Organometallics **1997,** *16,* 4889−4895

Hydrocarbon Activation with Metal Halides: Zirconium Tetrachloride Catalyzing the Jacobsen Reaction and Assisting the Trimerization of Alkynes via the Formation of η^6-Arene−Zirconium(IV) Complexes

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Received May 27, 1997[⊗]

Solubilization of the highly insoluble polymeric $ZrCl_4$ is achieved using 1,2,4,5-$Me_4C_6H_2$ (durene) as a carrier in a halogenated solvent, such as CH_2Cl_2, $CHCl_3$, 1,2-$Cl_2C_2H_4$, or *o*-$Cl_2C_6H_4$. Solubilization can reach the level of 40 g of $ZrCl_4$ in 100 mL of CH_2Cl_2 using an equimolar amount of durene. This is a very successful approach to making available soluble $ZrCl_4$ in a noncoordinating solvent. The solubilization occurs via the formation of a η^6-arene complex, which has been structurally characterized in the form of the hexamethylbenzene derivative $[(\eta^6\text{-}Me_6C_6)Zr_2(\mu\text{-}Cl)_3Cl_5]$ (**3**). This complex is in equilibrium, as revealed by the ^1H NMR spectrum in CH_2Cl_2, with free C_6Me_6 and a complex (**4**) which contains a higher Zr/C_6Me_6 ratio. A careful analysis of the CH_2Cl_2 solution, containing originally $ZrCl_4$ and durene, showed that durene underwent transformation to C_6Me_5H and C_6Me_6. These species have been trapped, bonded to zirconium in complex $[(\eta^6\text{-}C_6Me_5R)Zr_2(\mu\text{-}Cl)_3Cl_5]$ (**2**, R = H, 50%; R = Me, 50%), which has been structurally characterized. The methyl redistribution reaction in CH_2Cl_2 can result in the inconvenient formation of byproducts derived from the Zr-assisted Friedel−Craft reaction of CH_2Cl_2 on the arene. The intermediate of such a reaction has been isolated as $[C_6Me_6CHCl_2]^+[Zr_2Cl_9]^-$ (**5**), whose X-ray structure is available. In order to avoid the intervention of the solvent and to speed up the reaction, the $ZrCl_4$ rearrangement of methylbenzenes was carried out in neat hydrocarbon at 90 °C for 6 h. This rearrangement has a number of peculiarities: (i) unlike the original Jacobsen reaction, it involves intermolecular methyl transfer; (ii) it reaches an equilibrium of methyl distribution; and (iii) it is catalytic in zirconium. The very high stability of **3** accounts for the isolation of the same compound derived from the $ZrCl_4$-assisted trimerization of 2-butyne in *n*-hexane.

Introduction

The interaction of high oxidation state metal ions with hydrocarbons is a key step in their metal-assisted activation.[1] The primary interaction is supposed to occur via electron donation from the π-system or the σ C−H bonds[2] to the electron poor metal. Among the more interesting approaches, though not frequently employed, is the use of electrophilic metals.[3,4] This approach has a parallel in organic chemistry with the use of superacidic compounds.[5] A significant advantage of acidic metals over expensive, low-valent metals in elaborate coordination environments[1] is their straightforward preparation, low cost, and stability toward oxygen. We will consider in this context the formation

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[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1997.

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S0276-7333(97)00438-X CCC: $14.00

of labile d^0-arene complexes with zirconium(IV), which have had a number of unexpected consequences: (i) the solubilization in high concentrations of the polymeric form $(ZrCl_4)_n$ in halogenated solvents using methylbenzenes as carriers; (ii) the formation and isolation of unique metal(IV)–arene complexes; (iii) the catalytic rearrangement of methylbenzenes using $(ZrCl_4)_n$; and (iv) the trimerization of internal alkynes to the corresponding hexaalkylbenzenes. The key role in this chemistry is played by the solvent, and it will be examined in detail. A limited account of some aspects of this chemistry has already been communicated.[6]

