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Structural Characterization of the Acetylide Bridge in Dinuclear (μ-C≡CSiMe$_3$)–Al/Al and –Al/Zr Complexes

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Two rare examples of complexes that contain an acetylide ligand bridging between a main group metal (aluminum) and a transition metal (zirconium) are described. Such complexes are prepared by treatment of dimethylzirconocene with 2 molar equiv of (alkynyl)dimethylaluminum [(RC≡C)AlMe$_2$]$_2$ (R = –SiMe$_3$, –cyclohexyl, –CMe$_3$, –CH$_3$; **2a–d**). In this reaction an (η^2-alkyne)zirconocene complex is probably formed in situ which is then trapped by the excess (alkynyl)dimethylaluminum to yield the complexes Cp$_2$Zr(μ-η^1:η^2-RCCMe)(μ-C≡CR)AlMe$_2$ (**6a–d**). The complexes **6a** (R = SiMe$_3$) and **6b** (R = cyclohexyl) were characterized by X-ray diffraction. For comparison, we have also carried out the X-ray crystal structure analysis of the [(trimethylsilyl)ethynyl]dimethylaluminum dimer **2a**. The complexes **6** contain a dimetallabicyclic framework. One of the bridgehead positions is a carbon center which is planar-tetracoordinate. In these complexes the –C≡CR bridge between zirconium and aluminum can be described as being mainly of μ-(σ-acetylide) character.

The acetylide moiety (–C≡CR) bears some similarity to the metal-bonded carbonyl ligand (–C≡O). Like the ubiquitous carbonyl group, it serves as a potent σ-donor, able to bind and stabilize electron-deficient metal centers. Like the carbonyl group, σ-acetylide ligands can bind to a single metal center[1] but are also able to form σ-bridges between metal atoms.[2] In specific situations the –C≡CR unit can use its carbon–carbon π-electrons to introduce a second coordinating component and "lean over" to an adjacent metal center to form a σ,π-type bridge which is similar to many unsymmetrical ("semibridging") M^1[μ-η^1(C):η^2(C,O)]M^2 situations described in the literature. There are even cases of triply-bridging σ,π^2-C≡CR situations[3] which are structurally similar to the μ_3-C≡O coordination mode often encountered in late transition metal carbonyl cluster chemistry.

Of course, there are pronounced differences between MC≡CR/MC≡O and (MC≡CR)$_2$/(MC≡O)$_2$ pairs of complexes, respectively. The acetylide ligand bears a formal negative charge. Therefore, it predominantly binds to metals in high oxidation states. It forms strong σ-bonds to electron-poor main group metals and early transition metals. In contrast to comparable MC≡O linkages, the MC≡CR σ-bond is mostly devoid of a significant M–C$^\alpha$ π-bonding component.[4] This often results in a much larger metal–C(sp) separation in the metal acetylides as compared to similarly structured metal carbonyl complexes [e.g. Zr–C$^\alpha$(sp) = 2.249(1) Å in Cp$_2$Zr(C≡CCH$_3$)$_2$[2b] but 2.187(4) Å in Cp$_2$Zr(C≡O)$_2$[5]]. In the bridging situation, the μ-(σ-acetylide) ligand appears to exhibit a much softer bending potential than the μ-C≡O group. The bridging CO ligand rapidly develops a side-on π-bonding component when bending over to the adjacent metal center in a M^1-(μ-C≡O)M^2 complex. The M(μ-C≡CR)M complexes, in contrast, can show considerable deviation from the local C_{2v}-symmetric bridging situation without having the carbon–carbon triple bond interact with the other metal center.

Due to their specific coordination characteristics, bridging σ-acetylide ligands are very well suited to connect electropositive main group metals and/or early transition metal centers, forming strong dimetallic frameworks. We have extensively used this tendency of σ-acetylide ligands to construct zirconium/aluminum-containing heterodimetallic complexes serving as templates which have allowed for the electronic stabilization of a "square-planar" coordination geometry of carbon atoms[6] present in a second hydrocarbyl moiety bridging between these metal centers. In many of these cases, the high stability of the M^1(μ-C≡CR)M^2 bridge and its easy formation turned out to be very helpful in synthesizing such stable, isolable planar-tetracoordinate carbon compounds.[7] We here want to

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describe the structures of a pair of related complexes containing an Al(μ-C$\equiv$CSiMe$_3$)Al and a Zr(μ-C$\equiv$CSiMe$_3$)-Al bridge, respectively, and discuss the characteristic features of their bridging μ-acetylide ligands. The structure of an analogous complex containing planar-tetracoordinate carbon and a Zr(μ-C$\equiv$C(cyclohexyl))Al moiety is also reported for comparison.

Results and Discussion

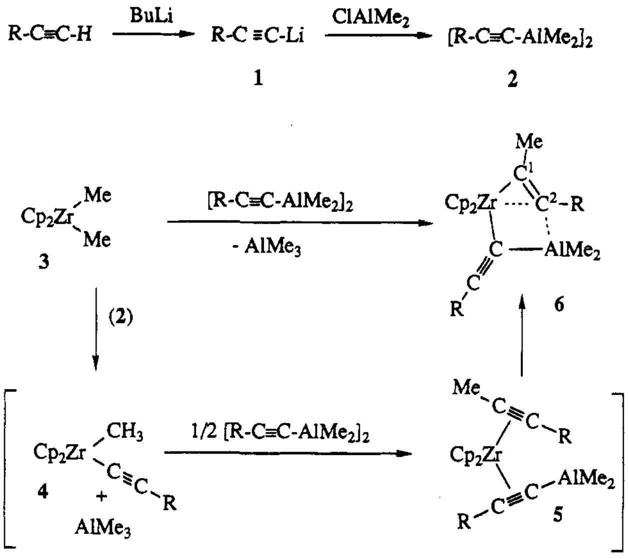
Synthesis of the μ-C$\equiv$CR Metal Complexes. Alkynylaluminum compounds can in some cases be prepared by the reaction of the CH-acidic terminal alkyne with a trialkylaluminum reagent. A typical example is (phenylethynyl)dimethylaluminum, which is prepared from PhC$\equiv$CH and trimethylaluminum dimer with evolution of methane.[8] The alkyl- and silyl-substituted alkynylaluminum reagents used in this study were prepared differently, namely by means of the reaction of dimethylaluminum chloride with the respective alkynyllithium reagents RC$\equiv$CLi [**1**, R = Me$_3$Si (**a**), cyclohexyl (**b**), *tert*-butyl (**c**), methyl (**d**)].[9]

Thus, [(trimethylsilyl)ethynyl]dimethylaluminum dimer (**2a**) was isolated in 67% yield as a white solid. Sublimation gave colorless needles of **2a** that were suited for the X-ray crystal structure analysis (see below). [Me$_3$SiC$\equiv$CAlMe$_2$]$_2$ shows two ^{1}H NMR singlets (in benzene-d_6) at δ 0.01 (SiMe$_3$) and -0.10 (AlMe$_2$). The ^{13}C NMR resonances (benzene-d_6) are observed at δ 139.8, 129.2 (C$\equiv$C), -0.9 (SiMe$_3$), and -6.0 (AlMe$_2$). The alkynylaluminum compounds **2b–d** were prepared analogously and isolated (ca. 50–90% yields). They were characterized by ^{1}H NMR spectroscopy and then directly used for the synthesis of the heterobimetallic aluminum/zirconium complexes.

