[Cp$_2$V(μ-η^2:η^4-butadiyne)MCp$'_2$] (M = Ti, Zr; Cp$'$ = C$_5$H$_5$, C$_5$H$_4$SiMe$_3$): Heterodimetallic Complexes from a Bis(alkynyl)metallocene and Vanadocene—Unexpected Structure of [Cp$_2$V(μ-η^2:η^4-butadiyne)Zr(C$_5$H$_4$SiMe$_3$)$_2$] Containing Two Planar-Tetracoordinate Carbon Atoms**

Christine Danjoy, Jianshe Zhao, Bruno Donnadieu, Jean-Pierre Legros, Lydie Valade, Robert Choukroun,* Antoine Zwick, and Patrick Cassoux

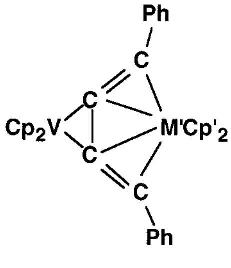
Abstract: The reaction of [Cp$_2$Ti(C≡CPh)$_2$], [Cp$_2$Zr(C≡CPh)$_2$], or [(C$_5$H$_4$SiMe$_3$)$_2$Zr(C≡CPh)$_2$] with vanadocene in toluene at room temperature gives [Cp$_2$V(μ-η^2:η^4-butadiyne)MCp$'_2$] **1** (M = Ti, Cp$'$ = C$_5$H$_5$), **2** (M = Zr, Cp$'$ = C$_5$H$_5$), or **3** (M = Zr, Cp$'$ = C$_5$H$_4$SiMe$_3$), respectively. These compounds, which have been characterized by elemental analysis, mass spectrometry, IR and Raman spectroscopy, exhibit similar magnetic susceptibilities. According to an X-ray diffraction analysis of **3**, the [Cp$_2$V] and Cp$'_2$Zr metallocene moieties are bonded to a butadiene (or butadiyne) framework through the two internal carbon atoms for [Cp$_2$V], and though the two internal and the two external carbon atoms for [Cp$'_2$Zr]. The two internal carbon atoms of the butadiene skeleton are planar and tetracoordinated.

Keywords: heterodimetallic complexes · structure elucidation · titanium · vanadium · zirconium

Introduction

The organometallic chemical vapor deposition (OMCVD) of thin films of complex materials, that is 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.[1] The ultimate goal of our work is to prepare heterodimetallic titanium–vanadium molecular complexes for use as single-source precursors in the OMCVD of ceramic thin films containing titanium, vanadium, carbon, and nitrogen.[2] From a more general point of view, the preparation of heterodimetallic complexes has recently attracted an increasing amount of attention. This is attributed to the new chemical reactivity that arises from the synergistic combination of the properties of both metals; this reactivity may be utilized in stoichiometric or catalytic reactions.[3] Most often, an electron-poor metal (Ti, Zr) is combined with an electron-rich metal (Rh, Ru).[4] The combination of two electron-poor metals in a single molecule is more unusual, and indeed, very few heterodimetallic compounds containing elements from Groups 4 and 5 have been described. Among the known compounds are the [Cl$_3$TiCl$_3$VCl$_3$](PPh$_4$) salt,[5] the oxygen-bridged [(Cl)(acacen)V-O-TiCl$_3$(thf)$_2$] compound (acacen = *N*,*N*$'$-bis(acetylacetone)ethylenediamine),[6] and the [(tBuη^5-C$_5$H$_4$)$_2$Zr(η^1-1,η^1-1$'$)(η^6-C$_6$H$_5$)$_2$V] complex.[7] A number of possible synthetic routes towards titanium–vanadium organometallic complexes have been previously explored in our group without much success.[2, 8]