Experimental Section

General Procedure. All reactions were carried out under an atmosphere of purified nitrogen. Solvents were dried and distilled by standard methods before use. ^1H NMR and IR spectra were recorded on AC-200, DPX-400 Bruker, and Perkin-Elmer FT 1600 instruments, respectively. GC and GC/MS analyses were carried out using a HP 5890 Series II system and a HP 5890A GC system, respectively. Hereafter, C_8, C_9, and C_{10} refer to the isomeric mixture of di-, tri-, and tetramethylbenzene, while C_{11} and C_{12} refer to penta- and hexamethylbenzene, respectively.

Solubilization of $ZrCl_4$ in CH_2Cl_2, $CHCl_3$, and $Cl_2C_2H_4$ and the Isolation of 2. Durene (1,2,4,5-$Me_4C_6H_2$, 23.0 g, 171 mmol) was added to a CH_2Cl_2 (100 mL) suspension of $ZrCl_4$ (40.0 g, 171 mmol). An orange suspension was obtained which turned to a red-violet clear solution after 10–15 h. The solution was treated with anhydrous THF and analyzed by gas chromatography after 24 h. It revealed a mixture of C_9, C_{10}, C_{11}, and C_{12} hydrocarbons in a 1:6.5:4.0:0.7 molar ratio. At longer times (2 months), the polymethylated (C_{10}, C_{11}, C_{12}) ratio changed to 1:2.5:2. The solution at this stage was evaporated to give a dark red solid, which on recrystallization from *o*-$Cl_2C_6H_4$ gave dark red crystals of **2**. Anal. Calcd for **2**, $C_{11.5}H_{17}Cl_8Zr_2$: C, 22.23; H, 2.76. Found: C, 22.54, H, 2.95. Crystals of **2**, -reacted with THF, gave quantitatively $ZrCl_4\cdot thf_2$ (>95% yield), C_6Me_6, and C_6Me_5H in a 1:1 molar ratio.

The durene-assisted solubilization of $ZrCl_4$ in $CHCl_3$ and 1,2-dichloroethane was carried out as above.

(a) $ZrCl_4$ (14.7 g, 63.0 mmol) dissolved in $CHCl_3$ (100 mL) in the presence of an equimolar amount of durene (8.45 g, 65.0 mmol) in 24 h to give a dark red clear solution. When all the $ZrCl_4$ has dissolved, the solution contains a mixture of C_9, C_{10}, C_{11}, C_{12}, and Me_5EtC_6 in a 1:8:6.5:0.6:0.5 molar ratio.

(b) $ZrCl_4$ (15.1 g, 65.0 mmol) dissolved in 1,2-$Cl_2C_6H_4$ in the presence of durene (8.71 g, 65.0 mmol) in 24 h to give a dark red-brown solution. The C_{10}, C_{11}, and C_{12} molar ratio at this stage was 3.3:1.5:1.

Synthesis of 3. $ZrCl_4$ (2.50 g, 10.7 mmol) was added to a 1,2-$Cl_2C_6H_4$ (150 mL) solution of C_6Me_6 (0.87 g, 5.37 mmol). The resulting suspension was refluxed until a clear solution was obtained, which was then allowed to cool to room temperature, affording **3** as a microcrystalline solid (90%). Anal. Calcd for **3**, $C_{12}H_{18}Cl_8Zr_2$: C, 22.94; H, 2.89. Found: C, 23.01; H, 2.97.

Synthesis of 5. C_6Me_6 (1.16 g, 7.16 mmol) was added to a CH_2Cl_2 (100 mL) suspension of $ZrCl_4$ (3.33 g, 14.3 mmol). The suspension became amber in a few hours and was then refluxed for 24 h until it reached a yellow-green color. The solid was extracted with the mother liquor to eliminate unreacted $ZrCl_4$. An amber crystalline solid was collected (60%). It was recrystallized from *o*-$Cl_2C_6H_4$. Anal. Calcd for **6**, $C_{13}H_{20}Cl_{10}Zr_2$: C, 21.89; H, 2.82. Found: C, 21.75; H, 2.90.

