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π-Conjugation and Dynamic Behavior in Doubly Acetylide-Bridged Binuclear Group 4 Bent Metallocene Complexes

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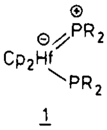
Bis(alkynyl)zirconocene and -hafnocene complexes $(R^1Cp)_2M(C\equiv CR)_2$ (**6**) were prepared by reacting metallocene dihalides $(R^1Cp)_2MCl_2$ (R^1 = H, CH_3, *tert*-butyl) with alkynyl anion equivalents. Subsequent comproportionation of **6** with additional $(R^1Cp)_2MCl_2$ yielded mono(alkynyl)metallocene chlorides **7**. Complexes **6** and **7** were treated with zirconocenes $(R^2Cp)_2Zr$, generated in situ from the corresponding (η^4-butadiene)metallocene systems to give binuclear alkynyl-bridged complexes $(R^1Cp)_2M(\mu\text{-}Cl)(\mu\text{-}C\equiv CR)Zr(CpR^2)_2$ (**9**) or $(R^1Cp_2)M(\mu\text{-}C\equiv CR)_2Zr(CpR^2)_2$ (**10**), respectively (M = Zr, Hf; R^1, R^2 = H, CH_3, *t*-Bu; R = CH_3, Ph). The X-ray crystal structure analysis of $Cp_2Zr(C\equiv CCH_3)_2$ (**6a**) revealed no noticeable conjugative interaction of the 16-electron d^0-configurated early-transition-metal center with the acetylenic π-system. Complex **6a** crystallizes in space group *Pnc*2 with cell constants a = 7.3099 (7) Å, b = 14.2440 (9) Å, c = 6.5299 (5) Å; d(Zr–C(1)) = 2.249 (3), C(1)–C(2) = 1.206 (4) Å; C(1)–Zr–C(1*) = 103.6 (1)°, Zr–C(1)–C(2) = 177.0 (3)°. In contrast, the metal–acetylide unit in the C_{2h} symmetric $(H_3CCp)_2Zr(C\equiv CPh)$ dimer (**10f**) has a much shorter Zr–C^α bond (2.188 (2) Å), as revealed by X-ray diffraction. Together with the other pertinent bonding features [$d(C^\alpha\equiv C^\beta)$ = 1.261 (2) Å; $Zr^*–C^\alpha/C^\beta$ = 2.431 (2)/2.407 (2) Å; Zr···Zr* = 3.506 (1) Å; $C^\alpha \cdots C^{\alpha *}$ = 3.018 (2) Å] this indicates a substantial π-interaction between the metal and the $C\equiv CR$ unit of the binuclear complexes of type **10**. Nevertheless, complexes **10** are highly fluxional—the alkynyl ligands undergo rapid intramolecular exchange between adjacent metal centers ($\Delta G^* \approx$ 12–15 kcal/mol). For one example, the $(t\text{-}BuCp)_2Zr(\mu\text{-}C\equiv CCH_3)_2ZrCp_2$ system, the temperature-dependent dynamic NMR spectra have disclosed the presence of a novel C_{2v} symmetric binuclear species (**13a**) equilibrating with the C_s symmetric doubly alkynyl-bridged complex **10d**. This may indicate that in such systems the automerization process by sequential σ-alkynyl ligand migrations (via **13**) is favored over the concerted exchange involving the common D_{2h} symmetric transition state.

Introduction

Organometallic group 4 bent metallocene complexes Cp_2MR_2 (M = Ti, Zr, Hf) of d^0 16-electron metal configuration are isolobal with the organic carbenium ions. They have one vacant orbital available for conjugative interaction with lone pairs or π-systems at adjacent σ-bonded ligands R.[1,2] Substantial ligand/metal π-interaction has been observed for R being PR_2[3] or $N{=}CR^1R^2$ groups[4] and also when ylidic σ-ligands $CHPR_3$[5] are attached to the early transition metals. Complexes **1**–**3** are typical examples.



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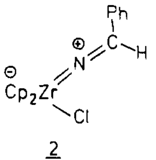

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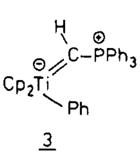

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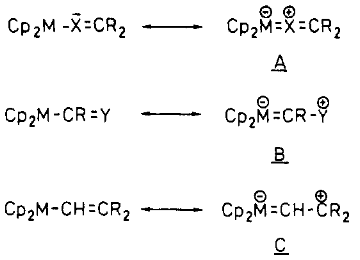
In contrast, there are no examples known of simple mononuclear compounds containing Cp_2M–alkenyl or –alkynyl moieties where there is unambiguous evidence of a substantial π-interaction between the electron-deficient metal center and the carbon–carbon multiple bond.[6] It appears that (in contrast to situation I or II, Scheme I) the resulting charge separation makes π-conjugation quite unfavorable for the neutral organometallic analogues (III) of the allyl or propargyl cation.

Scheme I

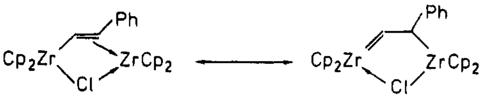


$Cp_2M\text{-}\bar{X}{=}CR_2 \longleftrightarrow Cp_2\overset{\ominus}{M}{=}\overset{\oplus}{X}{=}CR_2$ A

$Cp_2M\text{-}CR{=}Y \longleftrightarrow Cp_2\overset{\ominus}{M}{=}CR\text{-}\overset{\oplus}{Y}$ B

$Cp_2M\text{-}CH{=}CR_2 \longleftrightarrow Cp_2\overset{\ominus}{M}{=}CH\text{-}\overset{\oplus}{C}R_2$ C

There are indications that the π-interaction between the metal and the C=C bond in III becomes more favorable when the charge separation is reduced by adding a Cp_2M'–(μ-L) unit to the alkenyl metallocene moiety. For example, the Zr–C^α bond in complex **4** is remarkably short according to X-ray crystallography.[7]



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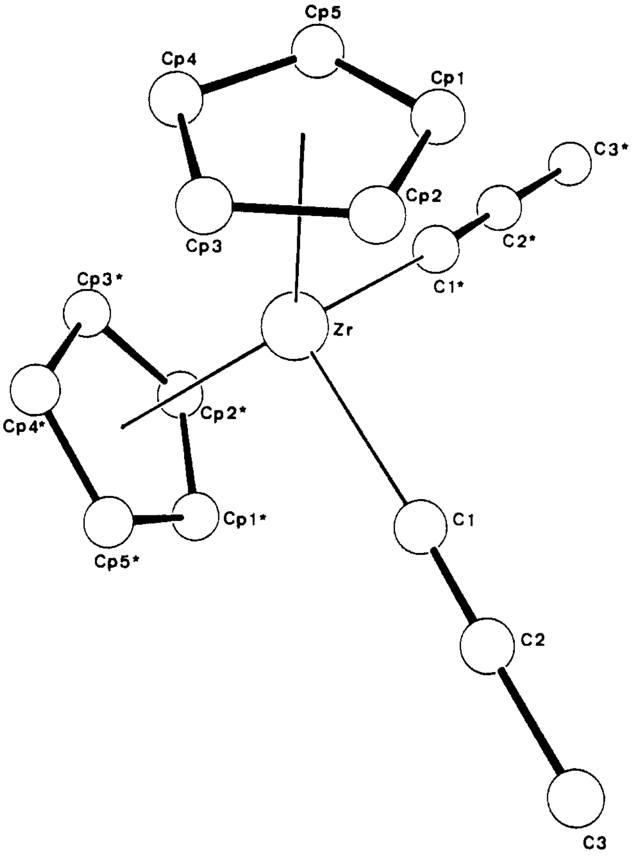


Figure 1. X-ray crystal structure determination of $Cp_2Zr(C{\equiv}CCH_3)_2$ (**6a**): molecular geometry and atom numbering scheme.

We have found an additional system showing this effect. The M–C^α bond length is reduced substantially, when bis(alkynyl)metallocene complexes $Cp_2M(C{\equiv}CR)_2$ (**6**) are converted into the binuclear doubly acetylide-bridged complexes $Cp_2M(\mu\text{-}C{\equiv}CR)_2M'Cp_2$ (**10**) by adding to them in situ generated Cp_2M' reagents.[8] Suitable labeling of the Cp groups with alkyl substituents revealed that complexes **6**, despite their increased M–C^α π-interaction, are dynamic molecules that undergo a remarkably facile σ-acetylide migration between the two metal centers.

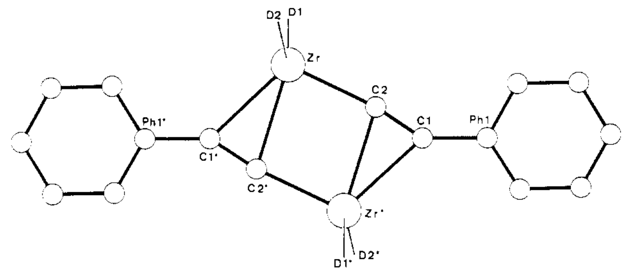
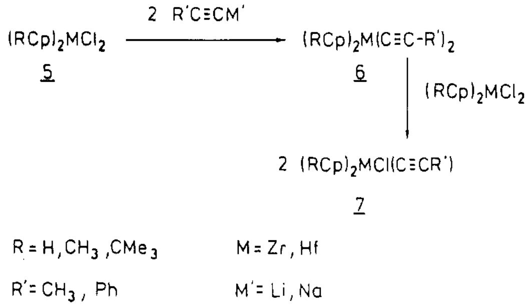


Figure 2. A view of the central coplanar section of $[(H_3CCp)_2Zr]_2(\mu\text{-}C{\equiv}CPh)_2$ (**10f**) as determined by X-ray diffraction. D1 and D2 denote centroids of the Cp ligands bonded to zirconium.

Results and Discussion

Mononuclear (σ-alkynyl)metallocene complexes were prepared by reacting $(RCp)_2MCl_2$ complexes **5** [M = Zr, R = H (**a**), CH_3 (**b**), *t*-Bu (**c**); M = Hf, R = H (**d**)] with $H_3CC{\equiv}CLi$ or $PhC{\equiv}CNa$. Reaction with 2 molar equiv of the alkynyl anion reagents thus yielded the bis(alkynyl)metallocenes **6**, $(RCp)_2Zr(C{\equiv}CCH_3)_2$ [R = H (**a**), CH_3 (**b**), *t*-Bu (**c**)], $(RCp)_2Zr(C{\equiv}CPh)_2$ [R = H (**d**), CH_3 (**e**), *t*-Bu (**f**)], and $Cp_2Hf(C{\equiv}C\text{-}R')_2$ [R' = CH_3 (**g**), Ph (**h**)]. Subsequent comproportionation of the dialkynylmetallocenes with 1 molar equiv of a zirconocene dihalide at temperatures between 25 and 50 °C in benzene solution gave the mononuclear monoalkynylmetallocene complexes **7**, $(RCp)_2Zr(C{\equiv}CCH_3)Cl$ [R = H (**a**), CH_3 (**b**)] and $(RCp)_2Zr(C{\equiv}CPh)Cl$ [R = H (**c**), CH_3 (**d**)].



Complexes **6** exhibit very characteristic spectroscopic features. In the ^{13}C NMR spectra, both σ-acetylide carbon atoms show absorptions at a much lower field than the parent non-metalated acetylenes $HC{\equiv}CPh$ [C(1), δ 83.8; C(2), δ 77.4] or $HC{\equiv}CCH_3$ [δ 86.8 ($^2J_{CH}$ = 10.6 Hz), 74.5 ($^3J_{CH}$ = 4.8 Hz)]. Typical values are δ 141.7 and 124.8 ($^3J_{CH}$ = 5.0 Hz) (C^β) for $Cp_2Zr(C^\alpha{\equiv}C^\beta Ph)_2$ (**6d**) or δ 131.6 ($^3J_{CH}$ = 4.1 Hz) and 120.0 ($^2J_{CH}$ = 9.5 Hz) for $Cp_2Zr(C^\alpha{\equiv}C^\beta CH_3)_2$ (**6a**).