We report here on the synthesis of the first titanium–vanadium and zirconium–vanadium organometallic complexes, [Cp$_2$V(μ-η^2:η^4-butadiyne)MCp$'_2$], **1** (M = Ti, Cp$'$ = C$_5$H$_5$), **2** (M = Zr, Cp$'$ = C$_5$H$_5$), and **3** (M = Zr, Cp$'$ = C$_5$H$_4$SiMe$_3$) from bi-



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[*] R. Choukroun, C. Danjoy, J. Zhao,[+] B. Donnadieu, J.-P. Legros, L. Valade, P. Cassoux
Equipe Précurseurs Moléculaires et Matériaux
Laboratoire de Chimie de Coordination du CNRS
UPR 8241 liée par convention à l'Université Paul Sabatier de Toulouse
205 Route de Narbonne, F-31077 Toulouse Cedex (France)
Fax: (33) 05-61-55-30-03
A. Zwick
Laboratoire de Physique des Solides
118 Route de Narbonne, 31062 Toulouse Cedex 4 (France)
Fax: (33) 05-61-55-62-33

[+] Permanent address ;
Department of Chemistry, Northwest University
Xi'an 710069 (P. R. China)

[**] Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/chemistry/ or from the author.

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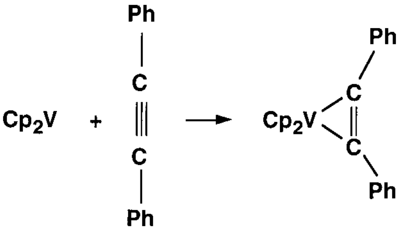
s(alkynyl)metallocene, $[Cp'_2M(C\equiv CPh)_2]$, and vanadocene. These compounds have been characterized by mass spectrometry, magnetic susceptiblity measurements, and IR and Raman spectroscopy. The structural arrangement in compounds has been confirmed by an X-ray crystal structure determination of compound **3**.

Results and Discussion

The reactivity of alkyne triple bonds in substituted titanocene and zirconocene compounds has recently been extensively studied.[9–13] In this regard, titanium–silver and titanium–copper compounds have been prepared by Lang et al,[14] and the oxidative addition of $[Cp_2Hf(C\equiv CPh)_2]$ by $[Cp_2Zr(butadiene)]$ has been found to give $[Cp_2Hf(\mu\text{-}C\equiv CPh)\text{-}ZrCp_2]$.[10a] In addition the formation mechanism of $[Cp_2V(\eta^2\text{-}R^1CCR^2)]$ (Scheme 1, $R^1 = R^2 = Ph$) has revealed



Scheme 1.

that the oxidative addition of vanadocene (the oxidation state of vanadium increases from II to IV) to $R^1C\equiv CR^2$ alkynes is possible.[15] Thus, a new route to heterodimetallic titanium–vanadium or zirconium–vanadium complexes can be envisaged based on the reaction of the appropriate acetylenic titanium or zirconium compounds with vanadocene.

Abstract in French: *La réaction de $[Cp_2Ti(C\equiv CPh)_2]$, $[Cp_2Zr(C\equiv CPh)_2]$, ou $[(C_5H_4SiMe_3)_2Zr(C\equiv CPh)_2]$, avec le vanadocène, dans le toluène et à la température ambiante, permet d'obtenir les composés de formule générale $[Cp_2V(\mu\text{-}\eta^2{:}\eta^4\text{-butadiyne})MCp'_2]$ avec, respectivement, $M = Ti$, $Cp' = C_5H_5$, (**1**), $M = Zr$, $Cp' = C_5H_5$ (**2**), ou $M = Zr$, $Cp' = C_5H_4SiMe_3$, (**3**). Ces composés ont été caractérisés par analyse élémentaire et spectrométrie de masse. Des mesures de susceptibilité magnétique indiquent que dans ces trois composés l'état d'oxydation formelle du vanadium est IV. Des études par spectroscopies IR et Raman montrent la disparition des liaisons C≡C des composés de départ, et leur remplacement dans les composés **1**–**3** par des liaisons C=C. Une étude de diffraction des rayons X a permis de déterminer la structure cristalline du composé **3**. Cette structure est caractérisée par le fait que l'entité $[Cp_2V]$ est liée aux atomes de carbone internes d'un fragment butadiène, tandis que l'entité $[Cp'_2Zr]$ est liée à la fois aux atomes de carbone internes et aux atomes de carbone externes de ce même fragment butadiène. La tétra-coordination des deux atomes de carbone internes du fragment butadiène est, de manière inattendue, située dans un plan.*

