of 90° is quite unusual for an sp^2 carbon atom such as C1, but the bonding attractors form with the carbon cores and hydrogen atoms a network of bond angles of 120°, as in the *cis*-butadiene, in agreement with the VSEPR model.

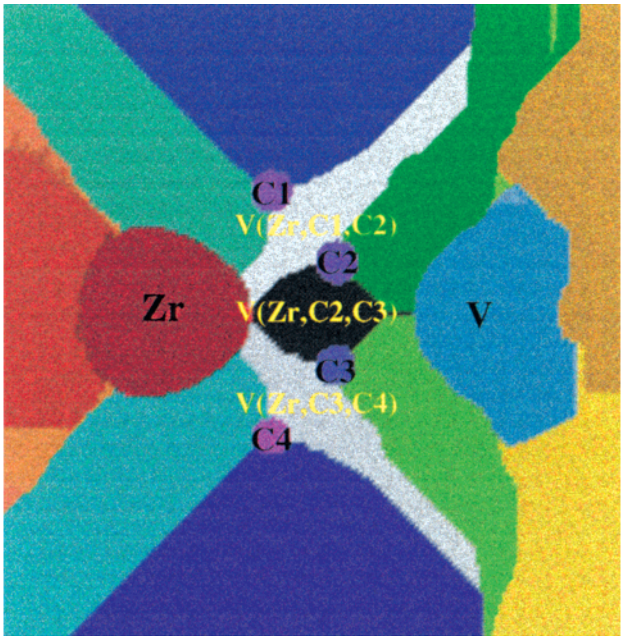


Figure 5. Basin partition map in the molecular symmetry plane of model **3b**. The trisynaptic basins are highlighted in yellow.

The basin partition map in the molecular symmetry plane of model **3b** is shown in Figure 5, whereas the assignment and basin populations are given in Table 4. The core basins of the carbon atoms are easily recognized in blue. Most valence basins are disynaptic because they share a borderline with only two core basins. However three trisynaptic basins may be distinguished, V(Zr,C2,C3), V(Zr,C1,C2), and V(Zr,C3,C4), revealing the existence of three multicentric bonds. The bond associated with the V(Zr,C2,C3) basin is a three-center/2.2-electron bond, whereas the two bonds associated with the V(Zr,C1,C2) and V(Zr,C3,C4) basins are three-center/3.2-electron bonds. This clearly appears from the analysis of the basin population (Table 4). C2 (and C3 as well) appears therefore to be a planar tetracoordinate carbon (for example, C2 is connected to Zr, V, C1, and C3, all lying in the same plane), but is only involved in three multicentric bonds, two of which are three-center bonds.

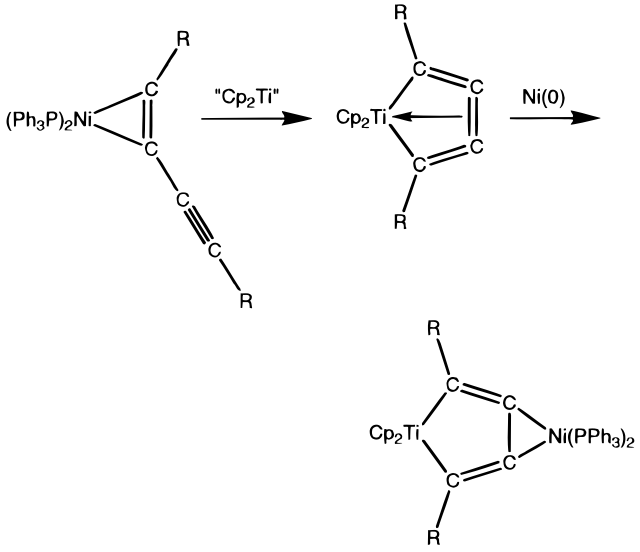
The ELF analysis of model **3a** was restricted to the first coordination sphere of the zirconium and vanadium

Table 5. Comparison of Selected Bonds Lengths (in Å) of the Various Models Studied in this Work

bond	models **3a**, **3b** crystal structure	model **3c**	complex **Ic**[a] crystal structure[18]	complex **Ib**[b] optimized geometry[18]
Zr−C1	2.239	1.742	2.182 ($Zr-C^1$)	2.085
Zr−C2	2.46	1.760	2.508 ($Zr-C^2$)	2.465
Zr−C3	2.46	1.726	2.324 ($Zr'-C^2$)	2.223
Zr−C4	2.207	1.742		
C1−C2	1.330	1.335	1.305	1.344
C2−C3	1.437	1.407		
C3−C4	1.330	1.335		
V−C2	2.129	1.949		
V−C3	2.110	1.949		
V−C1	2.41	2.131		
Zr−C1	2.445	1.969		

[a] Model complex **Ic**: $M = M' = Zr$; $R^1 = R^2 = CH_3$; $R^3 = Cp$; $X = C{\equiv}CPh$; $n = 2$; see Scheme 1. [b] Model complex **Ib**: $M = M' = Zr$; $R^1 = R^2 = CH_3$; $R^3 = Cl$; the Cp ligands of M being substituted by Cl atoms, and $n = 2$; see Scheme 1.