Similar chemical shifts have been observed for C^β in other metal σ-alkynyl complexes, while C^α shifts seem to

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cover a much wider range [see, for a comparison $Me_2Al(C{\equiv}CMe)$ δ 90.3 (C^α), 132.9 (9.6 Hz) (C^β),[10a] $Me_2Ga(C{\equiv}CMe)$ δ 89.8 (3.9 Hz), 122.4 (12.7 Hz),[10a] $Me_2In(C{\equiv}CMe)$ δ 90.9 (3.8 Hz), 122.4 (8.7 Hz),[10a] (dppe)Pt($C{\equiv}CR$) δ 107.0, 111.8 (R = Ph); δ 91.2, 105.3 (R = CH_3),[10b] and $Cp(CO)_2(PMe_3)W(C{\equiv}CPh)$ δ 96.3, 127.4[10c]].

A small decrease in the $\nu(C{\equiv}C)$ IR stretching frequency had been observed upon attaching a group 6 metallocene unit to an acetylide moiety [$\nu(C{\equiv}C)$ = 2090 cm^{-1} for $Cp_2Mo(C{\equiv}CPh)_2$, 2080 cm^{-1} for $Cp_2W(C{\equiv}CPh)_2$,[9b] and 2115 cm^{-1} for $HC{\equiv}CPh$]. A similar shift of the $\nu(C{\equiv}C)$ IR absorption results by introducing Cp_2Zr or Cp_2Hf moieties [$Cp_2Zr(C{\equiv}CPh)_2$ (**6d**), $\nu(C{\equiv}C)$ = 2075 cm^{-1}; $Cp_2Hf(C{\equiv}CPh)_2$ (**6h**), 2080 cm^{-1}; $Cp_2Zr(C{\equiv}CMe)_2$, 2085 cm^{-1}]. Substituting one of the σ-alkynyl ligands in complexes **6** for chloride leads to a slight increase in the $\nu(C{\equiv}C)$ IR frequencies [$Cp_2ZrCl(C{\equiv}C\text{-}CH_3)$, 2098 cm^{-1}; propyne, 2160 cm^{-1}].

The spectroscopic data of the alkynylzirconocene and -hafnocene complexes **6** and **7** provide no conclusive evidence for or against a π-bonding component between the coordinatively unsaturated early-transition-metal center and the carbon–carbon multiple bond of the π-bonded hydrocarbyl ligands. Therefore, the structure of bis(cyclopentadienyl)dipropynylzirconocene (**6a**), a typical example of this class of σ-alkynyl metallocene complexes, was determined by X-ray diffraction.

In the crystal, complex **6a** exhibits discrete $C_{16}H_{16}Zr$ molecular units. The central metal atom is surrounded by two Cp ligands and two σ-propynyl groups. The pairs of η-C_5H_5 and σ-$CCCH_3$ ligands are each symmetry-related. Metal–C(Cp) distances are in the usual range. The CpZrCp angle is typical for many group 4 bent metallocene complexes[1,2] [D(1)–Zr–D(1*) = 132.6°, where D(1) denotes the centroid of the cyclopentadienyl ring made up by the carbon centers Cp(1)–Cp(5) and D(1*) is the centroid of the symmetry-related η-Cp ligand attached to Zr]. The angle between the σ-ligands is larger than that found in, e.g., dimethylzirconocene [C(1)–Zr–C(1*) = 103.6 (1)° in **6a** and 95.6 (12)° in $Cp_2Zr(CH_3)_2$[11]], but is still within the range of L–M–L angles found in many zirconocene complexes [e.g. 101.2 (2)° in $Cp_2ZrCl(N{=}CHPh)$ (**2**); 106.5 (1)° in $Cp_2Zr(N{=}CPh_2)_2$[4]]. The σ-propynyl ligand exhibits a nearly linear carbon framework [C(1)–C(2)–C(3) = 179.4 (4)°]. The C(2)–C(3) distance [1.462 (5) Å] is typical for a C(sp)–C(sp^3) single bond. Very instructive is the C(1)–C(2) [1.206 (4) Å] bond distance, showing no noticeable deviation from typical $C{\equiv}C$ separations found in simple unperturbed organic or organometallic alkynes [$d(C{\equiv}C)$ = 1.21 Å ($HC{\equiv}CH$),[12] 1.207 Å ($HC{\equiv}CCH_3$),[13] 1.212 (20) Å ($Me_2InC{\equiv}CCH_3$), 1.207 (2) Å ($(Ph_2AlC{\equiv}CPh)_2$),[10a] 1.198 (5) Å (terminal $C{\equiv}CCH_3$ in $[(Me_3N)(H_3CC{\equiv}C)Be(\mu\text{-}C{\equiv}CCH_3)]_2$)[14]]. The Zr–C(1)–C(2) angle is 177.0 (3)° and the Zr–C(1) distance 2.249 (3) Å. This zirconium to carbon bond in **6a** is remarkably long. The linkage of the zirconium center to the sp-hybridized α-carbon of the propynyl ligand is almost as long as the Zr–C(sp^2) σ-bonds in bis(cyclopentadienyl)tetraphenylzirconacyclopentadiene $Cp_2Zr(C_4Ph_4)$ [2.265 (6) and 2.250 (5) Å].[15] Indeed, the zirconium-to-carbon bond in $Cp_2Zr(C{\equiv}CCH_3)_2$ (**6a**) is only about 0.03 Å shorter than a typical Zr–C(sp^3) σ-bond [2.280 (5), 2.273 (5) Å, as found in $Cp_2Zr(CH_3)_2$[11]]. Comparison with $Cp_2Zr(CO)_2$ [2.187 (4) Å; Zr–C–O = 178.6 (4)°[16]] or $(Me_5C_5)_2Zr(CO)_2$ [2.145 (9) Å; Zr–C–O = 179.3 (8)°[17]] also serves to demonstrate that the Zr–C(1) bond in **6a** is much longer than expected for a Zr–C(sp) σ-bond. Clearly there can be no significant π-conjugation between the d^0 configurated 16-electron zirconium center and the π-system of the organic alkynyl ligand in **6a**. Since its spectroscopic features show that complex **6a** is a typical representative of the mononuclear alkynylbis(cyclopentadienyl)zirconium complexes, we conclude that all these compounds appear to favor simple nonconjugated σ-hydrocarbyl structures.[18]

Mono(σ-alkynyl)metallocene complexes **6** and **7** were used as starting materials for the synthesis of binuclear alkyne-bridged binuclear bis(metallocene) complexes. For these reactions, the (η^4-butadiene)zirconocene complexes **8**, $(RCp)_2Zr(C_4H_6)$ [R = H (**a**), CH_3 (**b**), *t*-Bu (**c**)],[19,20] served as suitable starting materials for the in situ generation of the elusive $(RCp)_2Zr$ reagents to be added to the alkynyl metallocene educts **6** or **7**. Equilibrium mixtures of isomeric (*s-cis*-η^4-butadiene)- and (*s-trans*-η^4-butadiene)zirconocene complexes **8a** (*s-cis*/*s-trans* = 55:45), **8b** (60:40), and **8c** (95:5) were employed in each case. At room temperature, the rate of the (*s-cis-*/*s-trans*-diene)-metallocene isomerization is just sufficient to ensure equal use of both (η^4-diene)$Zr(CpR)_2$ geometric isomers as starting materials for generating $(RCp)_2Zr$.[21]

Treatment of $Cp_2ZrCl(C{\equiv}CR)$, **7a** (R = CH_3) or **7c** (R = Ph) with Cp_2Zr(butadiene) (**8a**) led to liberation of 1 equiv of butadiene in a moderately clean reaction to yield the binuclear μ-Cl, μ-alkynyl-bridged binuclear zirconocene complexes $Cp_2Zr(\mu\text{-}Cl)(\mu\text{-}C{\equiv}CR)ZrCp_2$, **9a** (R = CH_3) or **9b** (R = Ph), respectively. Complexes $(H_3CCp)_2ZrCl(C{\equiv}CR)$, **7b** (R = CH_3) and **7d** (R = Ph), similarly produced $(H_3CCp)_2Zr(\mu\text{-}Cl)(\mu\text{-}C{\equiv}CR)Zr(CpCH_3)_2$, **9c** (R = CH_3) and **9d** (R = Ph), respectively, when subjected to $(H_3CCp)_2Zr$, in situ generated from the (η^4-butadiene)-bis(methylcyclopentadienyl) zirconium system **8b**.

Doubly alkynyl-bridged binuclear bis(metallocene) complexes where formed when bis(σ-alkynyl)bis(cyclopentadienyl)zirconium complexes were treated with the (butadiene)metallocene reagents at ambient temperature for prolonged periods of time. The formation of the $M_2(\mu\text{-}C{\equiv}CR)_2$ species proceeded much more cleanly than that of the $Zr_2(\mu\text{-}C{\equiv}CR)$ complexes.

Thus, analytically pure $(Cp_2Zr)_2(\mu\text{-}C{\equiv}CCH_3)_2$ (**10a**) was

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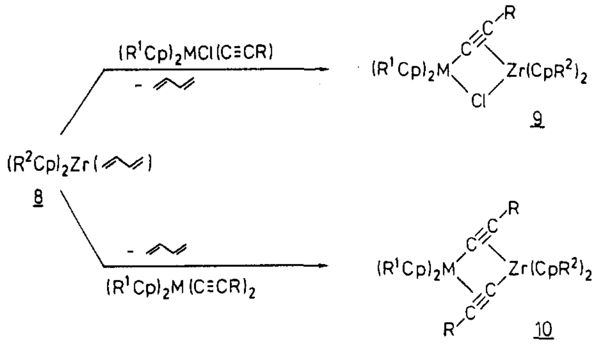
recovered in about 60% yield as a poorly soluble solid upon stirring $Cp_2Zr(C{\equiv}CCH_3)_2$ (**6a**) with the Cp_2Zr(butadiene) equilibrium mixture for 18 h in benzene at room temperature. The methyl Cp-substituted analogue $[(H_3CCp)_2Zr]_2(\mu\text{-}C{\equiv}CCH_3)_2$ (**10b**) was prepared analogously from $(H_3CCp)_2Zr(C{\equiv}CCH_3)_2$ and $(H_3CCp)_2Zr$(butadiene). Combination of two differently substituted zirconocene units to give the binuclear complex $(H_3CCp)_2Zr(\mu\text{-}C{\equiv}CCH_3)_2ZrCp_2$ (**10c**) was achieved by reacting **6b** with **8b**. The same complex was also formed, albeit in much poorer yield and purity, when $Cp_2Zr(CO)_2$ was irradiated in the presence of **6a** in toluene solution at −60 °C.



8

9

10

The photolysis of zirconocene dicarbonyl in the presence of $(t\text{-}BuCp)_2Zr(C{\equiv}CCH_3)_2$ (**6c**) produced $(t\text{-}BuCp)_2Zr(\mu\text{-}C{\equiv}CCH_3)_2ZrCp_2$ (**10d**). Again, the preparation of the binuclear complex via the (butadiene)metallocene route (here by reacting $(t\text{-}BuCp)_2Zr(\mu\text{-}C{\equiv}CCH_3)_2$ (**6c**) with the (η^4-butadiene)$ZrCp_2$ mixture of isomers) turned out to be preferable. It is interesting to note that the "unsymmetrically" substituted binuclear complex **10d** can also be prepared by reacting $Cp_2Zr(C{\equiv}CCH_3)_2$ (**6a**) with $(t\text{-}BuCp)_2Zr(C_4C_6)$ (**8c**) with loss of butadiene.

Complexes $(RCp)_2Zr(C{\equiv}CPh)_2$, **6a** (R = CH_3) or **6f** (R = *t*-Bu), reacted equally well with **8a** or **8b** to produce $(R^1Cp)_2Zr(\mu\text{-}C{\equiv}CPh)_2Zr(CpR^2)_2$, **10e** ($R^1 = CH_3$, R^2 = H), **10f** ($R^1 = R^2 = CH_3$), or **10g** (R^1 = *t*-Bu, R^2 = H). Finally, the binuclear mixed-metal complex containing hafnium and zirconium, $Cp_2Hf(\mu\text{-}C{\equiv}CCH_3)_2ZrCp_2$ (**10h**), was obtained by reacting bis(σ-propynyl)hafnocene (**6g**) with the (butadiene)zirconocene reagent.

