by the different behavior of complexes **2** and **3** with respect to their isomers **2′** and **3′** when they react with $AgClO_4$ in the presence of acetonitrile. The former give [PdR(bpy)(MeCN)]ClO_4 (**6**) and [PdR(phen)(MeCN)]ClO_4 (**7**), respectively, while the latter gives the cyclometalated [Pd(η^2-R′)(bpy)]ClO_4 (**8**) [ν(CO), 1510 cm^{-1}] and [Pd(η^2-R′)(phen)]ClO_4 (**9**) [ν(CO), 1505 cm^{-1}], respectively, although, in the last case, a mixture of **9** and some species containing MeCN (by IR), presumably [PdR′(phen)(MeCN)]ClO_4, was initially obtained; however, stirring this mixture in acetone removes MeCN, yielding pure **9**. The low solubilities of **6**–**9**, as well as **1**, have prevented measurements of their NMR spectra.

Crystal Structure of Complex 2. Figure 3 shows the expected tetracoordination of the metal center. The geometry at Pd is not exactly planar, because the atom N(2) lies 0.22 Å out of the plane of Pd, C(11), Cl, and N(1). The dihedral angle between the rings of the bpy ligand is 12°. Its bite angle is 79.6°. The Pd–N bond distances (Table III) show a clear difference in the trans influences of the aryl [Pd–N(1), 2.107 (3) Å] and chloro ligands [Pd–N(2), 2.039 (3) Å]; both are significantly shorter than those found[6] in the cationic complexes **5** and **5′** [2.143 (4), 2.137 (3) Å and 2.099 (4), 2.114 (3) Å, respectively] which can be explained as a consequence of greater Pd to N π-back-bonding in neutral complex **2** than in cationic **5** and **5′**. This difference is probably also responsible for the different orientation of the formyl group with respect to the palladium atom; in **5** and **5′** the formyl oxygen makes a short contact to Pd (2.921 (5) and 2.926 (3) Å, respectively) whereas in **2** the hydrogen atom is involved (Pd···H, 2.70 Å). All these formally nonbonded distances are appreciably longer than expected values for covalent bonds (Pd–O, 2.2 Å; Pd–H, 1.6 Å).[12] The Pd–C bond distance (1.992 (4) Å) is similar to those in **5** (2.010 (5) Å) and **5′** (1.986 (3) Å).

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Supplementary Material Available: Complete listings of bond lengths and angles, anisotropic displacement parameters, and H atom coordinates (4 pages). Ordering information is given on any current masthead page.

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(Aryne)metallocene- and (Alkyne)metallocene-Derived Dimetallic Zirconium/Aluminum Complexes Containing Planar-Tetracoordinate Carbon

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Compounds X-[M^2] of Lewis acidic main group metals can be added to very reactive alkyne–transition metal complexes (η^2-RC≡CR)[M^1] to form dimetallabicyclic organometallic compounds [M^1](μ-η^1:η^2-RCCR)(μ-X)[M^2] containing a planar-tetracoordinate carbon atom, which is stabilized by the combined σ-donor/π-acceptor properties of the specific metal/ligand combination. This general synthetic scheme has been used to prepare such planar-tetracoordinate carbon complexes by reacting e.g. (η^2-aryne)(PMe_3)$ZrCp_2$ (**12**) with 2 molar equiv of diisobutylaluminum hydride. Initial $Me_3P\cdot HAl(iBu)_2$ adduct formation generates the reactive (η^2-aryne)$ZrCp_2$ intermediate, which is then trapped by additional hydridoaluminum reagent to yield the thermodynamically stable complex $Cp_2Zr(\mu\text{-}\eta^1{:}\eta^2\text{-}C_6H_4)(\mu\text{-}H)Al(iBu)_2$ (**14a**). Complex **14a** crystallizes in space group $P2_1/n$ with cell parameters a = 16.749 (3) Å, b = 13.833 (1) Å, c = 20.178 (2) Å, β = 90.74 (1)°, R = 0.088, and R_w = 0.093. It contains a planar-tetracoordinate carbon center [C(2)] at the bridgehead position of the dimetallabicyclic framework which is bonded to two carbon atoms [d(C(2)–C(1)) = 1.37 (2) Å, d(C(2)–C(3)) = 1.41 (1) Å], the zirconium [d(C(2)–Zr) = 2.430 (8) Å], and the aluminum atom [d(C(2)–Al) = 2.09 (1) Å, all values averaged over the two independent molecules; the sum of bonding angles around C(2) is 360°]. The reaction between **12** and trimethylaluminum gave the analogously structured $Cp_2Zr(\mu\text{-}\eta^1{:}\eta^2\text{-}C_6H_4)(\mu\text{-}CH_3)AlMe_2$ complex **14b**; treatment of **12** with triethylaluminum furnished $Cp_2Zr(\mu\text{-}\eta^1{:}\eta^2\text{-}C_6H_4)(\mu\text{-}CH_2CH_3)AlEt_2$ (**14c**). Complex **14b** was characterized by X-ray diffraction (space group $P2_1/n$, a = 9.151 (1) Å, b = 14.022 (1) Å, c = 14.415 (1) Å, β = 104.56 (1)°, R = 0.042, R_w = 0.057). Again, carbon atom C(2) is planar-tetracoordinate [d(C(2)–C(1)) = 1.383 (4), d(C(2)–C(3)) = 1.423 (5), d(C(2)–Zr) = 2.481 (3), d(C(2)–Al) = 2.082 (3) Å; the sum of bonding angles at C(2) is 360°]. The general synthetic scheme for the preparation of dimetallabicyclic "anti-van't Hoff/LeBel compounds" can also be applied to reaction sequences starting from stable (η^2-alkyne)metallocene complexes. Thus, the reaction of (η^2-cyclohexyne)(PMe_3)$ZrCp_2$ (**11a**) or (η^2-diphenylacetylene)(PMe_3)$ZrCp_2$ (**11b**) with excess trimethylaluminum gave the respective $Cp_2Zr(\mu\text{-}\eta^1{:}\eta^2\text{-}RCCR)(\mu\text{-}CH_3)AlMe_2$ products (**7d,e**). The reaction between the (tolane)metallocene complex **11b** with a mixture of 9-BBN and triethylboron produced $Cp_2Zr(\mu\text{-}\eta^1{:}\eta^2\text{-}PhCCPh)(\mu\text{-}H)BEt_2$ (**15**) in low yield.

Since 1874, when van't Hoff's and LeBel's pioneering and imaginative thoughts and conclusions were independently published, it is well-known that tetracoordinate carbon in organic compounds favors a tetrahedral coor-

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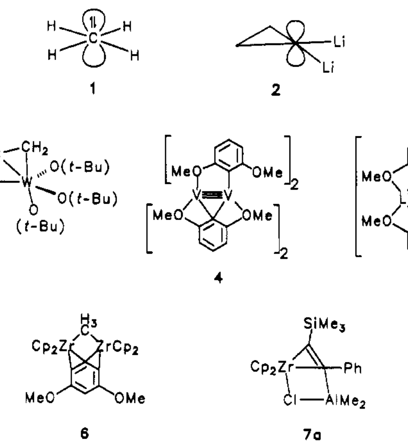
Chart I

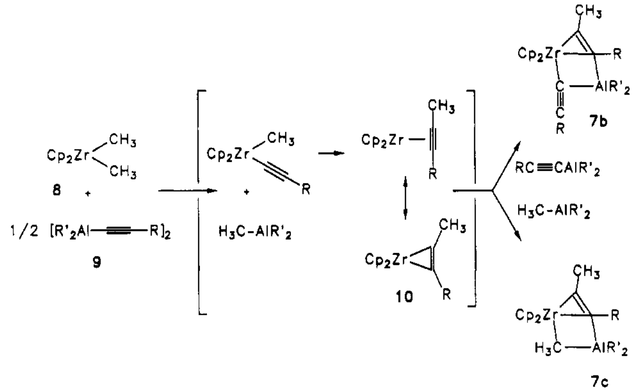


dination geometry.[1] Carbon atoms can rather easily make more than four bonds to surrounding groups or atoms ("hypervalent carbon chemistry"[2]), but it seemed to be rather difficult to have other than tetrahedral geometries being favored when a carbon center has only four tightly bonded neighboring atoms.