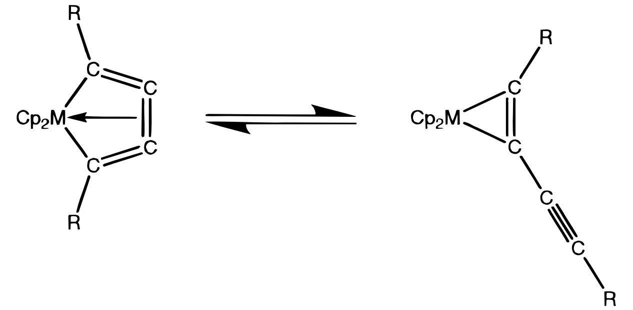
Scheme 3



atoms and is reported in Table 4. Localization domains and basin populations very similar to those of model **3b** are obtained, thus validating the simplifications made to generate model **3b**.

Geometry optimization of model **3b** at the restricted open spin level under C_{2v} symmetry constraint yields model **3c** (Table 5). The Zr−C distances are very much shorter than those determined by X-ray structure analysis from which the models used in this work are derived. Similar calculations, recently reported,[16f] yielded quite longer Zr−C bonds. These discrepancies may be attributed to a basis effect as well as to the replacement of Cp ligands by chlorine atoms and to the resulting electronic effect. A similar tendency was observed during the geometry optimization of complex **Ib** for which the calculations were carried out at a lower level than in the present work.[18] The SOMO of complex **3c** exhibits a large contribution of the d_{z^2} orbital of V, in agreement with the EPR measurements. Indeed the value of the isotropic hyperfine coupling constant $a(^{51}V) = 43$ G obtained for **3**−**5** can be compared to other similar $a(^{51}V)$ values (in the range of 40−45 G) observed for different vanadacyclopropene complexes in which the smaller C−V−C bond angle (35°) mainly reflects the contribution of the d_{z^2} orbital of V in the SOMO.[50c,51] The ELF analysis of model **3c** is in good agreement with the one carried out on model **3b**. In model **3c**, the trisynaptic basins V(Zr,C1,C2) and V(Zr,C3,C4) are now doubled due to the existence of a molecular symmetry plane, as is the case in *cis*-butadiene.

Scheme 4



Mechanism of Formation of Complexes 1−5. The physicochemical characterization of complexes **1**−**5**, the full structure solution of the crystal structure of complexes **3** and **4**, and the results of the ELF analysis have revealed the existence of two ptC's in these complexes. However, at this point, the mechanism of formation of these complexes is still unknown.

The crystal structures of the two [Ti,Ni] and [Zr,Ni] heterodimetallic complexes obtained by reaction of $Ni(PPh_3)(\eta^2\text{-}PhC{\equiv}CC{\equiv}CPh)$ and "Cp_2Ti" or "Cp_2Zr"[3] show the same skeletal arrangement as that observed in compounds **1**−**5**, and the formation of an intermediate zirconacyclocumulene species, $Cp_2Zr(\eta^4\text{:}1,2,3,4\text{-}PhC{=}C{=}C{=}CPh)$, was then suggested (Scheme 3).[3]

Likewise, $Cp_2M(\eta^4\text{:}1,2,3,4\text{-}RC{=}C{=}C{=}CR)$ metallacyclocumulene species (M = Ti, Zr; R = Me, *t*-Bu) have been obtained from $Cp_2Zr(C{\equiv}CMe)_2$ by adding a catalytic amount of $B(C_6F_5)_3$[63] or from $Cp_2Ti(C{\equiv}C\textit{t}\text{-}Bu)_2$ by $h\nu$ irradiation[3] and from $(C_5Me_5)_2Zr(C{\equiv}CR)_2$ (R = Ph, $SiMe_3$) after 4 days in the sunlight.[45,64] Finally, the study of the reactivity of the zirconacyclocumulene species led to a proposition of an equilibrium between the cumulene form and a $(\eta^2\text{-}RC{\equiv}C{-}C{\equiv}CR)$ complex (Scheme 4).[65] It is interesting to note that this proposition has been recently substantiated by the preparation of the $Li[Cp_2Zr(C{\equiv}CPh)(\eta^2\text{:}1,2\text{-}PhC{\equiv}C{-}C{\equiv}CPh)]\cdot 2THF$ complex, which does contain the $(\eta^2\text{:}1,2\text{-}RC{\equiv}C{-}C{\equiv}CR)$ fragment,[14] as well as by the also recent preparation of $(C_5Me_5)_2Ti)(\eta^2\text{:}1,2\text{-}Me_3SiC{\equiv}C{-}C{\equiv}CSiMe_3)]$.[64]