The reaction of $[Cp_2Ti(C\equiv CPh)_2]$ or $[Cp_2Zr(C\equiv CPh)_2]$ with vanadocene in toluene at room temperature afforded compounds **1** and **2** as brown solids in yields of 80 and 90%, respectively. Compound **1** seems to be moderately stable in air and is insoluble in common organic solvents. The same compounds are also obtained when these reactions are performed in THF. Elemental analysis and mass spectrometry (chemical ionization with methane)[16] gave results consistent with the $C_{36}H_{30}TiV$ formula. The IR absorption band corresponding to the alkynyl C≡C bonds, which appears at 2065 cm^{-1} in the IR spectrum of the starting $[Cp_2Ti(C\equiv CPh)_2]$ compound,[9] or at lower frequencies in the range between 1960 and 1850 cm^{-1} when alkynyl groups interact with another metal,[14, 17] is not present in the spectrum of the titanium–vanadium compound **1**.[16] Moreover, the measured magnetic moment of 1.73 μB is consistent with the presence of one single electron in the molecule and indicates that the formal oxidation state of vanadium has increased from II to IV. These findings provided the first clear indications that vanadocene had reacted with the two (C≡CPh) alkynyl groups.

The disappearance of the $\nu(C\equiv C)$ band in the IR spectrum of **1** should be accompanied by the formation of bands corresponding to C=C bonds;[18] however, this was not clear in the IR spectrum because of its complexity in the relevant spectral range, but was conspicuous in the Raman spectrum. Indeed, in the Raman spectrum of the starting $[Cp_2Ti(C\equiv CPh)_2]$ compound, the $\nu(C\equiv C)$ band is clearly observed at 2070 cm^{-1}. Another band found at 1600 cm^{-1} may be assigned to the aromatic phenyl groups.[16] This $\nu(C\equiv C)$ band is not observed in the spectrum of the titanium–vanadium compound **1**, but an intense band with a shoulder appears at 1600 cm^{-1}. This band is assigned to C=C bonds, and the shoulder is attributed to phenyl group bonds. The assignments were verified by comparing these Raman spectra with those of phenyl acetylene and styrene,[16] the Raman spectrum of phenyl acetylene displays a strong band corresponding to the C≡C bond at $\nu = 2090\ cm^{-1}$ and a less intense band for the phenyl group at $\nu = 1600\ cm^{-1}$, and the Raman spectrum of styrene, displays a strong band with a shoulder characteristic of the C=C bonds at 1570–1550 cm^{-1}.

As mentioned above, complex **1** is insoluble in most common organic solvents, and attempts at recrystallization of the compound, as well as at crystal growth by a slow diffusion reaction of the two component molecules were unsuccessful. Thus, since it is known that zirconium compounds usually crystallize better than their titanium analogues, we prepared the zirconium–vanadium analogue of **1** by using the analogous acetylenic zirconium complex $[Cp_2Zr(C\equiv CPh)_2]$. The resulting compound **2** was characterized by elemental analyses, mass spectrometry, [16] IR spectroscopy (no $\nu(C\equiv C)$ band was observed), [16] Raman spectroscopy ($\nu(C=C)$ bands observed at 1570 (sh) and 1550 (s) cm^{-1}), [16] and magnetic measurements (magnetic moment of 1.65 μB). In this case we were able to grow crystals of **2** by a slow diffusion reaction of the two component molecules. Although these crystals seemed, at first sight, to be of sufficient quality for an X-ray structural determination, examination of the profiles of the Bragg reflections indicated that all of the crystals were of very poor quality. However a set of diffraction intensities was collected (see Experimental Section). A tentative refinement of this data led to a disordered structure: the Fourier syntheses indicated that the electron density at both metal centers was almost identical. Nevertheless, the resulting overall molecular arrangement[16] was found to be similar to that observed in the fully resolved structure of $[Cp_2V(\mu\text{-}\eta^2{:}\eta^4\text{-butadiyne})Zr(C_5H_4SiMe_3)_2]$ (**3**, vide infra).