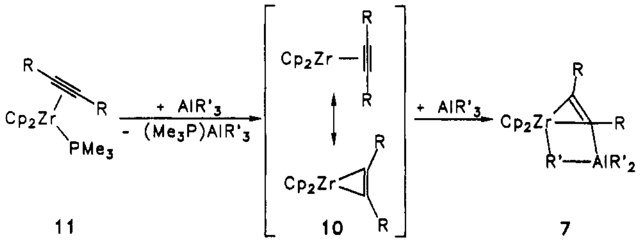
It has been tried to force four bonds to carbon coplanar by severe steric constraint (e.g. in fenestrane chemistry[3]) but not with ultimate success. In 1970 a paper authored by Hoffmann, Alder, and Wilcox appeared describing the essential factors to be met for stabilizing planar methane derivatives (1) electronically.[4] Planar-tetracoordinate carbon is sp^2-hybridized. Therefore, it contains an electron-deficient σ-system (six electrons making a total of four σ-bonds). The remaining electron pair occupies the p-orbital at carbon, which is oriented normal to the σ-plane (see Chart I). This energetically very unfavorable bonding situation can be stabilized by attaching suitable substituents at carbon (instead of hydrogen atoms) which increase the electron density of the σ-system and lower the energy of the doubly occupied p-orbital. Thus, a suitable combination of σ-donor and π-acceptor substituents may eventually lead to stable planar-tetracoordinate carbon compounds.

More sophisticated quantum-mechanical calculations (carried out e.g. by Schleyer et al.[5,6]) have indeed shown that a variety of dimetallamethane derivatives should possess stable square-planar ground states. A typical and

Scheme I



Scheme II



often cited example is 1,1-dilithiocyclopropane (2), which should be a thermodynamically stable planar-tetracoordinate carbon compound. Here the combined σ-donor/π-acceptor properties of lithium serve to stabilize the "unnatural" planar coordination geometry of the tetravalent carbon center.

Only very few examples of stable and isolable compounds containing planar-tetracoordinate carbon centers have been reported so far. The (μ-allene)ditungsten complex **3**, prepared by Chisholm et al.,[7] represents a rare example where the electronic features of which come close to those of the calculated 1,1-dimetallamethane systems. The few reported additional examples (**4**–**7**) have in common that the occupied p-orbital at the planar-tetracoordinate carbon center is part of a π-system. This may be an aromatic system (**4**–**6**)[8] or just a simple carbon–carbon double bond (**7**).[9]

The discovery that complex **7** contains a planar-tetracoordinate carbon center has opened simple new synthetic ways to novel thermodynamically stable "anti-van't

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Hoff/LeBel compounds". Thus, treatment of dimethylzirconocene (**8**) or -hafnocene with alkynylaluminum compounds RC≡CAlR′$_2$ (**9**) led to the formation of novel very stable examples of these unusually structured dimetallabicyclic compounds.[10] Depending on the reaction conditions, alkyl- or alkynyl-bridged complexes were isolated in high yield. All these reaction sequences probably have in common that a very reactive (η^2-alkyne)metallocene intermediate (**10**) is formed along the way which is then trapped by either the alkynealuminum reagent or by an alkylaluminum scavenger formed in the initial stages of the reaction (see Scheme I).

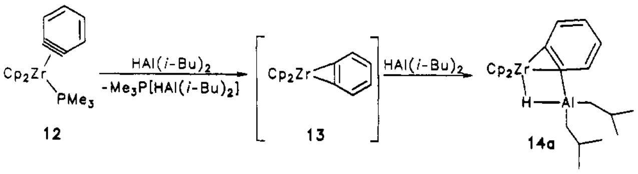
This general reaction scheme has allowed the development of an improved synthesis of stable dimetallic zirconium/aluminum complexes containing planar-tetracoordinate carbon. A variety of phosphane-stabilized (alkyne)zirconocene complexes of the general type (RC≡CR)(PMe$_3$)ZrCp$_2$ (**11**) are readily available.[11] From these the stabilizing trimethylphosphane ligand can be removed by treatment with a suitable Lewis-acid reagent (e.g. R′$_3$Al) to generate the reactive (η^2-alkyne)zirconocene intermediate (**10**). This can then be trapped e.g. by the added AlR′$_3$ reagent to give the respective dimetallabicyclic planar-tetracoordinate carbon compound **7** directly. This general synthetic route to differently substituted complexes **7** is depicted in Scheme II.

We have used this general reaction sequence to prepare a variety of organometallic planar-tetracoordinate carbon compounds containing zirconium and aluminum. We here describe several examples of such syntheses where (η^2-aryne)metallocenes derived from readily available (η^2-aryne)(PMe$_3$)ZrCp$_2$ (**12**)[12] are trapped by added Lewis acidic organoaluminum reagents. The (η^2-aryne)ZrCp$_2$ intermediate (**13**)[13] has bonding features that are very similar to those of the (η^2-alkyne)metallocene moiety used in Scheme II and can thus successfully be employed as an (alkyne)ZrCp$_2$-equivalent synthetic building block in this general synthetic scheme. The resulting dimetallabicyclic "anti-van't Hoff/LeBel compounds" obtained by the AlR$_3$/(η^2-aryne)zirconocene addition reaction exhibit properties similar to those of the planar-tetracoordinate carbon compounds (**4**–**6**) previously prepared and described by the groups of Schleyer and Brandsma, Cotton, and Buchwald, respectively.[8] In addition, three examples are described where similarly composed stable planar-tetracoordinate compounds have been prepared by means of the analogous reaction sequence starting from (η^2-alkyne)(trimethylphosphane)zirconocene complexes (**11**).

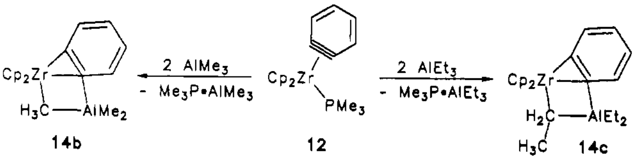
Results and Discussion

Synthesis and Spectroscopic Characterization of the Dimetallic Planar-Tetracoordinate Carbon Complexes. Dimetallic (μ-C$_6$H$_4$)Zr,Al complexes containing a planar-tetracoordinate carbon center were prepared by starting from (η^2-1,2-didehydrobenzene)(trimethylphosphane)zirconocene (**12**). This is a readily available starting material. For this study complex **12** was synthesized according to Buchwald's route by means of a thermally induced intramolecular benzene elimination from diphenylzirconocene in the presence of PMe$_3$.[12] Since (η^2-aryne)zirconocene cannot be prepared as an isolable compound and employed as such,[13] we have tried to generate the reactive (η^2-C$_6$H$_4$)ZrCp$_2$ intermediate (**13**) in situ in the presence of a suitable aluminum reagent as a scavenger. Many aluminum hydride or aluminum alkyl reagents react as strong Lewis acids with the PMe$_3$ Lewis base. Therefore, it was tempting to use in a variety of cases the added HAlR$_2$ or AlR$_3$ reagent to carry out both functions consecutively in the anticipated two-step reaction sequence and thus allow for a simple "one-pot" synthesis of the desired (μ-η^1:η^2-C$_6$H$_4$)Zr,Al complexes (**14**). This worked out beautifully in a variety of cases.

We have treated the aryne complex **12** with 2 molar equiv of diisobutylaluminum hydride in toluene solution at room temperature. A rapid reaction ensues which goes to completion within 2 h. Removal of the solvent and crystallization of the residue affords the dimetallic Cp$_2$Zr(μ-η^1:η^2-C$_6$H$_4$)(μ-H)Al(iBu)$_2$ complex **14a** crystalline in ca. 50% yield. Complex **14a** is air and moisture sensitive but rather thermally stable. It can be heated to about 80 °C before it decomposes. Complex **14a** was characterized spectroscopically and by X-ray diffraction (see below). It contains a planar-tetracoordinated carbon atom which is bridging between zirconium and aluminum and is part of the aromatic ring system. Both factors seem to be of importance for stabilizing this uncommon coordination geometry of carbon to make it thermodynamically favored.