The [(trimethylsilyl)ethynyl]dimethylaluminum dimer (**2a**) was mixed with dimethylzirconocene in a 2:1 molar ratio in toluene. A rapid reaction took place which was complete after about 3 h. Workup gave the heterodimetallic doubly hydrocarbyl-bridged Al/Zr complex **6a** in 83% yield. Recrystallization from pentane furnished crystals that were suited for the X-ray crystal structure analysis (see below).

We assume that this reaction is initiated by σ-ligand exchange between dimethylzirconocene and the R-C$\equiv$CAlMe$_2$ reagent to give [(trimethylsilyl)ethynyl]methylzirconocene (**4a**) and trimethylaluminum. Reductive coupling takes place consecutively, possibly aided by the addition of a hydrocarbylaluminum component. Formally, an (η^2-alkyne)zirconocene intermediate is formed (possibly **5a**). The favored pathway of stabilization in this case is not the usual metallacyclopentadiene formation.[10] We have rather observed the clean formation of the dimetallabicyclic product **6a**, which contains a planar-tetracoordinate carbon center as part of the μ-η^1(C2):η^2(C$\equiv$C)-Me$_3$Si–CC–Me ligand. Complex **6a** was isolated in good yield (83%). Recrystallization from pentane gave crystals suited for the X-ray crystal structure analysis.

Scheme I



R= Me$_3$Si- (**a**); Cyclohexyl- (**b**); Me$_3$C- (**c**); Me- (**d**)

In solution, complex **6a** exhibits C_s symmetry and thus gives rise to a single ^{1}H/^{13}C NMR Cp resonance at δ 5.38/106.7 (benzene-d_6). The ^{13}C NMR spectrum of complex **6a** shows four signals due to quarternary carbon atoms. We have assigned the resonance at δ 162.5 (in toluene-d_8) to the planar-tetracoordinate carbon center[6] [C(2) in Scheme I]. The signal at δ 224.0 originates from the adjacent olefinic carbon center C(1). We conclude that the remaining quarternary carbon resonances at δ 141.6 and 100.6 must then be due to the bridging μ-C$\equiv$CR alkynyl unit (R = SiMe$_3$). Complex **6a** exhibits an ^{27}Al NMR resonance at δ 169 ($\omega_{1/2}$ = 3700 Hz). This is in the typical range for tetracoordinated aluminum.[11] The IR spectrum of **6a** shows a $\nu_{\mathrm{C\equiv C}}$ band at 2003 cm^{-1}.

The reactions of dimethylzirconocene with (*tert*-butylethynyl)dimethylaluminum (**2c**) and (cyclohexylethynyl)dimethylaluminum (**2b**), respectively, proceeded similarly. The heterodimetallic alkynyl-bridged planar-tetracoordinate carbon compounds **6c** and **6b** were isolated in 66% and 52% yields, respectively. The alkynyl ^{13}C NMR resonances of **6c** are at δ 104.6 and 98.1 (in benzene-d_6). The planar-tetracoordinate carbon signal of **6c** is at δ 155.9, whereas the signal of the adjacent quarternary carbon is found at δ 208.4. Complex **6b** exhibits the respective ^{13}C NMR resonances at δ 107.6, 100.6 (–C$\equiv$CR), 151.9 (planar-tetracoordinate C), and 197.7 (C^1) (in toluene-d_8). The infrared $\nu_{\mathrm{C\equiv C}}$ bands of these complexes are monitored at 2068 (**6c**) and 2065 cm^{-1} (**6b**), respectively.

The reaction of dimethylzirconocene with (propynyl)dimethylaluminum (**2d**) takes a somewhat different course. Upon treatment of 1 molar equiv of Cp$_2$ZrMe$_2$ with a 2-fold excess of **2d**, one obtains a mixture of the propynyl-bridged planar-tetracoordinate carbon compound **6d** with its methyl-bridged analogue **6e**. It seems that in this case trimethylaluminum, which is formed as a stoichiometric product in the initial σ-ligand-exchange reaction between the zirconium and aluminum reagent, can successfully compete with (propynyl)dimethylaluminum for the in situ formed (η^2-2-butyne)ZrCp$_2$ intermediate. The reaction is more selective when carried out at low temperature. When

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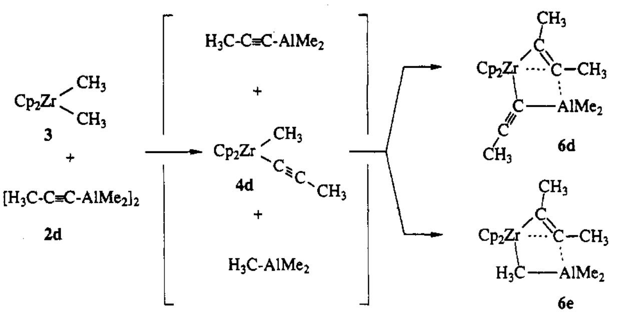

Cp_2ZrMe_2 was mixed with (propynyl)dimethylaluminum (**2d**) in an equimolar ratio at −78 °C and the mixture was allowed to warm to room temperature, only the formation of the methyl-bridged heterodimetallic product **6e** was observed.

X-ray Crystal Structure Analyses. Acetylide ligands can bridge two metal centers using a σ,π-type coordination mode (**C** in Chart I). This situation is sometimes encountered when at least one of the participating metal centers is a d- or f-block element. However, very often only the doubly occupied sp orbital at the acetylide terminus is involved in making the hydrocarbyl bridge and the π-system is left untouched. This situation sometimes leads to C_{2v}-symmetric cases as expected (**A** in Chart I), but often leaning of the σ-acetylide ligand toward one of the metal centers is observed (**B** in Chart I). The structural situations **B** and **C** may look similar but are electronically rather different and hence can be distinguished by the typical differences of the CCR moieties involved: predominant σ-binding does not involve the C≡C π-system and thus C≡C bond lengths close to the parent alkynes are expected, whereas the σ,π-type coordination mode leads to a substantial increase of the acetylide C(sp)–C(sp) separation.