Faced with this difficulty in distinguishing between the two metal centers in the structure solution, we prepared an analogue of compound **2** in which the two metal centers could be differentiated readily by the substituents on their respective cyclopentadienyl groups. Thus treatment of $[(C_5H_4SiMe_3)_2Zr(C{\equiv}CPh)_2]$ with vanadocene according to a procedure similar to that used for **2** resulted in a crystalline black product **3** in 55 % yield. Compound **3** was characterized by elemental analysis, IR spectroscopy (no ν(C≡C) band was observed),[16] Raman spectroscopy (ν(C=C) band observed at 1550 (s) cm^{-1}), and magnetic measurements (magnetic moment of 1.73 μB). This compound can be described, like compounds **1** and **2**, as a heterodimetallic structure containing vanadium(IV), zirconium atoms, and C=C bonds. Good quality single crystals of **3** were obtained by a slow diffusion reaction of the two component molecules, and the crystal structure was determined by X-ray diffraction.

Table 1. Selected intramolecular interatomic distances [Å] and bond angles [°] for compound **3**.

Zr–C1	2.224(3)	Si1–C5	1.869(4)
Zr–C2	2.458(3)	Si1–C6	1.874(4)
Zr–C3	2.459(3)	Si1–C7	1.864(4)
Zr–C4	2.235(3)	Si1–C21	1.864(4)
Zr–Cp$_1$*	2.260(av)	Si2–C8	1.878(5)
Zr–Cp$_2$	2.256(av)	Si2–C9	1.872(5)
V–C2	2.112(3)	Si2–C10	1.863(5)
V–C3	2.117(3)	Si2–C15	1.871(4)
V–Cp$_3$	1.937(av)	C1–C2	1.336(5)
V–Cp$_4$	1.947(av)	C1–C51	1.482(4)
		C2–C3	1.447(5)
		C3–C4	1.331(5)
		C4–C61	1.478(4)
C1-Zr-C2	32.7(1)	Zr-C1-C2	83.3(2)
C1-Zr-C3	66.9(1)	Zr-C1-C51	148.2(2)
C2-Zr-C3	34.2(1)	C2-C1-C51	128.4(3)
C1-Zr-C4	99.4(1)	Zr-C2-V	143.0(2)
C2-Zr-C4	66.7(1)	Zr-C2-C1	64.0(2)
C3-Zr-C4	32.5(1)	V-C2-C1	152.9(3)
Cp$_1$-Zr-Cp$_2$	133.7(av)	Zr-C2-C3	72.9(2)
C2-V-C3	40.0(1)	V-C2-C3	70.2(2)
Cp$_3$-V-Cp$_4$	142.0(av)	C1-C2-C3	136.9(3)
C5-Si1-C6	107.7(2)	Zr-C3-V	142.5(2)
C5-Si1-C7	107.8(2)	Zr-C3-C2	72.8(2)
C6-Si1-C7	110.3(2)	V-C3-C2	69.8(2)
C5-Si1-C21	106.6(2)	Zr-C3-C4	64.4(2)
C6-Si1-C21	110.1(2)	V-C3-C4	152.5(3)
C7-Si1-C21	114.1(2)	C2-C3-C4	137.2(3)
C8-Si2-C9	106.4(2)	Zr-C4-C3	83.0(2)
C8-Si2-C10	108.7(3)	Zr-C4-C61	148.0(2)
C9-Si2-C10	109.5(2)	C3-C4-C61	129.0(3)
C8-Si2-C15	116.8(2)		
C9-Si2-C15	107.0(2)		
C10-Si2-C15	108.4(2)		

[a] Cp are the centroids of the cyclopentadienyl rings. Cp$_1$: C11–C15; Cp$_2$: C21–C25; Cp$_3$: C31–C35; Cp$_4$: C41–C45.