The reaction probably proceeds straightforwardly as anticipated. The HAl(iBu)$_2$ reagent removes the trimethylphosphine ligand from the zirconium complex by means of Me$_3$P[HAl(iBu)$_2$] adduct formation. The resulting very reactive (η^2-benzyne)zirconocene intermediate is then effectively trapped by free HAl(iBu)$_2$ present in the solution to give the stable dimetallic reaction product (**14a**). Trialkylaluminum reagents can be used analogously. The reaction between the (aryne)metallocene complex (**12**) and trimethylaluminum proceeds equally easily at room temperature. Here the formed Me$_3$Al·PMe$_3$ adduct is removed from the reaction mixture together with the toluene solvent by vacuum distillation. Crystallization of the residue from pentane at low temperature gave the pure crystalline Zr,Al product **14b** in close to 80% yield. The Cp$_2$Zr(μ-η^1:η^2-aryne)(μ-ethyl)AlEt$_2$ complex **14c** was obtained analogously by reacting **12** with triethylaluminum (2 equiv).



These examples showed that the simple synthetic concept as outlined above could successfully be realized for the preparation of stable and isolable "anti-van't Hoff/LeBel compounds" by adding an organoaluminum reagent to in situ generated (η^2-aryne)zirconocene. This apparently simple access to planar-tetracoordinate carbon compounds

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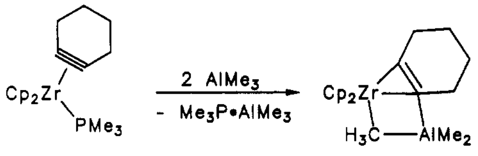
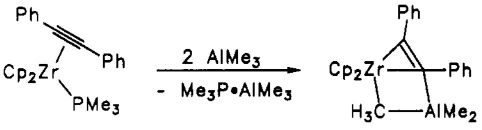
prompted us to check for the potential use of similarly structured (η^2-alkyne)(PMe_3)$ZrCp_2$ complexes (11) as starting materials in analogous synthetic sequences. The formation of the (μ-η^1:η^2-alkyne)(μ-X)Zr,Al complexes (7) (X = H, alkyl) turned out to be equally facile. (η^2-Cyclohexyne)(PMe_3)$ZrCp_2$ (**11a**) (prepared as described



11a **7d**

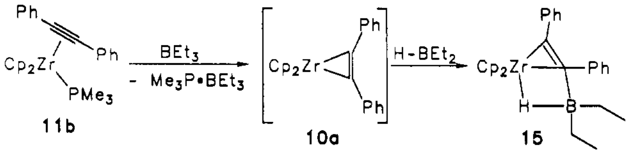


11b **7e**

by Buchwald et al.[11]) is a suitable starting material for our synthesis. It reacts with trimethylaluminum at room temperature in toluene solution to give a high yield (~ 70%) of the dimetallic Zr,Al complex **7d**, which contains a planar-tetracoordinate carbon center, bonded to the d element and the main group metal. In **7d** this carbon atom is part of an olefinic C=C moiety.

Acyclic alkynes bonded to an early transition metal can be used for the conversion into the (μ-η^1:η^2-RCCR)Zr,Al moiety as well. Thus, Cp_2Zr(μ-η^1:η^2-PhCCPh)(μ-CH_3)-$AlMe_2$ (**7e**) was formed when the (alkyne)zirconocene complex (PhC≡CPh)(PMe_3)$ZrCp_2$ (**11b**) was reacted with 2 molar equiv of trimethylaluminum at the usual reaction conditions. Complex **7e** was not obtained analytically pure but could be unambiguously identified by its characteristic NMR spectra (see below).

This synthetic scheme not only can be used for making Zr,Al compounds. In one case we used it successfully in the preparation of a dinuclear (μ-η^1:η^2-alkyne)Zr,B compound. However, here the overall reaction sequence was slightly more complicated. Triethylboron is known to effectively trap the phosphane from (L)(PR_3)$ZrCp_2$ complexes. When we added a mixture of triethylboron and 9-borabicyclo[3.3.1]nonane (9-BBN) to (η^2-tolane)-(PMe_3)$ZrCp_2$ (**11b**), a reaction did occur and we could



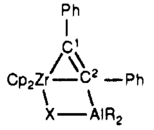
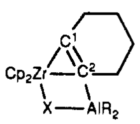
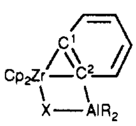
11b **10a** **15**

isolate a dimetallic (μ-alkyne)Zr,B complex, albeit in low yield (~10%). To our surprise, this did not contain the 9-borabicyclo[3.3.1]nonane moiety as a building block but rather turned out to be Cp_2Zr(μ-η^1:η^2-PhCCPh)(μ-H)BEt_2 (**15**). Thus, it is likely that the 9-BBN reagent had undergone some alkyl vs hydride exchange reaction with BEt_3 with concomitant formation of $HBEt_2$, which in turn was used to trap the in situ formed (tolane)$ZrCp_2$ intermediate to give the observed final product **15**.

The ^1H NMR spectrum of the Zr,B containing complex **15** shows the signals of the ethyl groups at boron at δ 1.13 (CH_3) and 0.98 (CH_2). There is a Cp singlet at δ 5.66 representing 10 hydrogens and the μ-H resonance at δ −2.07 (broad singlet).

The hydride resonance of the (μ-η^1:η^2-aryne)(μ-H)Zr,Al complex **14a** appears at δ −0.74. The Al center in **14a** is prochiral/tetracoordinate and thus exhibits an ABX type pattern of the $AlCH_2CH$ moieties [δ 0.52, 0.45 (CH_2), 2.26 (CH)]. The corresponding methyl groups of the $Al(iBu)_2$ building block are pairwise diastereotopic (δ 1.29; 1.26). The hydrogen atoms at the bridging C_6H_4 ring give rise to absorptions at δ 8.17 (1 H), 7.78 (1 H), and 7.18 (2 H). There is a sharp singlet at δ 5.40 representing 10 cyclopentadienyl hydrogens.

Table I. ^{13}C NMR Chemical Shifts of the μ-η^1:η^2-C≡C Moiety in the Dimetallabicyclic Complexes 7 and 14, Where C^2 Is Planar-Tetracoordinate[a]

				X-AlR_2
$\delta(C^1)$	206.1[b]	207.6[b]	193.4	H-$Al(iBu)_2$
$\delta(C^1)$	207.6	207.5	193.9	H_3C-$AlMe_2$
$\delta(C^2)$	143.5[b]	108.9[b]	114.9	H-$Al(iBu)_2$
$\delta(C^2)$	148.5	110.3	116.1	H_3C-$AlMe_2$

[a] Chemical shifts relative to tetramethylsilane, δ scale, measured in C_6D_6 solution. [b] From ref 10c,d.

The ^{13}C NMR spectrum of **14a** exhibits signals at δ 28.9 and 27.1 (diastereotopic methyl groups), 28.5 (CH), and 26.4 (CH_2) corresponding to the $Al(iBu)_2$ part of the molecule. The Cp resonance is at δ 105.6, and the expected four aromatic CH signals are observed at δ 137.4, 135.0, 134.7, and 134.3. Most interesting are the chemical shift values of the quaternary carbon centers (C^1 and C^2) of the μ-η^1:η^2-C_6H_4 bridge. The C^1 resonance is at δ 193.4. The characteristically high value of the C^1 resonance seems to be very typical of such dimetallic Zr,Al complex. For most complexes of this type C^1 chemical shifts > δ 180 have been observed.[10,14] Most values were found in a rather narrow range between ca. δ 180 and 220 (see Table I), although there are a few exceptions showing ^{13}C chemical shift values of the C^1 carbon atom as high as δ 290. The chemical shift of the planar-tetracoordinate carbon center C^2 is at markedly lower δ values, although still within the range of sp^2-hybridized olefinic carbon atoms. For complex **14a** we have observed the ^{13}C NMR resonance of the Zr,Al-bridging C^2 carbon atom at δ 114.9.

A comparison of two series of dimetallic Zr,Al complexes each containing a planar-tetracoordinate carbon center (C^2; see Table I) has revealed that the C^2 ^{13}C NMR chemical shift is not very dependent on the nature of the μ-X bridge (here CH_3 or H) although it does characteristically depend on the nature of the μ-η^1:η^2-alkyne type bridging system. Going from the aryne- to the cyclohexyne-bridged systems seems to result in a small reduction of the $\delta(C^2)$ values whereas a marked increase is noticed when one compares the μ-η^1:η^2-PhCCPh-bridged Zr,Al complexes. The Cp_2Zr(μ-η^1:η^2-C_6H_4)(μ-CH_2CH_3)$AlEt_2$ (**14c**) and Cp_2Zr(μ-η^1:η^2-PhCCPh)(μ-H)BEt_2 (**15**) systems fit very well into this overall chemical shift pattern [$\delta(C^1)$ at 193.9 (**14c**), 211.4 (**15**); $\delta(C^2)$ (planar-tetracoordinate) at 118.5 (**14c**) and 146.8 (**15**), respectively]. We thus conclude that the planar-tetracoordinate carbon center of the complexes described in this study seems to behave as expected for sp^2-hybridized carbon as judged from the ^{13}C NMR spectra. This appears also to hold for the IR spectra since complex **7d** exhibits an IR (C=C) band at ν = 1571 cm^{-1}.