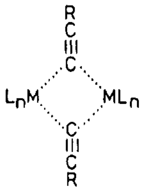
The typical (σ-alkynyl)metallocene ν(C≡C) band in the IR spectrum of the $(RCp)_2ZrCl(C{\equiv}CR')$ species **7** disappears upon complexation of the alkynyl ligand to a second zirconocene moiety.[22] We have not observed any distinctive new IR absorptions characteristic of the $Zr(\mu\text{-}C{\equiv}CR)Zr$ moiety of the binuclear product. However, the Raman spectra of the $[(RCp)_2Zr]_2(\mu\text{-}C{\equiv}C\text{-}CH_3)_2$ complexes exhibit characteristic absorption bands at ν = 1711 (m) and 1720 (sh) cm^{-1} (**9c**, R = CH_3) or ν = 1727 cm^{-1} (m) (**9a**, R = H), respectively.

Likewise, complexation to a metallocene unit leads to significant changes in the NMR features of the σ-C≡CR ligand. The ^{13}C NMR absorption of the propynyl methyl group is observed low field shifted at δ 20.3 ($^1J_{CH}$ = 127 Hz) in $[(H_3CCp)_2Zr]_2(\mu\text{-}C{\equiv}CCH_3)(\mu\text{-}Cl)$ (**9c**) as compared to its mononuclear component **7b** (δ 6.0). Even more drastically deshielded signals have been monitored for the alkynyl- sp carbon centers in the bridging ligand. π-Complexation to the additional metal center results in shifting these alkynyl resonances by up to 100 ppm to a lower field. In complex **9c**, the $C^\alpha{\equiv}C^\beta R$ resonances are found at δ 181.4 (C^β) and 228.5 (C^α), respectively. Phenyl substitution at the acetylide bridge, as found in complex **9b**, leads to even larger shifts (δ 187.3, 246.1).

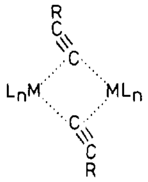
The deshielding of the sp-alkynyl carbon atoms upon complexation of the bis(σ-alkynyl)metallocenes to MCp_2 species is still pronounced but not quite as drastic as for compounds **9**. Typical examples are the complexes $(Cp_2Zr)_2(\mu\text{-}C{\equiv}CCH_3)_2$ (**10a**) or $[(H_3CCp)_2Zr]_2(\mu\text{-}C{\equiv}CPh)_2$ (**10f**), exhibiting ^{13}C NMR absorptions of the $\mu\text{-}C^\alpha{\equiv}C^\beta R$ ligands at δ 204.2 (C^α), 147.9 (C^β) and δ 227.7 (C^α), 155.4 (C^β), respectively.

In contrast to complexes **9**, the formation of **10** from **6** and the (η^4-butadiene)metallocene reagents coincides with the appearance of very characteristic IR absorptions in a region typical for carbon–carbon triple bonds side-on coordinated to a transition-metal center.[23] The doubly propynyl-bridged bis(zirconocene) complex $(Cp_2Zr)_2(\mu\text{-}C{\equiv}CCH_3)ZrCp_2$ thus exhibits two prominent ν(C≡C) absorptions at 1820 (m) and 1875 (w) cm^{-1}. Similar IR bands have been observed for all complexes containing $M(\mu\text{-}C{\equiv}CCH_3)_2M'$ moieties described in this paper. For the complexes containing $M(\mu\text{-}C{\equiv}CPh)_2M$ units, one of these absorptions is still clearly visible, albeit at a somewhat decreased wave number [e.g. $[(H_3CCp)_2Zr]_2(\mu\text{-}C{\equiv}CPh)_2$ (**10f**), ν(C≡C) = 1780 cm^{-1}].

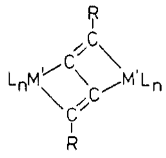
The X-ray crystal structure analysis shows that a typical example of the $[Zr]_2(\mu\text{-}C{\equiv}CR)_2$-type complexes, the binuclear species $[(H_3CCp)_2Zr]_2(\mu\text{-}C{\equiv}CPh)_2$ (**10f**), is formed from the bis(σ-alkynyl)metallocene $(H_3CCp)_2Zr(C{\equiv}CPh)_2$ (**6e**) and $Zr(CpCH_3)_2$ via migration of one σ-alkynyl group between the two transition-metal centers. Complexes **10** adopt a C_{2h}-symmetric molecular structure. Formally, two identical $(RCp)_2ZrC{\equiv}CR'$ units have been dimerized, forming a metallacyclic central organometallic framework consisting of the two early-transition-metal centers and the four acetylide ligand carbon atoms. The resulting structure is unique among the many known examples of $M(\mu\text{-}C{\equiv}CR)M'$ type complexes.[24] It can be regarded as adopting an intermediate position between the extreme bonding situations **11a**/**11b** (many examples of which have been described for bridging main-group metal acetylides) and **12** [$L_nM' = (RCp)_2Ti$], the transition-metal complex obtained by carbon–carbon bond formation between the acetylide ligands.[25]



11a



11b



12

The central C_4Zr_2 core atoms of **10f** are coplanar. Clearly, the C(2)···C(2*) separation (3.018 (2) Å) is much too large for any bonding interaction to be present. Surprisingly, there also appears to be no direct metal–metal interaction between the formally d^1-configurated single early-transition-metal centers. The Zr···Zr* distance is 3.506 (1) Å, significantly larger than the sum of the Zr van der Waals radii (3.10 Å).[26] The metal–metal separation

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[22] For related examples employing late-transition-metal complexes see: Cowie, M.; Loeb, S. J. *Organometallics* **1985**, *4*, 852 (loc. cit.).

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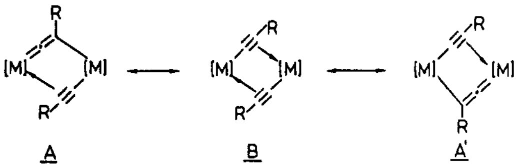
in **10f** is more than 0.3 Å larger than in the chloride-bridged Zr(d^1) dimer [$Cl_2(PR_3)_2Zr(\mu\text{-}Cl)_2Zr(PR_3)_2Cl_2$] with d(Zr–Zr) = 3.182 Å.[27] Metal–metal bonds between zirconium and late transition metals are usually shorter than 3 Å.[28] Apparently, electronic coupling between the group 4 transition-metal centers in **10** takes place via the unsaturated organic bridging ligand system. This results in a very characteristically altered set of typical structural data of the acetylide ligands as compared to the mononuclear $(RCp)_2Zr(C{\equiv}CR)_2$ complexes **6** (see above).

Despite the complexation of the acetylide π-system to the second metal center, the Zr–C(2)–C(1) unit remains almost linear (172.3 (1)°). In fact, the carbon atom C(1), bearing the phenyl substituent, is even slightly bent *toward* the side-on coordinated metal center Zr*, not away from it as is usually observed for transition-metal olefin or acetylene π-complexes. The C(2)–C(1)–Ph(1) angle is 146.8 (2)°. The C(2)–C(1) bond (1.261 (2) Å) in **10f** is significantly longer than in **6a** (1.206 (4) Å). The Zr–C(2) bond distance, in contrast, is much shorter in the binuclear μ-acetylide complex (2.188 (2) Å) than in the mononuclear reference (2.249 (3) Å).

In fact, the metal to carbon bond in **10f** is almost as long as the Zr–C(sp) bond in $Cp_2Zr(CO)_2$,[16] in which bond strengthening by back-donation from the d^2-configurated metal center certainly has to be taken into account.[29] Together with the remaining bonds being Zr*–C(2) = 2.431 (2) Å and Zr*–C(1) = 2.407 (2) Å, these very characteristic structural parameters seem to justify a description of complexes **10** by resonance formula A, B, and A′, attributing to these complexes a considerable π-interaction between the metal centers and the adjacent organic π-system across the connecting σ-bond.[30,31]



Despite the presence of an apparently quite strong Zr–C^α(alkynyl) bond, the $[Zr]_2(\mu\text{-}C{\equiv}CR)_2$-type complexes **10** exhibit pronounced dynamic behavior in solution. There is convincing evidence that the alkynyl ligands rapidly change places between the two early-transition-metal centers.

The complex $Cp_2Zr(\mu\text{-}C{\equiv}CCH_3)_2Zr(CpMe)_2$ (**10c**) is a typical example. At ambient temperature it shows only one propynyl ligand methyl singlet in the ^1H NMR spectrum at δ 2.57. Lowering the monitoring temperature results in a broadening of this CH_3 resonance, which is eventually observed to split into two separate signals in a 1:1 ratio at δ 2.55 and 2.57 ppm. This indicates that complex **10c** adopts the typical doubly acetylide-bridged structure in solution, that is equivalent to the general structural type found for complexes **10** in the solid state. In the special example of **10c**, however, the two bridging propynyl ligands are slightly different because the η-cyclopentadienyl ligands at one of the metal centers are methyl-substituted. For the coalescence temperature (267 K, at 1.879 T) a Gibbs activation barrier of $\Delta G^\ddagger$ = 14.6 ± 0.5 kcal/mol has been estimated.

Table I. Selected Bond Distances and Angles of 6a As Determined by X-ray Diffraction

	Bond Lengths (Å)		
Zr–C1	2.249 (3)	Cp1–Cp2	1.380 (4)
C1–C2	1.206 (4)	Cp2–Cp3	1.404 (6)
C2–C3	1.462 (5)	Cp3–Cp4	1.394 (6)
		Cp4–Cp5	1.399 (6)
Zr–Cp1	2.530 (3)	Cp5–Cp1	1.376 (6)
Zr–Cp2	2.530 (3)		
Zr–Cp3	2.488 (4)	Zr–D1	2.211
Zr–Cp4	2.490 (4)		
Zr–Cp5	2.502 (4)		
	Bond Angles (deg)		
C1–Zr–C1σ	103.6 (1)	Zr–Cp1–Cp2	74.2 (2)
Zr–C1–C2	177.0 (3)	Zr–Cp1–Cp5	73.0 (2)
C1–C2–C3	179.4 (4)	Zr–Cp2–Cp3	72.1 (2)
		Zr–Cp2–Cp1	74.2 (2)
Cp1–Zr–Cp2	31.6 (1)	Zr–Cp3–Cp4	73.8 (2)
Cp2–Zr–Cp3	32.5 (1)	Zr–Cp3–Cp2	75.4 (2)
Cp3–Zr–Cp4	32.5 (1)	Zr–Cp4–Cp5	74.2 (3)
Cp4–Zr–Cp5	32.6 (2)	Zr–Cp4–Cp3	73.6 (2)
Cp5–Zr–Cp1	31.7 (1)	Zr–Cp5–Cp1	75.3 (2)
		Zr–Cp5–Cp4	73.3 (2)
Cp1–Cp2–Cp3	108.1 (3)		
Cp2–Cp3–Cp4	107.5 (3)	D1–Zr–D1*	132.6
Cp3–Cp4–Cp5	107.6 (4)	C1–Zr–D1	105.1
Cp4–Cp5–Cp1	108.3 (3)	C1–Zr–D1*	103.7
Cp5–Cp1–Cp2	108.6 (4)		

Table II. Atomic Fractional Coordinates and Equivalent Isotropic Thermal Parameters (Å²) with Standard Deviations in Parentheses[a]

atom	x	y	z	U_{eq}
Zr	0.0000	0.0000	0.2500	0.031
C1	−0.1886 (4)	−0.0776 (2)	0.4629 (6)	0.043
C2	−0.2923 (4)	−0.1216 (2)	0.5696 (5)	0.044
C3	−0.4180 (6)	−0.1742 (3)	0.7006 (6)	0.065
Cp1	−0.1734 (5)	0.1534 (2)	0.2704 (8)	0.054
Cp2	−0.2990 (4)	0.0872 (2)	0.2072 (6)	0.051
Cp3	−0.2450 (5)	0.0543 (2)	0.0138 (7)	0.055
Cp4	−0.0875 (6)	0.1032 (3)	−0.0417 (7)	0.065
Cp5	−0.0434 (5)	0.1636 (3)	0.1197 (9)	0.064
H3a	−0.5431	−0.1529	0.7012	0.050
H3b	−0.3682	−0.1818	0.8434	0.050
H3c	−0.4218	−0.2455	0.6443	0.050
Hcp1	−0.1750	0.1889	0.4044	0.050
Hcp2	−0.4099	0.0628	0.2877	0.050
Hcp3	−0.3045	−0.0005	−0.0674	0.050
Hcp4	−0.0232	0.0921	−0.1767	0.050
Hcp5	0.0623	0.2102	0.1216	0.050

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*\bar{\mathbf{a}}_i\cdot\bar{\mathbf{a}}_j$.