Reaction of $ZrCl_4$ with Benzene in CH_2Cl_2. Benzene (1.63 g, 20.9 mmol) was added to a CH_2Cl_2 suspension of $ZrCl_4$ (5.0 g, 21.5 mmol). The suspension was stirred at room temperature for a month. Treatment with THF gave $ZrCl_4(thf)_2$, while the THF solution contains C_6H_6 and Ph_2CH_2 in the 2.2:1 molar ratio, and oligomeric methylene-bridged arenes. When the reaction was carried out in CD_2Cl_2, deuterated diphenylmethane was obtained.

Methyl Redistribution in Methylbenzenes Assisted by $ZrCl_4$ as a Function of the Solvent. **(A) Rearrangements in CH_2Cl_2. (i) Rearrangement of Mesitylene.** Mesitylene (14.3 g, 119 mmol) was added to a CH_2Cl_2 (100 mL) suspension of $ZrCl_4$ (13.9 g, 59.6 mmol) and then stirred until it became a dark red solution (~24 h). The $C_8/C_9/C_{10}$ ratio in the mixture was 1:11:2.3, with detectable amounts of oligomeric methylene-bridged arenes.

(ii) Rearrangement of Pentamethylbenzene. Me_5C_6H (3.2 g, 21.6 mmol) was added to a CH_2Cl_2 (100 mL) suspension of $ZrCl_4$ (5.0 g, 21.5 mmol). The suspension was stirred at room temperature for a month and then treated with THF, which gave $ZrCl_4(thf)_2$ and a solution containing C_{10}, C_{11}, and C_{12} in a 1/1/1 molar ratio, with detectable amounts of oligomeric methylene-bridged arenes.

(B) Rearrangements in Neat Hydrocarbons. The general procedure involved heating the $ZrCl_4$/hydrocarbon mixture for 16 h at 90 °C. The resulting orange solid was decomposed using THF, and then the THF solution, free from $ZrCl_4(thf)_2$, was analyzed (GC/MS).

Regardless of the starting materials, that is, (a) durene, (b) isodurene, (c) equimolar mixture of mesitylene, durene, and pentamethylbenzene, the composition of the final mixture is xylenes, 2.5%; trimethylbenzenes, 26%; durenes, 42%; pentamethylbenzene, 28%; hexamethylbenzene, 1.5%. The $ZrCl_4$/hydrocarbons molar ratio can vary from 1:1 to 1:100.

(C) Internal Alkynes Trimerization. (i) Synthesis of 3 via 2-Butyne Trimerization. 2-Butyne (11.9 g, 220.3 mmol) was added to an *n*-hexane suspension of $ZrCl_4$ (2.58 g, 11.1 mmol). The resulting yellow-orange suspension was stirred at room temperature for 1 week. The resulting yellow-orange solid was shown to be **3** (>95%). The solid was reacted with THF to form C_6Me_6 and $ZrCl_4(thf_2)$. The filtered solution did not contain any free C_6Me_6.

(ii) Reaction of 2-Butyne and $ZrCl_4$ in CH_2Cl_2. 2-Butyne (1.45 g, 26.8 mmol) was added to a CH_2Cl_2 (200 mL) suspension of $ZrCl_4$ (4.19 g, 26.8 mmol). The resulting deep-orange suspension was stirred at room temperature for 5 days and then reacted with THF to free the coordinated arene from the metal. The resulting THF solution contained 40% C_6Me_6, 30% 2,3,4,5-tetramethyl-2,5-dihydro-1,1′-dichlorocyclopent-3-ene (**8**), and 2% octamethylcyclooctatetraene and other unidentified products. In CD_2Cl_2, the same mixture of compounds was obtained, with 2,3,4,5-tetramethyl-2,5-dideuterio-1,1′-dichlorocyclopent-3-ene containing the deuterium atoms from the solvent.

