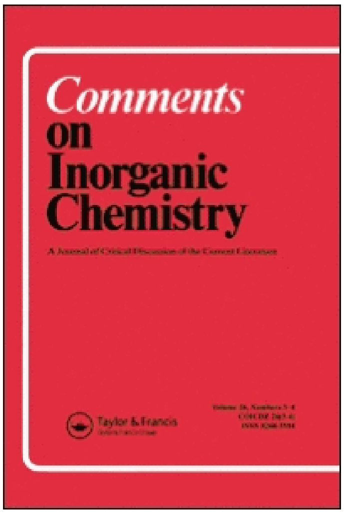

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Planar-Tetracoordinate Carbon: Making Stable Anti-van't Hoff/LeBel Compounds

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Planar-Tetracoordinate Carbon: Making Stable Anti-van't Hoff/LeBel Compounds

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Compounds containing planar-tetracoordinate carbon can be thermodynamically very stable. We have prepared a variety of examples of such compounds where the planar geometry of tetracoordinate carbon is stabilized by two metal substituents. A combination of two different metal centers, namely a transition metal (here: zirconium or hafnium) and a main group metal (here: aluminum or gallium) seems to be well suited to stabilize this "unnatural" coordination geometry of tetravalent carbon. Our new synthesis of such organometallic compounds is rather simple. The key step of the synthetic sequence is the addition of the main group metal reagent (e.g., AlR_3, AlR_2X, AlR_2H, GaR_3) to a reactive in situ generated (η^2-alkyne)metallocene intermediate which directly leads to the formation of the respective stable anti-van't Hoff/LeBel compound. The described variants of this general reaction only differ in the ways of generating the reactive alkyne transition metal component. The obtained planar-tetracoordinate carbon compounds were characterized spectroscopically. For more than ten examples X-ray crystal structure analyses have been carried out.

Key Words: *dimetallic main group/transition metal compounds, planar-tetracoordinate carbon, (alkyne) group 4 metallocenes, σ-donating/π-accepting metal centers*

Dedicated to Professor Friedrich Bickelhaupt on the occasion of his 60th birthday.

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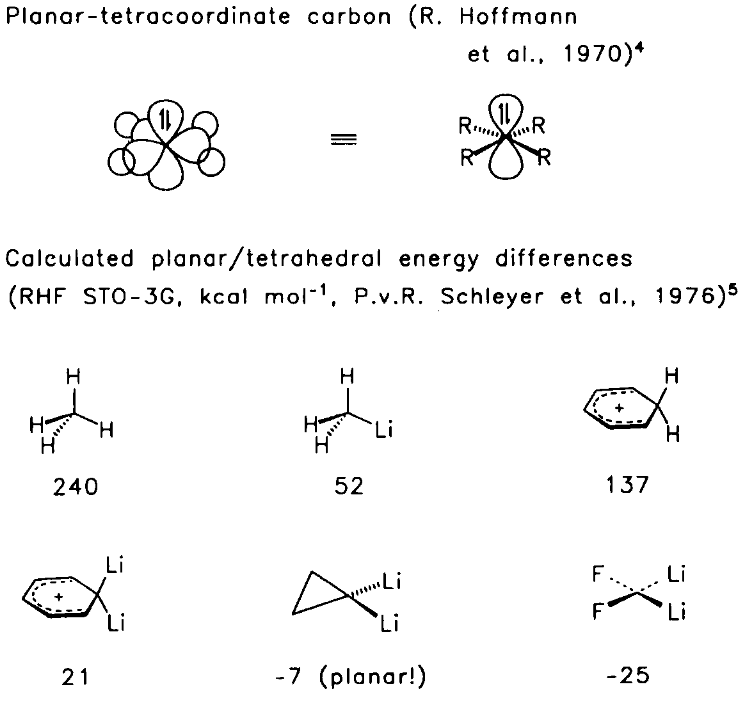
INTRODUCTION

It is well known that the element carbon makes many stable compounds in which it exceeds the coordination number of four. The favoured coordination geometry of such hypervalent carbon compounds is usually determined by the nature and the mutual interaction of the surrounding ligating groups or atoms.[1] It is commonly believed that tetracoordinate carbon behaves differently, namely that it is always surrounded by its four substituents in a tetrahedral or near tetrahedral geometry, regardless of what the special steric or electronic features of the surrounding σ-bonded groups might be. The basis of the very successful stereochemical concept of tetrahedral four-coordinate carbon was found and published more than 100 years ago independently by J. H. van't Hoff and J. A. LeBel in 1874. Since then it has provided an invaluable conceptual tool for understanding and developing organic chemistry.[2]

It is surprising how few organic chemists have challenged this concept and looked for ways to prepare stable "anti-van't Hoff/LeBel compounds," i.e., molecular substances containing tetracoordinate carbon in a non-tetrahedral coordination geometry. There have been some efforts to force sp^3-hydridized carbon into a planar-tetracoordinate σ-ligand environment by steric strain. The synthesis of the fenestranes and similar hydrocarbon systems marks attempts that, however, have led only a small distance towards experimentally realizing planar-tetracoordinate carbon compounds.[3]