The metal centers do not necessarily have to be different (by nature of the metals or RCp ligands bonded to them). Use of the monosubstituted RCp ligands $H_3CC_5H_4$ or $(H_3C)_3CC_5H_4$ is sufficient to provide an informative NMR probe for revealing σ-alkynyl mobility in the $(RCp)_2Zr(\mu\text{-}C{\equiv}CR')Zr(CpR)_2$ complexes. In the low-temperature-limiting "static" NMR spectra the C_{2h} molecular symmetry leads to the observation of a set of four cyclopentadienyl

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(30) For details concerning data collection, solution, and refinement of the X-ray crystal structure analysis of **10f** see ref 8.

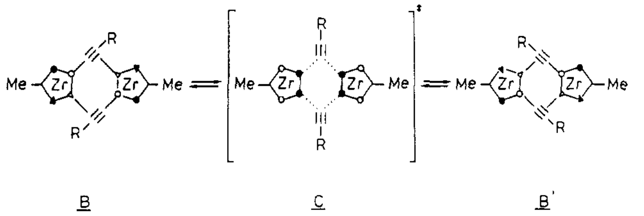
(31) For a comparison with related structural types see: Evans, W. J.; Hanusa, T. P.; Meadows, J. H.; Hunter, W. E.; Atwood, J. L. *Organometallics* **1987**, *6*, 295. Stahl, K.; Dehnicke, K. *J. Organomet. Chem.* **1986**, *316*, 85. Boncella, J. M.; Tilley, T. D.; Andersen, R. A. *J. Chem. Soc., Chem. Commun.* **1984**, 710. Evans, W. J.; Keyer, R. A.; Zhang, H.; Atwood, J. L. *Ibid.* **1987**, 837. Ustynyuk, N. A.; Vinogradova, V. N.; Korneva, V. N.; Kravtsov, D. N.; Andrianov, V. G.; Struchkov, Y. T. *J. Organomet. Chem.* **1984**, *277*, 285. Gotzig, J.; Otto, H.; Werner, H. *Ibid.* **1985**, *287*, 247. See also: Huffman, J. C.; Moloy, K. G.; Marsella, J. A.; Caulton, K. G. *J. Am. Chem. Soc.* **1980**, *102*, 3009.

Table III. Automerization Activation Barriers of Complexes 10[a]

complex	resonance	T_c, K	$\Delta G^\ddagger$
$Cp_2Zr(C{\equiv}CCH_3)_2HfCp_2$ (**10h**)	dynamic[b]		
$Cp_2Zr(C{\equiv}CCH_3)_2Zr(CpCH_3)_2$ (**10c**)	$C{\equiv}CCH_3$	267	14.6
$[(H_3CCp)_2Zr(C{\equiv}CCH_3)]_2$ (**10b**)	$H_3CC_5H_4$	288	14.6
$Cp_2Zr(C{\equiv}CPh)_2Zr(CpCH_3)_2$ (**10e**)	$H_3CC_5H_4$	283	13.9
$[(H_3CCp)_2Zr(C{\equiv}CPh)]_2$ (**10f**)	$H_3CC_5H_4$	297	14.8
$Cp_2Zr(C{\equiv}CPh)_2Zr(\textit{tert}\text{-butyl}Cp)_2$ (**10g**)	dynamic[b]		
$Cp_2Zr(C{\equiv}CCH_3)_2Zr(\textit{tert}\text{-butyl}Cp)_2$ (**10d**/**13a**)	Cp	218	12.6[c]

[a] $\Delta G^\ddagger$ values (±0.5 kcal/mol), estimated from the dynamic ^1H NMR resonance indicated at the coalescence temperature (T_c). [b] Spectra of the limiting low-temperature situation not obtained because of rearrangement taking place too rapidly. [c] $\Delta G^\ddagger$ for the **10d** ⇌ **13a** rearrangement.

Scheme II



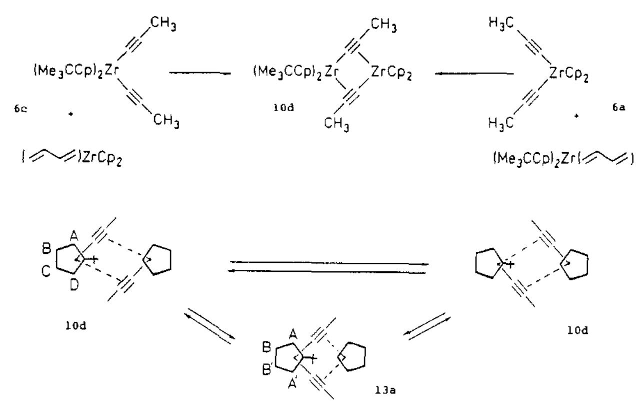
ring C–H resonances. In contrast, rapidly occurring intramolecular $C{\equiv}CR$ migration at high temperature reduces the number of observable RCp methine resonances to two, resulting in NMR spectra indicating apparent overall D_{2h} symmetry. This typical change has been observed for the temperature-dependent appearance of the NMR spectra of complexes $[(H_3CCp)_2Zr]_2(\mu\text{-}C{\equiv}CR)_2$, **10b** ($R = CH_3$) or **10f** (R = Ph). Estimated activation barriers are given in Table III.

Although the favored ground-state structures of many binuclear doubly acetylide-bridged complexes of the main-group metals and the lanthanides have symmetrical bridges similar to C (Scheme II), these NMR results do not require that the alkynyl ligand migration has to proceed via such an intermediate or transition state. In fact, in one instance we have obtained evidence for an unsymmetrically bridged $[Zr]_2(\mu\text{-}C{\equiv}CR)_2$-type complex of C_{2v} symmetry and similar energy content rapidly equilibrating with the automerizing $[Zr](\mu\text{-}C{\equiv}CR)$ dimer **10**.[32]

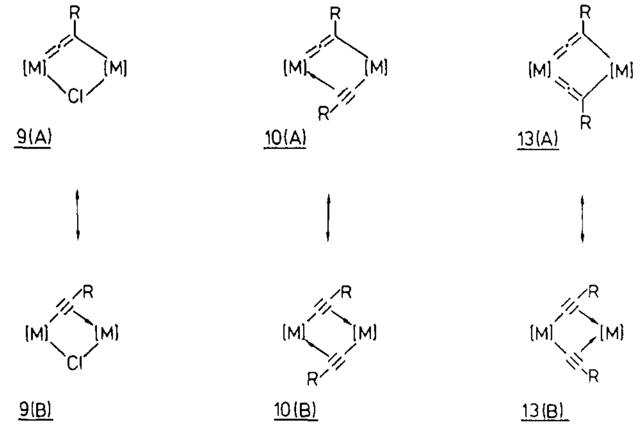
Complex **10d**, obtained by reacting either $(t\text{-}BuCp)_2Zr(C{\equiv}CCH_3)_2$ (**6c**) with Cp_2Zr(butadiene) or $Cp_2Zr(C{\equiv}CCH_3)_2$ (**6a**) with $(t\text{-}BuCp)_2Zr$(butadiene), at high temperature shows typical NMR spectra of the rapidly equilibrating $(t\text{-}BuCp)_2Zr(\mu\text{-}C{\equiv}CCH_3)_2ZrCp_2$ system (e.g. one propynyl ^1H NMR methyl singlet at δ 2.62; one Cp singlet at δ 5.16). Upon lowering the temperature, the usual line broadening takes place. However, at sufficiently low temperature a more complex splitting pattern than found for the other examples of complexes **10** is monitored. In addition to the expected NMR resonances of the "static" C_s symmetric complex **10d** [^1H NMR δ 2.57, 2.61 (CH_3), 5.25 (Cp); ^{13}C NMR δ 17.1, 19.1 (CH_3), 146.3, 149.8 ($C{\equiv}C^\beta$), 204.1, 208.5 ($C^\alpha{\equiv}C$)], a single set of signals due to the presence of an isomer of C_{2v} symmetry is observed [^1H NMR δ 2.67 (CH_3), 5.00 (Cp); ^{13}C NMR δ 18.6 (CH_3), 103.9 (Cp), 142.1, 178.1 ($C{\equiv}C$)].

This observation means that complex **10d** is equilibrating with one of the two possible "mixed-valence" zirconium(IV), zirconium(II) isomers **13**. We assume that the regioisomer **13a** is favored for steric reasons. Since the energies of **13a** and **10d** differ by only about 0.1 kcal/mol (equilibrium ratio of **13a**:**10d** ≈ 45:55, as deduced from the variable-temperature NMR experiments) and rates for the **13a** ⇌ **10d** isomerization and the **10d** automerization are experimentally undistinguishable, it is quite likely that the latter indeed proceeds via the formation of **13a** as an intermediate. It appears that shifting one σ-alkynyl group between the metal centers at a time is more favorable than the formation of the highly symmetrical intermediate geometry of type C (Scheme II).

Scheme III



Scheme IV



Conclusions

There are two major conclusions we would like to draw from the observations made. First, doubly acetylide-bridged binuclear complexes of group 4 transition metals of type $[M](\mu\text{-}C{\equiv}CR)_2[M]'$ can be obtained by combining readily available stable bis(σ-alkynyl)bis(cyclopentadienyl)zirconium or -hafnium(IV) complexes with the very reactive in situ generated group 4 metallocenes $(RCp)_2M$. Simple bis(alkyne)metallocene-type adducts (**13**) are probably formed first. When complexes with alkyl-substituted cyclopentadienyl groups are to be prepared, it is immaterial whether these are introduced on the Zr(IV) or Zr(II) building blocks because of the subsequent intramolecular σ-alkynyl migration reactions. Although there is a substantial π-contribution of the metal to the σ-alkynyl linkage in $(RCp)_2ZrC{\equiv}CR$ dimers **10** of C_{2h} symmetry, in at least one case the equilibration with the simple C_{2v}-symmetric binuclear bis(alkyne)metallocene-type complex **13** can be observed experimentally.

Generally, there seems to be an increase in metal-to-carbon π-interaction between zirconium and the σ-alkynyl

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[32] For related examples see: Warner, S.; Lippard, S. J. *Organometallics* **1986**, *5*, 1716. Lentz, D.; Brüdgam, I.; Hartl, H. *Angew. Chem.* **1984**, *96*, 511. Cotton, F. A. Duraj, S. A.; Roth, W. J. *J. Am. Chem. Soc.* **1984**, *106*, 6987.

ligand upon going from **13** through **10** to **9**. This can be deduced from systematic variations of several typical spectroscopic features, including the decreasing chemical shifts of the σ-propynyl α-carbon ^{13}C NMR resonance (**13a**, δ 178.1; **10d**, δ 204.1, 208.5; **9c**, δ 228.5). Apparently, on changing the μ-chloro ligand for stereochemically different types of bridging μ-alkynyl groups, the mesomeric structures of type A, exhibiting characteristics of the metal carbene complexes, become less important. This indicates that metal/carbon π-conjugative effects in such early-transition-metal complexes are increased when a means of back-donating charge is introduced.

Experimental Section

Reactions with organometallic compounds were carried out in an inert atmosphere (argon) using Schlenk type glassware. Solvents were dried and freshly distilled from potassium/benzophenone, lithium aluminum hydride, or P_4O_{10} under argon prior to use. Deuterated solvents benzene-d_6 and toluene-d_8 were treated with sodium/potassium alloy, and $CDCl_3$ and CD_2Cl_2 were treated with P_4O_{10} (Sikapent/Merck), distilled, and stored under argon. The following spectrometers were used: NMR, Bruker WP 80 FT (^{1}H, 80 MHz, variable temperature), Bruker WM 300 FT (^{13}C, 75.5 MHz), and Bruker WH 400 FT (^{1}H, 400 MHz; ^{13}C, 100.6 MHz); IR, Nicolet 7199 FT IR spectrometer; Raman, Coderg T 800 spectrometer (Krypton laser, 6471 Å); MS, Finnigan 311 A (70 eV), *m/e* values given correspond to isotopes of highest natural abundance. Elemental analyses were carried out by Dornis und Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, FRG. Melting points are uncorrected. Starting materials Cp_2ZrCl_2, Cp_2HfCl_2, $(H_3CCp)_2ZrCl_2$, and $(Me_3CCp)_2ZrCl_2$ were prepared according to published procedures.[20,33,34] Reagents sodium phenylacetylide and propynyllithium were synthesized by literature procedures.[25,35] The metallocene precursors zirconocene dicarbonyl,[36] hafnocene dicarbonyl,[37] and the (butadiene)metallocene reagents were obtained as described in recent publications.[19]

Dipropynylzirconocene (6a). A suspension of 0.7 g (2.4 mmol) of zirconocene dichloride and 0.25 g (5.4 mmol) of propynyllithium in 50 mL of ether was stirred for 20 h at ambient temperature. Solvent was evaporated in vacuo and the remaining solid stirred with 80 mL of benzene for 30 min. Lithium chloride was removed by filtration and the benzene solvent stripped in vacuo. The residue was treated with pentane (80 mL) to give **6a**: yield 0.4 g (56%); mp 178 °C dec; ^{1}H NMR (C_6D_6) δ 1.78 (s, 6 H, CH_3), 6.12 (s, 10 H, Cp); ^{13}C NMR (C_6D_6) δ 5.9 (q, $^1J_{CH}$ = 130 Hz, CH_3), 110.9 (d, $^1J_{CH}$ = 174 Hz, Cp), 120.0 (C^β, $^2J_{CH}$ = 9.5 Hz), 131.6 (C^α, $^3J_{CH}$ = 4.1 Hz); IR (KBr) 2085 (C≡C) cm^{-1}; MS (M^+) *m/e* 298. Anal. Calcd for $C_{16}H_{16}Zr$: C, 64.16; H, 5.38. Found: C, 64.24; H, 5.44.