The molecular structure of the alkynylaluminum compound **2a** was determined by X-ray diffraction. In the solid state [(trimethylsilyl)ethynyl]dimethylaluminum is a dimer. Its central atomic framework is located on a crystallographic mirror plane (i.e. $C2/m$); thus it contains two symmetry-equivalent dimethylaluminum units (Al–CH_3 = 1.916(6) Å, H_3C–Al–CH_3 = 121.0(3)°). The aluminum atoms are connected by a bridging (trimethylsilyl)acetylide ligand (the trimethylsilyl group is disordered). The central framework of the aluminum acetylide dimer **2a** comprises the atoms Al, C(1), C(2), and Si. Carbon atom C(1) of the bridging acetylide ligand is bonded to Al (Al–C(1) = 2.013(5) Å) and to Al* (Al*–C(1) = 2.229(6) Å). The central core of the dimetallic compound **2a** is C_{2h}-symmetric; each acetylide bridge leans over toward the aluminum center exhibiting the longer aluminum–C(1) separation. This geometric distortion brings the acetylide carbon center C(2) into a close contact with aluminum (Al*–C(2) = 2.536(5) Å). However, this does not exert a marked influence on the intrinsic bonding parameters of the acetylide ligand as compared to the parent HC≡CR alkyne. In **2a** the C(1)–C(2) bond length is very short at 1.212(7) Å (cf. C≡C distances: HC≡CH, 1.21 Å;[12] $HC{\equiv}CCH_3$, 1.207 Å; C(sp)≡C(sp), average 1.183–1.192 Å[13]) and the deviation of the $-C{\equiv}C-SiMe_3$ backbone from linearity is very small (Al–C(1)–C(2) = 175.3(5)°, C(1)–C(2)–Si = 173.2(5)°).

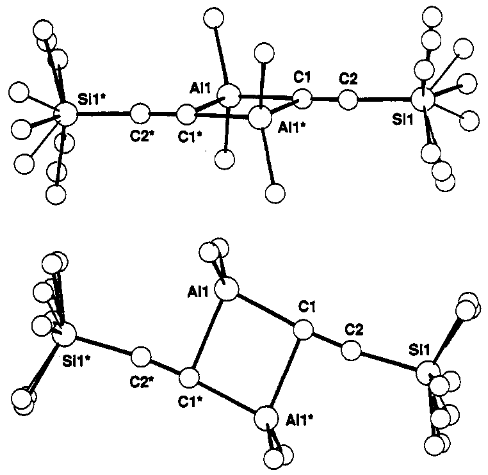

Figure 1. Two views of the molecule of [(trimethylsilyl)ethynyl]dimethyl aluminum (**2a**). Selected bond lengths (Å) and angles (deg): Si(1)–C(2) 1.859(5), Si(1)–C(4) 1.89(1), Si(1)–C(5) 2.00(2), Si(1)–C(6) 1.93(2), Al(1)–C(1) 2.013(5), Al(1)–C(3) 1.916(6), C(1)–C(2) 1.212(7), C(5)–C(6) 1.71(3); C(6)–Si(1)–C(5) 51.5(9), C(6)–Si(1)–C(4) 133.2(6), C(6)–Si(1)–C(2) 110.1(6), C(5)–Si(1)–C(4) 90.4(6), C(5)–Si(1)–C(2) 102.8(6), C(4)–Si(1)–C(2) 103.6(4), C(3)–Al(1)–C(1) 110.6(1), C(2)–C(1)–Al(1) 175.3(5), C(1)–C(2)–Si(1) 173.2(5), C(6)–C(5)–Si(1) 62(1), C(5)–C(6)–Si(1) 66(1).

Chart I

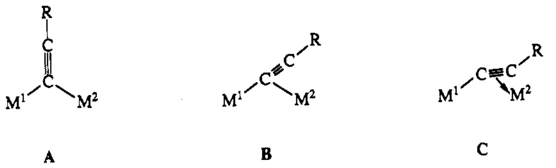

Table I. Atomic Coordinates of 2a

atom	*x*	*y*	*z*
Si(1)	0.1863(1)	0.0000	−0.0705(2)
Al(1)	0.5699(1)	0.0000	0.2244(2)
C(1)	0.4189(3)	0.0000	0.0821(8)
C(2)	0.3271(3)	0.0000	0.0097(8)
C(3)	0.6130(3)	−0.1434(5)	0.3593(8)
C(4)	0.1596(9)	0.0000	0.174(2)
C(4a)	0.1336(7)	−0.133(1)	−0.221(2)
C(5)	0.152(1)	−0.168(2)	−0.107(3)
C(5a)	0.156(2)	0.073(2)	0.149(4)
C(6)	0.130(2)	−0.085(2)	−0.318(4)

From these data, a description of **2a** similar to the structural type **B** in Chart I is suggested. The linear C≡C—R arrangement and the short C≡C bond place **2a** in a series of acetylide main group systems showing almost pure σ-bridging of the −C≡CR ligand. A typical series of examples is depicted in Chart II, and characteristic bonding features are listed in Table II. We notice that these examples cover a wide range of bending of the acetylide ligand over to one of the metals in the core of these metallacycles. The degree of this distortion from the C_{2v}-symmetric limiting situation is best described by the difference of the angles α^1 (M^1–C(1)–C(2), measured at the face opposite to the metal center M^2) and α^2 (defined

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Table II. Comparison of Structural Data for Dimeric Main Group Metal Acetylides

	2a	7	8	9[a]		10	11
L_nM^1	Me_2Al	Ph_2Al	Me_2Ga	$(MeCC)(Me_3N)Be$		Me_2Al	(tmpda)Li
L_nM^2	Me_2Al	Ph_2Al	Me_2Ga	$(MeCC)(Me_3N)Be$		Me_2Al	(tmpda)Li
R	Me_3Si	Ph	Ph	Me		Me	Ph
C^α–C^β	1.212(7)	1.207	1.183	1.200(5)	1.188(5)	1.229	1.220
M^1–C^α	2.013(5)	1.992	2.004(4)	1.763(7)	1.836(6)	2.050(15)	2.132(8)
M^2–C^α	2.229(6)	2.184	2.375(7)	2.042(6)	1.904(6)	2.153(27)	2.164(12)
$\Delta(\alpha,\alpha)$	0.22	0.19	0.37	0.28	0.07	0.10	0.03
α^1 [b]	175.3(5)	171.6	172.8(7)	168.6	154.9	158.3(19)	143.3
α^2	89.9(4)	96.7	93.9(5)	100.2	128.5	109.7(13)	143.4
$\Delta\alpha$	85.4	74.9	78.9	68.4	26.4	48.6	0.1
ref	*c*	14	15	16		17	18

[a] Two rather different independent molecules per unit cell. [b] $\alpha^1 = M^1$–C^α–C^β and $\alpha^2 = M^2$–C^α–C^β, as defined in Chart II. [c] This work.

