

Planar Tetracoordination of Carbon in Groups 4 and 5 Organometallic Chemistry

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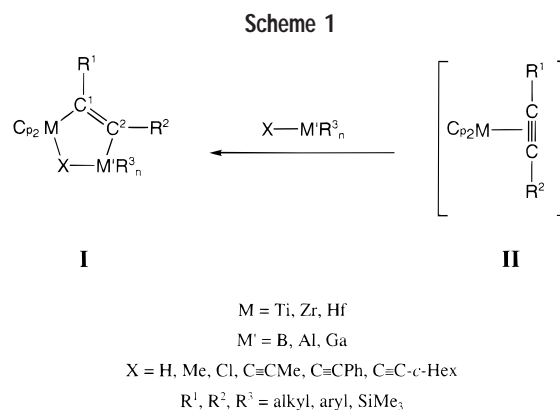
Introduction

Nowadays, when so many things are questioned again and again, tetrahedral sp^3 hybridization of tetravalent carbon seemed to be a rock solid concept since its proposal by van't Hoff and Le Bel.¹ Forget this! Planar tetracoordinate carbon is not as odd as a three-dollar bill and does exist.

In 1970, Hoffman et al. were the first to predict, on the basis of a theoretical approach, the possible existence of planar methane with an electronic structure involving a six-electron four-bond electron-deficient σ system and a two-electron-containing p_z -based orbital perpendicular to the σ plane.² Naturally, as the energy of planar methane is higher than that of tetrahedral methane,³ some kind of stabilization was needed if compounds containing planar tetracoordinate carbon (ptC) were to be prepared. Indeed, this prediction was experimentally confirmed,⁴ when Seidel et al. reported in 1976 the synthesis,^{4a} and Cotton et al. in 1977 the structure,^{4b} of $V_2(2,6\text{-dimethoxyphenyl})_4 \cdot \text{THF}$, a divanadium complex in which a ptC may be identified. Following on this seminal result, a number of other ptC compounds have been prepared, often inci-

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Patrick Cassoux was born in Hanoï, former French Indochina (Viet Nam), on September 5, 1941. He received the "Ingénieur" degree from the "Ecole Nationale Supérieure de Chimie de Toulouse", the master degree from the Paul Sabatier University at Toulouse, in 1965, and the "Doctorat d'Etat" (Ph.D.) from the same University, in 1971, under the direction of F. Gallais. He was a postdoctoral associate at the University of Michigan, Ann Arbor, with R. L. Kuczowski in 1973–74, and a visiting research fellow at the General Electric R&D Center, Schenectady, NY, with L. V. Interrante in 1979. He joined the French National Center for Research (CNRS) in 1966, where he rose through the ranks to become "Directeur de Recherche I" in 1989. His research interests include molecular coordination compounds with unusual solid-state properties and molecular organometallic precursors to ceramic materials.



dentally. Several recent important papers and exhaustive and comprehensive reviews have appeared at different stages of development of this research,⁵ and the reader is especially directed to the most recent one by Erker et al.⁶ Examination of the structural and electronic features of the various involved compounds indicates that the stabilization required for obtaining ptC compounds may result from the incorporation of a carbon atom into sterically rigid, small ring or polycyclic systems, or from the increase of the electron density in the σ system and its decrease in the π system. In the second case, variation of the electronic density may be obtained by use of appropriate σ -donor/ π -acceptor substituents, such as, for example, transition metals. As appears in the literature,⁶ most ptC compounds were obtained that way, and it may seem ironic that organometallic chemistry provides the most efficient route toward planar tetracoordinate carbon.

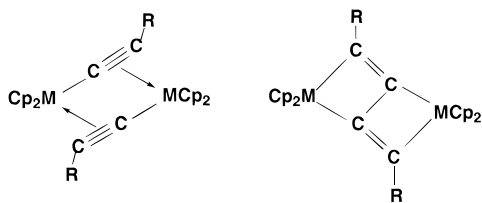
Planar Tetracoordinate Carbon in Groups 4 and 13 Dimetallic Complexes

From a general point of view, the preparation of dimetallic complexes associating two transition metals has recently attracted an increasing amount of attention. This is due to a new chemical reaction behavior resulting from the synergistic combination of the properties of both metals which may be utilized in stoichiometric or catalytic reactions.⁷ It happens that most of the ptC-containing transition metal complexes reported to date are dimetallic complexes of groups 4 and 13 (**I** in Scheme 1).⁶

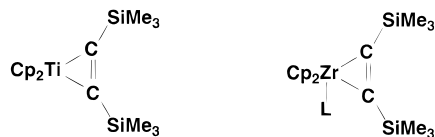
All the synthetic procedures described for preparing **I** are believed to involve an (alkyne)–metallocene intermediate compound **II** which reacts with another metal-containing species to afford the dimetallic complex **I** in which a $C^1=C^2$ bond is connected to both metals. The C^2 atom is the ptC in this system as shown by the planarity of the $MC^1C^2M'X$ cycle and the value close to 360° of the sum of the bond angles around C^2 . The preparation of ptC-containing, group 4 homodimetallic complex cations seems also to involve an (alkyne)–metallocene intermediate.^{6,8,9} Thus, the presence of this (alkyne)–metallocene

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Scheme 2



Scheme 3



intermediate, or, if available, an (alkyne)–metallocene-based reagent, seems crucial for obtaining group 4 and 13 dimetallic complexes containing one ptC.

On the other hand, more recently, implication of alkynyl moieties for incidental ptC generation was also observed by Rosenthal et al. in the reactivity of Ni⁰ complexes and titanocene (vide infra).¹⁰ Indeed, two heterobimetallic compounds (Ti–Ni, Zr–Ni) were prepared, and their crystal structure determination led to the identification of ptC in these compounds.

Acetylide Chemistry. π Donation as the First Step

The chemistry of acetylides is well suited for the preparation of new compounds of group 4 elements, either by oxidative addition of a diyne on the metal (initially Ti^{II} and Zr^{II}) of ligand-stabilized metallocene or by reaction of an alkyne compound of a group 4 element with a Lewis metal complex. 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 $[\text{Cp}_2\text{M}(\mu\text{-C}\equiv\text{CPh})_2]$ (Cp = cyclopentadienyl) (Scheme 2).^{11–14} Moreover, it has been shown by Rosenthal et al. that the $\text{Cp}_2\text{Ti}(\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3)$ and $\text{Cp}_2\text{Zr}(\text{THF})(\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3)$ compounds are convenient sources of transient Ti- and Zr-metallocene species (Scheme 3).¹⁵ Thus, the “Cp₂Ti” titanocene and “Cp₂Zr” zirconocene are the reactive moieties on alkynes and dialkynes and can self-organize to afford [Ti, Ti] and [Zr, Zr] homodimetallic, as well as heterodimetallic, [Ti, Zr] complexes.¹⁶ Alternately, the reactivity toward diynes of these transient “Cp₂M” species also allows the stabilization of these species. The subsequent reaction of these species with other diyne systems leads to the formation of new homo-