(iii) Reaction of 3-Hexyne with $ZrCl_4$ and Preparation of 7. $ZrCl_4$ (9.0 g, 38.6 mmol) was suspended in *n*-hexane (100 mL), and the hex-3-yne was added (10.0 g, 121.9 mmol). The suspension turned yellow in a few minutes. The resulting yellow-orange solid was collected and washed with *n*-hexane (>90%). Anal. Calcd for **7**, $C_{18}H_{30}Cl_8Zr_2$: C, 30.33; H, 4.21. Found: C, 30.12; H, 3.95. The yellow-orange solid reacted with THF and gave quantitatively C_6Et_6 and $ZrCl_4(thf)_2$.

X-ray Crystallography for Complexes 3 and 5. Suitable crystals were mounted in glass capillaries and sealed under nitrogen. The reduced cells were obtained using TRACER.[7] Crystal data and details associated with data collection are given in Tables 1 and S1. Data were collected at 295 K on a single-crystal diffractometer (Rigaku AFC6S). For intensities and background, the individual reflection profiles were analyzed.[8] The structure amplitudes were obtained after the

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Table 1. Experimental Data for the X-ray Diffraction Studies on Crystalline Complexes 3 and 5

	3	**5**
formula	$C_{12}H_{18}Cl_8Zr_2$	$(C_{13}H_{20}Cl)^+(Zr_2Cl_9)^-\cdot C_6H_4Cl_2$
a, Å	19.524(4)	17.857(3)
b, Å	13.218(3)	17.838(3)
c, Å	8.355(4)	10.298(2)
V, Å^3	2156.2(12)	3280.3(10)
Z	4	4
fw	628.3	860.3
space group	*Pnma* (No. 62)	*Pnma* (No. 62)
T, °C	22	22
λ, Å	0.710 69	0.710 69
ρ_{calc}, g cm^{-3}	1.936	1.742
μ, cm^{-1}	19.48	16.24
transmission coeff	0.778−1.000	0.789−1.000
R^a	0.042	0.047
wR2^b	0.093	0.143

[a] $R = \sum|\Delta F|/\sum|F_o|$ calculated on the unique observed data [$I > 2\sigma(I)$]. [b] $wR2 = [\sum w|\Delta F^2|^2/\sum w|F_o^2|^2]^{1/2}$ calculated on the unique total data with $I > 0$.

usual Lorentz and polarization corrections,[9] and the absolute scale was established by the Wilson method.[10] The crystal quality for both complexes was tested by ψ scans, showing that crystal absorption effects could not be neglected. Data for **3** and **5** were then corrected for absorption using a semiempirical method.[11] The function minimized during the least-square refinements was $\sum w(\Delta F^2)^2$. Anomalous scattering corrections were included in all structure factor calculations.[12 b] Scattering factors for neutral atoms were taken from ref 12a for nonhydrogen atoms and from ref 13 for H. Structure solutions were based on the observed reflections [$I > 2\sigma(I)$], while the refinements were based on the unique reflections having $I > 0$. The structures were solved by the heavy-atom method starting from a three-dimensional Patterson map.[14] Refinements were done by full matrix least-squares, first isotropically and then anisotropically, for all non-H atoms except for some disordered atoms in **5**. The hydrogen atoms were put in geometrically idealized positions and introduced in the refinements as fixed atoms contributions ($U_{iso} = 0.12$ and 0.08 Å^2 for **3** and **5**, respectively). In **5**, the H atoms associated with the C7 methyl carbon atom, which lies on a mirror plane, and with the disordered carbon atoms were ignored. In the last stage of refinement, the weighting scheme $w = 1/[\sigma^2(F_o^2) + (aP)^2]$ ($P = (F_o^2 + 2F_c^2)/3$) was applied, with a resulting in the values of 0.0363 and 0.0757 for **3** and **5**, respectively. All calculations were performed by using SHELX92.[15] The final difference maps showed no unusual features, with no significant peaks above the general background.