Interestingly, the formation of the zirconacyclocumulene is governed by the nature of the substituents attached to the alkyne. The precursor of "Cp_2Zr" obtained from $Cp_2Zr(L)Me_3SiC{\equiv}CSiMe_3$ (L = THF, pyridine), reacting with $\textit{t}\text{-}BuC{\equiv}CC{\equiv}C{-}C\textit{t}\text{-}Bu$ and $Me_3SiC{\equiv}C{-}C{\equiv}CSiMe_3$, led either to the $Cp_2Zr(\eta^4\text{:}1,2,3,4\text{-}\textit{t}\text{-}BuC{\equiv}C{-}C{\equiv}C\textit{t}\text{-}Bu)$ zirconacyclocumulene or to $[Cp_2Zr(\mu\text{-}\eta^1\text{:}\eta^2\text{-}C{\equiv}CSiMe_3)]_2$.[8] The nature of the substituents on the alkyne also conducts the reactivity between

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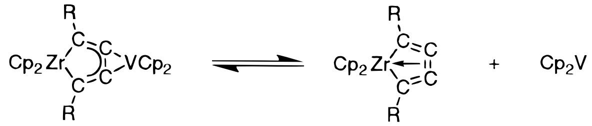
"Cp_2Ti" and $(PPh_3)_2Ni(0)(\eta^2\text{-}RC{\equiv}C{-}C{\equiv}CR')$ ($R = R' = Ph$; $R = Ph$, $R' = SiMe_3$; $R = R' = SiMe_3$) complexes, and three different compounds, depending on the nature of the substituents, were indeed reported by Rosenthal et al.,[66] especially $Cp_2Ti(\mu\text{-}\eta^2{:}\eta^4\text{-}PhC{\equiv}C{-}C{\equiv}CPh)Ni(PPh_3)_2$.[3] It should be also noted that in the $Cp_2Ti(\mu\text{-}\eta^2{:}\eta^4\text{-}PhC{\equiv}C{-}C{\equiv}CPh)Ni(PPh_3)_2$ compound obtained by Rosenthal et al.,[3] as well as in our compounds **1**−**5**, all possessing the same $(\mu\text{-}\eta^2{:}\eta^4\text{-}PhC{\equiv}C{-}C{\equiv}CPh)_5$ arrangement of the central fragment, a phenyl group attached to the alkyne. By contrast, attempts to prepare a similar heterodimetallic complex from Cp_2V and $Cp_2Zr(C{\equiv}CSiMe_3)_2$ failed.[11] On the other hand, the use of different electron-donating R groups on the Cp ring of the dialkyne zirconocene (H in **2**, $SiMe_3$ in **3**, *t*-Bu in **4**, and Me in **5**) does not change the nature of the resulting heterodimetallic [Zr,V] complex.

The transformation of the $(C_5H_4R)_2Zr(C{\equiv}CPh)_2$ (R = H, Me, *t*-Bu, $SiMe_3$) dialkynylzirconocene precursors (50−60 mmol dissolved in 0.50 mL of deuterated benzene or toluene) into the corresponding $(C_5H_4R)_2Zr(\eta^4{:}1,2,3,4\text{-}PhC{=}C{=}C{=}CPh)$ zirconacyclocumulene species was followed by ^1H NMR in a sealed tube in day light. After nearly 2 days, the formation of ≈70−80% $(C_5H_4R)_2Zr(\eta^4{:}1,2,3,4\text{-}PhC{=}C{=}C{=}CPh)$ was observed, and became complete 2 days later. The ^1H NMR spectra show the appearance of a characteristic doublet of multiplets for the *ortho* protons of the phenyl group at low field (≈8.15 ppm). Moreover an important high-field shift is observed for the protons of the cyclopentadienyl rings when comparing to the ^1H NMR of the starting dialkynyl zirconocene complexes ($\delta(C_5H_4R)$/ppm (C_6D_6), $(C_5H_4R)_2Zr(\eta^4{:}1,2,3,4\text{-}PhC{=}C{=}C{=}CPh)$ versus $(C_5H_4R)_2Zr(C{\equiv}CPh)_2$, R = H: 5.21/6.14; R = Me: 5.40, 0.92/6.22, 5.72, 2.34; R = *t*-Bu: 5.80, 5.56, 0.62/6.39, 5.78, 1.48; R = $SiMe_3$: 6.15, 5.67, −0.25/6.66, 6.00, 0.43; see Experimental Section). Likewise, the ^{13}C NMR spectrum shows peaks at ≈110 and 180 ppm similar to those observed in the spectrum of $Cp_2Zr(\eta^4{:}1,2,3,4\text{-}t\text{-}BuC(\alpha){=}C(\beta){=}C{=}Ct\text{-}Bu)$ at 105.5 and 186.4 ppm attributed to $C(\beta)$ and $C(\alpha)$, respectively.[45,64] These reactions do not occur in the absence of daylight when the probes were wrapped in aluminum foil. Finally, complexes **4** and **5** could be generated by treating the corresponding cyclocumulene species with a stoichiometric amount of Cp_2V.