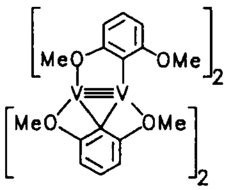
In 1970 R. Hoffmann *et al.* published a short paper describing the principles of how to stabilize planar-tetracoordinate carbon electronically.[4] Planar methane, the hypothetical high energy isomer of normal tetrahedral CH_4, contains an electron-deficient σ-system where only six electrons are available to make the bonds to four hydrogens in the main molecular plane. A p-orbital extending perpendicularly to the σ-ligand plane is doubly occupied. This overall very unfavourable electronic configuration should become stabilized by a combination of two electronic interactions. Substituting hydrogen atoms by strong σ-donor substituents would stabilize the electron-deficient σ-bond system of planar methane derivatives. Attaching π-acceptor groups at carbon would diminish the unfavourable p-electron localization. This concept of stabilizing the uncommon planar-tetracoordinate geometry over the usual tetrahedral one of methane-derivatives by a combined action of σ-donor/π-acceptor-substituents has very successfully been confirmed for a variety of specific molecular systems by means of computational chemistry. P. v. R. Schleyer *et al.* have calculated rather low activation barriers of inversion via a planar tetracoordinate carbon intermediate or transition state for a variety of metal substituted methane-derivatives. Hypothetical compounds such as, e.g., 1,1-dilithiomethane or difluorodilithiomethane were even computed to exhibit a planar ground state geometry (see Scheme 1).[5]

Before my group became concerned with these ideas there were only very few examples of stable, isolable compounds known exhibiting planar-tetracoordinate carbon. Probably the first one ever made and identified as such (**1**) came from F. A. Cotton's labo-



SCHEME 1

ratory.[6] Other singular examples (**2, 3**) were contributed by P. v. R. Schleyer's, L. Brandsma's, and S. L. Buchwald's groups, respectively.[7,8] These isolated and structurally thoroughly characterized compounds all have the planar-tetracoordinate carbon center attached to two identical σ-donating electropositive metal centers (two vanadiums, lithium's, or zirconiums). In all these cases the surplus p-electron density is effectively diminished by conjugative incorporation into the aromatic π-system.



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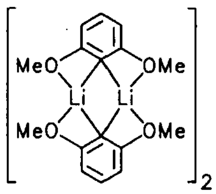

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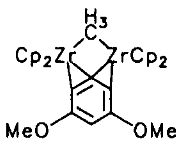


3

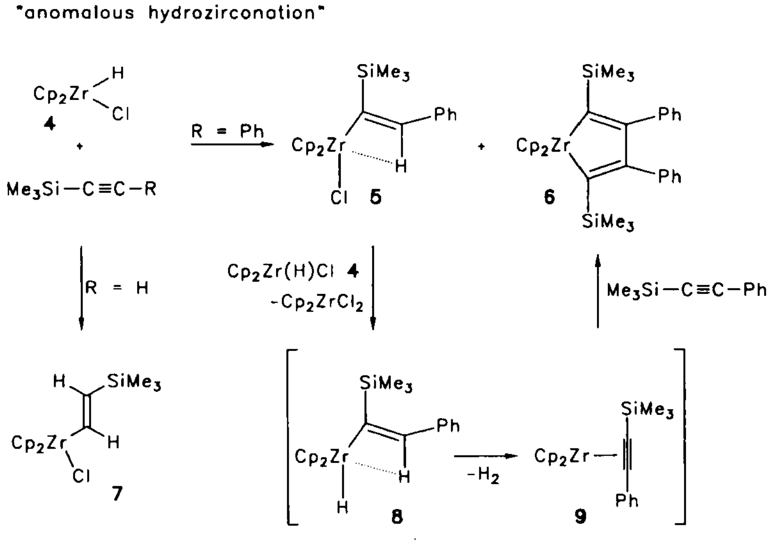
We have found a simple synthetic entry to a similar type of thermodynamically very stable organometallic compounds exhibiting a central planar-tetracoordinate carbon atom. These novel anti-van't Hoff/LeBel compounds all contain a combination of two non-identical σ-donating metal substituents. The π-delocalization here is taken care of by incorporating the planar-tetracoordinate carbon atom into a singular C═C double bond. This simple construction principle has allowed for the preparation, isolation, and characterization of many examples of stable anti-van't Hoff/LeBel compounds some of which are described and discussed in this account.

DISCOVERING A NEW WAY OF MAKING STABLE PLANAR-TETRACOORDINATE CARBON COMPOUNDS

My group became engaged with the planar-tetracoordinate carbon problem while studying the "anomalous" hydrozirconation reaction.[9] Usually the $Cp_2Zr(H)Cl$ hydrozirconation reagent (**4**) undergoes a straightforward addition to non-functionalized olefins or acetylenes; the latter reaction produces simple (σ-alkenyl)zirconocene complexes. It has been shown that the reaction between the hydrozirconation reagent and alkynes bearing bulky substituents may take a different mechanistic course which leads eventually to the formation of bis(cyclopentadienyl)zirconacyclopentadiene products. We have found out in a detailed study that this anomalous course of the hydrozirconation reaction takes place via β-agostic (alkenyl)zirconocene halide intermediates. In the cases looked at, the steric repulsion between the bulky former alkynyl substituents brings the β-alkenyl hydrogen close enough to the electron-deficient early transition metal center to overcome the barrier for making a favourable three-center-two-electron (i.e., "agostic") metal-hydrogen-sp^2-carbon interaction.

The agostic interaction acidifies the β-alkenyl hydrogen. Thus, chloride vs. hydride exchange taking place in the hydrozirconation reaction mixture gives an unstable product (i.e., **8** in Scheme 2) which rapidly loses dihydrogen. The resulting reactive (η^2-alkyne)zirconocene then adds another equivalent of the alkyne starting material to produce the five-membered metallacyclic CC-coupling product.