In **3**, the high values of the U_{ij} thermal parameters of the methyl carbons suggested the presence of some disorder related to a possible noncentrosymmetric structure. Attempts to refine the structure in the noncentrosymmetric $Pna2_1$ space group were unsuccessful because of strong correlations between pseudo-symmetry-related parameters. The centrosymmetric refinement was then considered satisfactory, and the high anisotropic thermal parameters were attributed to some rotation of the hexamethylbenzene molecule in the plane perpendicular to the Zr centroid direction.

In the cation of **5**, the methyl (C9) and the methyl chloride (C8, Cl7) groups associated with the C1 carbon atom were found to be statistically distributed over two positions, called A and B, refined with site occupation factors of 0.3 and 0.2, respectively. The disordered carbon atoms were refined isotropically, while the chlorine "partial" atoms were refined anisotropically. Severe problems were experienced in refining the dichlorobenzene solvent molecule of crystallization, which was found to be heavily disordered about a center of symmetry. The best fit was obtained by considering the three independent carbon atoms over five positions (C1S−C5S) and the independent chlorine atom over seven positions (Cl1S−Cl7S). The "partial" atoms, except C2S, which was anisotropically refined with unitary site occupation factor, were isotropically refined with site occupation factors of 0.5 for the carbon atoms and 0.1429 for the chlorine atoms. Attempts to remove disorder affecting the cation and the solvent molecule by refining the structure in the noncentrosymmetric $Pna2_1$ space group were unsuccessful because of strong correlations between pseudo-symmetry-related parameters.

Final atomic coordinates are listed in Tables S3 and S4 for non-H atoms and in Tables S5 and S6 for hydrogens. Thermal parameters are given in Tables S8 and S9 and bond distances and angles in Tables S11 and S12.[16]

Results and Discussion

This investigation originated from the general observation that the polymeric form of $ZrCl_4$[17] becomes soluble in the presence of durene in a number of noncoordinating, polyhalogenated solvents.

Solubilization of Polymeric $ZrCl_4$. The solubilization of the polymeric form of $ZrCl_4$ in noncoordinating solvents is unusual. It was obtained using durene ($1,2,4,5\text{-}Me_4C_6H_2$) or mesitylene ($1,3,5\text{-}Me_3C_6H_3$) as a carrier in a series of different halogenated solvents, such as CH_2Cl_2, $CHCl_3$ $o\text{-}Cl_2C_6H_4$, and $ClCH_2CH_2Cl$. The aromatic hydrocarbon should be used in 1:1 and 1:2 Zr/arene molar ratios for durene and mesitylene, respectively, regardless of the solvent employed. The nature of the solvent is, however, crucial in the following respects: (i) the highest concentration of $ZrCl_4$ was obtained in CH_2Cl_2; (ii) solubilization occurred within 10−15 h in CH_2Cl_2 to 24 h in $o\text{-}Cl_2C_6H_4$; and (iii) the degree of rearrangement of the carrier hydrocarbon is solvent dependent (*vide infra*).

In order to understand the solubilization mechanism of $ZrCl_4$ and the rearrangement (*vide infra*) of the carrier hydrocarbon, we tried to isolate from the CH_2Cl_2/durene/$ZrCl_4$ solutions an informative compound. The solvent was evaporated to dryness and the solid recrystallized from $o\text{-}Cl_2C_6H_4$. The arene−$ZrCl_4$ interaction is depicted as reported in Scheme 1, according to the nature of **2**.