X-ray diffraction data for $C_{16}H_{16}Zr$ (6a): crystal size 0.25 × 0.36 × 0.15 mm; orthorhombic; space group *Pnc*2; *a* = 7.3099 (7), *b* = 14.244 (1), *c* = 6.5299 (5) Å; *V* = 679.91 Å^3; *Z* = 2; d_{calcd} = 1.463 g cm^{-3}; μ(Mo) = 7.704 cm^{-1}; *F*(000) = 304; scan mode = Ω–2θ; *T* = 20 °C; $(\sin\theta)/\lambda_{max}$ = 0.7636; empirical absorption correction, min 0.855, max 1.023; 2773 measured reflections (±*h*,+*k*,+*l*); 1361 unique reflections; 1002 observed reflections ($I > 2.0\sigma(I)$); parameter varied 77; max shift/esd = 0.026; *R* = 0.0206; R_w = 0.0267; ρ(max) = 0.63 e Å^{-3}.

Bis(η-methylcyclopentadienyl)dipropynylzirconium (6b). A mixture of 9.3 g (29.0 mmol) of bis(η-methylcyclopentadienyl)zirconium dichloride and 2.9 g (63.0 mmol) of propynyllithium in 300 mL of ether was stirred for 1 h at room temperature. Then the ether was removed and the white solid residue taken up into benzene. Benzene was removed in vacuo after filtration and the remaining solid washed with 70 mL of pentane to give **6b**: yield 7.9 g (83%); mp 128 °C dec; ^{1}H NMR (C_6D_6) δ 1.76 (s, 6 H, CH_3), 2.29 (s, 6 H, MeCp), 5.76 (t, 4 H, MeCp), 6.16 (t, 4 H, MeCp); ^{13}C NMR (C_6D_6) δ 5.8 (q, $^1J_{CH}$ = 130 Hz, CH_3), 16.2 (q, $^1J_{CH}$ = 127 Hz, MeCp), 107.8 (d, $^1J_{CH}$ = 172 Hz, MeCp), 113.4 (d, $^1J_{CH}$ = 172 Hz, MeCp), 117.3 (C^β, $^2J_{CH}$ = 9.2 Hz), 125.5 (s, MeCp), 132.4 (C^α, $^3J_{CH}$ = 4.1 Hz); IR (KBr) 2080 (C≡C) cm^{-1}; MS (M^+) *m/e* 326. Anal. Calcd for $C_{18}H_{20}Zr$: C, 66.00; H, 6.15. Found: C, 65.98; H, 6.14.

Bis(η-*tert*-butylcyclopentadienyl)dipropynylzirconium (6c). A reaction mixture containing 1.2 g (3 mmol) of bis(η-*tert*-butylcyclopentadienyl)zirconium dichloride and 0.4 g (8.7 mmol) of propynyllithium in 100 mL of ether was stirred for 8 h at room temperature. Then the ether was removed. The light brown residue was stirred with 100 mL of benzene for 30 min. Filtration yielded a clear, dark red solution. Benzene solvent was evaporated in vacuo and the remaining oily precipitate stirred with 25 mL of pentane. Pentane was stripped from the filtrate to give **6c** as an amber solid: yield 0.8 g (65%); ^{1}H NMR (C_6D_6) δ 1.43 (s, 18 H, *t*-BuCp), 1.71 (s, 6 H, CH_3), 5.81 (t, 4 H, *t*-BuCp), 6.28 (t, 4 H, *t*-BuCp); ^{13}C NMR ($CDCl_3$) δ 5.9 (q, $^1J_{CH}$ = 130 Hz, CH_3), 31.4 (q, $^1J_{CH}$ = 126 Hz, *t*-BuCp), 32.7 (s, *t*-BuCp), 107.5 (d, $^1J_{CH}$ = 172 Hz, *t*-BuCp), 110.0 (d, $^1J_{CH}$ = 170 Hz, *t*-BuCp), 121.1 (C^β, $^2J_{CH}$ = 9.5 Hz), 131.3 (C^α, $^3J_{CH}$ = 4.1 Hz), 141.6 (s, *t*-BuCp); IR (KBr) 2090 (C≡C) cm^{-1}.

Bis(phenylethynyl)zirconocene (6d).[9b] A suspension of 1.2 g (4.1 mmol) of zirconocene dichloride and 1.1 g (8.9 mmol) of sodium phenylacetylide in 25 mL of ether was stirred for 5 h at room temperature. Ether was stripped in vacuo and the product extracted with 25 mL of benzene. Filtration followed by removal of the benzene solvent produced an oily residue. Pentane (25 mL) was added to give a precipitate of the alkynyl metallocene complex **6d**: yield 1.1 g (61%); ^{1}H NMR (C_6D_6) δ 6.14 (s, 10 H, Cp), 7.0 (m, 3 H, Ph), 7.5 (m, 2 H, Ph); ^{13}C NMR ($CDCl_3$) δ 111.2 (d, $^1J_{CH}$ = 175 Hz, Cp), 124.7 (s, Ph), 124.8 (C^β, $^3J_{CH}$ = 5.0 Hz), 127.3 (d, $^1J_{CH}$ = 160 Hz, Ph), 128.0 (d, $^1J_{CH}$ = 160 Hz, Ph), 131.4 (d, $^1J_{CH}$ = 162 Hz, Ph), 141.7 (C^α); IR (KBr) 2075 (C≡C) cm^{-1}. Anal. Calcd for $C_{26}H_{20}Zr$: C, 73.71; H, 4.76. Found: C, 73.93; H, 5.01.

Bis(η-methylcyclopentadienyl)bis(phenylethynyl)zirconium (6e).[9b] In a 500-mL Schlenk tube 9.9 g (30.9 mmol) of bis(η-methylcyclopentadienyl)zirconium dichloride and 7.8 g (62.9 mmol) of sodium phenylacetylide in 300 mL of ether were stirred for 1 h at room temperature. The etheral solvent was removed in vacuo. The brown solid residue was then extracted with 250 mL of benzene. Filtration from the sodium chloride precipitate gave a clear dark red solution. Removal of the benzene solvent gave a dark brown oily residue, which solidified upon prolonged treatment with pentane (150 mL). Filtration yielded 9.9 g (71%) of **6e**: mp 97 °C dec; ^{1}H NMR (C_6D_6) δ 2.30 (s, 6 H, MeCp), 5.80 (t, 4 H, MeCp), 6.20 (t, 4 H, MeCp), 6.95–7.05 (m, 6 H, Ph), 7.40–7.55 (m, 4 H, Ph); ^{13}C NMR ($CDCl_3$) δ 16.0 (q, $^1J_{CH}$ = 128 Hz, MeCp), 107.8 (d, $^1J_{CH}$ = 173 Hz, MeCp), 113.6 (d, $^1J_{CH}$ = 173 Hz, MeCp), 122.1 (C^β, $^3J_{CH}$ = 4.8 Hz), 125.0 (s, Ph), 126.2 (s, MeCp), 127.1 (d, $^1J_{CH}$ = 161 Hz, Ph), 128.0 (d, $^1J_{CH}$ = 160 Hz, Ph), 131.4 (d, $^1J_{CH}$ = 162 Hz, Ph), 142.8 (C^α); IR (KBr) 2070 (C≡C) cm^{-1}. Anal. Calcd for $C_{28}H_{24}Zr$: C, 74.45; H, 5.36. Found: C, 74.47; H, 5.37.

Bis(η-*tert*-butylcyclopentadienyl)bis(phenylethynyl)zirconium (6f). A suspension of 1.0 g (2.5 mmol) of bis(η-*tert*-butylcyclopentadienyl)zirconium dichloride and 1.1 g (8.9 mmol) of sodium phenylacetylide in 50 mL of ether was stirred for 20 h at 0 °C. Then the ether was removed and the light brown residue extracted with 50 mL of toluene. The residue resulting upon removal of the toluene solution after filtration was stirred with 50 mL of pentane to give 0.4 g (30%) of **6f** as a light brown solid: mp 125 °C dec; ^{1}H NMR (C_6D_6) δ 1.47 (s, 18 H, *t*-BuCp), 5.80 (t, 2 H, *t*-BuCp), 6.39 (t, 2 H, *t*-BuCp), 6.95 (m, 3 H, Ph), 7.50 (m, 2 H, Ph); ^{13}C NMR ($CDCl_3$) δ 31.7 (q, $^1J_{CH}$ = 126 Hz, *t*-BuCp), 33.0 (s, *t*-BuCp), 107.0 (d, $^1J_{CH}$ = 172 Hz, *t*-BuCp), 111.1 (d, $^1J_{CH}$ = 172 Hz, *t*-BuCp), 123.8 (C^β, $^3J_{CH}$ = 4.6 Hz), 125.2 (s, Ph), 127.0 (d, $^1J_{CH}$ = 161 Hz, Ph), 128.1 (d, $^1J_{CH}$ = 160 Hz, Ph), 130.9 (d, $^1J_{CH}$ = 162 Hz, Ph), 142.1 (s, *t*-BuCp), 143.7 (C^α); IR (KBr) 2078 (C≡C) cm^{-1}. Anal. Calcd for $C_{34}H_{36}Zr$: C, 76.21; H, 6.77. Found: C, 76.17; H, 6.92.

Bis(phenylethynyl)hafnocene (6h).[9b] A mixture of 1.2 g (3.2 mmol) of hafnocene dichloride and 0.9 g (7.3 mmol) of sodium

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phenylacetylide in 25 mL of ether was stirred for 3 h at ambient temperature. Ether was removed in vacuo. The organometallic product was recovered from the residue by extraction with 25 mL of benzene. Filtration and distillation of the benzene solvent in vacuo produced an oil, which solidified upon stirring with 25 mL of pentane. Filtration yielded 1.0 g (62%) of **6h**: ^{1}H NMR (C_6D_6) δ 6.1 (s, 10 H, Cp), 7.0 (m, 3 H, Cp), 7.5 (m, 2 H, Ph); ^{13}C NMR (CD_2Cl_2) δ 110.7 (d, $^{1}J_{CH}$ = 175 Hz, Cp), 125.3 (s, Ph), 127.8 (d, $^{1}J_{CH}$ = 161 Hz, Ph), 128.3 (C^{β}, $^{3}J_{CH}$ = 4.8 Hz), 128.6 (d, $^{1}J_{CH}$ = 160 Hz, Ph), 131.6 (d, $^{1}J_{CH}$ = 162 Hz, Ph), 151.1 (C^{α}); IR (KBr) 2080 (C≡C) cm^{-1}. Anal. Calcd for $C_{26}H_{20}Hf$: C, 61.12; H, 3.95. Found: C, 61.08; H, 4.15.