Chart II

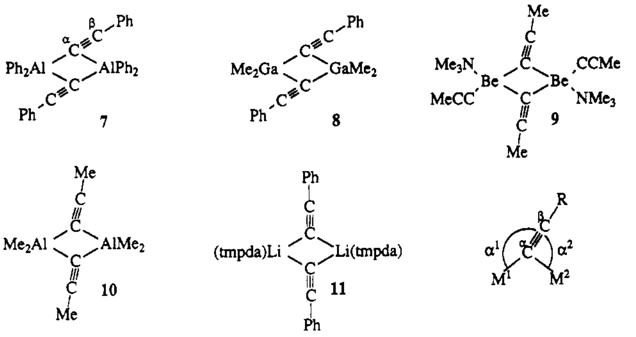
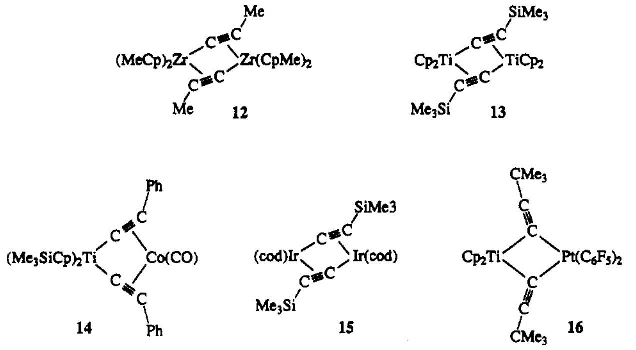


Chart III



as M^2–C(1)–C(2); see Chart II). For an ideal nonbent structure, α^1 should be equal to α^2 and hence their difference $\Delta\alpha$ should be zero. This situation is almost met in the lithium acetylide dimer **11**.[18] From Table II it becomes evident that there are a large range of compounds showing varying degrees of bending. In view of the large $\Delta\alpha$ value (85.4°) obtained from this X-ray crystal structure analysis, [(trimethylsilyl)ethynyl]dimethylaluminum (**2a**) occupies an extreme position in this series. It shows even larger bending than was previously observed for $[PhC{\equiv}CAlPh_2]_2$ (**7**)[14] or $[PhC{\equiv}CGaMe_2]_2$ (**8**).[15]

Acetylide-bridged dinuclear transition metal complexes possess a wider variability of bonding arrangements of the unsaturated μ-C≡CR hydrocarbyl ligand.[1-3] In contrast to the situation found in most main group metal $M^1(\mu$-C≡CR$)M^2$ compounds, the introduction of electron-deficient coordinatively unsaturated d-block metal complex moieties may allow for a participation of the acetylide π-system in connecting the metal centers. In some cases the σ,π-acetylide bridges may also be used for hyperexchange coupling between d-metal L_nM pairs having unpaired electrons.[2b,19,20]

Complexes **12** and **13** (see Chart III) are typical examples of dinuclear group 4 metal systems exhibiting μ-(σ,π-acetylide) bridges. This structural situation of the acetylide ligand is characterized by the occurrence of very short metal–C^α bonds [**12**, 2.188(2) Å;[2b] **13**, 2.056(11) Å[19]] and an increased C^α–C^β separation [**12**, 1.261(2) Å; **13**, 1.253(15) Å] relative to the parent acetylene system or to typical μ-(σ-acetylide)systems (see Tables II and III for a comparison). The π-component in the bridge leads to almost equal M^2–C^α and M^2–C^β bond lengths. Very typically, the acetylide bridge leans over strongly toward M^2. A large value for the $\alpha^1 - \alpha^2$ difference (as defined in Chart II) is characteristically observed for this bonding situation [**12**, $\Delta\alpha$ = 113.9°; **13**, $\Delta\alpha$ = 113.0° (see also Tables II and III)].

The acetylide bridge in complex **6a** is part of a planar central core of atoms containing the atoms Zr, C(11), C(12), C(13), Si(1), Al, C(19), C(20), and Si(2). Both cyclopentadienyl ligands show a nearly 50:50 disorder. There is also a rotational disorder of the $(CH_3)_3Si(2)$ and the $(CH_3)_3$-Si(1) groups; the latter could not be resolved.

The C(19)–C(20)–Si(2) acetylide in **6a** bridges between zirconium and aluminum. The coordination geometry at C(19) is distorted trigonally planar. The sum of bonding angles at C(19) is 359.9(5)° [Zr–C(19)–C(20) = 169.0(5)° (=α^1); Al–C(19)–C(20) = 105.5(5)° (=α^2); Al–C(19)–Zr = 85.4(2)°]. The C(19)–C(20)–Si(2) unit is almost linear (177.0(6)°). The $\Delta\alpha$ value (see Table III) is 63.5°, so the bridging acetylide ligand is leaning over toward the aluminum side. However, its deviation from a symmetrical bridging situation is much less pronounced than e.g. observed for the dinuclear (μ-acetylide)metallocene complexes **12** or **13** that were mentioned above.[2b,19,20] In **6a** the Zr–C(19) bond is long at 2.316(6) Å. The C(19)–C(20) linkage is short. At 1.220(8) Å it is in the typical range of an undisturbed C≡C triple bond.[13] The Al–C(19)/Al–C(20) bond lengths' difference is $|\Delta(\alpha,\beta)|$ = 0.20 Å. All these data taken together (and taking the numerical uncertainties induced by the disorder into account) looked at in comparison to the representative examples listed in Tables II and III indicate that the $C^\alpha{\equiv}C^\beta$ bond of the acetylide ligand in complex **6a** is not strongly involved in bridging between the main group metal aluminum and the transition metal zirconium. In a comparison with

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Table III. Comparison of Selected Structural Data for Dimetallic $M^1(\mu\text{-}C{\equiv}CR)M^2$ Complexes Containing Transition Metals

	12	**13**	**14**	**15**	**6a**	**6b**	**16**
L_nM^1	$(MeCp)_2Zr$	Cp_2Ti	$(Me_3SiCp)_2Ti$	(cod)Ir	Cp_2Zr	Cp_2Zr	Cp_2Ti
L_nM^2	$(MeCp)_2Zr$	Cp_2Ti	(CO)Co	(cod)Ir	Me_2Al	Me_2Al	$(F_5C_6)_2Pt$
R	Ph	Me_3Si	Ph	Me_3Si	Me_3Si	cyclohexyl	Me_3C
$C^\alpha–C^\beta$	1.261(2)	1.253(15)	1.260(4)	1.22(2)	1.220(8)	1.195(6)	1.216(16)
$M^1–C^\alpha$	2.188(2)	2.056(11)	2.070(1)	1.99(2)	2.316(6)	2.338(4)	2.249(10)
$M^2–C^\alpha$	2.431(2)	2.395(7)	1.981(3)	2.24(2)	2.116(6)	2.098(4)	2.016(11)
$\Delta(\alpha,\alpha)$	0.24	0.34	–0.09	0.25	–0.20	–0.24	–0.23
$M^2–C^\beta$	2.407(2)	2.312(8)	2.000(3)	2.18(2)	2.711(6)	2.67	~3.3
$\Delta(\alpha,\beta)$	–0.02	–0.08	0.02	–0.06	0.60	0.67	~1.3
α^1 [a]	187.7(1)	183.9(7)	199.6(2)	185(1)	169.0(5)	168.7(4)	117.0(8)
α^2	73.8(1)	70.9(6)	88.2(2)	76.5(6)	105.5(5)	106.0(3)	159.8(8)
$\Delta\alpha$	113.9	113.0	111.4	108.5	63.5	62.7	–42.8
ref	2b	19, 20	21	22	*b*	*b*	23

[a] For definitions of the angles, see Table II and Chart II. [b] This work.