X-ray Crystal Structure Analyses of 14a,b. In view of the spectral data (see above), it was necessary to have X-ray crystal structure analyses of representative examples of this new class of compounds to reveal their extraordi-

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(14) Erker, G.; Schlund, R.; Krüger, C. *Organometallics* **1989**, *8*, 2349.

Table II. Selected Bond Lengths (Å) and Angles (deg) for the Two Independent Molecules of 14a in the Crystal

	mol 1	mol 2
Zr(1)–C(1)	2.166 (9)	2.160 (9)
Zr(1)–C(2)	2.436 (9)	2.425 (9)
Zr(1)–H(0)	1.90	1.81
Al(1)–C(2)	2.09 (1)	2.08 (1)
Al(1)–C(15)	1.94 (2)	1.94 (1)
Al(1)–C(19)	2.08 (2)	2.05 (1)
Al(1)–H(0)	1.85	1.80
C(1)–C(2)	1.37 (1)	1.37 (2)
C(1)–C(6)	1.39 (1)	1.40 (1)
C(2)–C(3)	1.41 (1)	1.41 (1)
C(3)–C(4)	1.37 (2)	1.37 (2)
C(4)–C(5)	1.35 (2)	1.35 (2)
C(5)–C(6)	1.37 (2)	1.39 (2)
H(0)–Zr(1)–C(2)	83.7	82.1
H(0)–Zr(1)–C(1)	117.6	116.1
C(2)–Zr(1)–C(1)	33.9 (4)	34.1 (4)
C(19)–Al(1)–C(15)	117.9 (7)	116.1 (5)
C(19)–Al(1)–C(2)	108.8 (5)	108.4 (4)
C(15)–Al(1)–C(2)	107.3 (5)	110.7 (5)
H(0)–Al(1)–C(2)	95.6	92.8
C(6)–C(1)–C(2)	122.5 (9)	121.0 (9)
C(6)–C(1)–Zr(1)	153.6 (8)	155.1 (8)
C(2)–C(1)–Zr(1)	84.0 (6)	83.7 (6)
C(3)–C(2)–C(1)	116.9 (8)	117.2 (9)
C(3)–C(2)–Al(1)	101.5 (7)	101.4 (7)
C(3)–C(2)–Zr(1)	179.0 (7)	176.0 (7)
C(1)–C(2)–Al(1)	141.6 (7)	141.4 (7)
C(1)–C(2)–Zr(1)	62.2 (5)	62.3 (5)
Al(1)–C(2)–Zr(1)	79.4 (3)	79.1 (3)
C(4)–C(3)–C(2)	121 (1)	122 (1)
C(5)–C(4)–C(3)	120 (1)	120 (1)
C(6)–C(5)–C(4)	121 (1)	120 (1)
C(5)–C(6)–C(1)	118 (1)	120 (1)
Zr(1)–H(0)–Al(1)	101.3	105.9

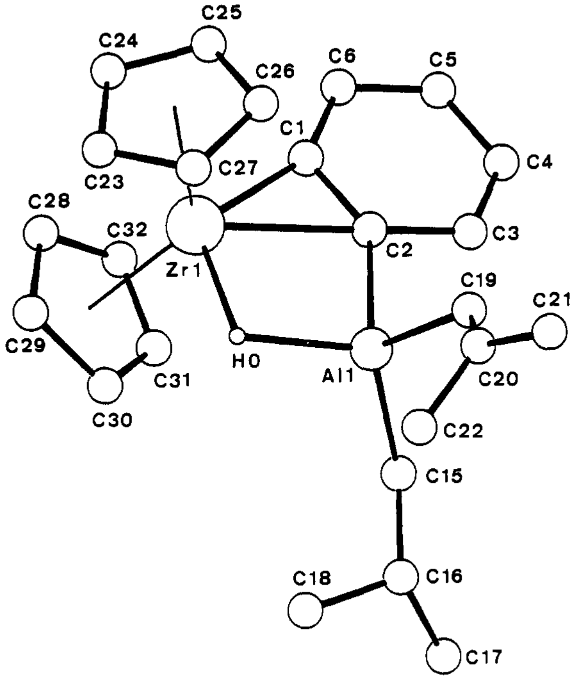

Figure 1. View of the molecular geometry of complex **14a** in the solid state. Only one of the chemically equivalent independent molecular entities observed is depicted.

nary structural feature, namely the presence of a central planar-tetracoordinate carbon atom. We have obtained crystals of the (aryne)metallocene-derived Zr,Al complexes **14a,b** that were suitable for X-ray crystal structure determinations.

Complex **14a** crystallizes in space group $P2_1/n$, with $Z = 8$. The only numerical values of bonding parameters presented and discussed are averaged over the two observed independent molecular entities of **14a** in the solid state (Tables II and III).

Table III. Positional Parameters for 14a

atom	*x*	*y*	*z*
Zr(1)	0.4695 (1)	0.2190 (1)	0.2164 (1)
Zr(1a)	0.5968 (1)	0.6844 (1)	0.2919 (1)
Al(1)	0.4338 (2)	0.2084 (2)	0.3565 (2)
Al(1a)	0.5849 (2)	0.6797 (2)	0.1494 (2)
C(1)	0.4145 (5)	0.0777 (6)	0.2223 (5)
C(2)	0.4079 (5)	0.0994 (6)	0.2280 (5)
C(3)	0.3714 (6)	0.0296 (8)	0.3285 (5)
C(4)	0.3462 (6)	−0.0567 (8)	0.3029 (7)
C(5)	0.3554 (6)	−0.0764 (7)	0.2378 (7)
C(6)	0.3889 (6)	−0.0101 (8)	0.1958 (5)
C(15)	0.3331 (9)	0.255 (1)	0.3904 (7)
C(16)	0.312 (1)	0.331 (1)	0.4328 (9)
C(17)	0.2293 (9)	0.338 (1)	0.4609 (7)
C(18)	0.330 (1)	0.419 (1)	0.4044 (9)
C(19)	0.518 (1)	0.157 (1)	0.4246 (8)
C(20)	0.558 (2)	0.198 (3)	0.462 (2)
C(21)	0.616 (1)	0.171 (1)	0.5177 (9)
C(22)	0.559 (1)	0.299 (2)	0.469 (1)
C(23)	0.6059 (7)	0.266 (1)	0.183 (1)
C(24)	0.5842 (7)	0.188 (1)	0.1418 (6)
C(25)	0.5803 (7)	0.108 (1)	0.181 (1)
C(26)	0.5987 (7)	0.135 (1)	0.2455 (9)
C(27)	0.6150 (6)	0.233 (1)	0.2464 (8)
C(28)	0.410 (1)	0.287 (1)	0.1136 (7)
C(29)	0.4321 (9)	0.368 (1)	0.155 (1)
C(30)	0.376 (1)	0.363 (1)	0.2074 (7)
C(31)	0.3316 (7)	0.286 (1)	0.1979 (9)
C(32)	0.3490 (9)	0.239 (1)	0.1441 (9)
C(1a)	0.4701 (6)	0.6624 (6)	0.2780 (5)
C(2a)	0.4886 (5)	0.6629 (6)	0.2123 (5)
C(3a)	0.4264 (7)	0.6434 (7)	0.1668 (5)
C(4a)	0.3501 (6)	0.6240 (8)	0.1869 (7)
C(5a)	0.3333 (6)	0.6229 (8)	0.2519 (8)
C(6a)	0.3923 (7)	0.6442 (7)	0.2987 (5)
C(15a)	0.6015 (8)	0.5636 (9)	0.0978 (6)
C(16a)	0.671 (1)	0.551 (1)	0.0538 (9)
C(17a)	0.669 (1)	0.467 (2)	0.014 (1)
C(18a)	0.743 (1)	0.548 (2)	0.098 (1)
C(19a)	0.5690 (8)	0.8051 (8)	0.0964 (6)
C(20a)	0.642 (1)	0.841 (1)	0.0556 (9)
C(21a)	0.611 (1)	0.934 (1)	0.0161 (9)
C(22a)	0.712 (1)	0.845 (2)	0.089 (1)
C(23a)	0.6771 (7)	0.816 (1)	0.340 (1)
C(24a)	0.610 (1)	0.8093 (9)	0.3798 (6)
C(25a)	0.5452 (8)	0.8368 (9)	0.3409 (9)
C(26a)	0.571 (1)	0.8626 (8)	0.2801 (9)
C(27a)	0.652 (1)	0.8522 (9)	0.2810 (8)
C(28a)	0.634 (2)	0.575 (1)	0.3836 (6)
C(29a)	0.6997 (9)	0.582 (1)	0.348 (1)
C(30a)	0.686 (2)	0.538 (2)	0.291 (1)
C(31a)	0.610 (2)	0.504 (1)	0.289 (1)
C(32a)	0.5791 (9)	0.526 (2)	0.344 (2)
H(0)	0.4794	0.2918	0.2961
H(0a)	0.6542	0.6982	0.2173