Scheme 2 depicts the course taken upon hydrozirconation of some trimethylsilyl-substituted acetylenes to illustrate for a se-

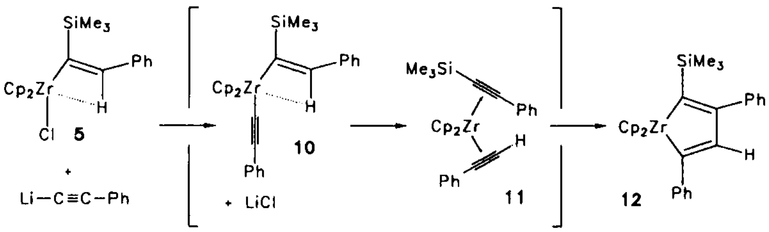


SCHEME 2

lected series of examples the general mechanistic alternatives outlined above. Trimethylsilylacetylene reacts with hydridozirconocenechloride (**4**) to give the normal hydrozirconation product **7**. In contrast, (trimethylsilyl)phenylacetylene has sufficiently bulky substituents to direct the system into the anomalous hydrozirconation alternative. This leads to a mixture of the β-agostic alkenylzirconocene halide **5** and the zirconacyclopentadiene **6**. Their ratio is complicatedly dependent on the reaction temperature and the concentrations of the reagents employed. This is a kinetic consequence of the complex reaction scheme featuring the key compound **5** as both a final product and a reactive intermediate for the subsequent reaction pathway eventually leading to the formation of **6**.

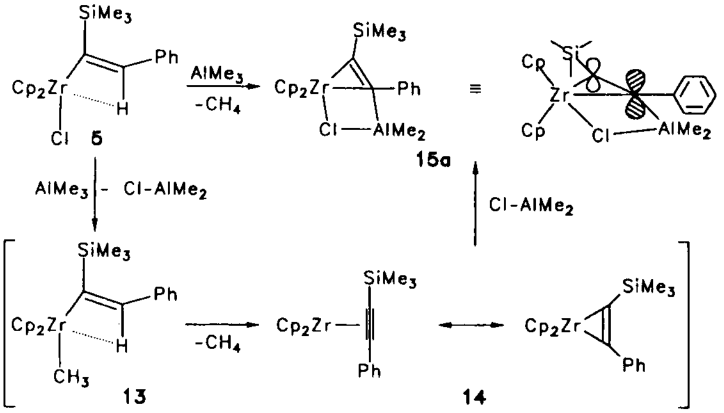
Complexes **5** and **6** were separated and both characterized by X-ray diffraction. The Zr–Cl bond length of the σ-alkenylzirconocene moiety in **5** is 2.209(4) Å. The metal to β-alkenyl carbon distance (Zr–C2) is 2.623(2) Å. The agostic Zr–H–C interaction leads to an unusually small Zr–C1–C2 angle at 89.9(2)°. The Zr–H2 separation is 2.29(2) Å.

Complex **5** undergoes a few unusual reactions. The reaction with excess lithium iodide or bromide leads to halide exchange at zirconium. The same is observed upon treatment of the alkenylzirconocene chloride **5** with the Grignard reagent benzylmagnesium bromide. We have obtained the corresponding alkenylzirconocene bromide, not the anticipated benzylated alkenylzirconocene complex. With alkynylanion equivalents a clean metathetical exchange is observed, followed by a rapid subsequent reductive elimination reaction which makes use of the acidified agostic β-alkenyl hydrogen and leads eventually to specifically substituted metallacyclopentadienyl systems such as **12** (characterized by X-ray diffraction).[9]



The most interesting reaction was observed when the alkenyl-metallocene complex **5** was treated with a stoichiometric quantity of trimethylaluminum.[10] The C–H acidic agostic σ-alkenylzirconocene complex reacts readily with the aluminum alkyl at ambient temperature in toluene solution. One equivalent of methane is evolved and a dimetallic complex of the molecular composition of $Cp_2Zr(Me_3SiCCPh)ClAlMe_2$ (**15a**) is isolated in about 90% yield. Scheme 3 provides a tentative picture of the reaction sequence taking place. The overall reaction sequence is probably initiated by methylation of the zirconium halide complex with concomitant formation of one molar equivalent of $ClAlMe_2$. The resulting σ-hydrocarbylzirconium complex **13** is not stable under the applied reaction conditions but decomposes to give methane plus a reactive (η^2-alkyne)zirconocene species (**14**). This then adds the $ClAlMe_2$ formed during the first reaction step to produce the observed reaction product **15a**.

It is the molecular structure of the obtained (η^2-alkyne)zirconocene/dimethylaluminumchloride addition product that makes this reaction sequence such an unusual one. In the course of the last step of this reaction sequence, the Cl–Al unit is attached in plane edge-bridging to the triangular framework of the (η^2-alkyne)metallocene building block. During this addition reaction the overall connectivities of both reagents have remained unaltered. The $Cl–AlMe_2$ reagent has just added to the ZrCPh edge of the (η^2-$Me_3SiCCPh$)$ZrCp_2$ intermediate and become connected



SCHEME 3

to zirconium by means of Zr–Cl bond formation and to carbon by means of forming a new C–Al linkage; the Cl–Al bond is retained in this reaction. This addition reaction has thus led to the formation of a novel type of dimetallic organometallic species that contains a single carbon center that is connected to four neighboring atoms in one common plane by means of σ-bonds. In other words, complex **15a** contains a planar-tetracoordinate carbon atom. This complex constitutes the first example of a novel type of thermodynamically stable, isolable anti-van't Hoff/LeBel compound.