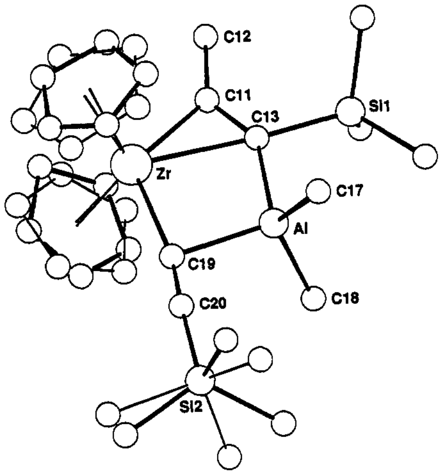

Figure 2. View of the molecular structure of **6a** with (unsystematical) atom-numbering scheme. Characteristic bond lengths (Å) and angles (deg): Zr–C(11) 2.158(6), Zr–C(13) 2.477(5), Zr–C(19) 2.316(6), Al–C(13) 2.071(6), Al–C(17) 1.948(7), Al–C(18) 1.946(8), Al–C(19) 2.116(6), Si(1)–C(13) 1.904(6), Si(2)–C(20) 1.842(6), C(11)–C(12) 1.52(1), C(11)–C(13) 1.316(8), C(19)–C(20) 1.220(8); C(19)–Zr–C(13) 87.5(2), C(19)–Zr–C(11) 119.5(2), C(13)–Zr–C(11) 32.0(2), C(19)–Al–C(18) 106.1(3), C(19)–Al–C(17) 105.0(3), C(19)–Al–C(13) 104.8(2), C(18)–Al–C(17) 122.1(4), C(18)–Al–C(13) 107.9(3), C(17)–Al–C(13) 109.7(3), C(13)–C(11)–C(12) 134.7(6), C(13)–C(11)–Zr 87.5(4), C(12)–C(11)–Zr 137.8(5), C(11)–C(13)–Si(1) 114.6(4), C(11)–C(13)–Al 142.8(5), C(11)–C(13)–Zr 60.5(3), Si(1)–C(13)–Al 102.6(3), Si(1)–C(13)–Zr 175.0(3), Al–C(13)–Zr 82.3(2), C(20)–C(19)–Al 105.5(5), C(20)–C(19)–Zr 169.0(5), Al–C(19)–Zr 85.4(2), C(19)–C(20)–Si(2) 177.0(6).

related systems (Table III), complex **6a** attains a position near one extreme of the overall range of bonding situations where the simple μ-(σ-acetylide) bridging mode is by far dominating.

The μ-(σ-C≡C(cyclohexyl)) bridge in the related heterodimetallic zirconium/aluminum complex **6b** shows almost identical bonding characteristics. Here, the μ-C≡C– triple bond is even shorter [C(12)–C(13) = 1.195(6)Å, C(12)–C(13)–C(14) = 175.5(5)°]. The Zr–C^α bond in **6b** is even longer [Zr–C(12) = 2.338(4) Å] than that in **6a**. The Al–C(12) distance in **6b** is 2.098(4) Å, which is 0.67 Å shorter than the Al–C(13) separation. Again, the μ-(σ-acetylide) bridge in **6b** is much less bent toward the main group metal ($\Delta\alpha$ = 62.7; see Chart II and Table III) than observed for the $M^1(\mu\text{-}C{\equiv}CR)M^2$ complexes **12**–**15**.

We conclude that the μ-C≡CR ligand in complexes **6** is predominantly σ-bridging. It occupies only one of the three valence orbitals at the bent metallocene unit and thus leaves the remaining two available for bonding of the other bridging hydrocarbyl ligand. It is the overall bonding situation of the μ-η^1:η^2-R^1CCR^2 ligand, involving a planar-tetracoordinate carbon center [C(13) in **6a**; C(3) in **6b**], that makes these complexes structurally unusual. The carbon center C(13) in **6a** contains four close neighbors oriented with C(13) in a single plane. These neighboring atoms are all within bonding distance. The C(13)–Si(1) bond length is 1.904(6) Å. The C(13)–C(11) distance is 1.316(8) Å which is in the C=C double bond range. The C(13)–Zr distance is 2.477(5) Å. This is in a range as also typically found for Zr–C(Cp) separations. Finally, the C(13)–Al bond is 2.071(6) Å long. The adjacent Al–C(methyl) bonds are slightly shorter at 1.948(7) and 1.946(8) Å.

Complex **6b** shows similar structural parameters around the planar-tetracoordinate carbon center [C(3); see Figure 3 and Table VI]. Here the Zr–C(3) distance is 2.467(4) Å. Both complexes **6a** and **6b** fit a description of the bonding features of planar-tetracoordinate carbon that involves an sp^2-hybridized carbon center that forms a three-center–two-electron bond to the coordinated metal centers in the σ-plane.[24,25] The observed structural parameters are in accord with a description where three of the substituents at the planar-tetracoordinate carbon serve as σ-donors (Al, Si(2), and C(11) in **6a**; Al, C(4), and C(1) in **6b**), whereas the zirconocene unit serves as a strong σ-acceptor, using its available empty valence orbital in the central σ-ligand plane for bonding.[26] It may be that a small additional contribution from a conjugative interaction between Cp_2Zr and the adjacent C=C bond (being effective normal to the σ-ligand plane) helps to stabilize this unusual coor-

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Table IV. Details of the X-ray Crystal Structure Analyses of the Dimetallic μ-Acetylide Compounds 2a,[a] 6a,[b] and 6b[c]

	2a	6a	6b
mol formula	$C_{14}H_{30}Al_2Si_2$	$C_{23}H_{37}Si_2AlZr$	$C_{29}H_{41}AlZr$
mol wt	308.5	487.9	507.9
cryst color	white	light brown	yellow
cryst syst	monoclinic	monoclinic	monoclinic
space group [No.]	$C2/m$ [12]	$P2_1/c$ [14]	$P2_1/c$ [14]
a, Å	13.990(1)	15.696(3)	12.245(2)
b, Å	11.624(1)	9.119(1)	8.418(1)
c, Å	7.084(1)	19.172(2)	26.272(1)
β, deg	109.62(1)	95.56(1)	90.59(1)
V, Å^3	1085.1	2731.4	2707.7
Z	2	4	4
D_{calcd}, g cm^{-3}	0.94	1.19	1.25
μ, cm^{-1}	2.27	5.19	4.43
$\lambda(K\alpha)$, Å	0.710 69	0.710 69	0.71069
$F(000)$, e	336	1024	1072
diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Enraf-Nonius CAD4
scan mode	ω–2θ	ω–2θ	ω–2θ
$[(\sin\theta)/\lambda]_{max}$, Å^{-1}	0.77	0.65	0.65
T, °C	20	20	20
no. of measd rflns	4337 ($\pm h,\pm k,+l$)	6814 ($\pm h,+k,+l$)	6736 ($\pm h,+k,+l$)
no. of indep rflns	2121	6222	6172
no. of obsd rflns ($I > 2\sigma(I)$)	951	3838	4537
no. of refined params	53	231	280
R	0.072	0.065	0.055
R_w ($w = 1/\sigma^2(F_o)$)	0.086	0.066	0.065
resid electron dens, e Å^{-3}	0.42	0.66	1.45
structure solution	heavy-atom method	heavy-atom method	heavy-atom method

[a] The H atom positions were calculated and kept fixed in the final refinement stages; $SiMe_3$ group 50:25:25 disordered. [b] The H atom positions were calculated and kept fixed in the final refinement stages; Cp rings and $Si(2)Me_3$ group 50:50 disordered. [c] The H atom positions were calculated and kept fixed in the final refinement stages.