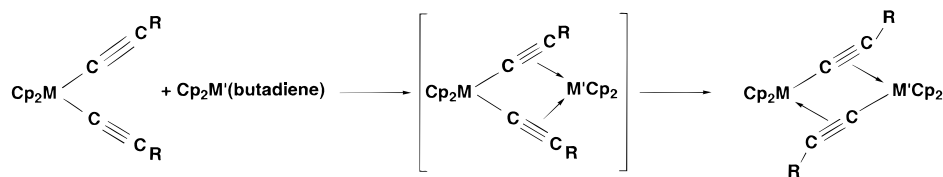
and heterodimetallic complexes with various structural configurations. For example, Lang et al. have successfully used the reactivity of alkynes coordinated to titanium or zirconium to prepare heterodimetallic complexes in which the second metal is an element of group 11.^{17,18} These opportunities have also been exploited by Erker et al. who used Cp₂Zr(butadiene) as a source of zirconocene. Reaction of “Cp₂Zr” with Cp₂M(C≡CPh)₂ (M = Zr, Hf) is followed by a redistribution process which affords either the dimeric $[\text{Cp}_2\text{Zr}(\mu\text{-C}\equiv\text{CPh})_2]$ or the heterodimetallic Cp₂Zr(μ-C≡CPh)₂HfCp₂ complexes (Scheme 4).¹⁹ This research line was further explored by studying the protonation of $[\text{Cp}_2\text{Zr}(\mu\text{-C}\equiv\text{CPh})_2]$, which led to the formation of ptC.¹⁹

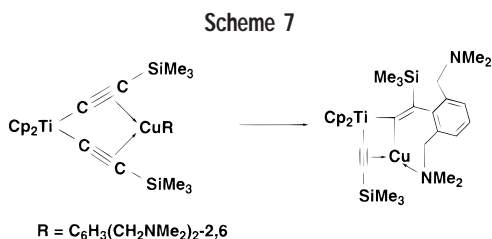
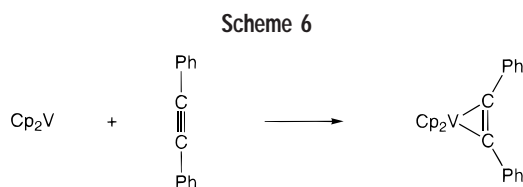
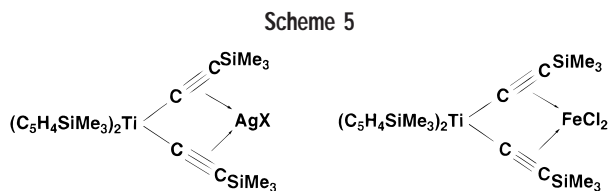
Synthesis and Characterization of Groups 4 and 5 Dimetallic Complexes

All the ptC-containing dimetallic complexes reported until recently had only one planar tetracoordinate carbon atom. We were able to prepare and characterize dimetallic complexes of groups 4 and 5 containing two ptCs.²⁰ This result was obtained in our group rather incidentally as our primary goal was then the synthesis of dimetallic vanadium–titanium complexes for use as molecular precursors in the organometallic chemical vapor deposition of carbonitride ceramics containing both these metals.^{21,22} In many heterodimetallic complexes, an electron-poor metal (Ti, Zr) is associated with an electron-rich metal (Rh, Ru).^{7,23} The association in a single molecule of two electron-poor metals is more unusual, and indeed, very few heterodimetallic compounds of groups 4 and 5 elements have been described.^{24–26} The reaction behavior of alkyne triple bonds in substituted titanocene and zirconocene compounds has recently been extensively studied.^{17,18,27–30} In particular, the preparation by oxidative addition of titanium–silver and titanium–copper heterodimetallic compounds from $[(\text{C}_5\text{H}_4(\text{SiMe}_3))_2\text{Ti}(\text{C}\equiv\text{CSiMe}_3)_2]$ and MCl₂ (M = Fe, Co, Ni) or M'X (M' = Ag, Cu; X = Cl, R) has been reported by Lang et al. (Scheme 5).¹⁸

Likewise, a similar oxidative addition of Cp₂Hf(C≡CPh)₂ by Cp₂Zr(butadiene) has led to the preparation of Cp₂Hf(μ-C≡CPh)₂ZrCp₂.¹⁹ 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 $[\text{Cp}_2\text{V}(\eta^2\text{-R}^1\text{C}=\text{CR}^2)]$ compound (Scheme 6)³¹ indicated that the oxidative addition of vanadocene Cp₂V (the oxidation state of vanadium increases from II to IV) on R¹C≡CR² alkynes was possible.³² Thus, a new route toward M–vanadium heterodi-

Scheme 4





metallic complexes by reaction between the appropriate M^{IV} alkyne compound ($M = \text{Ti}, \text{Zr}$) and vanadocene was explored. A series of M^{IV} alkyne compounds, namely, $\text{Cp}_2\text{-Ti}(\text{C}\equiv\text{CPh})_2$ and $\text{Cp}'_2\text{Zr}(\text{C}\equiv\text{CPh})_2$ with $\text{Cp}' = \text{C}_5\text{H}_5, \text{C}_5\text{H}_4\text{-Me}, \text{C}_5\text{H}_4\text{SiMe}_3,$ and $\text{C}_5\text{H}_4t\text{-Bu}$, were reacted with vanadocene. Physicochemical characterization of all resulting compounds gave similar indications.^{20,33} Elemental analyses and mass spectra were consistent with a formula corresponding to a 1:1 adduct of the two starting components. The infrared absorption band corresponding to the alkynyl $\text{C}\equiv\text{C}$ bonds, which is clearly observed at $\sim 2065\text{ cm}^{-1}$ in the infrared spectrum of the starting M^{IV} alkyne compound,^{13,17a} or at lower frequencies in the range of $1960\text{--}1850\text{ cm}^{-1}$ when alkynyl groups interact with another metal,^{14,34} was not present in the spectrum of the metal–vanadium adduct. The measured magnetic moment ($\sim 1.73\ \mu_B$), corresponding to one single electron in the molecule, indicated that the formal oxidation state of vanadium has been increased from II to IV. These observations gave the first clear indication that vanadocene has reacted with both $(\text{C}\equiv\text{CPh})$ alkynyl groups. An intense $\nu(\text{C}=\text{C})$ band at 1600 cm^{-1} is observed in the Raman spectra (along with a shoulder attributed to phenyl group bonds), whereas no $\nu(\text{C}\equiv\text{C})$ band is present. Thus, all the obtained metal–vanadium adducts can be described as heterodimetallic systems containing vanadium(IV) and zirconium atoms, and $\text{C}=\text{C}$ double bonds.

It is interesting to note, however, that the reactivity of M^{IV} alkyne compounds depends on the substituents carried by the alkyne.^{30d,34} For example, no reaction is observed with vanadocene and when the substituent on the alkyne is the SiMe_3 group.²¹ In relation to the previously mentioned formation of a heterodimetallic compound from titanium dialkynes and CuR , an interesting reaction concerns the 1,2-addition of the CuR moiety on the alkynyl Ti ligand when R is $[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-}2,6]$ (Scheme 7).¹⁸

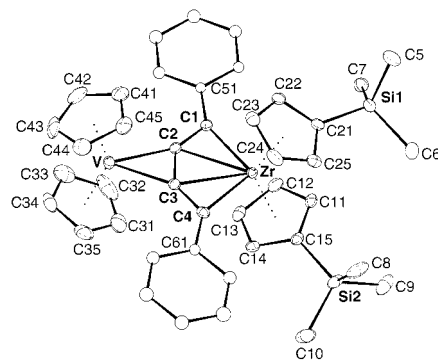


FIGURE 1. Molecular structure and atom numbering scheme for $\text{Cp}_2\text{V}(\mu\text{-}\eta^2\text{-}\eta^4\text{-butadiene})\text{Zr}(\text{C}_5\text{H}_4\text{SiMe}_3)_2$, **1**. Reprinted with permission from ref 20. Copyright 1998 Wiley-VCH.