Complex **2**, which has been fully characterized including X-ray analysis,[18] contains 50% of C_6Me_5H and 50% of C_6Me_6 bound to the zirconium dimer. This was proved by decomposing **2** with THF to give quantitative $ZrCl_4(thf)_2$ and a 1:1 mixture of C_6Me_5H and C_6Me_6. Complex **2** can originate from **1** by an exchange of durene with C_6Me_5H or C_6Me_6 derived from the durene rearrangement. The complexation of the $[Zr_2Cl_8]$ dimer by an electron-rich arene causes the solubilization of the

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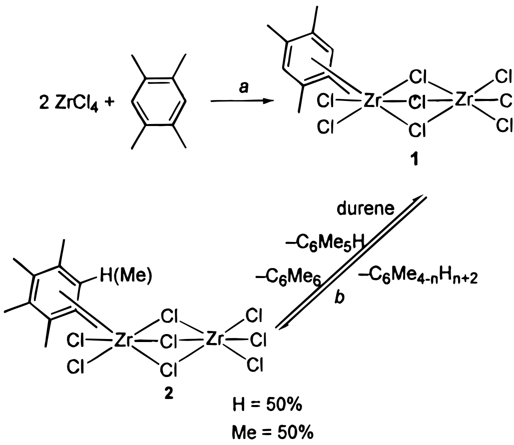
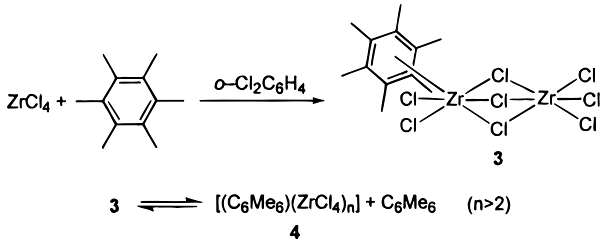
Scheme 1



Scheme 2



polymeric $ZrCl_4$. Reactions in Scheme 1 are driven to the right depending on the arene basicity. In fact, the higher basicity of durene allowed, better than in the case of mesitylene, the use of smaller amounts of hydrocarbon for shifting the reaction to the right. The more basic hexamethylbenzene, while very effective in shifting the reaction to the right, is less convenient as a $ZrCl_4$ carrier, due to the lower solubility of the corresponding arene complex. The reaction of $ZrCl_4$ with hexamethylbenzene, however, when carried out in *o*-$Cl_2C_6H_4$, became the best method for obtaining the zirconium−arene complex **3**, analogous to **2** but containing exclusively C_6Me_6 (Scheme 2).[19]

Complex **3** was obtained in very high yield as a crystalline solid following the procedure given in the Experimental Section. The structure of **3** is shown in Figure 1, and the structural parameters listed in Table 2.

Complex **3** has an imposed crystallographic mirror plane running through the zirconium atoms and the Cl1 and Cl5 chlorine atoms and bisecting the aromatic ring at the middle point of the C1−C1′ and C3−C3′ bonds. The coordination polyhedron around Zr2 is a distorted octahedron of chlorine atoms. The best equatorial plane runs through the Cl2, Cl2′, Cl4, Cl4′ atoms, defining a perfect plane (for symmetry requirements), from which Zr2 is displaced by 0.173(1) Å. The coordination geometry around Zr1 is octahedral, with the equatorial plane defined by Cl2, Cl2′, Cl3, Cl3′, Zr1 being displaced by 0.583(1) Å from it. The η^6-bonding mode of the hexamethylbenzene is supported by the narrow range of the Zr−C distances [2.723(8)−2.772(7) Å]. Zr1−Cl1 is the only bond distance significantly affected by the η^6- C_6Me_6 *trans* to it [Zr1−Cl1, 2.760(2) Å], all the other Zr−Cl distances being in the usual range.