The observed reaction between the bis(phenylethynyl)metallocene and vanadocene and the formation of the heterodimetallic [M,V] compounds may be understood as resulting from the partial transfer of the phenylethynyl group from M to vanadium. With this hypothesis, the most reasonable mechanism would involve the migration of the $C{\equiv}CPh$ moiety from the Zr environment to the vanadium environment, while the zirconium atom would establish bonding to four carbon atoms within a $\mu\text{-}\eta^2{:}\eta^4$-butadiyne arrangement. The possible involvement of Cp_2V as catalyst to form the zirconacyclocumulene-containing complex $(C_5H_4R)_2Zr(\eta^4{:}1,2,3,4\text{-}PhC{=}C{=}C{=}CPh)$ was also checked by ^1H NMR. The reaction was carried out in a sealed tube in the absence of daylight and monitored from time to time. $(C_5H_4R)_2Zr(C{\equiv}CPh)_2$ (R = H, Me, *t*-Bu, $SiMe_3$) was completely transformed within 2−3 days into $(C_5H_4R)_2Zr(\eta^4{:}1,2,3,4\text{-}PhC{=}C{=}C{=}CPh)$ by adding a catalytic amount of Cp_2V (ratio 10:1). Thus, both pathways, i.e., irradiation and/or Cp_2V catalysis, lead to the same zirconacyclocumulene species, and their relative importance in our reactions is difficult to assess. Nevertheless, our results clearly show that (i) the two $C{\equiv}CPh$ alkynyl moieties of $Cp'_2Zr(C{\equiv}CPh)_2$ undergo a C−C coupling, vanadocene being actually involved in the mechanism of formation of compounds **1**−**5** through a transfer of the $C{\equiv}CPh$ moiety from Zr to V, and (ii) a zirconacyclocumulene species is a key intermediate in this mechanism.

Scheme 5



The formerly intriguing presence of sharp NMR signals corresponding to the zirconacyclocumulene species in the ^1H and ^{13}C NMR spectra of **3** and **4** despite the presence of a paramagnetic center in those molecules[13] may be now explained by some partial dissociation of these complexes in solution (Scheme 5). This dissociation was estimated by EPR spectroscopy to 10−20% for a solution of **3** and **4** in THF by comparison to the EPR spectrum of a known standardized solution of $V(NMe_2)_4$ (the signal of the Cp_2V is EPR silent at room temperature[67]).

The formation of the zirconacyclocumulene species may proceed through the catalytic cycle proposed in Scheme 6.

The formation of complexes **2**−**5** from the reaction of Cp_2V with the $(C_5H_4R)_2Zr(\eta^4{:}1,2,3,4\text{-}PhC{=}C{=}C{=}CPh)$ zirconacyclocumulene species may restrain the catalytic process. Whereas the existence of the intermediate zirconacyclocumulene species has been evidenced by NMR studies, their actual involvement in the formation of **1**−**5** as depicted in Scheme 6 remains to be proven. However, it should be noted that analogous homo- and heterodimetallic $Cp_2Ti(C{\equiv}CR)_2]MX$ compounds (M = Cu, Ag) (type {*A*} in Scheme 6),[68] namely, $[(Me_2Si(C_5H_4)_2)Ti(\sigma\text{-}C{\equiv}CR)]_2$, $Cp_2M(\mu\text{-}\eta^1{:}\eta^2\text{-}C{\equiv}CR)(\mu\text{-}\eta^1{:}\eta^2\text{-}C{\equiv}CR)M'Cp_2$ (M = M′ = Ti; M = M′ = Zr; M = Ti, M′ = Hf), as well as Cp_2Ti(1,4-disubstituted ($\mu\text{-}\eta(1,3)\eta(2{-}4)$-*trans*,*trans*-butadiene)$TiCp_2$ (type {*B*}[69] or {*B*′})[70] compounds, have been described in the literature and could mimic the proposed {*A*} and {*B*} intermediate species.[4e] However, another mechanism based on a pathway from *A* to *C* via the thermodynamically more stable zirconacyclocumulene species, possibly present at a very low concentration in the solution, cannot be excluded.[16f]