Dipropynylhafnocene (6g). The reaction mixture of 3.0 g (7.9 mmol) of hafnocene dichloride and 0.9 g (19.1 mmol) of propynyllithium in 300 mL of ether was stirred for 18 h at room temperature. The ether was removed in vacuo and the solid residue stirred for 1 h with 400 mL of benzene. A yellow solution was obtained after filtration. Benzene was distilled off in vacuo. The residue was stirred with 200 mL of pentane. Product **6g** precipitated and was recovered by filtration: yield 2.1 g (69%); mp 208 °C dec; ^{1}H NMR (C_6D_6) δ 1.72 (s, 6 H, CH_3), 6.04 (s, 10 H, Cp); ^{13}C NMR (C_6D_6) δ 6.0 (q, $^{1}J_{CH}$ = 130 Hz, CH_3), 109.9 (d, $^{1}J_{CH}$ = 174 Hz, Cp), 123.7 (C^{β}, $^{2}J_{CH}$ = 9.5 Hz), 141.1 (C^{α}, $^{3}J_{CH}$ = 4.1 Hz); IR (KBr) 2085 (C≡C) cm^{-1}; MS (M^+) *m/e* 388. Anal. Calcd for $C_{16}H_{16}Hf$: C, 49.68; H, 4.17. Found: C, 49.67; H, 4.14.

Propynylzirconocene Chloride (7a). A mixture containing 1.7 g (5.7 mmol) of dipropynylzirconocene (**6a**) with 1.5 g (5.1 mmol) of zirconocene dichloride in 150 mL of benzene was stirred for 4 days at room temperature. The benzene was stripped and the resulting amber solid residue stirred with 50 mL of pentane. The resulting solid (2.4 g, 79%) consisted of a 80/20 mixture of propynylzirconocene chloride (**7a**) and zirconocene dichloride. This product mixture was used for subsequent reactions without further purification. **7a**: ^{1}H NMR (C_6D_6) δ 1.77 (s, 3 H, CH_3), 5.90 (s, 10 H, Cp); ^{13}C NMR (C_6D_6) δ 6.0 (q, $^{1}J_{CH}$ = 130 Hz, CH_3), 113.0 (d, $^{1}J_{CH}$ = 175 Hz, Cp), 121.8 (C^{β}, $^{2}J_{CH}$ = 9.7 Hz), C^{α} resonance hidden by solvent peaks; IR (KBr) 2098 (C≡C) cm^{-1}.

Bis(η-methylcyclopentadienyl)propynylzirconium Chloride (7b). A mixture of 8.8 g (26.9 mmol) of dipropynylbis(η-methylcyclopentadienyl)zirconium (**6b**) and 7.8 g (24.3 mmol) of bis(η-methylcyclopentadienyl)zirconium dichloride in 300 mL of benzene was stirred for 6 days at 50 °C. The solvent was removed in vacuo. The residue was treated with 150 mL of pentane. The resulting yellow precipitate was recovered by filtration and dried in vacuo to give 9.8 g (62%) of a product mixture containing nonreacted zirconocene dihalide (20%) and **7b**. No **6b** was found to be present by ^{1}H NMR spectroscopy. This crude material was used without further purification. **7b**: ^{1}H NMR (C_6D_6) δ 1.79 (s, 3 H, CH_3), 2.18 (s, 6 H, MeCp), 5.7 (m, MeCp), 6.1 (m, MeCp); IR (KBr) 2098 (C≡C) cm^{-1}.

(Phenylethynyl)zirconocene Chloride (7c). A mixture of 1.0 g (2.3 mmol) of bis(phenylethynyl)zirconocene (**6d**) and 0.6 g (2.1 mmol) of zirconocene dichloride in 50 mL of toluene was stirred for 3 days at room temperature. The resulting equilibrium mixture consisted of ca. 90% **7c**. The toluene was removed in vacuo and the oily dark brown residue stirred with 50 mL of pentane. **7c** precipitated as a light brown solid. It was recovered by filtration and dried in vacuo: yield 1.2 g (71%); ^{1}H NMR (C_6D_6) δ 6.00 (s, 10 H, Cp), 7.03 (m, 3 H, Ph), 7.51 (m, 2 H, Ph); IR (KBr) 2074 (C≡C) cm^{-1}. Anal. Calcd for $C_{18}H_{15}ClZr$: C, 60.39; H, 4.22. Found: C, 61.52; H, 4.33.

Bis(η-methylcyclopentadienyl)(phenylethynyl)zirconium Chloride (7d). Bis(phenylethynyl)bis(η-methylcyclopentadienyl)zirconium (**6e**) (4.5 g, 9.9 mmol) and 1.8 g (5.6 mmol) of bis(η-methylcyclopentadienyl)zirconium dichloride in 250 mL of benzene were stirred for 6 days at 50 °C. Benzene was removed in vacuo. The oily dark brown residue was treated with 150 mL of pentane to give a light brown solid. Filtration yielded 3.6 g (83%) of a crude product, containing ca. 80% of the alkynylmetallocene chloride **7d**. This was used without purification for further reactions: ^{1}H NMR (C_6D_6) δ 2.20 (s, 6 H, MeCp), 5.68 (m, 4 H, MeCp), 5.91 (q, 2 H, MeCp), 6.06 (m, 2 H, MeCp), 7.03 (m, 3 H, Ph), 7.48 (m, 2 H, Ph); IR (KBr) 2070 (C≡C) cm^{-1}.

(μ-η^{1}(C1):η^{2}(C≡C)-Propynyl)(μ-chloro)bis(zirconocene) (9a). Propynylzirconocene chloride (**7a**) (1.1 g, 3.7 mmol) was stirred with 1.2 g (4.3 mmol) of (butadiene)zirconocene in 50 mL of benzene for 20 h at room temperature. The benzene was removed in vacuo and the resulting orange solid washed with 50 mL of pentane to give 1.2 g (62%) of product. This crude material contained ca. 60% of the desired binuclear complex **9a**. The product was purified by crystallization. A sample of 0.4 g (0.8 mmol) of the crude reaction product was dissolved in 10 mL of methylene chloride and kept at −35 °C for 3 days. Cube-shaped red crystals of **9a** were obtained, which lost incorporated CH_2Cl_2 in vacuo to give 0.1 g (25%) of analytically pure **9a**: mp 267 °C; ^{1}H NMR (C_6D_6) δ 2.62 (s, 3 H, CH_3), 5.29 (s, 10 H, Cp), 5.37 (s, 10 H, Cp); ^{13}C NMR (CD_2Cl_2) δ 21.3 (q, $^{1}J_{CH}$ = 127 Hz, CH_3), 104.2 (d, $^{1}J_{CH}$ = 172 Hz, Cp), 105.8 (d, $^{1}J_{CH}$ = 172 Hz, Cp), 178.2 (s, C2), 223.1 (s, C1); Raman 1727 (C≡C) cm^{-1}; MS (M^+) *m/e* 514. Anal. Calcd for $C_{23}H_{23}Zr_2Cl$: C, 53.40; H, 4.48. Found: C, 53.08; H, 4.73.

(μ-η^{1}(C1):η^{2}(C≡C)-Propynyl)(μ-chloro)bis[bis(η-methylcyclopentadienyl)zirconium] (9c). A sample of 1.7 g (3.7 mmol) of bis(η-methylcyclopentadienyl)propynylzirconium chloride and 1.2 g (3.9 mmol) of (butadiene)bis(η-methylcyclopentadienyl)zirconium in 100 mL of benzene was stirred for 2 days at room temperature. Benzene was evaporated in vacuo. The brown residue was extracted with 100 mL of pentane and filtered to give a clear red solution. Distillation of the pentane solvent produced **9c** as an orange solid: yield 1.2 g (57%); mp 76 °C; ^{1}H NMR (C_6D_6) δ 2.02 (s, 6 H, MeCp), 2.07 (s, 6 H, MeCp), 2.63 (s, 3 H, CH_3), 4.88 (q, 4 H, MeCp), 5.05 (q, 4 H, MeCp), 5.24 (q, 4 H, MeCp), 5.56 (q, MeCp); ^{13}C NMR (CD_2Cl_2) δ 15.0 (q, $^{1}J_{CH}$ = 127 Hz, MeCp), 15.7 (q, $^{1}J_{CH}$ = 127 Hz, MeCp), 20.3 (q, $^{1}J_{CH}$ = 127 Hz, CH_3), 100.4 (d, $^{1}J_{CH}$ = 171 Hz, MeCp), 102.7 (d, $^{1}J_{CH}$ = 173 Hz, MeCp), 104.1 (d, $^{1}J_{CH}$ = 171 Hz, MeCp), 106.1 (d, MeCp), 106.3 (d, MeCp), 107.7 (d, $^{1}J_{CH}$ = 170 Hz, MeCp), 108.3 (d, $^{1}J_{CH}$ = 171 Hz, MeCp), 108.6 (d, $^{1}J_{CH}$ = 171 Hz, MeCp), 116.0 (s, MeCp), 118.2 (s, MeCp), 181.4 (s, C2), 228.5 (s, C1); Raman 1711 (m), 1720 (sh) cm^{-1}; MS (M^+) *m/e* 570. Anal. Calcd for $C_{27}H_{31}Zr_2Cl$: C, 56.55; H, 5.45. Found: C, 56.79; H, 5.70.

(μ-η^{1}(C1):η^{2}(C≡C)-Phenylethynyl)(μ-chloro)bis(zirconocene) (9b). A suspension of 0.5 g (1.4 mmol) of (phenylethynyl)zirconocene chloride and 0.4 g (1.5 mmol) of (butadiene)zirconocene in 50 mL of toluene was stirred overnight at room temperature to give a clear dark red solution. Solvent was evaporated in vacuo and the dark red oily residue stirred with 100 mL of pentane. The resulting orange precipitate was collected by filtration and dried in vacuo to give 0.5 g containing ca. 60% of the desired product. **9b**: ^{1}H NMR (C_7D_8) δ 5.34 (s, 10 H, Cp), 5.35 (s, 10 H, Cp), 7.39 (m, 1 H, Ph), 7.48 (m, 1 H, Ph), 7.58 (m, 1 H, Ph), 7.72 (m, 1 H, Ph), 7.84 (m, 1 H, Ph).

(μ-η^{1}(C1):η^{2}(C≡C)-Phenylethynyl)(μ-chloro)bis[bis(η-methylcyclopentadienyl)zirconium] (9d). A mixture of 1.1 g (2.8 mmol) of bis(η-methylcyclopentadienyl)(phenylethynyl)zirconium chloride and 0.9 g (3.0 mmol) of (butadiene)bis(η-methylcyclopentadienyl)zirconium in 50 mL of toluene was stirred for 3 days at room temperature. Toluene was removed in vacuo. The red solid residue was stirred with 50 mL of pentane. The resulting orange solid was filtered and dried in vacuo to give 0.7 g (40%) of reasonably pure **9d**: mp 158 °C; ^{1}H NMR (C_6D_6) δ 1.97 (s, 6 H, MeCp), 2.07 (s, 6 H, MeCp), 4.88 (q, 4 H, MeCp), 5.10 (q, 4 H, MeCp), 5.27 (q, 4 H, MeCp), 5.61 (q, 4 H, MeCp), 7.34 (m, 1 H, Ph), 7.45 (m, 1 H, Ph), 7.53 (m, 1 H, Ph), 7.75 (m, 1 H, Ph), 7.84 (m, 1 H, Ph); ^{13}C NMR (C_6D_6) δ 15.2 (q, $^{1}J_{CH}$ = 127 Hz, MeCp), 15.5 (q, $^{1}J_{CH}$ = 127 Hz, MeCp), 100.3 (d, $^{1}J_{CH}$ = 172 Hz, MeCp), 102.7 (d, $^{1}J_{CH}$ = 173 Hz, MeCp), 104.4 (d, $^{1}J_{CH}$ = 171 Hz, MeCp), 106.3 (d, $^{1}J_{CH}$ = 169 Hz, MeCp), 106.5 (d, $^{1}J_{CH}$ = 169 Hz, MeCp), 107.0 (d, $^{1}J_{CH}$ = 169 Hz, MeCp), 107.4 (d, $^{1}J_{CH}$ = 168 Hz, MeCp), 110.0 (d, $^{1}J_{CH}$ = 172 Hz, MeCp), 117.9 (s, MeCp), 118.1 (s, MeCp), 126.7 (d, $^{1}J_{CH}$ = 160 Hz, Ph), 128.7 (d, $^{1}J_{CH}$ = 160 Hz, Ph), 131.2 (d, $^{1}J_{CH}$ = 158 Hz, Ph), 140.0 (s, Ph), 187.3 (s, C2), 246.1 (s, C1); MS (M^+) *m/e* 632.