Crystal Structure of Groups 4 and 5 Dimetallic Complexes: Identification of Two Planar Tetracoordinate Carbons

Determination of the crystal structure of the above-described groups 4 and 5 dimetallic complexes was possible in several cases and gave a rather unexpected molecular arrangement.²⁰ For example, in the structure of compound **1** resulting from the reaction of $(\text{C}_5\text{H}_4\text{-SiMe}_3)_2\text{Zr}(\text{C}\equiv\text{CPh})_2$ and vanadocene (Figure 1), the vanadium atom adopts a metallacyclopropane environment: the $\text{V}\text{-C}(2)$ and $\text{V}\text{-C}(3)$ bond lengths are those expected for a $\text{V}\text{-C}$ σ bond,³⁵ and the $\text{C}(2)\text{-C}(3)$ distance, 1.447 \AA , is characteristic of a single $\text{C}\text{-C}$ bond in a conjugated system. The metallacyclopropane vanadium core observed in **1** is quite different from a metallacyclopentene in which the corresponding $\text{C}=\text{C}$ bond length is typically $1.25\text{--}1.28\text{ \AA}$.^{31,35}

Moreover, the $\text{C}(2)\text{-C}(1)\text{-C}(51)$ and $\text{C}(3)\text{-C}(4)\text{-C}(61)$ bond angles in **1** are 128.4° and 129.0° , respectively, *i.e.*, out of the range observed for the corresponding angles ($134\text{--}148^\circ$) in systems containing π -bonded alkynyl $\text{C}\equiv\text{C}$ triple bonds.³⁶ The environment around the zirconium atom could be regarded as a η^4 -diene (or η^4 -diyne) zirconium structure.³⁷ Indeed, the $\text{C}(1)\text{-C}(2)$ and $\text{C}(3)\text{-C}(4)$ distances (1.336 and 1.331 \AA , respectively) are in the range of a $\text{C}=\text{C}$ double bond linkage and similar to the $\text{C}=\text{C}$ bond length observed in the zirconacyclopentene complex $\text{Cp}_2\text{Zr}(\text{RC}\equiv\text{CR}')(\text{PMe}_3)$ ($\text{R} = \text{H}, \text{R}' = \text{Bu}; \text{R} = \text{R}' = \text{Ph}$).³⁸ The distances of Zr to $\text{C}(1)$ and $\text{C}(4)$, 2.224 and 2.235 \AA , respectively, are as expected for a $\text{Zr}\text{-C}$ σ bond (2.27 \AA in Cp_2ZrMe_2).³⁹ The distances from Zr to $\text{C}(2)$ and $\text{C}(3)$ are 2.458 and 2.459 \AA , respectively, which indicates that the Zr atom is coordinated in an olefinic σ -plane fashion to both internal carbon atoms of the butadiene skeleton.^{5,9b} These $\text{Zr}\text{-C}(2)$ and $\text{Zr}\text{-C}(3)$ distances (mean value 2.46 \AA) are smaller than those of $\text{Zr}\text{-C}(\text{Cp})$ (mean value 2.55 \AA), but close to the sum of the corresponding van der Waals radii (2.42 \AA). The specific connections of $\text{C}(2)$ and $\text{C}(3)$ to their four neighboring atoms ($\text{Zr}, \text{V}, \text{C}(1), \text{C}(3)$ and $\text{Zr}, \text{V}, \text{C}(2), \text{C}(4)$, respectively) make $\text{C}(2)$ and $\text{C}(3)$ planar and tetracoordinated, and the sum of the angles around $\text{C}(2)$, as well as around $\text{C}(3)$, is 360° . These results show that the zirconium atom is 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 $\text{Cp}_2\text{Zr}(\eta^4\text{-}s\text{-}cis\text{-}2,3\text{-dimethylbutadiene})$ corresponds to similar Zr–C distances (2.300 and 2.597 Å).⁴⁰ Thus, two planar tetracoordinate carbons seem to have been identified in the crystal structure of compound **1**, which could be designated as $\text{Cp}_2\text{V}(\mu\text{-}\eta^2\text{:}\eta^4\text{-butadiyne})\text{Zr}(\text{C}_5\text{H}_4\text{SiMe}_3)_2$.

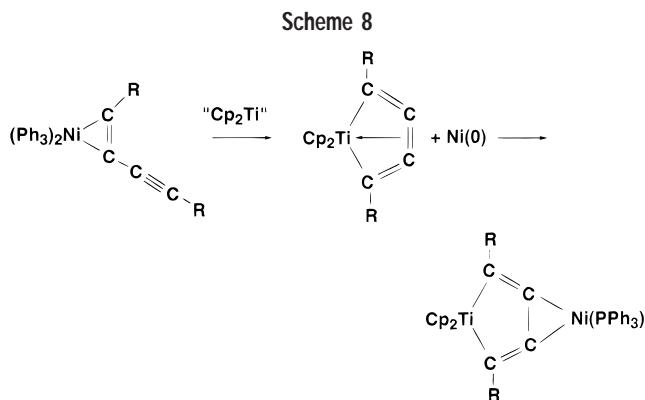
It may be noted that atoms C(2) and C(3) could also be considered as unsaturated, and in that case, their planar tetracoordination could have been expected. Thus, one might alternately consider that the Zr–C(2) and Zr–C(3) interactions may be just enforced by the butadiene framework. The question as to whether there is an actual electron density between the Zr atom and the C(2) and C(3) atoms may be addressed by the determination of this density (using, for example, a topological analysis of the electron localization function (ELF) which is in progress³³).

A similar molecular structure was observed for the $\text{Cp}_2\text{V}(\mu\text{-}\eta^2\text{:}\eta^4\text{-butadiyne})\text{Zr}(\text{C}_5\text{H}_4t\text{-Bu})_2$ analogue compound, **2**, obtained from the reaction of $(\text{C}_5\text{H}_4t\text{-Bu})_2\text{Zr}(\text{C}\equiv\text{CPh})_2$ and vanadocene.⁴¹ Although crystals of compounds **3** and **4** obtained from the reaction of $\text{Cp}_2\text{Zr}(\text{C}\equiv\text{CPh})_2$ and $(\text{C}_5\text{H}_4\text{-Me})_2\text{Zr}(\text{C}\equiv\text{CPh})_2$ with vanadocene, respectively, seemed at first sight to be of sufficient quality for an X-ray structural determination, difficulties due to a statistical disorder were encountered throughout the refinement. Nevertheless, for both compounds **3** and **4**, the resulting overall molecular arrangement^{20,41} was found to be similar to that observed in the fully resolved structure of **1** described above. Crystals of insufficient quality for an X-ray structural determination were obtained for compound **5** prepared by reaction of $\text{Cp}_2\text{Ti}(\text{C}\equiv\text{CPh})_2$ and vanadocene.

Nevertheless, the physicochemical characterizations of compounds **1–5** (elemental analysis and mass spectroscopy, IR spectroscopy [no $\nu(\text{C}\equiv\text{C})$ band observed], Raman spectroscopy ($\nu(\text{C}=\text{C})$ band observed at 1550 (s) cm^{-1}), and magnetic measurements (magnetic moment of $\sim 1.73 \mu_B$) are so consistent that it is probable that all these compounds have a similar $\text{Cp}_2\text{V}(\mu\text{-}\eta^2\text{:}\eta^4\text{-butadiyne})\text{Zr}(\text{Cp})_2$ structure containing two ptCs.