We know about the very unusual coordination geometry of the carbon atom C2 in complex **15a** from an X-ray crystal structure analysis (Fig. 1). It has revealed that C2 is coordinated to four substituents by means of strong bonds all located within a singular plane. The pertinent bonding angles around C2, summing to 360°, are 62.6(2)° [C1,C2,Zr], 120.8(2)° [C1,C2,C(Ph)], 89.8(2)° [C(Ph), C2,Al], and 87.0(1)° [Zr,C2,Al]. The C1–C2 bond distance is in the olefin C=C range at 1.326(4) Å. The Zr–C2 bond length is 2.453(3) Å; this is shorter than the average Zr–C(Cp) distance but longer than the (unusually short) Zr–C1 separation (2.186(3) Å). The Zr–C(Ph) bond length is 1.513(4) Å, the C1–Al distance is 2.121(3) Å.

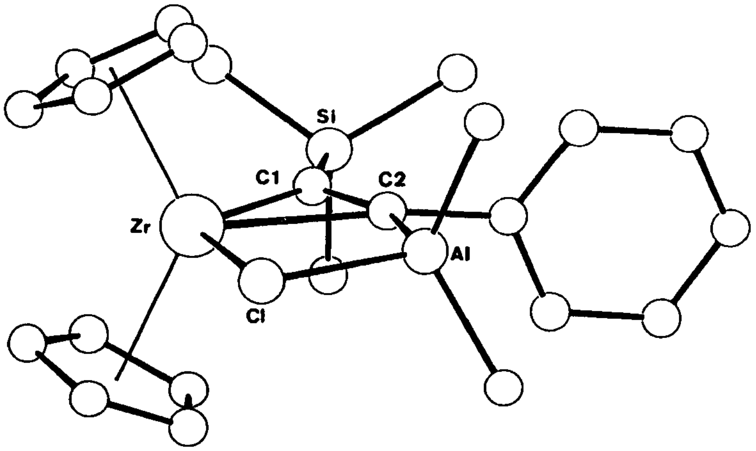


FIGURE 1 A view of the molecular structure of complex **15a**, featuring the planar-tetracoordinate geometry of the carbon atom C2.

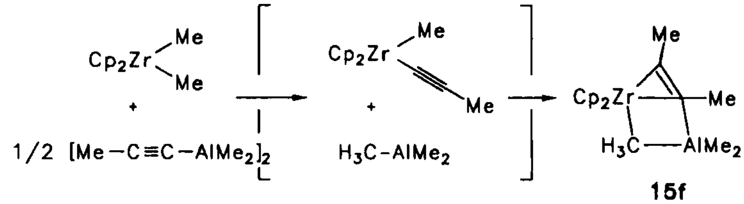
EXPLORING OUR NOVEL SYNTHESIS OF ANTI-VAN'T HOFF/LEBEL COMPOUNDS

With the reaction of the β-CH agostic (alkenyl)zirconocene halide complex **5** with trimethylaluminum we have found another singular example of forming an organometallic compound featuring a planar-tetracoordinate carbon atom. The underlying reaction principle seems to be that certain aluminum compounds (and possibly related reagents) may add to reactive (η^2-alkyne) metal complexes of the early transition metal zirconium (and potentially to alkyne complexes of other d- and f-elements as well) with preservation of the metal-alkyne connectivity, thus leading to the formation of thermodynamically stable planar-tetracoordinate carbon compounds. This simple synthetic concept turned out to be very successful for designing synthetic procedures for the preparation of many new examples of stable main group-/transition-metal substituted planar-tetracoordinate carbon compounds. These syntheses all have in common that a reactive (η^2-alkyne) transition metal complex is in situ generated in the presence of a suitable main group metal complex trapping reagent. Up to now more than twenty new examples of hitherto very rare anti-van't Hoff/LeBel compounds have been prepared along these lines and were isolated and characterized. Here are several selected examples which are representative for this development.[11]

Dimethylzirconocene reacts with (phenylalkynyl)dimethylaluminum (**16a**; two equivalents) to give trimethylaluminum and the new dimetallic complex **15b**. This product contains a phenylacetylide ligand bridging between zirconium and aluminum and a μ-(H_3C)CCPh moiety which is η^2-bonded to zirconium and η^1-coordinated to aluminum. The bridging carbon atom of the latter ligand is planar-tetracoordinate.

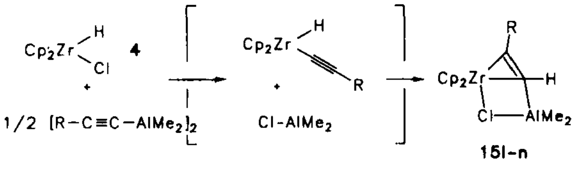
The reaction sequence leading to **15b** probably starts with a σ-ligand metathesis between dimethylzirconocene and the $RC{\equiv}C-AlMe_2$ reagent. The resulting methylzirconocene acetylide (**17**) seems to be unstable in the presence of the aluminum alkyl and undergoes a reductive elimination which generates the (H_3C)CCPh ligand system at zirconium. Additional [Al]-substituted alkyne reagent is here not cycloadded as usual to give a metallacyclopentadiene system but is rather used to build up the framework of the anti-van't Hoff/LeBel compound **15b**. It is a remarkable incidence that in this competing situation the formation of the stable planar-tetracoordinate carbon compounds **15b** is even favoured over the coupling of two acetylene ligands at zirconium, a reaction that for many examples is known to be kinetically extremely fast and thermodynamically favourable.[12]

Many differently substituted examples of **15** have been prepared in this way. In all these preparations the trimethylaluminum co-product was removed from the reaction mixture. However, it can in a few cases be used as a coupling component for the synthesis of the dimetallic (alkyne)zirconocene/R_3Al-coupling product as well. For example, from the reaction of Cp_2ZrMe_2 with one molar equivalent of (propynyl)dimethylaluminum we have obtained the methyl-bridged anti-van't Hoff/LeBel compound **15f**. In this case both monometallic building blocks have been formed in situ by means of the rate-determining σ-hydrocarbyl ligand metathesis reaction and then coupled in the subsequent rapid addition reaction.