Table V. Atomic Coordinates of 6a

atom	x	y	z
Zr	0.3115(1)	0.1521(1)	0.2288(1)
Al	0.1970(1)	0.1158(2)	0.0947(1)
Si(1)	0.0692(1)	0.3466(2)	0.1419(1)
Si(2)	0.3436(2)	−0.1961(2)	0.0077(1)
C(11)	0.2062(4)	0.3004(7)	0.2382(3)
C(12)	0.1776(5)	0.408(1)	0.2917(4)
C(13)	0.1751(3)	0.2576(6)	0.1753(3)
C(14)	0.0852(7)	0.546(1)	0.1420(5)
C(15)	0.0217(6)	0.305(1)	0.0523(6)
C(16)	−0.0109(6)	0.288(2)	0.1990(7)
C(17)	0.2217(6)	0.2278(9)	0.0125(4)
C(18)	0.1092(5)	−0.0353(8)	0.0901(4)
C(19)	0.3134(4)	0.0096(6)	0.1290(3)
C(20)	0.3277(4)	−0.0735(7)	0.0816(3)
C(1)	0.240(1)	0.058(2)	0.3314(7)
C(1a)	0.2187(9)	0.017(2)	0.312(1)
C(2)	0.231(1)	−0.051(2)	0.280(1)
C(2a)	0.245(1)	−0.092(2)	0.2647(8)
C(3)	0.308(1)	−0.112(2)	0.2692(8)
C(3a)	0.339(1)	−0.101(2)	0.279(1)
C(4)	0.361(1)	−0.047(2)	0.317(1)
C(4a)	0.377(1)	−0.001(2)	0.3288(9)
C(5)	0.329(1)	0.074(2)	0.3553(8)
C(5a)	0.296(1)	0.064(2)	0.3513(9)
C(6)	0.441(1)	0.299(2)	0.275(1)
C(6a)	0.416(1)	0.343(2)	0.279(1)
C(7)	0.383(1)	0.400(2)	0.243(1)
C(7a)	0.372(1)	0.410(2)	0.208(1)
C(8)	0.380(1)	0.372(2)	0.174(1)
C(8a)	0.402(1)	0.310(2)	0.1521(8)
C(9)	0.430(1)	0.261(2)	0.166(1)
C(9a)	0.4581(9)	0.195(2)	0.1865(9)
C(10)	0.464(1)	0.218(2)	0.222(1)
C(10a)	0.4693(9)	0.211(2)	0.2605(9)
C(21)	0.414(1)	−0.337(2)	0.036(1)
C(21a)	0.460(1)	−0.293(2)	0.025(1)
C(22)	0.236(1)	−0.250(2)	−0.0345(8)
C(22a)	0.264(1)	−0.352(2)	0.011(1)
C(23)	0.3887(9)	−0.074(2)	−0.0619(7)
C(23a)	0.337(1)	−0.104(2)	−0.073(1)

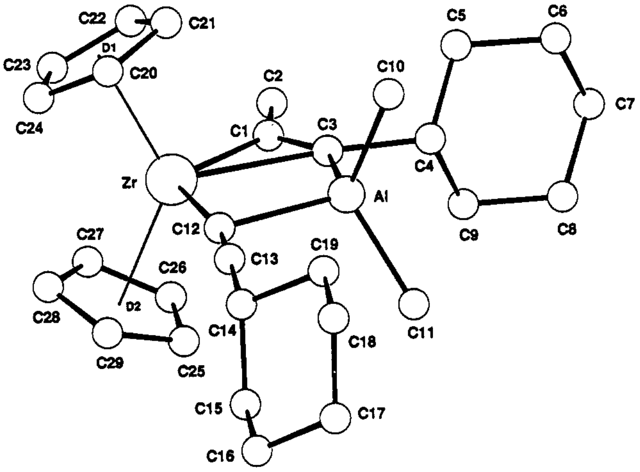

Figure 3. View of the molecular geometry of **6b**.

dination geometry at carbon. The very short Zr—C═C distances [**6a**, Zr–C(11) = 2.158(6) Å; **6b**, Zr–C(1) = 2.192(5) Å] could be an indication of this additional stabilizing effect.[6,7]

Conclusions

We and others have accumulated convincing evidence that the reaction of reactive group 4 metallocene alkyne complexes $[M^1(\eta^2\text{-RC}{\equiv}\text{CR})]$ with X–M^2 components leads to the formation of very stable complexes exhibiting a dimetallabicyclic framework and containing a planar-tetracoordinate carbon atom.[6,7,27,28] From theoretical investigations[26] and an experimental study,[29] it is quite clear that the unusually structured dimetallabicyclic form is much more stable thermodynamically than its "normal" monocyclic isomer.

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Table VI. Selected Bond Lengths (Å) and Angles (deg) for 6b

Zr–C(1)	2.192(5)	Zr–C(3)	2.467(4)
Zr–C(12)	2.338(4)	Zr–D(1)	2.224
Zr–D(2)	2.230	Al–C(3)	2.117(5)
Al–C(10)	1.959(5)	Al–C(11)	1.959(5)
Al–C(12)	2.098(4)	C(1)–C(2)	1.499(8)
C(1)–C(3)	1.291(7)	C(3)–C(4)	1.583(6)
C(12)–C(13)	1.195(6)	C(13)–C(14)	1.477(6)
D(2)–Zr–D(1)	129.2(1)	D(2)–Zr–C(12)	101.6(1)
D(2)–Zr–C(3)	113.0(1)	D(2)–Zr–C(1)	102.8(1)
D(1)–Zr–C(12)	101.5(1)	D(1)–Zr–C(3)	112.2(1)
D(1)–Zr–C(1)	103.7(1)	C(12)–Zr–C(3)	88.4(1)
C(12)–Zr–C(1)	119.8(2)	C(3)–Zr–C(1)	31.5(2)
C(12)–Al–C(11)	105.9(2)	C(12)–Al–C(10)	108.0(2)
C(12)–Al–C(3)	105.3(2)	C(11)–Al–C(10)	119.2(2)
C(11)–Al–C(3)	109.6(2)	C(10)–Al–C(3)	108.0(2)
C(3)–C(1)–C(2)	134.0(5)	C(3)–C(1)–Zr	86.1(3)
C(2)–C(1)–Zr	139.8(4)	C(4)–C(3)–C(1)	123.3(4)
C(4)–C(3)–Al	92.9(3)	C(4)–C(3)–Zr	173.9(3)
C(1)–C(3)–Al	143.8(4)	C(1)–C(3)–Zr	62.4(3)
Al–C(3)–Zr	81.3(1)	C(13)–C(12)–Al	106.0(3)
C(13)–C(12)–Zr	168.7(4)	Al–C(12)–Zr	84.9(2)
C(14)–C(13)–C(12)	175.5(5)		