Mechanism of Formation of Compounds 1–5

Whereas the sole determination of the crystal structure of compounds **1–5** reveals the existence of two ptCs in these complexes, it does not help much in understanding their mechanism of formation. The observed reaction between the bis(phenylethynyl)zirconocene and vanadocene and the formation of the heterodimetallic [Zr, V] compounds may be understood as resulting from the transfer of the phenylethynyl group from zirconium to vanadium to give $\text{Cp}_2\text{V}(\text{C}\equiv\text{CPh})_2$ and zirconocene “ Cp_2Zr ” (or $\text{Cp}_2\text{V}(\text{C}\equiv\text{CPh})$ and “ $\text{Cp}_2\text{Zr}(\text{C}\equiv\text{CPh})$ ”). Just as the latter species, which has been extensively studied for its high reactivity,⁴² $\text{Cp}_2\text{V}(\text{C}\equiv\text{CPh})_2$ should also be considered as a transient species.²⁷ 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 metallacyclopentadiene vanadium. Thus, the most straightforward explanation would involve the migration of the $\text{C}\equiv\text{CPh}$ moiety from the Zr environment to the vanadium environment, while the zirconium atom would establish bonding to the four C(1), C(2), C(3), and C(4) carbon atoms within a $\mu\text{-}\eta^2\text{:}\eta^4\text{-butadiyne}$ arrangement.

On the other hand, as mentioned above, two [Ti, Ni] and [Zr, Ni] heterodimetallic compounds have been prepared by Rosenthal et al. by reaction of $\text{Ni}(\text{PPh}_3)(\eta^2\text{-PhC}\equiv\text{CC}\equiv\text{CPh})$ and Cp_2Ti or Cp_2Zr .¹⁰ The crystal structures of both complexes have the same skeletal arrangement as that observed in compounds **1–5**, i.e., involving two ptCs. Moreover, the formation of a zirconacyclocumulene species, $\text{Cp}_2\text{Zr}(\eta^4\text{-PhC}=\text{C}=\text{C}=\text{CPh})$, as a reactive intermediate toward the nickel(0) complex fragment was suggested (Scheme 8).¹⁰

Likewise, a cumulene-based complex was also claimed to be obtained from acetylide Ti and Zr complexes, $\text{Cp}_2\text{M}(\text{C}\equiv\text{C}t\text{-Bu})_2$ ($\text{M} = \text{Ti}, \text{Zr}$) and $\text{Cp}_2\text{Zr}(\text{C}\equiv\text{CMe})_2$, by either $h\nu$ irradiation or adding a catalytic amount of $\text{B}(\text{C}_6\text{F}_5)_3$.⁴³ $\text{Cp}_2\text{M}(\eta^4\text{-RC}=\text{C}=\text{C}=\text{CR})$ ($\text{M} = \text{Ti}, \text{Zr}; \text{R} = t\text{-Bu}$) was characterized by an X-ray structure determination (Scheme 9).^{16,30e}

The study of the reactivity of the zirconacyclocumulene species led to a recent proposition by Rosenthal et al. of an equilibrium between the cumulene form and a $(\eta^2\text{-RC}\equiv\text{C}-\text{C}\equiv\text{CR})$ complex (Scheme 10).⁴⁴ This latter form was revealed in the formation of the $[\text{Cp}_2\text{Zr}(\text{C}\equiv\text{CPh})(\eta^2\text{-RC}\equiv\text{C}-\text{C}\equiv\text{CR})]^-$ complex anion obtained by the reaction of Cp_2ZrCl_2 with $\text{LiC}\equiv\text{CPh}$. (Figure 2).⁴¹

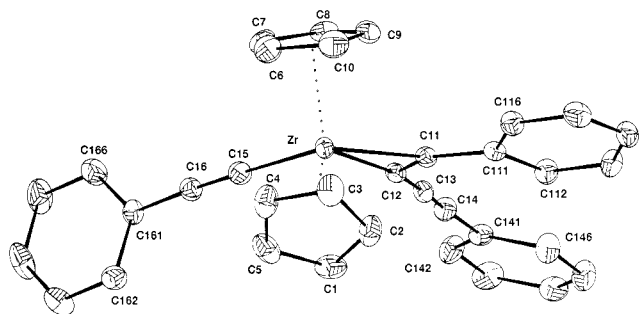
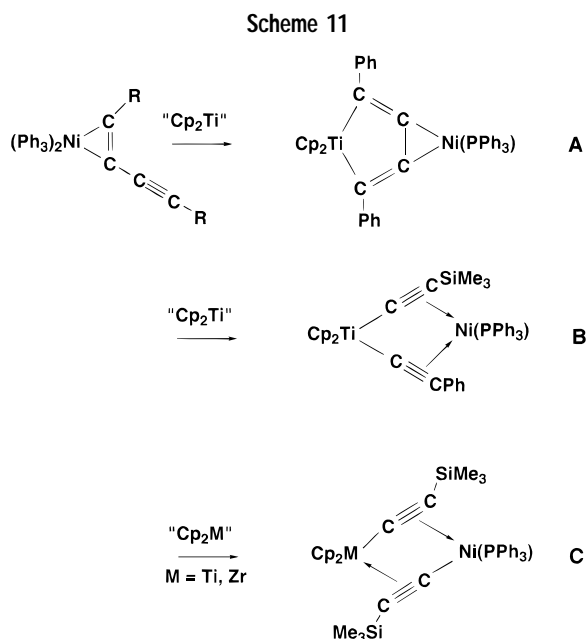


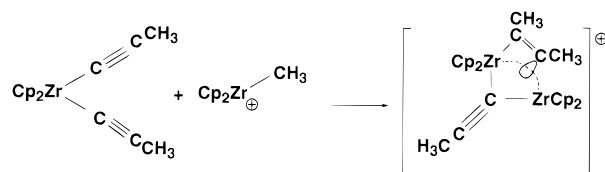
FIGURE 2. Molecular structure and atom numbering scheme for $[\text{Cp}_2\text{Zr}(\text{C}\equiv\text{CPh})(\eta^2\text{-RC}\equiv\text{C}-\text{C}\equiv\text{CR})]^-$.⁴¹



We suspect that in this case $\text{LiC}\equiv\text{CPh}$ reacts with the zirconacyclocumulene or the $[\text{Cp}_2\text{Zr}(\eta^2\text{-RC}\equiv\text{C}-\text{C}\equiv\text{CR})]$ form (see Scheme 10) to stabilize the $[\text{Cp}_2\text{Zr}(\text{C}\equiv\text{CPh})(\eta^2\text{-RC}\equiv\text{C}-\text{C}\equiv\text{CR})]^-$ complex anion.

It should be noted that the formation of the zirconacyclocumulene is governed by the nature of the substituents attached to the alkyne. The precursor synthon of “ Cp_2Zr ” obtained from $\text{Cp}_2\text{Zr}(\text{L})\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3$ ($\text{L} = \text{THF}$, pyridine), reacting with $t\text{-BuC}\equiv\text{CC}t\text{-Bu}$ and $\text{Me}_3\text{SiC}\equiv\text{CC}\equiv\text{CSiMe}_3$, leads to either the zirconacyclocumulene $\text{Cp}_2\text{Zr}(\eta^4\text{-}t\text{-BuC}\equiv\text{CC}\equiv\text{C}t\text{-Bu})$ or $[\text{Cp}_2\text{Zr}(\mu\text{-}\eta^1\text{:}\eta^2\text{-C}\equiv\text{CSiMe}_3)_2]$.¹⁶ The substituents on the alkyne also conduct the reactivity between Cp_2M and $\text{Ni}(0)$ complexes, and three situations were observed by Rosenthal et al.⁴⁵ (Scheme 11). Thus, a subtle balance between the electronic effects of the different substituents attached to the diyne determine the nature of the final complex (A, B, and C in Scheme 11). It should be noted that the $\text{Cp}_2\text{Ti}(\mu\text{-}\eta^2\text{:}\eta^4\text{-PhC}\equiv\text{C}-\text{C}\equiv\text{CPh})\text{Ni}(\text{PPh}_3)_2$ compound mentioned by Rosenthal et al.¹⁰ and our $\text{Cp}'_2\text{Zr}(\mu\text{-}\eta^2\text{:}\eta^4\text{-PhC}\equiv\text{C}-\text{C}\equiv\text{CPh})\text{VCp}_2$ compounds ($\text{Cp}' = \text{C}_5\text{H}_4\text{SiMe}_3$ and $\text{C}_5\text{H}_4t\text{-Bu}$), studied in the stabilization of the zirconacyclocumulene either with $\text{Ni}(0)$ or with vanadocene, were observed with a phenyl group attached to the alkyne. In this context, it should also be noted that our attempts to prepare the