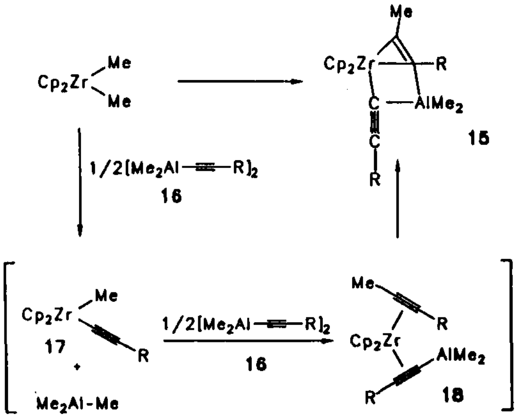
15f

A similar reaction is observed to take place between alkynylaluminum compounds and $Cp_2Zr(H)Cl$. The hydride is eventually added to the alkynyl carbon center α to aluminum to give the dinuclear Zr,Al-complexes **15l-m** (R = Ph, CH_3, or cyclohexyl). The stereochemical attachment of substituents at the central bridging C═C unit indicates that these complexes are probably not formed by means of a hydrozirconation reaction but rather result from a reaction sequence similar to the one described above and depicted in Scheme 4. We assume that alkynyl vs. chloride exchange takes place initially giving rise to the formation of CpZr(H)(−C≡CR) and $ClAlMe_2$ which then may recombine forming the observed dimetallic complexes **15**.



(R = Ph, Me, cyclo-C$_6$H$_{11}$)

A variety of trialkylphosphate-stabilized (η^2-alkyne)zirconocenes and related complexes are readily available.[13] These can very conveniently be used as starting materials for our synthesis of stable organometallic anti-van't Hoff/LeBel compounds as well. The reaction of the (η^2-aryne)(trimethylphosphane)zirconocene complex **19** with various aluminum compounds is a typical example. Treatment of **19** with excess trimethylaluminum induces the fragmentation of the (phosphane)zirconocene complex by $Me_3P{\cdot}AlMe_3$ adduct formation. The reactive (η^2-1,2-didehydrobenzyne)zirconocene intermediate thus generated in situ then readily takes up another equivalent of trimethylaluminum to form the dimetallic complex **15n**. Similarly, exposure of the zirconium(II)complex **19** to diisobutylaluminumhydride in toluene solution at ambient temperature rapidly leads to the formation of the Zr,Al-complex **15s**. Both compounds contain a central planar-

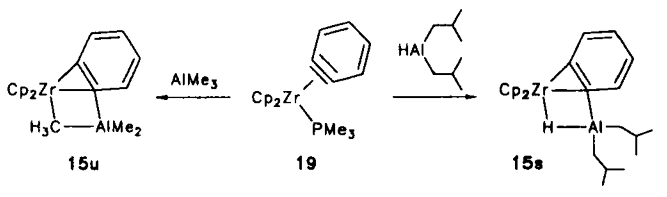


R = -Ph; -cyclo-C$_6$H$_{11}$; -SiMe$_3$; -CMe$_3$

[M] = Cp$_2$Zr (15b-d); (MeC$_5$H$_4$)$_2$Zr (15g); Cp$_2$Hf (15h-k).

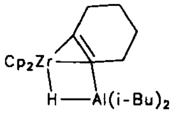
SCHEME 4

tetracoordinate carbon atom that is part of an aromatic system bridging two metal centers. This structural composition of the complexes **15s** and **15n** is reminiscent of the early examples of isolated organometallic compounds containing planar-tetracoordinate carbon (complexes **1–3**, vide supra).[6–8]

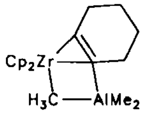


15u **19** **15s**

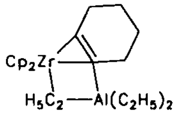
True (η^2-alkyne)(trimethylphosphane)ZrCp$_2$ complexes react analogously. We have prepared the cyclohexendiyl-annulated complexes **15r**, **15t**, and **15v** by reacting (η^2-cyclohexyne)(trimethylphosphane)zirconocene with diisobutylaluminumhydride, trimethyl- or triethylaluminum, respectively. (η^2-Tolane)(trimethylphosphane)ZrCp$_2$ yields the planar-tetracoordinate carbon compound **15p** upon treatment with HAl(iBu)$_2$.