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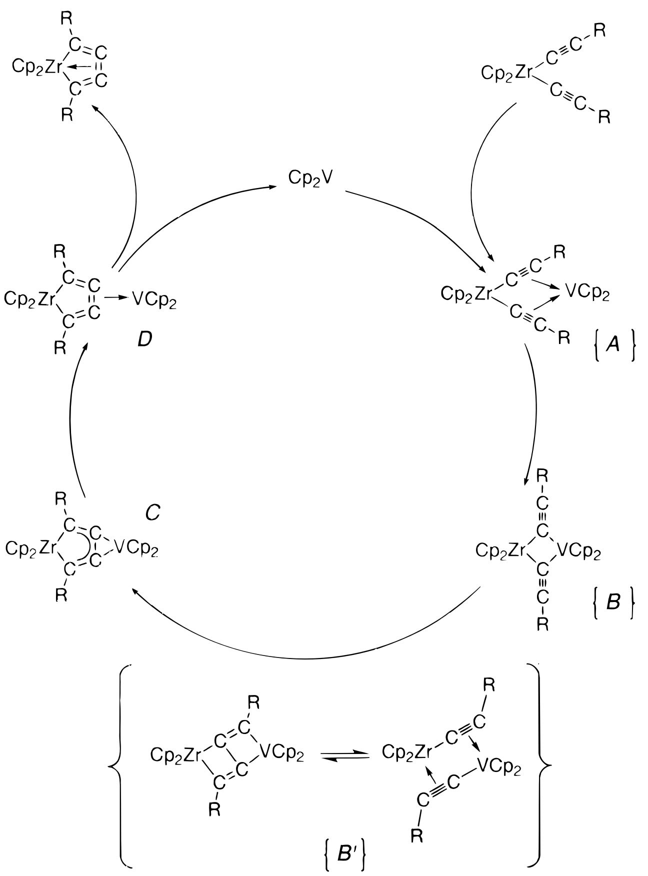
Scheme 6



It may be quite possible that the mechanism proposed above, involving a zirconacyclocumulene intermediate, also applies in the case of other diacetylenic Zr and Ti complexes. A similar mechanism was proposed for the reaction of monoacetylenic complexes with group 11 elements, in which the acetylene is π-bounded to the Zr(II) species.[62a]

Conclusions

The synthesis and characterization of five $[Cp_2V(\mu\text{-}\eta^2:\eta^4\text{-butadiyne})MCp'_2]$ heterodimetallic complexes ($M = Ti, Zr$; $Cp' = C_5H_5$, $C_5H_4SiMe_3$, $C_5H_5t\text{-}Bu$, $C_5H_4\text{-}Me$), and some striking features in their structure, led us to postulate that these complexes may contain two planar tetracoordinate carbon atoms (ptC).

This claim was confirmed by ELF analysis, which reveals the existence of three multicentric bonds involving the Zr atom and the four carbon atoms of the butadiyne fragment. The existence of electron-shared interactions between each of the two central carbon atoms of the butadiyne fragment and four neighbors (for example, C2 interacts with Zr, V, C1, and C3) is established. Both these central carbon atoms are each involved in three bonds, two of which are three-center bonds. Therefore, these central carbon atoms may be considered as planar tetracoordinate.

A mechanism of formation of the $[Cp_2V(\mu\text{-}\eta^2:\eta^4\text{-butadiyne})MCp'_2]$ compounds **1**−**5** is proposed that involves, as experimentally confirmed, the catalytic production of a zirconacyclocumulene species, the existence of which was previously suggested in the formation of similar heterodimetallic Ti−Ni and Zr−Ni complexes.[3] This mechanism may be generalized and applied to the formation of a number of related metal complexes, containing only one ptC electronically stabilized by σ-donor/π-acceptor interaction.[16,17,71]

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Supporting Information Available: Tables giving full crystallographic details, positional and thermal parameters, and bond distances and angles for **6**, **7**, **8**, and **4**. An X-ray crystallographic file, in CIF format, is also available. This material is available free of charge via the Internet at http://pubs.acs.org.

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[71] See Chart 1 in ref 14.