Scheme 12



heterodimetallic complex from Cp_2V and $\text{Cp}_2\text{Zr}(\text{C}\equiv\text{CSiMe}_3)_2$ failed.²¹ Furthermore, the use of different electron-donating or -accepting R groups on the Cp ring of the dialkyne zirconocene does not change the nature of the resulting heterodimetallic $[\text{Zr}, \text{V}]$ complex.⁴¹

These results prompted us to produce, and characterize by ^1H and ^{13}C NMR, a zirconacyclocumulene species within 2–3 days by adding a catalytic amount of Cp_2V to $(\text{Cp}'_2\text{Zr}(\text{C}\equiv\text{CPh})_2)$ ($\text{Cp}' = \text{C}_5\text{H}_5$, $\text{C}_5\text{H}_4t\text{-Bu}$) (1:10 ratio).^{41,46} This means that (i) vanadocene is actually involved in the mechanism of formation of compounds 1–5 through a transfer of the $\text{C}\equiv\text{CPh}$ moiety from Zr to V and (ii) a zirconacyclocumulene species is a key intermediate in this mechanism.

From another point of view, we now understand why the heterodimetallic complexes $\text{Cp}_2\text{V}(\mu\text{-}\eta^2\text{:}\eta^4\text{-butadiyne})\text{Zr}(\text{C}_5\text{H}_4\text{SiMe}_3)_2$, **1**, and $\text{Cp}_2\text{V}(\mu\text{-}\eta^2\text{:}\eta^4\text{-butadiyne})\text{Zr}(\text{C}_5\text{H}_4t\text{-Bu})_2$, **2**, show very sharp NMR signals, despite the presence of a paramagnetic center in the molecule.²⁰ This is probably due to some dissociation of **1** and **2** in solution, giving some Cp_2V and the zirconacyclocumulene. Indeed, the ^{13}C NMR spectra of solutions of **1** and **2** in deuterated toluene or THF show signals corresponding to a quaternary carbon atom at ~ 181 and ~ 115 ppm. The same ^{13}C NMR chemical shifts were observed when $(\text{C}_5\text{H}_4\text{-SiMe}_3)_2\text{Zr}(\text{C}\equiv\text{CPh})_2$ and $(\text{C}_5\text{H}_4t\text{-Bu})_2\text{Zr}(\text{C}\equiv\text{CPh})_2$ were treated with a catalytic amount of Cp_2V .^{41,46} This shows that a relatively easy access to the metallacyclocumulene component is available, and possibly to ptC systems with an appropriate choice of the second metal-containing reagent.

The Chemistry of ptC. Extension of This Mechanism to Other ptC Systems

It may be quite possible that the mechanism proposed above, involving the key zirconacyclocumulene intermediate, also applies in the case of other diacetylenic Zr and Ti complexes. Recent results by Erker et al.^{9b} have shown that the formation of ptC is observed when a diacetylenic zirconium complex is reacted with the cationic species $[\text{Cp}_2\text{ZrMe}(\text{THF})]^+$ (Scheme 12).

If Cp_2V and $\text{B}(\text{C}_6\text{F}_5)_3$ are able to catalyze the formation of a zirconacyclocumulene intermediate, why should this not happen when $\text{Cp}'_2\text{Zr}(\text{C}\equiv\text{CPh})_2$ is placed in the presence of the cationic species $[\text{Cp}_2\text{ZrMe}(\text{THF})]^+$? Indeed, when $(\text{C}_5\text{H}_4\text{Me})_2\text{Zr}(\text{C}\equiv\text{CPh})_2$ is mixed with a catalytic amount of $[\text{Cp}_2\text{ZrMe}(\text{THF})]^+$ in THF (in a 10:1 ratio), the characteristic peaks of the corresponding zirconacyclocumulene, $(\text{C}_5\text{H}_4\text{Me})_2\text{Zr}(\eta^4\text{-PhC}\equiv\text{C}=\text{C}=\text{CPh})$, are observed in the ^1H and ^{13}C spectra of the resulting solution (nearly

Scheme 13

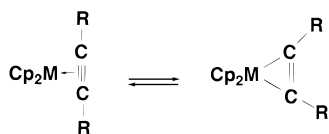
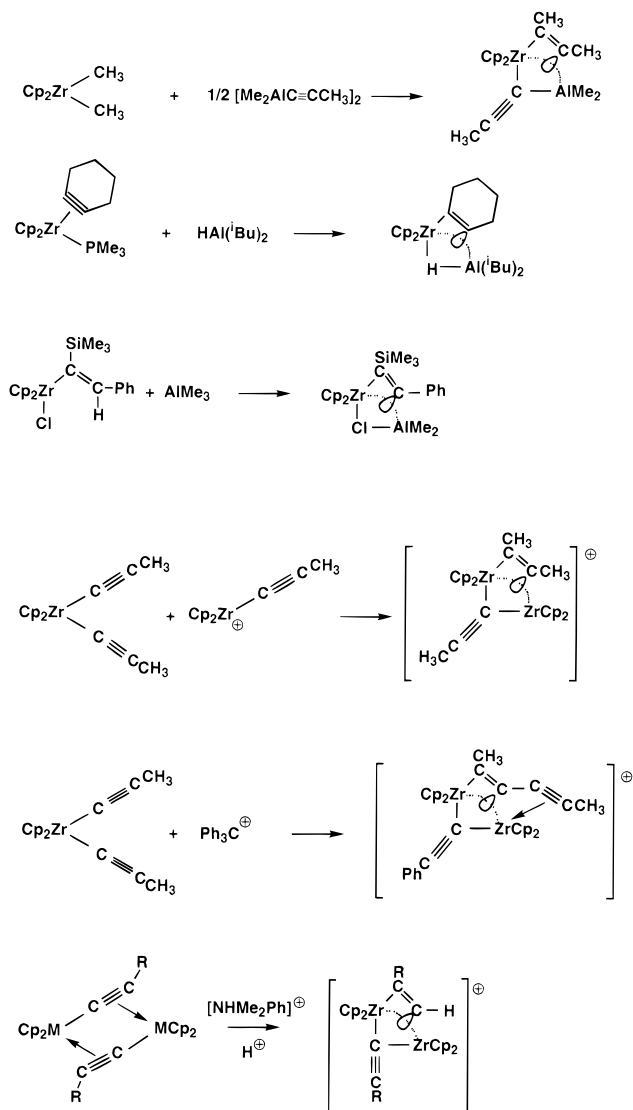


Chart 1



100% of $(C_5H_4Me)_2Zr(\eta^4-PhC=C=C=CPh)$ is obtained within 2 days).^{41,46} This experiment confirms that the cationic species $[Cp_2ZrMe(THF)]^+$ does catalyze the CC coupling of $(C_5H_4Me)_2Zr(C\equiv CPh)_2$.

This result, involving a zirconacyclocumulene as a key intermediate, shed more light on the reaction scheme proposed by Erker et al. in the case of diacetylenic complexes.^{9b} As a matter of fact, these authors made a proposition which seems similar to ours when monoacetylenic complexes are engaged in a reaction with group 11 elements and where the acetylene is π -bonded to the Zr(II) species (Scheme 13).^{9a}

Different routes toward ptC-containing systems were proposed by Erker et al.,^{5,6} and some are depicted in Chart 1, offering a simple method to prepare a variety of metal

complexes containing one ptC electronically stabilized by σ -donor/ π -acceptor interaction.