Table VII. Atomic Coordinates of 6b

atom	*x*	*y*	*z*
Zr	0.3727(1)	0.0988(1)	0.1461(1)
Al	0.1683(1)	0.2235(1)	0.0965(1)
C(1)	0.2416(4)	–0.0428(6)	0.1796(2)
C(2)	0.2264(5)	–0.1755(7)	0.2169(2)
C(3)	0.1759(4)	0.0389(5)	0.1511(2)
C(4)	0.0483(3)	0.0095(5)	0.1487(2)
C(5)	–0.0074(4)	0.0315(6)	0.1993(2)
C(6)	–0.1304(4)	0.0031(7)	0.1940(2)
C(7)	–0.1561(4)	–0.1553(8)	0.1710(3)
C(8)	–0.1003(4)	–0.1756(6)	0.1206(2)
C(9)	0.0226(4)	–0.1518(6)	0.1261(2)
C(10)	0.0936(4)	0.4047(6)	0.1274(2)
C(11)	0.1140(4)	0.1391(6)	0.0316(2)
C(12)	0.3312(3)	0.2888(5)	0.0840(2)
C(13)	0.3287(3)	0.3845(5)	0.0504(2)
C(14)	0.3282(3)	0.4926(5)	0.0061(2)
C(15)	0.3484(4)	0.4027(6)	–0.0433(2)
C(16)	0.3484(4)	0.5145(7)	–0.0884(2)
C(17)	0.2475(4)	0.6117(7)	–0.0923(2)
C(18)	0.2247(4)	0.7013(6)	–0.0432(2)
C(19)	0.2221(4)	0.5898(6)	0.0023(2)
C(20)	0.4253(6)	0.3644(6)	0.1843(2)
C(21)	0.3416(5)	0.306(1)	0.2142(3)
C(22)	0.3813(6)	0.1692(9)	0.2386(2)
C(23)	0.4878(5)	0.1473(7)	0.2236(2)
C(24)	0.5146(4)	0.2679(7)	0.1903(2)
C(25)	0.3973(5)	–0.0765(7)	0.0694(2)
C(26)	0.3996(5)	–0.1775(6)	0.1118(3)
C(27)	0.4912(6)	–0.1425(7)	0.1399(2)
C(28)	0.5479(4)	–0.0224(9)	0.1132(3)
C(29)	0.4885(5)	0.0168(7)	0.0716(2)

The electronic means of stabilizing planar-tetracoordinate carbon are now principally well understood.[24,25] Each of them has two metal-containing substituents attached at the "square-planar" C atom, which serve to diminish the electron-deficiency of the σ-system. A few examples of isolated planar-tetracoordinate carbon compounds have been reported in the literature.[30] Complexes **6** and related systems, of which ca. 50 stable examples have been prepared and characterized so far,[6,7,27-29] are slightly different from the symmetrically substituted examples calculated or experimentally observed. The dimetallic Zr/Al compounds described above use their metal centers in a complementary way: the d-block metal uses its unique σ-acceptor abilities inside the bent metallocene environment,[31] whereas the other metal center predominantly serves as a strong σ-donor substituent. This situation requires that these two components are connected by a ligand that behaves electronically as an insulator, i.e. a group that holds the two metal centers physically close together but does not allow for a pronounced compensation of the Lewis acidity of the transition metal. The μ-(σ-acetylide) seems to serve this purpose very well. In the Zr/Al combination, it is almost completely σ-bridging. Its π-system is apparently not interacting with zirconium, which can concentrate its acceptor power to stabilize the adjacent planar-tetracoordinate carbon center.

Experimental Section

All reactions were carried out in an inert atmosphere (argon) using Schlenk type glassware. Solvents were dried and distilled under argon prior to use. For other experimental details including a listing of spectrometers used for characterization see ref 6c. Alkynyllithium reagents RC≡CLi (**1**) (R = –SiMe$_3$, –cyclohexyl, –CMe$_3$, –CH$_3$) were prepared according to literature procedures.[9] The corresponding (alkynyl)dimethylaluminum compounds $[(\mathrm{RC{\equiv}C})\mathrm{AlMe_2}]_2$ (**2a–d**) were also synthesized as described in the literature.[9] Complexes **6** are sensitive to moisture and oxygen but stable in an inert atmosphere up to their respective decomposition temperatures given below.

Preparation of [(Trimethylsilyl)ethynyl]dimethylaluminum (2a). Chlorodimethylaluminum (0.90 g, 9.73 mmol) was dissolved in 10 mL of pentane, and the solution was added dropwise during 1 h to a suspension of 1.00 g (9.62 mmol) of [(trimethylsilyl)ethynyl]lithium in 20 mL of pentane at 0 °C. The mixture was stirred for 24 h at ambient temperature and then filtered. Solvent was removed from the filtrate in vacuo to give **2a** as a white solid (1.00 g, 67%). Sublimation at 30 °C (ambient pressure over several days) yielded crystals suitable for an X-ray crystal structure analysis (for details see Table IV). ^{1}H NMR (benzene-d_6): δ 0.01 (s, 9H, SiMe$_3$), –0.10 (s, 6H, AlMe$_2$). ^{13}C NMR (benzene-d_6): δ 139.8, 129.2 (C≡C), –0.9 (SiMe$_3$), –6.0 (br, AlMe$_2$).

Preparation of $\mathrm{Cp_2Zr}(\mu\text{-}\eta^1{:}\eta^2\text{-MeCCSiMe_3})(\mu\text{-C{\equiv}CSiMe_3})\text{-}\mathrm{AlMe_2}$ (6a). Dimethylzirconocene (815 mg, 3.24 mmol) was dissolved in 5 mL of toluene. A solution of 1.00 g (6.50 mmol) of [(trimethylsilyl)ethynyl]dimethylaluminum in 5 mL of toluene was added, and the mixture was stirred for 3 h at room temperature. Solvent was removed in vacuo to give 1.17 g (83%) of **6a**. Recrystallization from pentane gave red crystals of **6a** suited for the X-ray crystal structure analysis (see Table IV); mp 105 °C dec. Anal. Calcd for $\mathrm{C_{23}H_{37}AlSi_2Zr}$ (M_r = 487.9): C, 56.62; H, 7.64. Found: C, 55.36; H, 7.80. ^{1}H NMR (toluene-d_8): δ 5.36 (s, 10H, Cp), 2.68 (s, 3H, Me), 0.36 (s, 9H), 0.27 (s, 9H, SiMe$_3$), –0.16 (s, 6H, AlMe$_2$). ^{13}C NMR (toluene-d_8): δ 224.0 (ZrC=), 162.5 (planar-tetracoordinate C), 141.6, 100.6 (–*C*≡*C*-SiMe$_3$, 106.7 ($^1J_{\mathrm{CH}}$ = 172 Hz, Cp), 26.6 ($^1J_{\mathrm{CH}}$ = 126 Hz, CH$_3$), 3.2 ($^1J_{\mathrm{CH}}$ = 120 Hz), –0.4 ($^1J_{\mathrm{CH}}$ = 120 Hz), –1.5 ($^1J_{\mathrm{CH}}$ = 114 Hz, SiMe$_3$ and AlMe$_2$). ^{27}Al NMR (toluene-d_8, 104 MHz, 333 K): δ 169 ($\omega_{1/2}$ = 3700 Hz). IR (KBr), $\tilde{\nu}$ (cm^{-1}): 3101; 1444, 1010, 810 (Cp); 2003 (C≡C); 1563 (C=C).