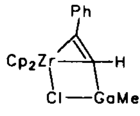
15r



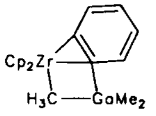
15t



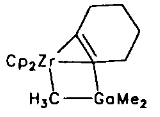
15v



15o



15w



15x

All these reactions as described above represent variations of a rather simple general reaction scheme, namely the addition of aluminum alkyl, hydride, or halide compounds, respectively, to in situ generated reactive (η^2-alkyne)zirconocene type complexes to give organometallics exhibiting dimetallatricyclic frameworks each containing a planar-tetracoordinate carbon atom in the central bridgehead position. We have obtained evidence that this synthetic concept may be used to prepare many stable anti-van't Hoff/LeBel compounds in such a simple and straightforward manner as well where other combinations of metals and substituents can be utilized to thermodynamically stabilize this uncommon coordination geometry of four-coordinate carbon. The first examples that were just prepared and isolated in my laboratory include the aluminum/hafnium complexes **15h, i**, and **k** that were already mentioned above. In addition we have recently obtained first examples of analogously structured zirconium/gallium compounds (**15v, w**, and **x**) and we have found indications that boron containing compounds (possibly $Cp_2Zr(\mu\text{-}\eta^2{:}\eta^2\text{-}PhCCPh)(\mu\text{-}H)B(C_2H_5)_2$ **15y**) of similar composition can be obtained as well.

STRUCTURE AND BONDING OF THE PLANAR-TETRACOORDINATE CARBON COMPOUNDS 15

The anti-van't Hoff/LeBel complexes **15**, prepared from in situ generated (η^2-alkyne)metallocenes by the different variants of our general synthetic scheme as outlined above were systematically characterized by NMR-spectroscopy and by X-ray diffraction. The ^{13}C NMR feature of the carbon atom C1 of the bridging $\mu\text{-}\eta^1{:}\eta^2\text{-}C^1R^1{=}C^2R^2$ unit is generally observed at rather low field. Chemical shift values of around δ 200 seem to be typical. In a few instances δ-values of >250 may be observed (e.g., complexes **15f, 15l, 15n, 15o**, see Table I). The planar-tetracoordinate carbon atom exhibits ^{13}C NMR absorptions in the low field olefinic range. As illustrated by the selected examples listed in Table I, most planar-tetracoordinate carbon resonances of the dimetallabicyclic complexes **15** have been observed in a very narrow range between δ 142 and 156. If these values are corrected for typical R^1 and R^2 substituent effects by a commonly used ^{13}C NMR increment system[14] one obtains a value of about δ 140 ± 2 for the C^2 ^{13}C NMR absorption in the parent system derived from acyclic disubstituted $\mu\text{-}\eta^1{:}\eta^2\text{-}C^1R^1{=}C^2R^2$ bridging components.

The analogously corrected value for the planar-tetracoordinate carbon ^{13}C NMR absorption in the $Cp_2M(\mu\text{-}\eta^1{:}\eta^2\text{-}C^1R^1{=}C^2H)(\mu\text{-}X)AlR_2$ and $-GaR_2$ systems is slightly different at δ 157 ± 7. For

TABLE I

Selected NMR data of $Cp_2M(\mu\text{-}\eta^1:\eta^2\text{-}C^1R^1{=}C^2R^2)(\mu\text{-}X)M'R_2$ complexes **15** (C^2 is planar-tetracoordinate).

Compound	M	R^1	R^2	X	$M'R_2$	δC^1	δC^2
15b	Zr	CH_3	Ph	$C{\equiv}CPh$	$AlMe_2$	208.6	144.2
15c	Zr	CH_3	C_6H_{11}	$C{\equiv}CC_6H_{11}$	$AlMe_2$	197.7	151.9
15e	Zr	CH_3	CMe_3	$C{\equiv}CCMe_3$	$AlMe_2$	208.4	155.9
15f	Zr	CH_3	CH_3	CH_3	$AlMe_2$	281.5	147.3
15h	Hf	CH_3	Ph	$C{\equiv}CPh$	$AlMe_2$	211.6	146.2
15i	Hf	CH_3	C_6H_{11}	$C{\equiv}CC_6H_{11}$	$AlMe_2$	201.0	153.6
15l	Zr	H	Ph	Cl	$AlMe_2$	282.9	147.2[a]
15m	Zr	H	CH_3	Cl	$AlMe_2$	198.8	142.1[a]
15n	Zr	H	C_6H_{11}	Cl	$AlMe_2$	275.5	153.7
15o	Zr	H	Ph	Cl	$GaMe_2$	258.9	146.8[b]
15p	Zr	Ph	Ph	H	$AliBu_2$	206.1	143.5
15r	Zr	CH_2CH_2-	CH_2CH_2-	H	$AliBu_2$	207.6	108.9
15s	Zr	$CH{=}CH$-	$CH{=}CH$-	H	$AliBu_2$	193.4	114.9
15w	Zr	$CH{=}CH$-	$CH{=}CH$-	CH_3	$GaMe_2$	187.3	117.3
15x	Zr	CH_2CH_2-	CH_2CH_2-	CH_3	$GaMe_2$	197.3	109.3

[a] $^1J(CH)$ = 150 Hz.
[b] $^1J(CH)$ = 154 Hz.

these complexes slightly decreased "olefinic" $^1J(C^2H)$ coupling constants are found (150 Hz). The ^1H NMR shift of the hydrogen at C^2 is in the olefinic region. Sometimes rather large $^4J(H,H)$ coupling constants are found for these hydrogen atoms [$=C^2H$ (**15l**): δ 8.05 (s); (**15m**): 6.93 (q, ^4J = 6 Hz), (**15n**): 6.78 (d, ^4J = 6 Hz).

The cyclohexyne and benzyne derived complexes show C^1R ^{13}C NMR chemical shifts in the expected range [e.g., δ 207.5 (**15t**), δ 193.9 (**15n**)]. However, the planar-tetracoordinate carbon centers in these complexes, which are exhibiting a dimetallatricyclic framework, show considerably lower ^{13}C NMR shift values than their dimetallabicyclic analogues. For the complexes **15r**, **s**, and **15u–x** we have observed chemical shift values between δ 109 and δ 118 for the central planar-tetracoordinate carbon atom.