The work by Rosenthal et al.¹⁰ and our recent findings describe a new situation (should an actual electron density between the involved M and C atoms be confirmed) where two ptCs are included in the same molecule via a unifying mechanism involving the formation of a zirconacyclocumulene.

This Account results from our modest contribution and from the extensive work of U. Rosenthal and G. Erker in the chemistry of group 4 elements and more especially on ptC-containing complexes. We thank both these colleagues for fruitful discussion on this Account prior to publication. We are indebted to L. Valade, J.-S. Zhao, and D. De Caro, whose parallel research project on molecular precursors to ceramics was the driving force of this work. We thank J.-P. Legros and B. Donnadiou for cunningly solving tricky crystal structures.

References

- (1) (a) Van't Hoff, J. H. Sur les Formules de Structure dans l'Espace. *Arch. Néerl. Sci. Exactes Nat.* **1874**, 445–54. (b) Le Bel, J. A. *Bull. Soc. Chim. Fr.* **1874**, 22, 337–347.
- (2) Hoffmann, R.; Alder, R. W.; Wilcox Jr., C. F. Planar Tetracoordinate Carbon. *J. Am. Chem. Soc.* **1970**, *92*, 4992–4993.
- (3) Sorger, K.; Ragué Schleyer, P. V. Planar and Inherently Non-Tetrahedral Tetracoordinate Carbon: a Status Report. *J. Mol. Struct.* **1995**, *338*, 317–346.
- (4) (a) Seidel, W.; Kreisel, G.; Mennenga, H. Bis(2-6-dimethoxyphenyl)vanadium—a diamagnetic vanadium (II) compound. *Z. Chem.* **1976**, *16*, 492–493. (b) Cotton, F. A.; Millar, F. The Probable Existence of a Triple Bond between Two Vanadium Atoms. *J. Am. Chem. Soc.* **1977**, *99*, 7886–7891.
- (5) (a) Erker, G. Planar-Tetracoordinate Carbon: Making Stable Anti-Van't Hoff/LeBel Compounds. *Comments Inorg. Chem.* **1992**, *13*, 111–131. (b) Albrecht, M.; Erker, G.; Krüger, C. The Synthesis of Stable, Isolable Planar-Tetracoordinate Carbon Compounds. *Synlett* **1993**, 441–448. (c) Pellny, P.-M.; Peulecke, N.; Burlakov, V. V.; Tillack, A.; Baumann, W.; Spannenberg, A.; Kempe, R.; Rosenthal, U. Twofold C–C Single Bond Activation and Cleavage in the Reaction of Octatetraynes with Titanocene and Zirconocene Complexes. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2615–2617. (d) Jones, W. M.; Klosin, J. Transition-Metal Complexes of Arynes, Strained Cyclic Alkynes and Strained Cyclic Cumulenes. *Adv. Organomet. Chem.* **1998**, *42*, 147–221. (e) Pulst, S.; Kirchbauer, F. G.; Heller, B.; Baumann, W.; Rosenthal, U. The First Metathesis of C–C Single Bonds in Homogeneous Solution: Titanocene-Mediated and Photocatalyzed Cleavage and Recombination of Disubstituted Butadiynes. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1925–1927. (f) Jemmis, E. D.; Giju, K. T. Novel mechanism for Interesting C–C Coupling and Cleavage Reactions and Control of Thermodynamic Stability Involving $[L_2M(\mu-CCR)_2ML_2]$ and $[L_2M(\mu-RCC-CCR)_2ML_2]$ Complexes (M = Ti, Zr; L = $\mu^5-C_5H_5$, Cl, H; R = H, F, CN): A Theoretical Study. *J. Am. Chem. Soc.* **1998**, *120*, 6952–6964.
- (6) Röttger, D.; Erker, G. Compounds Containing Planar-Tetracoordinate Carbon. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 812–827.