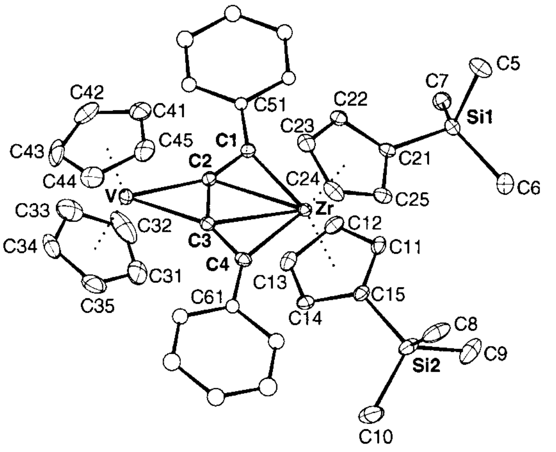
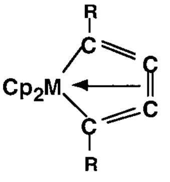
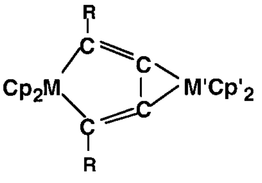


Figure 1. Molecular structure and atom numbering scheme for compound **3** (for clarity only one atom has been labeled for the phenyl rings).

The molecular structure of **3** is shown in Figure 1 and selected bond lengths and angles are listed in Table 1. Several striking features of the bonding arrangement in **3** are worthy of mention. First, the vanadium atom resides in a metallacyclopropane environment: the V–C2 and V–C3 bond lengths are in the range expected for a V–C σ bond,[18] and the C2–C3 distance (1.447 Å) is characteristic of a C–C single bond in a conjugated system. Thus, to our knowledge, a metallacyclopropane vanadium core is observed for the first time. By comparison, the corresponding C=C bond length in a metallacyclopropene is typically 1.25–1.28 Å.[15, 18] Moreover, the C2-C1-C51 and C3-C4-C61 bond angles in compound **3** are 128.4 and 129.0°, respectively, that is, out of the range observed for the corresponding angles (134–148°) in systems containing π-bonded alkynyl C≡C bonds.[19] The environment around the zirconium atom could be regarded as a η^4-diene (or η^4-diyne) zirconium structure.[20] First, the C1–C2 and C3–C4 distances (1.336 and 1.331 Å, respectively) are in the range of a C=C bond linkage and similar to the C=C bond length observed in the zirconacyclopropene complex $[Cp_2Zr(Me_3SiCCPh)(PMe_3)]$.[21] Second, the Zr–C1 and Zr–C4 distances of 2.224 and 2.235 Å, respectively, are in the range expected for a Zr–C σ bond (2.27 Å in $[Cp_2ZrMe_2]$[22]). Third, the Zr–C2 and Zr–C3 distances are 2.458 and 2.459 Å, respectively, which indicates that the Zr atom is coordinated in an olefinic σ-plane fashion to both internal carbon atoms of the butadiene skeleton.[23] The specific connections of C2 and C3 to their four neighboring atoms (Zr, V, C1, C3 and Zr,V, C2, C4, respectively) reveal that they reside in planar environments and are tetracoordinated; the sum of the angles around C2, and around C3, is 360°.[23] It may be noted that atoms C2 and C3 may be considered as unsaturated and, thus, their planar tetracoordination could have been expected. The planes Cp(centroid)-V-Cp(centroid) and Cp′(centroid)-Zr-Cp′(centroid) are nearly perpendicular to the plane defined by the butadiene skeleton C1-C2-C3-C4 (the corresponding angles are 91 and 84°, respectively), and the line connecting the Zr to the V atom is orthogonal to the C2–C3 bond. These results show that the zirconium atom is connected symmetrically to a four-carbon chain that can be described as a butadiene (or butadiyne) fragment. For comparison, similar Zr–C distances are displayed (2.300 and 2.597 Å) in the bonding of the Zr atom to the diene in [$Cp_2Zr(\eta^4$-s-*cis*-2,3-dimethylbutadiene)].[20b] Compound **3** could be compared to similar titanocene and zirconocene species, **A** and **B** , described by Rosenthal et al.[13f,g] The zirconocene diyne **A** (M = Zr) contains a cumulene structure in which the central C=C bond coordinates to the metal center. Another arrangement, observed in complexes **B** and **3**, consists of the interaction of the central C=C bond with a second metal center.