The NMR spectra alone do not allow for a positive identification of the complexes **15** as belonging to a class of compounds featuring a planar-tetracoordinate carbon atom. Therefore, up to now more than ten examples of the differently substituted complexes **15** described above were characterized by X-ray crystal structure analyses and thus correctly assigned as anti-van't Hoff/LeBel compounds.

All these structures have confirmed the presence of a coplanarly oriented dimetallabicyclic central complex framework. The "bridgehead" carbon atom C2, which is coordinated to both metal centers, is planar-tetracoordinated—its sum of bonding angles is 360°. This is illustrated for a typical example in Fig. 2, giving a projection of the molecular structure of the Zr,Al containing anti-van't Hoff/LeBel compound **15b**. The compounds **15** are not forced into this bicyclic bonding arrangement by any steric constraints. Simple molecular model studies have shown that for the given composition the occurrence of a five-membered monocyclic ZrCCAlX skeleton would be possible without any steric restriction. In such a "natural" bonding situation the Zr,C1,C2 angle would be found at about 120°. The Zr–C2 separation would be between 2.9 Å to 3.1 Å. In all the examples looked at (see above), the systems **15** "voluntarily" undergo a substantial ring contraction and prefer to make a rather strong Zr–C2 bond, even if this results in a dramatic reduction of the Zr,C1,C2 bonding angle. Quite uniformly for all the examples looked at (see Table II) we have

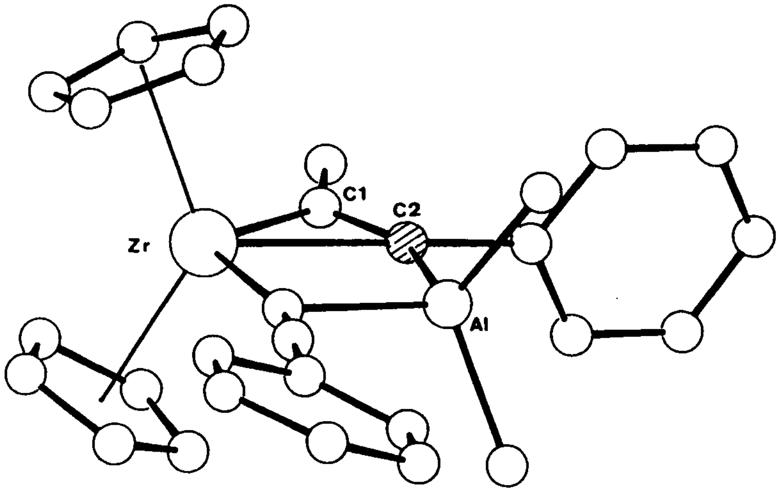


FIGURE 2 A projection of the molecular structure of **15b**.

TABLE II

Selected structural parameters of planar-tetracoordinate carbon compounds $Cp_2M(\mu\text{-}\eta^1{:}\eta^2\text{-}C^1R^1{=}C^2R^2)(\mu\text{-}X)M'R_2$ **15**.

Compound	M,M′	Zr,C1,C2 (°)	Zr–C1 (Å)	Zr–C2 (Å)	C1–C2 (Å)
15a	Zr,Al	84.9(2)	2.186(3)	2.453(3)	1.326(4)
15b	Zr,Al	86.6(6)	2.163(3)	2.47(1)	1.324(4)
15c	Zr,Al	86.1(3)	2.192(5)	2.467(4)	1.291(7)
15h	Hf,Al	87.7(4)	2.120(6)	2.432(6)	1.280(9)
15p	Zr,Al	82.4(3)	2.184(4)	2.401(4)	1.326(6)
15r	Zr,Al	83.4(2)	2.155(4)	2.389(4)	1.311(5)
15x	Zr,Ga	86.2(3)	2.126(5)	2.423(5)	1.314(7)

found Zr,C1,C2 bonding angles between 82° and 88°. The Zr–C2 distances are all shorter than the Zr–C(Cp) bonds. The planar-tetracoordinate carbon to transition metal bonds are all typically in a range between 2.39 and 2.47 Å.

The ring-closure reaction from a hypothetical monocyclic five-membered metallacycle (which does not necessarily have to correlate to any real intermediate or transition state during the formation of the complexes **15**) to the dimetallatricycle was modelled by an ab initio calculation (STO-3G-level). R. Gleiter *et al.* have found that the metallacycle $Cl_2ZrCH{=}CHAl(H)_2Cl$ (starting geometry: angle Zr,C1,C2 = 120°, *d* (Zr–C2) = 2.90 Å) is unstable with regard to exothermic (ΔE = −47 kcal/mol^{-1}) formation of the $Cl_2ZrCH{=}CHAl(H)_2Cl$ bicyclus.[15] The calculated geometry of the final product is characterized by an even slightly more pronounced Zr–C2 interaction at 2.252 Å than experimentally observed for the metallocene derived systems **15**. The Zr,C1,C2 angle of the calculated model system turned out to be 79.2°. The calculated C1–C2 distance is 1.333 Å. This is not far from the experimentally observed C–C bond lengths in **15**, which are in the C=C double bond region. The Zr–C1 distance in this calculation was found at 2.081 Å. This is a shorter bond than observed. However, the corresponding Zr–C1 values listed in Table II confirm that the results from our simplified calculated model show the correct tendency. All these examples exhibit extremely low values of the transition metal to C1 bond distance. For the hafnium complex **15h** (see Table II and Fig. 3), featuring a hydride bridge between Hf and Al, the Cp_2M–C1 bond is as short as 2.120(6)