The Zr,Al complex **14a** contains a bent group 4 metallocene unit. The Zr–C(Cp) bond distances are in the usual range (2.47–2.54 Å). The σ-ligand angle [C(1)–Zr–H(0) = 116.9°; see Figure 1] is rather large. This indicates the presence of three coordinative interactions in the σ-ligand plane of the bent metallocene complex.[15] Indeed, complex **14a** exhibits an unusual dimetallabicyclic central framework oriented in the major plane of the bent metallocene moiety, i.e. the plane bisecting the Cp(centroid)–Zr–Cp(centroid) angle. This central dimetallabicyclo[2.1.0]pentane type framework consists of the metal atoms zir-

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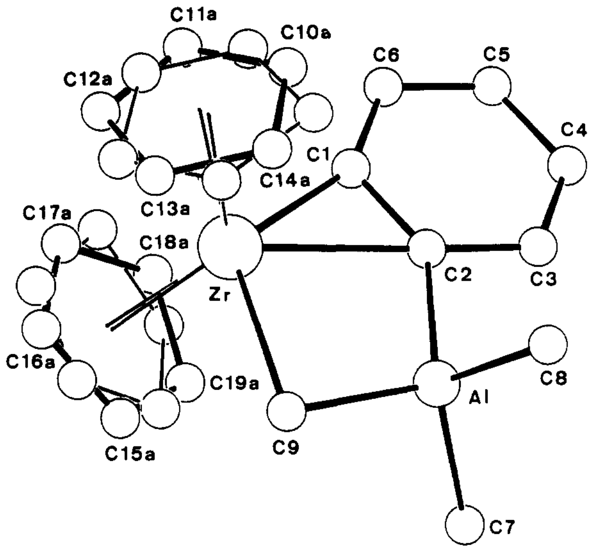

Figure 2. Projection of the molecular structure of **14b**.

conium and aluminum and the μ-hydride ligand bridging between them [d(Zr–H(0)) = 1.86, d(Al–H(0)) = 1.83 Å][16] and is completed by the C_6H_4 ligand. The latter is oriented in the σ-ligand plane and is bonded η^1 to aluminum and η^2 to zirconium. The aromatic ring annulated to the central dimetallabicyclic framework is only slightly distorted. Three bonds of the nearly hexagonal perimeter are close to the expected aromatic C(sp^2)–C(sp^2) bond lengths [C(1)–C(2), C(3)–C(4), C(5)–C(6) = 1.37 (2) Å; C(4)–C(5) = 1.35 (2) Å]. Only the C(1)–C(6) and C(2)–C(3) bond distances are marginally longer at 1.40 (1) and 1.41 (3) Å, respectively. The C–C–C bonding angles within the six-membered ring are close to 120°. The adjacent aluminum center is tetracoordinate. It is bonded to carbon atoms C(2), C(15), and C(19) and to the μ-hydride ligand H(0) (see Table I).

The extraordinary structural feature of **14a** (Figure 2) is that it contains a planar-tetracoordinate carbon. The carbon atom C(2) is coordinated to four adjacent atoms. The corresponding bond lengths are 1.37 (2) Å [C(2)–C(1)], 1.41 (1) Å [C(2)–C(3)], 2.09 (1) Å [C(2)–Al], and 2.431 (9) Å [C(2)–Zr]. All four bonds are coplanar. The sum of the bonding angles at C(2) is 360°. The corresponding bond angles are as follows: 117.1 (9)° [C(1)–C(2)–C(3)], 101.5 (7)° [C(3)–C(2)–Al], 79.3 (3)° [Zr–C(2)–Al], and 62.3 (5)° [C(1)–C(2)–Zr]. In addition to the decreased metal–carbon–metal bonding angle at C(2) the corresponding metal to C(2) bond lengths point to a three-center-two-electron bonding situation for the Zr–C(2)–Al moiety. The C(2)–Al bond length is slightly longer than the average of the Al–C(15)/C(19) separation. The C(2)–Zr distance of 2.430 (9) Å is markedly larger than the standard Cp_2Zr–C(sp^2) situation [cf. the Zr–C(sp^2) σ-bond lengths in (Me_3C-Cp)$CpZrPh_2$ of 2.305 (7) and 2.317 (6) Å; the corresponding Zr–C(sp^2) distances in difurylzirconocene are 2.296 (3) and 2.304 (3) Å, respectively].[17] The reported Zr–C(sp^3) σ-bond length in dimethylzirconocene is 2.28 Å[18]. The Zr–C(1) bond in **14a** is extremely short at 2.163 (9) Å [cf. the reference values of a formal Cp_2Zr–C(sp^2) σ-bond cited above]. It is even as short as the Zr–C(sp) distance observed in the (carbonyl)zirconocene complexes $Cp_2Zr(CO)_2$[19] [d(Zr–C(carbonyl)) = 2.18 Å] or $Cp_2Zr(CO)[P(OMe)_3]$[20] [d(Zr–C(carbonyl)) = 2.153 (4), 2.167 (5) (two independent molecules)]. The Zr–C(1) bond is by ca. 0.08 Å shorter than the Zr–C(sp) σ-bond in $Cp_2Zr(C{\equiv}CCH_3)_2$.[21]

Table IV. Selected Bond Lengths (Å) and Angles (deg) for 14b

Zr–C(1)	2.165 (3)	Zr–C(2)	2.481 (3)
Zr–C(9)	2.559 (5)	Al–C(2)	2.082 (3)
Al–C(7)	1.966 (5)	Al–C(8)	1.952 (5)
Al–C(9)	2.101 (5)	C(1)–C(2)	1.383 (4)
C(1)–C(6)	1.400 (5)	C(2)–C(3)	1.423 (5)
C(3)–C(4)	1.372 (6)	C(4)–C(5)	1.371 (6)
C(5)–C(6)	1.374 (6)		
C(9)–Zr–C(2)	87.8 (1)	C(9)–Zr–C(1)	121.5 (1)
C(2)–Zr–C(1)	33.8 (1)	C(9)–Al–C(8)	105.0 (2)
C(9)–Al–C(7)	105.4 (2)	C(9)–Al–C(2)	113.4 (2)
C(8)–Al–C(7)	116.3 (2)	C(8)–Al–C(2)	107.2 (2)
C(7)–Al–C(2)	109.6 (2)	C(6)–C(1)–C(2)	121.5 (3)
C(6)–C(1)–Zr	152.7 (3)	C(2)–C(1)–Zr	85.8 (2)
C(3)–C(2)–C(1)	117.4 (3)	C(3)–C(2)–Al	101.6 (2)
C(3)–C(2)–Zr	177.9 (2)	C(1)–C(2)–Al	141.0 (3)
C(1)–C(2)–Zr	60.5 (2)	Al–C(2)–Zr	80.5 (1)
C(4)–C(3)–C(2)	120.1 (4)	C(5)–C(4)–C(3)	121.6 (4)
C(6)–C(5)–C(4)	119.6 (4)	C(5)–C(6)–C(1)	119.8 (3)
Al–C(9)–Zr	78.3 (1)		