- (7) (a) Roberts, D. A.; Geoffroy, G. L. Compounds with Heteronuclear Bonds between Transition Metals. In *Comprehensive Organometallic Chemistry*, Wilkinson, G., Stone, F. G. A., Abel E. W., Eds.; Pergamon: Oxford, 1982; Vol. 6, Chapter 40. (b) Stephan, D. W. Early-Late Heterobimetallics. *Coord. Chem. Rev.* **1989**, *95*, 41–107.
- (8) Hornton, A. D.; Orpen, A. G. A Structurally Distorted Ligand in an Electron-Deficient Dizirconocene Cation: Unusual 1, 2- and 1,1-Dimetallalkenes. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 876–878.
- (9) (a) Erker, G.; Röttger, D. The Energetic Stabilization Caused by a Planar-Tetracoordinate Carbon Atom: a Dynamic NMR Spectroscopic Study of the Dimetallabicyclo [(Cp₂Zr)₂(μ-C≡CCH₃)(μ-H₃CCCCH₃)]BPh₄. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1623–1625. (b) Röttger, D.; Erker, G.; Fröhlich, R.; Grehl, M.; Silverio, S. J.; Hyla-Kryspin, I.; Gleiter, R. Determination of the Stabilization Energy of Planar-Tetracoordinate Carbon in Dynamic Dinuclear (μ-hydrocarbyl)bis(zirconocene) Cation Complexes and Detection of an Organometallic Memory Effect in their Formation. *J. Am. Chem. Soc.* **1995**, *117*, 10503–10512. (c) Röttger, D.; Erker, G.; Fröhlich, R.; Kotila, S. Stabilization of a Planar-Tetracoordinate Carbon Center in an Organometallic Complex Containing both a Zirconocene and a Hafnocene Moiety. *Chem. Ber.* **1996**, *129*, 1–3.
- (10) Pulst, S.; Arndt, P.; Heller, B.; Baumann, W.; Kempe, R.; Rosenthal, U. Nickel(0) Complexes of Five-Membered Titana- and Zirconacyclocumulenes as Intermediates in the Cleavage of C–C Bonds of Disubstituted Butadiynes. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1112–1114.
- (11) Rosenthal, U.; Ohff, A.; Baumann, W.; Kempe, R.; Tillack, A.; Burlakov, V. V. Synthesis and Structure of the Smallest Cyclic Cumulene; Reaction of 1,3-Diyne with Zirconocene Complexes. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1605–1607.
- (12) Chisholm, M. H. Metalla-enes and Metalla-ynes. From Small Molecules to Infinite Polymers. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 673–674.
- (13) (a) Nast, R. Coordination Chemistry of Metal Alkynyl Compounds. *Coord. Chem. Rev.* **1982**, *47*, 89–124. (b) Lotz, S.; Van Rooyen, P. H.; Meyer, R. σ,π-Bridging Ligands in Bimetallic and Trimetallic Complexes. *Adv. Organomet. Chem.* **1995**, *37*, 219–313.
- (14) Lang, H.; Köhler, K.; Blau, S. η²-Alkyne Copper(I) and Silver(I) Compounds; from Polymeric [M^R]_n to Monomeric [M^R] Units (M = Cu, Ag). *Coord. Chem. Rev.* **1995**, *143*, 113–168.
- (15) (a) Burlakov, V. V.; Rosenthal, U.; Petrovskii, V. V.; B. Shur, V.; Vol'pin, E. Complex of Titanocene with Bis(trimethylsilyl) Acetylene. *Metalloorg. Khim.* **1988**, *1*, 953–954. (b) Rosenthal, U.; Görls, H.; Burlakov, V. V.; Shur, V. B.; Vol'pin, E. Alkinkomplexe des Titanocens und Permethyltitanocens ohne zusätzliche Liganden—Erste Strukturvergleiche. *J. Organomet. Chem.* **1992**, *426*, C53–C57. (c) Lefeber, C.; Ohff, A.; Tillack, A.; Baumann, W.; Kempe, R.; Burlakov, V. V.; Rosenthal, U.; Görls, H. Darstellung und regioselektive Reaktionen des phosphinfreien Zirconocen-Alkin-Komplexes Cp₂Zr(THF)(^tBuC₂SiMe₃). *J. Organomet. Chem.* **1995**, *501*, 179–188. (d) Rosenthal, U.; Ohff, A.; Baumann, W.; Tillack, A.; Görls, H.; Burlakov, V. V.; Shur, V. B. Struktur, Eigenschaften und NMR-spektroskopische Charakterisierung von Cp₂Zr(Pyridin)(Me₃SiC≡CSiMe₃). *Z. Anorg. Allg. Chem.* **1995**, *621*, 77–83. (e) Lefeber, C.; Ohff, A.; Tillack, A.; Baumann, W.; Kempe, R.; Burlakov, V. V.; Rosenthal, U. Darstellung und regioselektive Reaktionen des phosphinfreien Zirconocen-Alkin-Komplexes Cp₂Zr(THF)(^tBuC₂SiMe₃). *J. Organomet. Chem.* **1995**, *501*, 189–194.
- (16) Burlakov, V. V.; Ohff, A.; Lefeber, C.; Tillack, A.; Baumann, W.; Kempe, R.; Rosenthal, U. The First Titanacyclic Five-Membered Cumulene. Synthesis, Structure, and Reactivity. *Chem. Ber.* **1995**, *128*, 967–971.
- (17) (a) Lang, H.; Seyfert, D. Synthese und Reaktivität von Alkynyl-substituierten Titanocen-Komplexen. *Z. Naturforsch.* **1990**, *45b*, 212–220. (b) Janssen, M.; Herres, M.; Zsolnai, L.; Grove, D. M.; Spek, A. L.; Lang, H.; van Koten, G. A Stable Bimetallic Copper(I) Titanium Acetylide. *Organometallics* **1995**, *14*, 1098–1100. (c) Lang, H.; Frosch, W.; Wu, I. Y.; Blau, S.; Nuber, B. Reaction Chemistry of Alkynyl-Functionalized Titanocenes. X-ray Structure Analyses of (η⁵-C₅H₄SiMe₃)₂Ti(Cl)(CH₂SiMe₃) and [(η⁵-C₅H₄SiMe₃)₂Ti(Cl)(C≡CSiMe₃)]CuBr. *Inorg. Chem.* **1996**, *35*, 6266–6272.
- (18) Janssen, M. D.; Köhler, K.; Herres, M.; Dedieu, A.; Smeets, W. J. J.; Spek, A. L.; Grove, D. M.; Lang, H.; van Koten, G. Monomeric Bis(η²-alkyne) Complexes of Copper(I) and Silver(I) with η¹-Bonded Alkyl, Vinyl and Aryl Ligands. *J. Am. Chem. Soc.* **1996**, *118*, 4817–4829 and references therein.
- (19) Schottek, J.; Erker, G.; Fröhlich, R. Formation of Metallocene-Stabilized Planar-Tetracoordinate Carbon Compounds by a Protonation Route. *Eur. J. Inorg. Chem.* **1998**, 551–558.
- (20) Danjoy, C.; Zhao, J.; Donnadiou, B.; Legros, J.-P.; Valade, L.; Choukroun, R.; Zwick, A.; Cassoux, P. [Cp₂V(μ-η²:η⁴-butadiene)MCp'₂] (M = Ti, Zr; Cp' = C₅H₅, C₅H₄SiMe₃): Heterodimetallic Complexes from a Bis(alkynyl)metallocene and Vanadocene-Unexpected Structure of [Cp₂V(μ-η²:η⁴-butadiene)Zr(C₅H₄SiMe₃)₂] Containing Two Planar-Tetracoordinate Carbon Atoms. *Chem. Eur. J.* **1998**, *4*, 1100–1105.
- (21) Danjoy, C. Complexes du titane et du vanadium. Vers le système céramique quaternaire V.Ti.C.N par dépôt chimique en phase vapeur. Ph.D. Thesis, Institut National Polytechnique de Toulouse, France, 1996, No. 1197.
- (22) Valade, L.; Choukroun, R.; Danjoy, C.; Chansou, B.; De Caro, D.; Cassoux, P. Possibilités d'obtention de dépôts dans le système céramique Ti–V–C–N à partir de sources moléculaires. *Ann. Chim. Sci. Mater.* **1998**, *23*, 721–732.
- (23) (a) Choukroun, R.; Dahan, F.; Gervais, D.; Rifai, C. Substituted Cyclopentadienyl Phosphinomethyl Complexes of Zirconium. Synthesis, Chemical Characteristics, Complexation with Rhodium Complexes, and Catalytic Properties. Molecular and Crystal Structure of (η⁵-t-BuC₅H₄)₂Zr(CH₂PPh₂)₂[Rh₂(μ-S-t-Bu)₂(CO)₂]. *Organometallics* **1990**, *9*, 1982–1987 and references therein. (b) Trzeciak, A. M.; Ziolkowski, J. J.; Choukroun, R. New Bimetallic Rhodium–Zirconium Catalysts for Homogeneous Olefin Hydroformylation. *J. Mol. Catal.* **1996**, *110*, 135–139 and references therein.
- (24) Friebel, C.; Scherfise, K. D.; Willing, W.; Mueller, U.; Dehnicke, K. EPR- und Ligandenfeld-Spektren von Chlorovanadaten(IV). Die Kristallstruktur von PPh₄[V_xTi_{2-x}Cl₉] (x = 0, 15). *Z. Anorg. Allg. Chem.* **1987**, *546*, 21–32.