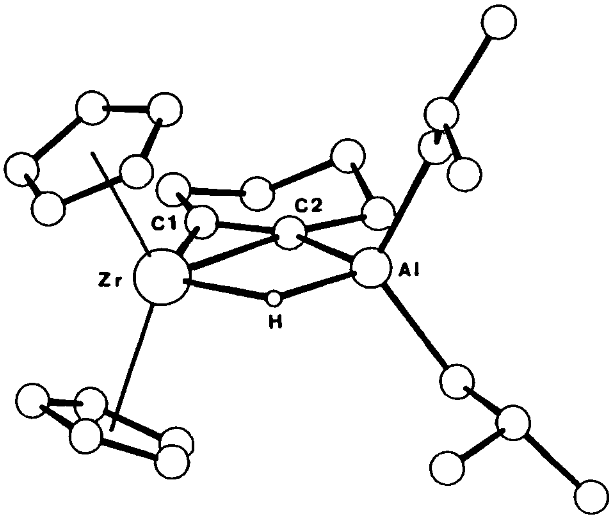
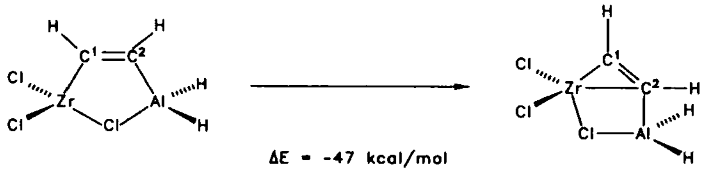


FIGURE 3 View of the molecular structure of the Hf/Al anti-van't Hoff/LeBel compound **15h**.

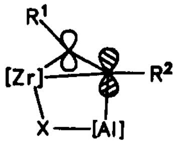
Å. The median of the observed Zr–C1 range (2.15–2.19 Å) is at or even below the reported Zr–C(sp) distance in zirconocenedicarbonyl.[16] This indicates that there is a significant π-interaction between the C1–C2 carbon carbon double bond and an acceptor orbital at zirconium oriented normal to the σ-ligand plane.[17] This may have found some confirmation in a recent X–X electron difference density study, carried out by C. Krüger *et al.* on complex **15b**, showing positive deformation density between zirconium and carbon in the region above and below the Zr–C1 vector.[18]

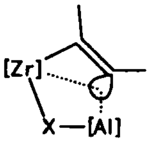


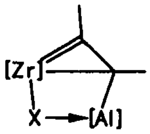
CONCLUSIONS

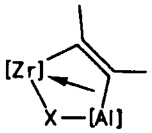
We have found that many (η^2-alkyne) group 4 metallocene complexes and related compounds very cleanly add aluminumalkyl,

-hydride, or -halide reagents, and also similar gallium and some boron compounds, to yield stable, isolable dimetallic main group metal/transition metal complexes which contain a planar-tetracoordinate carbon atom. Many examples of such unusually structured substances have been prepared. Due to their number and in view of the apparent ease of their formation such anti-van't Hoff/LeBel compounds should no longer be considered as being extremely rare exceptions to normally structured organic and organometallic carbon compounds. The bonding pattern observed for the complexes **15** is in principle as was predicted for electronically stabilized planar-tetracoordinate carbon by the theoretical work of R. Hoffmann *et al.*, P. v. R. Schleyer *et al.*, and others.[4,5,19]









The planar-tetracoordinate carbon center (C2) in our complexes seems to form a three-center-two-electron interaction with, e.g., zirconium and aluminum. This probably leads to a sufficient stabilization of the electron-deficient σ-system. A priori it is not equally clear to what extent the π-electron density is removed by metal–carbon interaction from the p-orbital at C2. Of course, the planar-tetracoordinate carbon center is part of the C1–C2 carbon–carbon double bond; but it appears that a further π-delocalization involving a metal center is a key point for the observed great thermodynamic stability of the complexes **15**. From the Zr–C1 bonding distances (see Table II) and the high resolution X–X study mentioned above the presence of a marked Zr–C1 π-interaction is likely. The overall bonding picture thus includes a π-conjugative C2–C1–Zr component which may effectively diminish the surplus p-electron density at the planar-tetracoordinate carbon center C2 by some C═C to metal back-donation. A metal alkylidene type resonance structure may be used to depict this bonding component and complement other valence structures in attempting to formulate simple pictures for describing the complexes **15**.

It may turn out that using a combination of two different metals greatly helps to electronically stabilize the "unnatural" planar geometry of tetracoordinate carbon compounds. The σ- as well as π-interaction could very much benefit from the interaction of the M^1–C system with a second metal M^2 different from the first one because this may allow for a better energetic match of the involved orbitals.[20] A number of cases can be envisaged where the use of two different metals should be superior to the electronic stabilization that can possibly be exerted by the interaction of carbon with two identical metal fragments in the planar-tetracoordinate situation. Finally, I would like to note that the many synthesized and characterized examples of complexes **15** show that stable planar-tetracoordinate carbon compounds seem not to be spectroscopically very conspicuous. Therefore, it may well be that many more examples of such compounds have been prepared but their very nature has not been disclosed for that very reason. It is possible that stable anti-van't Hoff/LeBel compounds are more common than was previously thought.

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