Table V. Positional Parameters for 14b

atom	x	y	z
Zr	0.8479 (1)	0.7649 (1)	0.5765 (1)
Al	0.6795 (1)	0.7649 (1)	0.7272 (1)
C(1)	0.9811 (3)	0.8604 (2)	0.6828 (2)
C(2)	0.8758 (3)	0.8426 (2)	0.7346 (2)
C(3)	0.8968 (4)	0.8888 (3)	0.8249 (3)
C(4)	1.0163 (5)	0.9497 (3)	0.8565 (3)
C(5)	1.1178 (5)	0.9679 (3)	0.8032 (3)
C(6)	1.1013 (4)	0.9235 (3)	0.7162 (3)
C(7)	0.7176 (5)	0.6678 (4)	0.8288 (3)
C(8)	0.5191 (5)	0.8563 (4)	0.7281 (4)
C(9)	0.6043 (5)	0.6891 (3)	0.5983 (3)
C(10a)	0.7782 (8)	0.9298 (4)	0.5065 (4)
C(10b)	0.695 (2)	0.915 (1)	0.514 (1)
C(11a)	0.8864 (7)	0.8905 (5)	0.4625 (5)
C(11b)	0.832 (2)	0.9222 (9)	0.4902 (9)
C(12a)	0.8197 (8)	0.8147 (5)	0.4051 (4)
C(12b)	0.846 (2)	0.858 (1)	0.428 (1)
C(13a)	0.6713 (8)	0.8042 (4)	0.4169 (4)
C(13b)	0.730 (2)	0.7950 (9)	0.4051 (9)
C(14a)	0.6465 (7)	0.8752 (6)	0.4817 (5)
C(14b)	0.629 (1)	0.833 (1)	0.452 (1)
C(15a)	0.8935 (8)	0.5862 (5)	0.5927 (7)
C(15b)	0.905 (2)	0.595 (1)	0.547 (2)
C(16a)	0.9280 (9)	0.6161 (5)	0.5059 (6)
C(16b)	0.989 (2)	0.641 (1)	0.506 (1)
C(17a)	1.056 (1)	0.6761 (6)	0.5311 (6)
C(17b)	1.102 (2)	0.697 (1)	0.570 (2)
C(18a)	1.1046 (7)	0.6871 (5)	0.6336 (5)
C(18b)	1.068 (2)	0.657 (1)	0.651 (1)
C(19a)	1.0048 (8)	0.6290 (5)	0.6690 (4)
C(19b)	0.947 (3)	0.605 (1)	0.639 (2)

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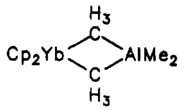
We assume that there is some zirconium–carbon π-interaction associated with the extremely short Zr–C(1) distance observed in complex **14a**.

The Zr–C(1) bond in the methyl-bridged Zr,Al complex **14b** is equally short at 2.165 (3) Å (Tables IV and V). In **14b** the Zr–C(1)–C(2) angle is 85.8 (2)°. This complex also exhibits a dimetallatricyclic σ-framework and contains a planar-tetracoordinate carbon center [C(2): bond lengths C(2)–C(1) = 1.383 (4), C(2)–C(3) = 1.423 (5), C(2)–Zr = 2.481 (3), C(2)–Al = 2.082 (3) Å; bond angles C(1)–C(2)–C(3) = 117.4 (3), C(3)–C(2)–Al = 101.6 (2), Zr–C(2)–Al = 80.5 (1), = C(1)–C(2)–Zr = 60.5 (2)°]. A comparison with typical bonding parameters (see above) again points to the presence of a three-center-two-electron bonding situation of the Zr–C(2)–Al moiety.

In **14b** there is a methyl group between zirconium and aluminum. The bridging carbon to aluminum bond [C(9)–Al] is rather long at 2.101 (5) Å. It is slightly longer then the C(2)–Al linkage (see above) and increased by about 0.13 Å as compared to the terminal methyl–aluminum bonds [Al–C(7) = 1.966 (5) Å, Al–C(8) = 1.952 (5) Å]. The carbon–aluminum bond distance and angle [Zr–C(9)–Al = 78.3 (1)°] is in the same range as observed for the Al–CH_3–Al bridges in dimeric trimethylaluminum[22] [μ-CH_3–Al = 2.125 (2), 2.123 (2) Å, Al–C–Al = 75.7 (1)°]. The C(9)–Zr bond (2.559 (5) Å) is very long. Similar zirconium–carbon distances have been observed for the Zr–μ-CH_3–Zr situation in Buchwald's complex **6**[8d] [*d*(Zr–C) = 2.617 (6) and 2.591 (6) Å, Zr–C–Zr = 84.9 (2)°]. Related bonding parameters were found for the M–CH_3–M′ linkage in $Cp_2Yb(\mu\text{-}CH_3)_2AlMe_2$ (**16**)[23] [*d*(Yb–C) = 2.609 (23) Å, *d*(C–Al) = 2.165 (22) Å; Yb–C–Al = 77.7 (7)°]. The bonding situation of the μ-CH_3 complex **17** is slightly different[24] [Zr–μ-CH_3–Zr unit: *d*(Zr–C) = 2.483 (4), 2.564 (4) Å, Zr–C–Zr 152.4 (2)°], in this case resembling the near to sp^2-hybridization of an almost linear M–CH_3–M bridge as in **18**[25] [Lu–μ-CH_3–Lu: *d*(Lu–C) = 2.440 (9), 2.756 (9) Å, Lu–C–Lu = 170 (4)°].



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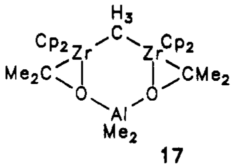

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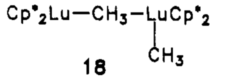


$Cp^*_2Lu{-}CH_3{-}Lu(CH_3)Cp^*_2$

18

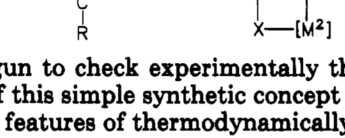
Thus, it appears that the carbon atom of the bridging methyl group in **14b** is near to sp^3-hybridized. The five-coordinate carbon center C(9) thus forms another three-center-two-electron linkage between zirconium and aluminum. Here the curious situation arises that both electropositive metal centers, the d^0-configurated early transition metal and the group 13 main group metal, are linked by means of forming two slightly different types of electron-deficient σ-bond systems, one containing a hypervalent sp^3-hybridized carbon center [C(9)] and the other made by a sp^2-hybridized carbon atom which is planar-tetracoordinate.

Conclusions

This study shows, as did our preceding papers in this series,[9,10] that compounds containing planar-tetracoordinate carbon can sometimes be quite thermodynamically stable. The complexes described in this paper all contain an sp^2-hybridized carbon center which is closely surrounded by four adjacent substituents perfectly oriented in a single common plane. These complexes seem to contain a planar-tetracoordinate carbon center which is stabilized electronically in the way predicted by the theoretical studies carried out by the groups of Hoffmann and Schleyer, respectively, that were cited in the introductory paragraph.[4-6] Spectroscopic and structural data point to a bonding situation where the planar carbon [C(2)] is sp^2-hybridized and part of an aromatic π-system (just like the examples **4**–**6** shown in Scheme I) and is coordinated to two metal centers in addition to the bonds to the two adjacent ring carbon atoms by means of a three-center-two-electron connection. It appears that the combined electron-donor properties of the two metallic "substituents" help to a great extent to stabilize this uncommon coordination geometry of tetravalent carbon. In addition there seems to be an effective way of removing some of the p-electron density from that particular carbon center [C(2)] by conjugative interaction. From the structural studies on the complexes **14a**,**b** discussed above as well as related X-ray structural investigations[10] we are led to assume that there is a substantial π-interaction (normal to the σ-ligand framework) between the carbon centers C(2) and C(1) and the Zr atom that represents a substantial contribution to the overall thermodynamic stabilization of the planar-tetracoordinate carbon bonding situation. The observed extremely short Zr–C(1) bond length is a result of this interaction.

The apparent ease of formation of the new "anti-van't Hoff/LeBel complexes" described above leads us to believe that many more examples of this type of compounds will be prepared and described in the future. It may well be that a number of related examples have already been synthesized but not been recognized as belonging to this class of carbon compounds because of their "unsuspicious" spectroscopic properties.