A

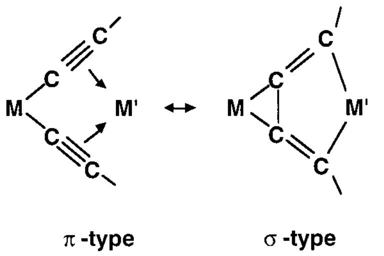


B

The observed reaction between the bis(phenylethynyl)zirconocene and vanadocene and the formation of the heterodimetallic zirconium–vanadium compound **3** may be understood as resulting from the transfer of the phenylethynyl group from zirconium to vanadium to give [$Cp_2V(CCPh)_2$] and zirconocene Cp_2Zr. Just like the latter species, which has been extensively studied because of its high reactivity,[24] [$Cp_2V(CCPh)_2$] should also be considered as a transient species.[9] Both species certainly are extremely reactive and stabilization of the bis(ethynyl)vanadocene by Cp_2Zr implies the reductive coupling of alkynes via the formation of the metallacyclopropane vanadium.

Conclusion

The first heterodinuclear organometallic complexes containing titanium and vanadium, or zirconium and vanadium, namely **1**–**3**, have been prepared and characterized by elemental analysis and mass spectrometry, and exhibit similar magnetic susceptibilities, IR and Raman spectra. Compound **1** is formed by the reaction of vanadocene with the two alkyne groups of [$Cp_2Ti(C{\equiv}CPh)_2$]. These results were confirmed by the preparation and characterization of the zirconium–vanadium analogue **2**. Finally, the structural arrangement of these types of compounds has been further confirmed by the determination of the crystal structure of the trimethylsilyl-substituted zirconium–vanadium analogue **3**. The structure consists of a zirconocene complex σ-bonded to a butadiene (or butadiyne) ligand containing two internal planar coordinated carbon atoms that are also bonded to a vanadocene moiety. This structure could be formally considered as the conceptual σ-boundary form of the σ-π bonding description in the alkynyl homo- and heterodimetallic systems studied so far (Scheme 2).



Scheme 2.

Future research along this line is aimed at the preparation of titanium–vanadium organometallic complexes with a better solubility or volatility. These compounds would be potential single-source precursors for the preparation of ceramic thin films containing titanium, vanadium, carbon, and nitrogen. In this respect, the trimethylsilyl-substituted zirconium–vanadium analogue **3** is soluble in common organic solvents and potentially could be used as a single-source precursor in spray pyrolysis techniques.