Preparation of $\mathrm{Cp_2Zr}(\mu\text{-}\eta^1{:}\eta^2\text{-MeCC(cyclohexyl)})(\mu\text{-C{\equiv}C}\text{-(cyclohexyl)})\mathrm{AlMe_2}$ (6b). A solution of 765 mg (3.05 mmol) of dimethylzirconocene in 5 mL of toluene was charged with 1.00

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g (6.10 mmol) of (cyclohexylethynyl)dimethylaluminum dissolved in 5 mL of toluene. The resulting yellow solution was stirred for 20 h at room temperature. Solvent was then removed in vacuo. The residue was washed with 5 mL of pentane to yield the heterodimetallic complex **6b** as a yellow solid (785 mg, 52%). Recrystallization from pentane at −30 °C gave crystals for the X-ray crystal structure determination (Table IV); mp 121 °C dec. Anal. Calcd for $C_{29}H_{41}AlZr$ (M_r = 507.9): C, 68.59; H, 8.14. Found: C, 68.43; H, 8.46. ^1H NMR (toluene-d_8): δ 5.50 (s, 10H, Cp), 2.92 (m, 1H, cyclohexyl CH), 2.56 (s, 3H, CH_3), 2.34 (m, 1H cyclohexyl CH), 1.78–1.10 (m, 20H, cyclohexyl CH_2), −0.22 (s, 6H, $AlMe_2$). ^{13}C NMR (toluene-d_8): δ 197.7 (ZrC=), 151.9 (planar-tetracoordinate C), 107.6 (br), 100.6 (−*C*≡*C*(cyclohexyl)), 107.1 ($^1J_{CH}$ = 173 Hz, Cp), 43.3 ($^1J_{CH}$ = 121 Hz), 32.6 ($^1J_{CH}$ = 130 Hz, cyclohexyl *C*H), 32.2 ($^1J_{CH}$ = 128 Hz), 31.4 ($^1J_{CH}$ = 127 Hz), 27.9 ($^1J_{CH}$ = 126 Hz), 26.9 ($^1J_{CH}$ = 127 Hz), 26.0 ($^1J_{CH}$ = 127 Hz), 25.2 ($^1J_{CH}$ = 127 Hz, cyclohexyl CH_2), 23.8 ($^1J_{CH}$ = 126 Hz, CH_3), −6.33 ($AlMe_2$). ^{27}Al NMR (toluene-d_8, 104 MHz, 333 K): δ 159 ($\omega_{1/2}$ = 4750 Hz). IR (KBr), $\tilde{\nu}$ (cm^{-1}): 3092; 1447, 1012, 804 (Cp); 2065 (C≡C); 1612 (C=C).

Preparation of $Cp_2Zr(\mu\text{-}\eta^1{:}\eta^2\text{-}MeCCCMe_3)(\mu\text{-}C{\equiv}CCMe_3)AlMe_2$ (6c). A mixture of 0.90 g (6.52 mmol) of (*tert*-butylethynyl)dimethylaluminum and 0.82 g (3.26 mmol) of dimethylzirconocene in 10 mL of toluene was stirred for 20 h at ambient temperature. Solvent was evaporated to give a black oil. Recrystallization from pentane gave **6c** as a yellow solid: yield 0.70 g (66%); mp 68 °C dec (DSC). Anal. Calcd for $C_{25}H_{34}AlZr$ (M_r = 455.8): C, 65.88, H, 8.18. Found: C, 63.92; H, 8.14. ^1H NMR (benzene-d_6): δ 5.62 (s, 10H, Cp), 2.28 (s, 3H, CH_3), 1.22, 1.17 (s, 9H each, CMe_3), −0.17 (s, 6H, $AlMe_2$). ^{13}C NMR (benzene-d_6): δ 208.4 (ZrC=), 155.9 (planar-tetracoordinate C), 107.2 (Cp), 104.6, 98.1 (−C≡C−), 39.0, 35.8 (*C*Me_3), 30.5, 29.9 (C(CH_3)$_3$), 17.2 (CH_3), −4.3 ($AlMe_2$). IR (KBr), $\tilde{\nu}$ (cm^{-1}): 3114; 1457, 1019, 800 (Cp); 2068 (C≡C); 1573 (C=C).

Reaction of Dimethylzirconocene with (Propynyl)dimethylaluminum. (a) Dimethylzirconocene (250 mg, 1.00 mmol) was dissolved in 5 mL of toluene. (Propynyl)dimethylaluminum (190 mg, 2.00 mmol) dissolved in 3 mL of toluene was added and the mixture kept for 3 h at room temperature. Solvent was removed in vacuo to give a yellow wax, which turned out to be an approximately 1:1 mixture of **6d** and **6e** [^1H NMR of **6d** (benzene-d_6): δ 5.65 (s, 10H, Cp), 1.91, 1.66, 1.43 (s, each 3H, CH_3), −0.26 (s, 6H, $AlMe_2$)].

(b) Dimethylzirconocene (1.77 g, 7.05 mmol) was reacted with 672 mg (7.00 mmol) of (propynyl)dimethylaluminum in 30 mL of toluene at −78 °C. Warmup to room temperature gave a red solution. Solvent was removed in vacuo and the resulting red oil extracted with 20 mL of pentane. Solvent was removed from the clear pentane phase at −30 °C to give **6e** as a yellow-orange wax, which was only characterized spectroscopically: yield 1.05 g (43%); mp 71–75 °C. ^1H NMR (benzene-d_6): δ 5.51 (s, 10H, Cp), 1.88, 1.60 (s, 3H each, CH_3), −0.30 (s, 6H, $AlMe_2$), −1.05 (s, 3H, μ-CH_3). ^{13}C NMR (benzene-d_6): δ 281.5 (Zr*C*=), 147.3 (planar-tetracoordinate C), 107.1 ($^1J_{CH}$ = 178 Hz, Cp), 30.9 ($^1J_{CH}$ = 128 Hz, CH_3), 25.6 ($^1J_{CH}$ = 125 Hz, CH_3), −6.9 ($^1J_{CH}$ = 105 Hz, $AlMe_2$), −11.4 ($^1J_{CH}$ = 112, μ-CH_3). IR (KBr), $\tilde{\nu}$ (cm^{-1}): 3100; 1438, 1014, 802 (Cp); 1596 (C=C).

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Supplementary Material Available: Tables giving details of the X-ray crystal structure analyses, bond lengths and angles, hydrogen atomic coordinates, and thermal parameters for **2a**, **6a**, and **6b** (20 pages). Ordering information is given on any current masthead page.

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