Bis[(μ-propynyl)zirconocene] (10a). A mixture of 0.3 g (1.0 mmol) of dipropynylzirconocene and 0.3 g (1.1 mmol) of a (butadiene)zirconocene equilibrium mixture in 20 mL of benzene was stirred for 18 h at room temperature. During this time, the product **10a** precipitated. It was collected by filtration and washed with pentane: yield 0.3 g (60%); mp >320 °C; ^{1}H NMR (C_6D_6) δ 2.59 (s, 3 H, CH_3), 5.19 (s, 10 H, Cp); ^{13}C NMR (C_6D_6) δ 18.1 (q, $^{1}J_{CH}$ = 129 Hz, CH_3), 102.6 (d, Cp), 147.9 (s, C2), 204.2 (s, C1); IR (KBr) 1820 (C≡C) cm^{-1}; MS (M^+) *m/e* 518. Anal. Calcd for

$C_{26}H_{26}Zr_2$: C, 59.95; H, 5.03. Found: C, 60.13; H, 5.14.

Bis(μ-propynyl)dicyclopentadienylhafniumdicyclopentadienylzirconium (10h). A sample of 0.7 g (1.8 mmol) of dipropynylhafnocene and 0.7 g (2.5 mmol) of (butadiene)zirconocene in 100 mL of toluene was stirred for 18 h at room temperature. The resulting precipitate of pure **10h** was filtered, washed with 25 mL of pentane, and dried in vacuo: yield 0.5 g (46%); mp >320 °C; ^{1}H NMR (C_7D_8, 193 K) δ 2.66 (s, 6 H, CH_3), 5.09 (s, 10 H, Cp), 5.15 (s, 10 H, Cp); ^{13}C NMR (CD_2Cl_2, 223 K) δ 18.7 (q, $^1J_{CH}$ = 129 Hz, CH_3), 19.1 (q, $^1J_{CH}$ = 129 Hz, CH_3), 101.2 (d, Cp), 101.6 (d, Cp), 146.8 (C2, $^2J_{CH}$ = 8 Hz), 148.9 (C2′, $^2J_{CH}$ = 8 Hz), 201.8 (C1, $^3J_{CH}$ = 5 Hz), 206.6 (C1′, $^3J_{CH}$ = 5 Hz); IR (KBr) 1810 (C≡C) cm^{-1}; MS (M^+) *m/e* 608. Anal. Calcd for $C_{26}H_{26}HfZr$: C, 51.35; H, 4.31. Found: C, 51.66; H, 4.46.

Bis(η-methylcyclopentadienyl)zirconiumbis(μ-propynyl)dicyclopentadienylzirconium (10c). A solution of 1.3 g (4.0 mmol) of bis(η-methylcyclopentadienyl)dipropynylzirconium and 1.4 g (5.1 mmol) of the (butadiene)zirconocene equilibrium mixture in 100 mL of benzene was kept for 20 h at room temperature. Then the solvent was evaporated in vacuo and the solid brown residue stirred with 100 mL of pentane. Product **10c** precipitated as a yellow solid: yield 1.8 g (82%); mp 195 °C dec; ^{1}H NMR (C_6D_6, ambient temperature) δ 2.57 (s, 6 H, CH_3), 2.08 (s, 6 H, MeCp), 4.90 (m, 4 H, MeCp), 5.10 (m, 4 H, MeCp), 5.18 (s, 10 H, Cp); ^{1}H NMR (C_7D_8, 233 K) δ 2.11 (s, 6 H, MeCp), 2.55 (s, 3 H, CH_3), 2.57 (s, 3 H, CH_3), 4.62 (q, 2 H, MeCp), 4.96 (m, 2 H, MeCp), 5.02 (q, 2 H, MeCp), 5.18 (s, 10 H, Cp), 5.29 (m, 2 H, MeCp); automerization activation barrier derived from the coalescence of the propynyl methyl groups, $\Delta\nu$(253 K) = 2.6 ± 0.1 Hz, ΔG^*(267 K) = 14.6 ± 0.3 kcal/mol; ^{13}C NMR (C_7D_8, 353 K) δ 15.7 (q, MeCp), 17.1 (q, CH_3), 102 (br signal, MeCp), 102.7 (d, Cp), 105 (br signal, MeCp), 105.1 (d, MeCp), 116.2 (s, MeCp), 148.6 (s, C2), 207.7 (s, C1); ^{13}C NMR (C_7D_8, 233 K) δ 15.9 (q, $^1J_{CH}$ = 127 Hz, MeCp), 17.6 (q, $^1J_{CH}$ = 129 Hz, CH_3), 17.7 (q, $^1J_{CH}$ = 129 Hz, CH_3), 102.4 (d, $^1J_{CH}$ = 171 Hz, Cp), 97.9 (d, $^1J_{CH}$ = 172 Hz, MeCp), 104.3 (d, $^1J_{CH}$ = 167 Hz, MeCp), 104.9 (d, $^1J_{CH}$ = 167 Hz, MeCp), 105.9 (d, $^1J_{CH}$ = 170 Hz, MeCp), 147.5 (C2, $^2J_{CH}$ = 8 Hz), 148.3 (C2′, $^2J_{CH}$ = 8 Hz), 204.6 (C1, $^3J_{CH}$ = 5 Hz), 207.5 (C1′, $^3J_{CH}$ = 5 Hz); automerization activation barrier derived from the coalescence of the propynyl methyl groups, $\Delta\nu$(273 K) = 15.1 ± 0.5 Hz, ΔG^*(281.8 K) = 14.5 ± 0.3 kcal/mol; IR (KBr) 1815 (C≡C) cm^{-1}; MS (M^+) *m/e* 546. Anal. Calcd for $C_{28}H_{30}Zr_2$: C, 61.26; H, 5.51. Found: C, 61.22; H, 5.57.

Photolysis of Dipropynylbis(η-methylcyclopentadienyl)zirconium in the Presence of Zirconocene Dicarbonyl at Low Temperature. A sample containing 60 mg (0.18 mmol) of dipropynylbis(η-methylcyclopentadienyl)zirconium (**6b**) and 50 mg (0.18 mmol) of zirconocene dicarbonyl in 0.4 mL of toluene-d_8 was irradiated in a 5-mm NMR tube for 40 min at −60 °C (HPK 125, Pyrex filter). The ^{1}H NMR spectrum at −60 °C revealed the presence of the binuclear alkynyl-bridged complex **10c** plus residual starting material.

Reaction of Dipropynylbis(η-methylcyclopentadienyl)zirconium with (Butadiene)zirconocene. A sample of 60 mg (0.18 mmol) of dipropynylbis(η-methylcyclopentadienyl)zirconium (**6b**) is mixed with 0.03 g (0.10 mmol) of (butadiene)zirconocene in 0.4 mL of toluene-d_8 at −40 °C. The reaction was monitored by ^{1}H NMR spectroscopy at various increasing temperatures. Reaction was observed to take place at 0 °C. The observed reaction product is **10c**, which was identified by its characteristic ^{1}H NMR spectrum.

Bis(μ-propynyl)bis[bis(η-methylcyclopentadienyl)zirconium] (10b). The reaction mixture of 1.6 g (4.9 mmol) of bis(η-methylcyclopentadienyl)dipropynylzirconium (**6b**) and 1.4 g (4.6 mmol) of the bis(η-methylcyclopentadienyl)(butadiene)zirconium equilibrium mixture in 100 mL of benzene was stirred for 2 days at ambient temperature. Benzene was stripped and the resulting red oil stirred with 100 mL of pentane. Product **10b** precipitated as an amber solid: yield 0.8 g (30%); mp 278 °C; ^{1}H NMR (C_6D_6, ambient temperature) δ 2.12 (s, 6 H, MeCp), 2.55 (s, 3 H, CH_3), 4.90 (m, 4 H, MeCp), 5.10 (m, 4 H, MeCp); ^{1}H NMR (C_7D_8, 233 K) δ 2.13 (s, 6 H, MeCp), 2.53 (s, 6 H, CH_3), 4.65 (2 H, MeCp), 5.03 (4 H, MeCp), 5.30 (2 H, MeCp); automerization activation barrier from the coalescence of the methylcyclopentadienyl signals, $\Delta\nu$(243 K) = 21.5 ± 0.5 Hz, ΔG^*(288 K) = 14.6 ± 0.3 kcal/mol; ^{13}C NMR (CD_2Cl_2, 233 K) δ 15.3 (q, $^1J_{CH}$ = 127 Hz, MeCp), 16.5 (q, $^1J_{CH}$ = 129 Hz, CH_3), 97.2 (d, $^1J_{CH}$ = 170 Hz, MeCp), 103.7 (d, $^1J_{CH}$ = 168 Hz, MeCp), 104.6 (d, $^1J_{CH}$ = 167 Hz, MeCp), 105.2 (d, $^1J_{CH}$ = 170 Hz, MeCp), 115.1 (s, MeCp), 148.7 (C2, $^2J_{CH}$ = 8 Hz), 207.7 (C1, $^3J_{CH}$ = 5 Hz); IR (KBr) 1817 (m), 1870 (w) (C≡C) cm^{-1}; MS (M^+) *m/e* 574. Anal. Calcd for $C_{30}H_{34}Zr_2$: C, 62.44; H, 5.94. Found: C, 62.46; H, 5.95.

Bis(η-methylcyclopentadienyl)zirconiumbis(μ-phenylethynyl)dicyclopentadienylzirconium (10e). A mixture of 0.5 g (1.1 mmol) bis(η-methylcyclopentadienyl)bis(phenylethynyl)zirconium (**6e**) and 0.3 g (1.1 mmol) of the (butadiene)zirconocene equilibrium mixture in 25 mL of benzene was stirred overnight at room temperature. The orange precipitate was filtered and washed once with 5 mL of pentane: yield 0.3 g (45%); mp 293 °C; ^{1}H NMR (CD_2Cl_2) δ 2.16 (s, 6 H, MeCp), 5.1 (m, MeCp), 5.44 (s, 10 H, Cp), 7.31 (m, Ph), 7.43 (m, Ph), 7.60 (m, Ph), 7.68 (m, Ph); automerization activation barrier from the coalescence of the MeCp signals, $\Delta\nu$(233 K) = 49.8 ± 1.0 Hz, ΔG^*(283 K) = 13.9 ± 0.5 kcal/mol; ^{13}C NMR (CD_2Cl_2, 223 K) δ 15.5 (q, $^1J_{CH}$ = 128 Hz, MeCp), 97.8 (q, $^1J_{CH}$ = 171 Hz, MeCp), 102.2 (q, $^1J_{CH}$ = 172 Hz, MeCp), 104.1 (d, $^1J_{CH}$ = 165 Hz, MeCp), 104.6 (d, $^1J_{CH}$ = 170 Hz, MeCp), 106.0 (d, $^1J_{CH}$ = 172 Hz, MeCp), 116.5 (s, MeCp), 126.5 (d, $^1J_{CH}$ = 161 Hz, Ph), 126.6 (d, $^1J_{CH}$ = 161 Hz, Ph), 128.2 (d, $^1J_{CH}$ = 161 Hz, Ph), 128.4 (d, $^1J_{CH}$ = 161 Hz, Ph), 130.9 (d, $^1J_{CH}$ = 161 Hz, Ph), 132.0 (d, $^1J_{CH}$ = 159 Hz, Ph), 133.3 (s, Ph), 134.2 (s, Ph), 153.9 (s, C2), 224.2 (s, C1), 227.7 (s, C1′); IR (KBr) 1783 (C≡C) cm^{-1}; MS (M^+) *m/e* 670. Anal. Calcd for $C_{38}H_{34}Zr_2$: C, 67.81; H, 5.09. Found: C, 67.69; H, 4.99.