Experimental Section

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 by syringe or cannula. All solvents were dried by conventional methods, distilled under argon, and degassed before use. [Cp_2V],[25] [$Cp_2Ti(C{\equiv}CPh)_2$],[9] [$Cp_2Zr(C{\equiv}CPh)_2$],[11b] and [$(C_5H_4SiMe_3)_2ZrCl_2$][26] were prepared according to previously reported procedures. Elemental analyses were performed at the laboratory (C, H, N) and by the Service National de Microanalyses du CNRS (Si, Ti, V, Zr). Mass spectrometry analysis (chemical ionization with methane) was conducted on a Nermag, Model R10-10, spectrometer. The intensity ratios of the peaks are consistent with the distribution of the isotopes of titanium and zirconium. Magnetic susceptibility measurements were carried out by Faraday's method. IR spectra were obtained in Nujol by using a Perkin-Elmer, Model 983G, spectrometer. Raman spectra were obtained by using a XY-DILOR Raman spectrometer with a CCD-OMA4 detector and a Notch filter.

[$(C_5H_4SiMe_3)_2Zr(C{\equiv}CPh)_2$]: A 1M solution of LiC≡CPh (4.8 mL, 4.8 mmol) in THF was added dropwise at ambient temperature to a solution of [$(C_5H_4SiMe_3)_2ZrCl_2$] (1.06 g, 2.4 mmol) in toluene (40 mL). The resulting reaction mixture was stirred at room temperature for 3 h and then filtered. The reaction mixture was concentrated to 7 mL under vacuum, pentane (30 mL) was slowly added, and the resulting solution was left overnight in a freezer. A solid (brown crystals), which was very sensitive to air and moisture, precipitated, was filtered off, washed with pentane, and dried under vacuum. Yield: 460 mg (34%); $C_{32}H_{36}Si_2Zr$ (M_r = 568.0 g mol^{-1}) calcd C 67.66 H 6.39; found C 67.01, H 5.96. ^{1}H NMR (250 MHz, C_6D_6): δ = 7.51 (m, 4H, Ph), 7.05 (m, 6H, Ph), 6.66 (t, J = 2.4 Hz, 4H, C_5H_4), 5.99 (t, J = 2.6 Hz, 4H, C_5H_4), 0.43 (s, 18H, $SiMe_3$). IR (Nujol): ν = 2072 cm^{-1} (C≡C).

[$Cp_2V(\mu$-η^2:η^4-butadiyne)$TiCp_2$] (1): A solution of [$Cp_2Ti(C{\equiv}CPh)_2$] (700 mg, 1.8 mmol) in toluene (10 mL) was added dropwise at room temperature to a solution of [Cp_2V] (332 mg, 1.8 mmol) in toluene (10 mL). A brown solid immediately precipitated. This solid was filtered off, washed with toluene, and dried under vacuum. Yield: 910 mg (90%); $C_{36}H_{30}TiV$ (M_r = 561.5 g mol^{-1}) calcd C 77.01, H 5.38, Ti 8.53, V 9.08; found C 76.5, H 5.4, Ti 8.9, V 8.0; MS (70 eV, CI/methane): *m/z*: 562 ($C_{36}H_{30}TiV$ + H), 381 ($C_{26}H_{20}Ti$ + H), 182 ($C_{10}H_{10}V$ + H); Raman: ν = 1570 (s; C=C), 1550 cm^{-1} (sh; C=C(Ph)).

[Cp$_2$V(μ-η^2:η^4-butadiyne)ZrCp$_2$] (2): Compound **2** was prepared analogously to **1** by using [Cp$_2$Zr(C≡CPh)$_2$] instead of [Cp$_2$Ti(C≡CPh)$_2$] as starting material. Yield: 980 mg (90 %); $C_{36}H_{30}ZrV$ ($M_r = 604.8$ g mol^{-1}) calcd C 71.49, H 4.95, Zr 15.08, V 8.42; found C 71.2, H 5.1, Zr 15.8, V 8.0; MS (70 eV, CI/methane): m/z: 643 ($C_{36}H_{30}ZrV + C_3H_5$), 422 ($C_{26}H_{20}Zr + H$), 182 ($C_{10}H_{10}V + H$); Raman: $\nu = 1570$ (s; C=C), 1550 cm^{-1} (sh; C=C(Ph)).