The synthetic scheme used and developed here for the preparation of the complexes **7** and **14** seems to be very simple and straightforward. The successful preparation of the examples described above may indicate that a variety of other stable planar-tetracoordinate carbon compounds could become available by synthetic pathways following this general route, namely by the addition of Lewis-acidic main group or transition metal complexes X-[M^2] to reactive alkyne metal reagents [M^1](RC≡CR).



We have begun to check experimentally the scope and limitations of this simple synthetic concept and to study the chemical features of thermodynamically stable compounds containing planar-tetracoordinate carbon.

Experimental Section

Preparations and handling of the organometallic compounds were carried out in an inert atmosphere using Schlenk type glassware (argon) or a glovebox (nitrogen). Solvents were dried and distilled under argon prior to use. Spectrometers used are

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Table VI. Details of the X-ray Crystal Structure Analyses of 14a[a] and 14b[b]

	14a	**14b**
mol formula	$C_{24}H_{33}AlZr$	$C_{19}H_{23}AlZr$
mol wt	439.7	369.6
cryst color	colorless	white
cryst syst	monoclinic	monoclinic
space group (No.)	$P2_1/n$ (14)	$P2_1/n$ (14)
a, Å	16.749 (3)	9.151 (1)
b, Å	13.833 (1)	14.022 (1)
c, Å	20.178 (2)	14.415 (1)
β, deg	90.74 (1)	104.56 (1)
V, Å^3	4674.6	1790.4
Z	8	4
D_{calcd}, g cm^{-3}	1.25	1.37
μ, cm^{-1}	5.03	6.44
Mo Kα radiation λ, Å	0.710 69	0.710 69
$F(000)$, e	1840	760
diffractometer	Enraf-Nonius CAD4	
scan mode	ω–2θ	ω–2θ
$[(\sin\theta)/\lambda]_{max}$, Å^{-1}	0.65	0.65
T, °C	20	20
no. of measd rflns ($\pm h,+k,+l$)	11 388	4422
no. of indep rflns	10 592	4081
no. of obsd rflns ($I > 2\sigma(I)$)	5356	3438
no. of refined params	389	180
R	0.088	0.042
R_w ($w = 1/\sigma^2(F_o)$)	0.093	0.057
resid electron dens, e Å^{-3}	0.95	0.56
structure solution	heavy-atom method	

[a] μ-H atom positions were found; the other H atom positions were calculated and kept fixed in the final refinement stage, with no separation of the disordered atoms at the iBu groups. [b] H atom positions were calculated (except for C(9) where they were omitted) and kept fixed in the final refinement stage. Cp rings are 70:30 disordered.

as follows: Bruker AC 200 P NMR spectrometer (^{1}H, 200 MHz; ^{13}C, 50 MHz); Nicolet 5 DX C FT IR spectrometer. Melting points were determined by DSC (DuPont 2910 DSC, STA Instruments). The complexes $Cp_2Zr(\eta^2\text{-}C_6H_4)(PMe_3)$ (**12**), $Cp_2Zr(\eta^2\text{-}C_6H_8)(PMe_3)$ (**11a**), and $Cp_2Zr(\eta^2\text{-}PhC{\equiv}CPh)(PMe_3)$ (**11b**) were prepared according to literature procedures.[11,12]

Preparation of Cp$_2$Zr(μ-η^1:η^2-1,2-didehydrobenzene)(μ-H)Al(iBu)$_2$ (14a). To a solution of 500 mg (1.34 mmol) of the (aryne)(PMe$_3$) zirconocene complex **12** in 5 mL of toluene is added at ambient temperature a solution of 400 mg (2.82 mmol) of diisobutylaluminum hydride in 5 mL of toluene. The mixture is then stirred for 2 h. Solvent is removed from the resulting red solution in vacuo. The oily residue is recrystallized from pentane at −30 °C to give colorless crystals of **14a**, mp 88 °C (dec, DSC). Yield: 280 mg (48%). Anal. Calcd for $C_{24}H_{33}AlZr$ (439.7): C, 65.55; H, 7.56. Found: C, 65.10; H, 7.20. ^{1}H NMR (benzene-d_6): δ 8.17 (m, 1 H), 7.78 (m, 1 H), 7.18 (m, 2 H, C_6H_4), 5.40 (s, 10 H, Cp), 2.26 (m, 2 H, C*H*Me$_2$), 1.29 and 1.26 (each: d, 6 H, CH$_3$), 0.52 and 0.45 (each: m, 2 H, Al–CH$_2$), −0.74 (br s, 1 H, μ-H). ^{13}C NMR (benzene-d_6): δ 193.4 (ZrC=), 137.4, 135.0, 134.7, 134.3 (arom *C*H), 114.9 (C$_{planar}$), 105.6 (Cp), 28.9 (CH$_3$), 28.5 (CH), 27.1 (CH$_3$), 26.4 (br, AlCH$_2$). X-ray crystal structure analysis: see Table VI.

Preparation of Cp$_2$Zr(μ-η^1:η^2-1,2-didehydrobenzene)(μ-CH$_3$)AlMe$_2$ (14b). Trimethylaluminum (220 mg, 3.06 mmol) is dissolved in 5 mL of toluene, and the solution is added to a solution of 550 mg (1.35 mmol) of the (aryne)zirconocene complex **12** in 10 mL of toluene at room temperature. The mixture is stirred for a period of 2 h, and then the solvent is removed in vacuo. The resulting oil is extracted with 10 mL of pentane. A portion of 150 mg of white amorphous **14b** remains. From the pentane extract one obtains crystalline **14b** upon cooling to −30 °C [mp: 119 °C (dec, DSC)]. Combined yield: 390 mg (78%). Anal. Calcd for $C_{19}H_{23}AlZr$ (369.6): C, 61.75; H, 6.27. Found: C, 61.08; H, 6.17. IR (KBr): ν 1442, 1013, 808 cm^{-1} (Cp). ^{1}H NMR (benzene-d_6): δ 8.24 (m, 1 H), 7.57 (m, 1 H), 7.20 (m, 2 H, arom C*H*), 5.24 (s, 10 H, Cp), −0.10 (s, 3 H, μ-CH$_3$), −0.23 (s, 6 H, AlMe$_2$). ^{13}C NMR (benzene-d_6): δ 193.9 (ZrC=), 139.0, 138.1, 132.2, 128.3 (arom *C*H), 116.1 (C$_{planar}$), 109.2 (Cp), −4.7 (AlMe$_2$), −14.9 (μ-CH$_3$). X-ray crystal structure analysis: see Table VI.

Preparation of Cp$_2$Zr(μ-η^1:η^2-1,2-didehydrobenzene)(μ-CH$_2$CH$_3$)AlEt$_2$ (14c). To a solution of 560 mg (1.55 mmol) of the (aryne)zirconocene complex **12** in 10 mL of toluene is added at room temperature triethylaluminum (450 mg, 4.02 mmol) dissolved in 5 mL of toluene. The reaction mixture is stirred for 1 h. Then the solvent is removed in vacuo to give an oil. Recrystallization from pentane gives colorless crystals of **14c** [mp: 90 °C (dec, DSC)]. Yield: 480 mg (77%). Anal. Calcd for $C_{22}H_{29}AlZr$ (411.7): C, 64.19; H, 7.10. Found: C, 62.98; H, 7.09. IR (KBr): ν 1396, 1015, 801 cm^{-1} (Cp). ^{1}H NMR (benzene-d_6): δ 8.23 (m, 1 H), 7.48 (m, 1 H), 7.21 (m, 2 H, arom C*H*), 5.34 (s, 10 H, Cp), 1.42 (t, 3 H, μ-CH$_2$C*H*$_3$), 1.40 (t, 6 H, AlCH$_2$C*H*$_3$), 0.45 and 0.35 (m, each 2 H, −CH$_2$−), 0.21 (m, 2 H, μ-CH$_2$). ^{13}C NMR (benzene-d_6): δ 196.3 (ZrC=), 138.3, 132.3, 127.5 (double intensity, arom *C*H), 118.5 (C$_{planar}$), 109.4 (Cp), 13.3 and 11.3 (CH$_3$), 3.9 (br, CH$_2$), −12.6 ($^1J_{CH}$ = 109 Hz, μ-CH$_2$).