- (25) Mazzanti, M.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. (*N,N'*-Ethylenebis(acetylacetonate iminato))vanadium(III) Derivatives: Syntheses and Substitution Reactions at the V–Cl Bond. *Inorg. Chem.* **1986**, *25*, 4158–4164.
- (26) Elschenbroich, C.; Schmidt, E.; Metz, B.; Harms, K. Zircona[1]metallocyclophanes: Synthesis, Properties, and Structure of (tBu- η^5 -C₅H₄)₂Zr(η^1 -1, η^1 -1')-(η^6 -C₆H₅)₂V and its Chromium Analog. *Organometallics* **1995**, *14*, 4043–4045.
- (27) Teuben, J. H.; De Liefde Meijer, H. J. Phenylethynyl Complexes of Titanocene and Vanadocene. *J. Organomet. Chem.* **1969**, *17*, 87–93.
- (28) (a) Erker, G.; Frömberg, W.; Mynott, R.; Gabor, B.; Krüger, C. Unusual Bridging of the Metal Centers in Dimeric Bis(η -methylcyclopentadienyl)-phenylethynylzirconium. *Angew. Chem., Int. Ed. Engl.* **1986**, *98*, 463–464. (b) Erker, G.; Frömberg, W.; Benn, R.; Mynott, R.; Angermund, K.; Krüger, C. π -Conjugation and Dynamic Behavior in Doubly Acetylide-Bridged Binuclear Group 4 Bent Metallocene Complexes. *Organometallics* **1989**, *8*, 911–920.
- (29) Jimenez, R.; Barral, M. C.; Moreno, V.; Santos, A. Synthesis and Properties of Bis(η^5 -cyclopentadienyl)-Bis(alkynyl)zirconium(IV) Complexes. *J. Organomet. Chem.* **1979**, *182*, 353–359.
- (30) (a) Warner, B. P.; Davis, W. M.; Buchwald, S. L. Synthesis and X-ray Structure of a Zirconocene Complex of Two Alkynes. *J. Am. Chem. Soc.* **1994**, *116*, 5471–5472. (b) Rosenthal, U.; Ohff, A.; Baumann, W.; Kempe, R.; Tillack, A.; Burlakov, V. V. Reaction of Disubstituted 1,3-Butadiynes R¹≡CC≡CR² with Zirconocene Complexes: Cleavage of the Central C–C Single Bond to Form Symmetrically and Unsymmetrically Doubly Acetylide-Bridged Metallocene Complexes. *Organometallics* **1994**, *13*, 2903–2906. (c) Varga, V.; Hiller, J.; Polasek, M.; Thewalt, U.; Mach, K. Synthesis and Structure of Titanium(III) Tweezer Complexes with Embedded Alkali Metal Ions: [η^5 -C₅HMe₄]₂Ti(η^1 -C≡CSiMe₃)₂][–]M⁺ (M = Li, Na, K and Cs). *J. Organomet. Chem.* **1996**, *515*, 57–64. (d) Ohff, A.; Pulst, S.; Lefebvre, C.; Peulecke, N.; Arndt, P.; Burlakov, V. V.; Rosenthal, U. Unusual Reactions of Titanocene- and Zirconocene-Generating Complexes. *Synlett* **1996**, *2*, 111–118. (e) Rosenthal, U.; Ohff, A.; Baumann, W.; Kempe, R.; Tillack, A.; Burlakov, V. V. Synthesis and Structure of the Smallest Cyclic Cumulene; Reaction of 1,3-Diynes with Zirconocene Complexes. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1605–1607. (f) Peulecke, N.; Baumann, W.; Kempe, R.; Burlakov, V. V.; Rosenthal, U. Stability of Bridged and Unbridged η^2 -alkyne-Titanocene and -Zirconocene Complexes – Influence of Metals, Alkyne Substituents, Cp Substitution and Additional Ligands. *Eur. J. Inorg. Chem.* **1998**, 419–424.
- (31) (a) Sekutowski, D.; Stucky, G. D. Oxidative Coupling of the Phenylethynyl Group in μ -(1-3 η :2-4 η -trans-trans-1,4-Diphenylbutadiene)-bis(bis(η^5 -Methylcyclopentadienyl) Titanium) and the Reaction of 1,4-Diphenyl-1,3-Butadiene with Bis(cyclopentadienyl)titanium(II). *J. Am. Chem. Soc.* **1976**, *98*, 1376–1382. (b) Fachinetti, G.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. Vanadium-Olefin and -Acetylene Complexes: Structural Studies on (η^2 -Diethyl Fumarato-C,C)- and (η^2 -Dimethyl Acetylenedicarboxylato-C,C)bis(η -Cyclopentadienyl) Vanadium. *Inorg. Chem.* **1979**, *18*, 2282–2287. (c) Petersen, J. L.; Griffith, L. Electron Paramagnetic Resonance and Structural Studies of Small-Ring Metallacycles. Bonding in a Metallacyclopentene Formed by the Oxidative Addition of an Acetylene to Vanadocene. *Inorg. Chem.* **1980**, *19*, 1852–1858.
- (32) Razuvaev, G. A.; Abakumov, G. A.; Cherkasov, V. K. Paramagnetic d¹-Complexes of Biscyclopentadienylvanadium. *Russ. Chem. Rev.* **1985**, *54*, 724–738 (translated from *Usp. Khim.* **1985**, *54*, 1235–1259).
- (33) Zhao, J.; Valade, L.; Choukroun, R.; Cassoux, P. Unpublished results.
- (34) (a) Janssen, M. D.; Herres, M.; Zsolnai, L.; Grove, D. M.; Spek, A. L.; Lang, H.; van Koten, G. A Stable Bimetallic Copper(I) Titanium Acetylidyne. *Organometallics* **1995**, *14*, 1098–1100. (b) Yasufuku, K.; Yamazaki, H. Novel route to mixed transition-metal complexes. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 2664.
- (35) Choukroun, R.; Donnadieu, B.; Malfant, I.; Haubrich, S.; Frantz, R.; Guerin, C.; Henner, B. Homobimetallic Vanadium d¹-d¹ Complexes: Structure and Magnetism. *J. Chem. Soc., Chem. Commun.* **1997**, 2315–2316.
- (36) Takahashi, T.; Nishihara, Y.; Sun, W.-H.; Fischer, R.; Nakajima, K. Reaction of Alkenylzirconocenes with Dialkylzirconocenes: Unexpected Formation of Bimetallic (μ -alkynyl)zirconocene Complexes. *Organometallics* **1997**, *16*, 2216–2219.
- (37) Erker, G.; Wicher, J.; Engel, K.; Rosenfeld, F.; Dietrich, W.; Krüger, C. Synthesis, Structure, and Equilibration of s-Cis- and s-Trans- η^4 -Conjugated Diene-Zirconocene Complexes. *J. Am. Chem. Soc.* **1980**, *102*, 6344–6346.
- (38) Buchwald, S. L.; Watson, B. T.; Huffman, J. C. The Synthesis, Reactions, and Molecular Structure of Zirconocene-alkyne Complexes. *J. Am. Chem. Soc.* **1987**, *109*, 2544–2546.
- (39) Hunter, W. E.; Hrnčir, D. C.; Vann Bynum, R.; Penttilä, R. A.; Atwood, J. L. The Search for Dimethylzirconocene. Crystal Structures of Dimethylzirconocene, Dimethylhafnocene, and (μ -Oxo)-bis(methylzirconocene). *Organometallics* **1983**, *2*, 750–755.
- (40) Kai, Y.; Kanehisa, N.; Miki, K.; Kasai, N.; Mashima, K.; Nagasuna, K.; Yasuda, H.; Nakamura, A. X-ray Evidence for a Mononuclear s-trans- η^4 -1,3-diene Complex; Molecular Structure of Zr(η^5 -C₅H₅)₂(s-trans-PhCH=CH–CH=CHPh). *J. Chem. Soc., Chem. Commun.* **1982**, 191–192.
- (41) Donnadieu, B.; Choukroun, R.; Cassoux, P. Unpublished results.
- (42) (a) Binger, P.; Podubrin, S. Metallocene(II) Complexes of Zirconium and Hafnium. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G., Wilkinson, G., Eds.; Pergamon Press: Fort Collins, 1995; Vol. 4, pp 439–463. (b) Broene, R. D. Transition Metal Alkyl Complexes: Reductive Dimerization of Alkenes and Alkynes. *Ibid.*; Vol. 12, pp 323–347. (c) Buchwald, S. L.; Broene, R. D. Transition Metal Alkyne Complexes: Zirconium-benzynes Complexes. *Ibid.*; pp 771–784.
- (43) Temme, B.; Erker, G.; Frölich, R.; Grehl, M. Heterodimetal-Betaine Chemistry: Catalytic and Stoichiometric Coupling of Alkynyl Ligands under the Joint Influence of Zirconium and Boron Centers. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1480–1482.
- (44) Burlakov, V. V.; Peulecke, N.; Baumann, W.; Spannenberg, A.; Kempe, R.; Rosenthal, U. Reactions of the Phenyl-Substituted Five-Membered Titanacyclocumulene. Unusual Coupling of a 1,4-Disubstituted 1,3-Butadiyne with Two Titanium Atoms. *J. Organomet. Chem.* **1997**, *536–537*, 293–297.

(45) Rosenthal, U.; Pulst, S.; Arndt, P.; Ohff, A.; Tillack, A.; Baumann, W.; Kempe, R.; Burlakov, V. V. Heterobimetallic σ,π -Acetylide-Bridged Complexes from Disubstituted 1,3-Butadiynes. *Organometallics* **1995**, *14*, 2961–2968.

(46) This catalytic conversion is also observed in the absence of light.

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