[Cp$_2$V(μ-η^2:η^4-butadiyne)Zr(C$_5$H$_4$SiMe$_3$)$_2$] (3): A solution of [Cp$_2$V] (89 mg, 0.49 mmol) in toluene (8 mL) was added at room temperature to a solution of [(C$_5$H$_4$SiMe$_3$)$_2$Cp$_2$Zr(C≡CPh)$_2$] (280 mg, 0.49 mmol) in toluene (5 mL). The reaction mixture was concentrated to 6 mL under vacuum, pentane (6 mL) was slowly added, resulting in a two-phase solution. After three days of slow diffusion, black crystals were filtered off, washed with pentane, and dried under vacuum. Yield : 200 mg (54 %); $C_{42}H_{46}Si_2VZr$ ($M_r = 749.1$ g mol^{-1}) calcd C 67.34, H 6.19, V 6.80, Zr 12.18; found C 66.51, H 5.59, V 7.0, Zr 11.90; ^{1}H NMR (250 MHz, C_6D_6): $\delta = 8.12$ (d, 4 H, *para* H, Ph), 7.38 (t, 4 H, *meta* H, Ph), 7.18 (m, obscured by C_6D_6, *ortho* H, Ph), 6.15 (t, $J = 2.4$ Hz, 4 H, C_5H_4), 5.67 (t, $J = 2.6$ Hz, 4 H, C_5H_4), -0.25 (s, 18 H, SiMe$_3$); Raman: $\nu = 1550$ cm^{-1} (s; C=C).

Attempted X-ray study of compound 2: Selected crystals, sensitive to air and humidity, were protected in Vaseline oil and put into capillaries. Diffraction data were collected on a CAD4 ENRAF-NONIUS diffractometer at 293 and 150 K. Examination of the profiles of the Bragg reflections indicated that all crystals were of very poor quality. However, a set of diffraction intensities was collected,[27] but no quantitative data could be drawn from this study.

X-ray structure determination of compound 3: The selected crystal, sensitive to air and humidity, was protected in Vaseline oil and put into a capillary. Diffraction data were collected on a STOE IPDS diffractometer at 180 K. Relevant crystal data and data collection parameters are summarized in Table 2. The structure was determined by using direct methods,[28] and refined by standard full-matrix least-squares and Fourier techniques by using the CRYSTALS program package.[29] Phenyl rings were treated as rigid groups with an isotropic temperature factor refined for each individual carbon atom. Hydrogen atoms were located on the final difference Fourier maps and their contribution was included in the structure factor calculations by using idealized geometry and arbitrary isotropic temperature factors. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100799. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Table 2. Crystal data and details of the structure refinement for compound **3**.

structural formula	$C_{42}H_{46}Si_2VZr$
formula weight	749.2
crystal size [mm^3]	$0.5 \times 0.4 \times 0.3$
crystal system	orthorhombic
space group	*Pna*2$_1$ (no. 33)
a [Å]	18.640(2)
b [Å]	14.033(1)
c [Å]	14.008(1)
V [Å^3]	3664.1(9)
Z	4
F(000)	1545.8
ρ_{calcd} [g cm^{-3}]	1.36
diffractometer	STOE IPDS
radiation, wavelength [Å]	Mo$_{K\alpha}$, 0.71073
μ [cm^{-1}]	6.2
temperature [K]	180
scan mode	imaging plate
$2\theta_{\max}$ [°]	47.9
absorption correction	none
number of collected reflections [$I > 0$]	16341
number of independent reflections [$I > 0$]	2961
merging R_{int} [%]	3.55
number of observed reflections [$I > 2\sigma(I)$]	2799
number of refined parameters	331
R [%] refinement against |F|	2.44
R_w [%] refinement against |F|	2.72
S	1.11
weighting scheme	optimized Chebychev series
residual electron density (min/max) [e Å^{-3}]	0.28/0.56

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