Preparation of Cp$_2$Zr(μ-η^1:η^2-cyclohexyne)(μ-CH$_3$)AlMe$_2$ (7d). To a solution of 700 mg (1.86 mmol) of the (cyclohexyne)zirconocene complex **11a** in 10 mL of toluene is added at ambient temperature 500 mg (6.94 mmol) of trimethylaluminum dissolved in 10 mL of toluene. The mixture is stirred for 3 h. Then the solvent is removed in vacuo together with the formed trimethylaluminum/trimethylphosphane adduct. The residue is recrystallized from pentane at −30 °C to give 470 mg (68%) of crystalline **7d** [mp: 96 °C (dec, DSC)]. Anal. Calcd for $C_{19}H_{27}AlZr$ (373.6): C, 61.08; H, 7.28. Found: C, 60.25; H, 7.42. IR (KBr): ν 3104, 1443, 1011, 804 (Cp), 1571 cm^{-1} (C=C). ^{1}H NMR (benzene-d_6): δ 5.28 (s, 10 H, Cp), 2.50 (m, 4 H, 2 × CH$_2$), 1.49 (m, 4 H, 2 × CH$_2$), −0.13 (s, 3 H, μ-CH$_3$), −0.33 (s, 6 H, AlMe$_2$). ^{13}C NMR (toluene-d_8): δ 207.5 (ZrC=), 110.3 (C$_{planar}$), 108.5 (Cp), 35.1, 30.4, 25.0 (double intensity, CH$_2$), −6.7 ($^1J_{CH}$ = 112 Hz, AlMe$_2$), −17.0 ($^1J_{CH}$ = 114 Hz, μ-CH$_3$). ^{27}Al NMR (toluene-d_8, 93 MHz, 330 K): δ 170 ($w_{1/2}$ = 1500 Hz).[26]

Preparation of Cp$_2$Zr(μ-η^1:η^2-diphenylacetylene)(μ-CH$_3$)AlMe$_2$ (7e). Trimethylaluminum (150 mg, 2.08 mmol), dissolved in 5 mL of toluene, is added at room temperature to a solution of 400 mg (0.84 mmol) of the (η^2-tolane)zirconocene complex **11b** in 5 mL of toluene. The mixture is stirred for 1 h. Solvent is then removed in vacuo. An ^{1}H NMR spectrum of a sample of the residue revealed that the reaction was only ca. 50% complete. The residue is dissolved in 5 mL of toluene and an additional quantity of trimethylaluminum (300 mg, 4.17 mmol) added. The mixture is stirred for 1 h at ambient temperature, and then the solvent and the volatile reaction products are removed in vacuo. The resulting residue is washed with pentane to give 350 mg (88%) of **7e** [mp: 57 °C (dec, DSC)], which was only characterized spectroscopically. IR (KBr): ν 3054, 1438, 1014, 808 (Cp), 1590, 1565, 1486 cm^{-1} (Ph and C=C). ^{1}H NMR (benzene-d_6): δ 7.14–6.87 (m, 10 H, Ph), 5.48 (s, 10 H, Cp), 0.00 (s, 3 H, μ-CH$_3$), −0.44 (s, 6 H, AlMe$_2$). ^{13}C NMR (benzene-d_6): δ 207.6 (ZrC=), 148.5 (C$_{planar}$), 143.2, and 141.7 (ipso-C, Ph), 131.2, 129.7, 128.5, 127.0, 125.9, 125.5 [*C*H(phenyl)], 109.3 (Cp), −4.9 ($^1J_{CH}$ = 115 Hz, AlMe$_2$), −14.0 ($^1J_{CH}$ = 115 Hz, μ-CH$_3$).

Preparation of Cp$_2$Zr(μ-η^1:η^2-diphenylacetylene)(μ-H)BEt$_2$ (15). The (tolane)zirconocene complex **11b** (500 mg, 1.05 mmol) is dissolved in 15 mL of toluene. To this solution is added 9-BBN (260 mg, 1.06 mmol) and 120 mg (1.23 mmol) of triethylboron, both dissolved in 5 mL of toluene each. The mixture is stirred for 30 h at ambient temperature. Then the solvent and volatile reaction products are removed in vacuo. The oily residue is washed with pentane (three 10-mL portions) and then three times recrystallized from ca. 10 mL of toluene at −30 °C. This gives **15** as a white solid [mp: 131 °C (dec, DSC)]. Yield: 60 mg (12%). Anal. Calcd for $C_{28}H_{31}BZr$ (469.6): C, 71.62; H, 6.65. Found: C, 70.42; H, 6.45. ^{1}H NMR (benzene-d_6): δ 7.05 (m, 5 H, Ph), 6.80 (m, 5 H, Ph), 5.66 (s, 10 H, Cp), 1.13 (t, 6 H, CH$_3$), 0.98 (m, 4 H, CH$_2$), −2.07 (br s, 1 H, μ-H). ^{13}C NMR (benzene-d_6): δ 211.4 (ZrC=), 146.8 (C$_{planar}$), 128.8, 126.1, 125.0, 124.7 [4 CH (phenyl), remaining Ph resonances not located], 108.8 (Cp), 18.4 (br, B–CH$_2$), 13.3 (CH$_3$).

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Registry No. 7d, 143733-05-5; **7e**, 143733-06-6; **11a**, 105253-58-5; **11b**, 113177-54-1; **12**, 105102-80-5; **14a**, 143733-02-2; **14b**, 143733-03-3; **14c**, 143733-04-4; **15**, 143733-07-7; $AlMe_3$, 75-24-1; $AlEt_3$, 97-93-8; BEt_3, 97-94-9.

Supplementary Material Available: Tables listing details of the X-ray structure analyses of **14a** and **14b** and complete listings of bond lengths and angles (18 pages). Ordering information is given on any current masthead page.

OM920215K

Regioselective Hydroformylation of Cyclic Vinyl and Allyl Ethers with Rhodium Catalysts. Crucial Influence of the Size of the Phosphorus Cocatalyst

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In the course of studies aimed at developing new catalytic systems, we have explored the possibilities offered by the modification of thiolato bridges in dinuclear rhodium complexes, together with the influence of the cocatalyst, on the selective hydroformylation of cyclic vinyl and allyl ethers. The dinuclear complex $[Rh_2(\mu\text{-}S(CH_2)_3NMe_2)_2(cod)_2]$ (cod = 1,5-cyclooctadiene) has been prepared, and its reactivity with CO, phosphines, and phosphites has been investigated. The complex crystallizes in the monoclinic space group $C2/c$ with $Z = 8$, $a = 22.543$ (4) Å, $b = 12.040$ (2) Å, $c = 21.547$ (3) Å, and $\beta = 98.77$ (1)°. For the determination of the structure 4091 unique reflections were used, and the final refinement gave $R = 4.1\%$ and $R_w = 4.4\%$. The molecular structure reveals that the two rhodium atoms are bridged by the two thiolato ligands, and the cyclooctadiene completes the coordination of the metal atoms. The amine groups are not bonded to the rhodium. The dinuclear complex has been used in the hydroformylation of 2,3-dihydrofuran, 2,5-dihydrofuran, 3,4-dihydro-2*H*-pyran, and 3,6-dihydro-2*H*-pyran. Hydroformylation reactions of dihydrofurans required conditions milder than those for dihydropyrans. The major product in the hydroformylation of 3,4-dihydro-2*H*-pyran or 3,6-dihydro-2*H*-pyran was tetrahydropyran-2-carbaldehyde. A systematic study of the influence of the reaction parameters on the selectivity of the hydroformylation of 2,3-dihydrofuran and 2,5-dihydrofuran was undertaken. The study allowed the rationalization of the observed selectivity and the optimization of the yields and regioselectivities. Thus, by modification of the reaction parameters, tetrahydrofuran-3-carbaldehyde was obtained in quantitative yields from 2,5-dihydrofuran and tetrahydrofuran-2-carbaldehyde can be prepared from either 2,3-dihydrofuran or 2,5-dihydrofuran in approximately 75% yield.

Introduction

The hydroformylation of propene is one of the few processes in which homogeneous catalysts are employed on a large industrial scale.[1] Although the reaction has been known for many years, much work has recently been devoted to the preparation of new, active, highly selective catalytic systems,[2,3] the recovery of the catalyst,[4] the study of the reaction mechanism,[5] and the use of the process in the synthesis of fine chemicals.[6] With regard to this last point, the hydroformylation of functionalized alkenes has recently been reviewed.[7] The reactions of cyclic functionalized alkenes are a special case. The hydroformylation of some of these substrates yields aldehydes which are of interest for the preparation of intermediates for the synthesis of natural products or pharmaceuticals.[8] However,

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