Bis[(μ-phenylethynyl)bis(η-methylcyclopentadienyl)zirconium] (10f). A solution of 1.5 g (3.3 mmol) of bis(η-methylcyclopentadienyl)bis(phenylethynyl)zirconium (**6e**) and 1.1 g (3.6 mmol) (butadiene)bis(η-methylcyclopentadienyl)zirconium in 25 mL of benzene was kept at room temperature for 20 h. During this time the orange colored product precipitated. It was collected by filtration, washed with 5 mL of pentane, and dried in vacuo: yield 1.4 g (61%); mp 257 °C; ^{1}H NMR (C_7D_8, 243 K) δ 4.67 (q, 2 H, MeCp), 5.14 (t, 4 H, MeCp), 5.60 (q, 2 H, MeCp), 7.46 (m, 6 H, Ph), 7.81 (m, 4 H, Ph); absorption of the MeCp methyl group hidden under solvent; automerization activation barrier from the coalescence of the MeCp signals, $\Delta\nu$(243 K) = 35.6 ± 0.5 Hz, ΔG^*(297 K) = 14.8 ± 0.3 kcal/mol; ^{13}C NMR (CD_2Cl_2, 223 K) δ 15.5 (q, $^1J_{CH}$ = 127 Hz, MeCp), 97.6 (d, $^1J_{CH}$ = 170 Hz, MeCp), 103.9 (d, $^1J_{CH}$ = 169 Hz, MeCp), 104.3 (d, $^1J_{CH}$ = 169 Hz, MeCp), 105.8 (d, $^1J_{CH}$ = 172 Hz, MeCp), 116.6 (s, MeCp), 126.5 (d, $^1J_{CH}$ = 161 Hz, Ph), 128.4 (d, $^1J_{CH}$ = 159 Hz, Ph), 131.9 (d, $^1J_{CH}$ = 159 Hz, Ph), 133.8 (s, Ph), 154.7 (s, C2), 228.9 (s, C1); IR (KBr) 1780 (s) (C≡C) cm^{-1}; MS (M^+) *m/e* 698. Anal. Calcd for $C_{40}H_{38}Zr_2$: C, 68.52; H, 5.46. Found: C, 68.61; H, 5.46.

Bis(η-*tert*-butylcyclopentadienyl)zirconiumbis(μ-phenylethynyl)dicyclopentadienylzirconium (10g). A reaction mixture of 0.7 g (1.3 mmol) of bis(η-*tert*-butylcyclopentadienyl)bis(phenylethynyl)zirconium (**6f**) and 0.7 g (2.5 mmol) of (butadiene)zirconocene in 50 mL of benzene was stirred for 3 days at room temperature. The benzene solvent was removed in vacuo. The brown residue was stirred with 50 mL of pentane. The remaining brown solid was filtered and dried in vacuo: yield 0.5 g (54%) of **10g**: mp 193 °C; ^{1}H NMR (C_7D_8, 400 MHz, 193 K) δ 1.20 (s, 18 H, *t*-BuCp), 4.99 (s, 2 H, *t*-BuCp), 5.11 (s, 2 H, *t*-BuCp), 5.25 (s, 10 H, Cp), 5.37 (s, 2 H, *t*-BuCp), 5.63 (s, 2 H, *t*-BuCp), 7.26 (m, 2 H, Ph), 7.33 (m, 4 H, Ph), 7.69 (m, 4 H, Ph; ^{13}C NMR (CD_2Cl_2, 193 K) δ 31.1 (q, $^1J_{CH}$ = 126 Hz, *t*-BuCp), 32.1 (s, *t*-BuCp), 95.6 (d, $^1J_{CH}$ = 170 Hz, *t*-BuCp), 101.3 (d, $^1J_{CH}$ = 170 Hz, *t*-BuCp), 102.3 (d, $^1J_{CH}$ = 172 Hz, Cp), 104.2 (d, $^1J_{CH}$ = 173 Hz, *t*-BuCp), 104.6 (d, $^1J_{CH}$ = 168 Hz, *t*-BuCp), 125.0 (d, $^1J_{CH}$ = 161 Hz, Ph), 125.9 (d, $^1J_{CH}$ = 160 Hz, Ph), 126.7 (d, $^1J_{CH}$ = 160 Hz, Ph), 127.9 (d, $^1J_{CH}$ = 162 Hz, Ph), 128.1 (d, $^1J_{CH}$ = 160 Hz, Ph), 130.4 (d, $^1J_{CH}$ = 160 Hz, Ph), 132.5 (s, *t*-BuCp), 135.3 (s, Ph), 136.7 (s, Ph), 148.1 (C2, $^3J_{CH}$ = 4 Hz), 154.5 (C2′, $^3J_{CH}$ = 4 Hz), 211.5 (s, C1), 225.8 (s, C1′); IR (KBr) 1770 (s), 1870 (m) (C≡C) cm^{-1}; MS (M^+) *m/e* 754. Anal. Calcd for $C_{44}H_{46}Zr_2$: C, 69.79; H, 6.12. Found: C, 69.69; H, 6.20.

Bis(η-*tert*-butylcyclopentadienyl)zirconiumbis(μ-propynyl)dicyclopentadienylzirconium (10d, 13a). A solution containing 0.7 g (1.7 mmol) of bis(η-*tert*-butylcyclopentadienyl)dipropynylzirconium (**6c**) and 0.7 g (2.5 mmol) of the (butadiene)zirconocene equilibrium mixture in 75 mL of benzene was stirred for 3 days at room temperature. The benzene solvent was removed in vacuo. The oily residue was stirred with 25 mL of pentane. The yellow product was collected by filtration and dried in vacuo: yield 0.2 g (20%); mp 141 °C; ^{1}H NMR (C_7D_8, 400 MHz, 203 K). At low temperature the spectra of the isomeric complexes **10d** and **13a** have been observed in a 45:55 ratio. **10d**: δ 1.38 (s, 18 H, *t*-BuCp), 2.57 (s, 3 H, CH_3), 2.61 (s, 3 H, CH_3), 4.76 (br s, 4 H, *t*-BuCp), 5.14 (br s, 4 H, *t*-BuCp), 5.25 (s, 10 H, Cp). **13a**: δ 1.44 (s, 18 H, *t*-BuCp), 2.67 (s, 6 H, CH_3), 5.00 (s, 10 H, Cp), 5.21 (br s, 4 H, *t*-BuCp), 5.45 (br s, 4 H, *t*-BuCp); estimation of the activation barrier of the **10d** $\rightleftharpoons$ **13a** rearrangement from the Cp coalescence (80 MHz), $\Delta\nu$(208 K) = 18.5 ± 0.5 Hz, $\Delta G^{\ddagger}$(218 K) = 12.6 ± 0.5 kcal/mol; ^{13}C NMR: **10d**, δ 17.1 (q, $^1J_{CH}$ = 128 Hz, CH_3), 19.1 (q, $^1J_{CH}$ = 127 Hz, CH_3), 32.3 (q, $^1J_{CH}$ = 125 Hz, *t*-BuCp), 32.5 (s, *t*-BuCp), 102.4 (d, $^1J_{CH}$ = 169 Hz, Cp), 132.7 (s, *t*-BuCp), 146.3 (s, C2), 149.8 (s, C2′), 204.1 (s, C1), 208.5 (s, C1′); **13a**, δ 18.6 (q, $^1J_{CH}$ = 128 Hz, CH_3), 31.7 (s, *t*-BuCp), 32.8 (q, $^1J_{CH}$ = 125 Hz, *t*-BuCp), 103.9 (d, $^1J_{CH}$ = 169 Hz, Cp), 133.2 (s, *t*-BuCp), 142.1 (C2, J_{CH} = 8.0 Hz), 178.1 (C1, J_{CH} = 4.4 Hz); IR (KBr) 1870 (w), 1815 (m) ($C{\equiv}C$) cm^{-1}; MS (M^+) *m/e* 630. Anal. Calcd for $C_{34}H_{42}Zr_2$: C, 64.50; H, 6.69. Found: C, 64.60; H, 6.67.

Photolysis of Dipropynylbis(η-*tert*-butylcyclopentadienyl)zirconium (6c) in the Presence of Zirconocene Dicarbonyl at Low Temperature. A solution containing 60 mg (0.14 mmol) of dipropynylbis(η-*tert*-butylcyclopentadienyl)zirconium (**6c**) and 40 mg (0.14 mmol) of zirconocene dicarbonyl in 0.4 mL of toluene-d_8 was irradiated for 40 min at −40 °C (HPK 125, Pyrex filter). The solution was then directly analyzed by ^{1}H NMR spectroscopy at −40 °C. Formation of **10d**/**13a** as the only reaction products was observed at about 20% conversion rate, achieved under these conditions. No further reaction products or intermediates were found.

Reaction of Dipropynylzirconocene (6a) with (Butadiene)bis(η-*tert*-butylcyclopentadienyl)zirconium. A mixture of 0.4 g (1.4 mmol) of dipropynylzirconocene (**6a**) and 0.4 g (1.0 mmol) of (butadiene)bis(η-*tert*-butylcyclopentadienyl)zirconium in 10 mL of toluene was stirred for several days at room temperature. The progress of the reaction was followed by ^{1}H NMR spectroscopy. After 12 days, most of the dipropynylzirconocene starting material had been consumed, while there was still some unused butadiene metallocene reagent around. In addition to the unsymmetrically substituted binuclear product **10d**/**13a** some $[Cp_2Zr]_2(\mu\text{-}C{\equiv}CCH_3)_2$ (**10a**) was formed (ratio 3:1).

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Registry No. **6a**, 103111-51-9; **6b**, 105036-32-6; **6c**, 119071-19-1; **6d**, 72982-57-1; **6e**, 72951-38-3; **6f**, 119071-20-4; **6g**, 119071-21-5; **6h**, 84879-48-1; **7a**, 119071-22-6; **7b**, 119071-22-6; **7c**, 119071-23-7; **7d**, 119071-24-8; **9a**, 119071-25-9; **9b**, 119071-27-1; **9c**, 119071-26-0; **9d**, 119071-28-2; **10a**, 119108-44-0; **10b**, 119108-46-2; **10c**, 119144-91-1; **10d**, 119144-92-2; **10e**, 119108-47-3; **10f**, 101518-71-2; **10g**, 119108-48-4; **10h**, 119108-45-1; **13a**, 119108-49-5; zirconocene dichloride, 1291-32-3; propynyllithium, 4529-04-8; bis(η-methylcyclopentadienyl)zirconium dichloride, 12109-71-6; bis(η-*tert*-butylcyclopentadienyl)zirconium dichloride, 32876-92-9; sodium phenylacetylide, 1004-22-4; hafnocene dichloride, 12116-66-4; (butadiene)zirconocene, 75374-50-4; (butadiene)bis(η-methylcyclopentadienyl)zirconium, 101518-70-1; zirconocene dicarbonyl, 59487-85-3; (butadiene)bis(η-*tert*-butylcyclopentadienyl)zirconium, 113667-86-0.

Supplementary Material Available: Detailed information on the crystal structure determination of **6a** including tables of atomic thermal parameters, atom coordinates, and interatomic distances and angles (6 pages); a listing of structure factors for **6a** (5 pages). Ordering information is given on any current masthead page.

Synthesis and Crystal Structure of the New Mixed-Metal, Mixed-Ligand Cluster Compound $Zn_4Ni_2(C_5H_5)_4(C_5Me_5)_2$

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The reaction of equimolar amounts of $Zn(C_5H_5)_2$, $Zn(C_5Me_5)_2$, and $Ni(COD)_2$ afforded the zinc-containing mixed-metal, mixed-ligand cluster compound $Zn_4Ni_2(C_5H_5)_4(C_5Me_5)_2$. Crystals of the title compound are monoclinic, space group $P2_1/n$, with unit-cell dimensions a = 10.87 (1) Å, b = 14.86 (1) Å, c = 11.60 (1) Å, β = 96.12 (5)°, and Z = 2. The structure refinement converged at R_F = 0.063. The cluster $Zn_4Ni_2(C_5H_5)_4(C_5Me_5)_2$ is the first characterized example of a metal complex containing an isolated, η^2-coordinating, main-group metal bonded cyclopentadienyl ring, in this case a pentamethyl-substituted one. The unsubstituted rings are bonded to zinc and nickel in an η^2–η^3 and η^5 mode, respectively. This compound has provided further support for the previously proposed mechanism for the formation of related ZnNi clusters, and the selectivity of the reaction has enabled us to identify the rate-determining step in these cluster-forming reactions. The surprisingly high yield, compared to that of $Zn_4Ni_2(C_5H_5)_6$, with which the new cluster is formed can be explained by assuming a stabilizing influence of the pentamethylcyclopentadienyl ligand on the key-trimetallic radical intermediate. Zinc-bonded cyclopentadienyl rings easily adapt to steric interference by changing their hapticity. This occurs in particular when their size increases through the introduction of substituents and is in accord with the largely ionic character of the zinc–cyclopentadienyl interaction.

Introduction

Recently, we reported the preparation and crystal structure determination of the first zinc–nickel cluster compound $Zn_4Ni_2(C_5H_5)_6$ which was obtained from the reaction of dicyclopentadienylzinc with bis(1,4-cyclooctadiene)nickel [$Ni(COD)_2$].[1] The fact that this heter-