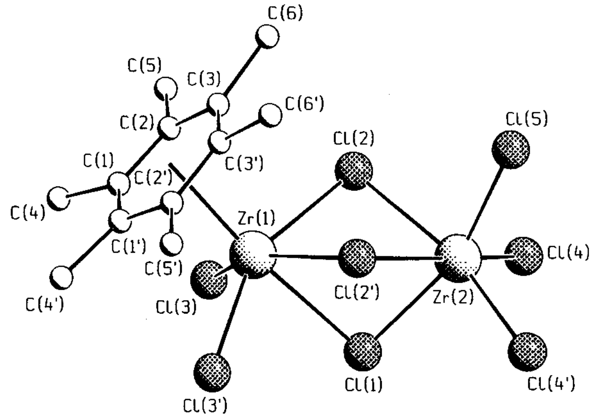


Figure 1. SCHAKAL drawing of **3**. Prime denotes a transformation of *x*, 0.5 − *y*, *z*.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 3

Zr(1)−Cl(1)	2.760(2)	Zr(1)−C(3)	2.772(7)
Zr(1)−Cl(2)	2.585(2)	Zr(2)−Cl(1)	2.518(3)
Zr(1)−Cl(3)	2.373(2)	Zr(2)−Cl(2)	2.608(2)
Zr(1)−Cb	2.369(8)	Zr(2)−Cl(4)	2.345(2)
Zr(1)−C(1)	2.750(6)	Zr(2)−Cl(5)	2.359(4)
Zr(1)−C(2)	2.721(8)		
Cl(3)−Zr(1)−Cl(3)′	94.0(1)	Cl(2)−Zr(2)−Cl(4)	91.1(1)
Cl(2)−Zr(1)−Cl(3)	87.5(1)	Cl(2)−Zr(2)−Cl(2)′	77.3(1)
Cl(2)−Zr(1)−Cl(2)′	78.2(1)	Cl(1)−Zr(2)−Cl(5)	161.4(1)
Cl(1)−Zr(1)−Cb	174.6(2)	Zr(1)−Cl(1)−Zr(2)	88.4(1)
Cl(4)−Zr(2)−Cl(4)′	99.3(1)	Zr(1)−Cl(2)−Zr(2)	90.3(1)

[a] Prime denotes a transformation of *x*, 0.5 − *y*, *z*. Cb refers to the centroid of the aromatic ring.

We should mention that d^0 η^6-arene compounds of zirconium(IV) are quite rare. Some related complexes, where zirconium has, however, additional organic ligands, diplay either a zwitterionic $[Zr(CH_2Ph)_3(\eta^6\text{-}PhBPh_3)]$,[20] or $[Zr(CH_2Ph)_3\{(\eta^6\text{-}PhCH_2B(C_6F_5)_3\}]$,[21] or a cationic $[Cp_2ZrMe_2(\eta^6\text{-arene})][MeB(C_6F_5)_3]$ form.[22]

The ^1H NMR spectrum of **3** recorded in CD_2Cl_2, however, showed three singlets at 2.55, 2.40, and 2.20 ppm, indicating the existence of an equilibrium. The presence of both **3** and free C_6Me_6 (2.20 ppm),[23] along with the absence of any insoluble $ZrCl_4$, requires the presence of a soluble species having a Zr/C_6Me_6 ratio higher than 2, herein called **4**. This can be explained if we assume an equilibrium between **3**, **4**, and free C_6Me_6. The assignment of the singlets in the ^1H NMR spectrum can be as follows: 2.55 (**4**), 2.40 (**3**), and 2.20 ppm (free C_6Me_6): The equilibrium between **3** and **4** is largely shifted to the right, as monitored by the relative intensity of the three peaks (1.5:0.2:1) for **4**/**3**/C_6Me_6. The least soluble under those conditions is **3**; thus, any attempt to isolate **4** gave exclusively **3**. Support for this hypothesis and the ^1H NMR assignments comes from a number of related experiments. Running the spectrum of **3** in the presence of a large excess of $ZrCl_4$ led to the increase of **4** with the concomitant disappearance of the signals due to free C_6Me_6 and **3**. We cannot exclude

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(19) The synthesis of the same compound, following our procedure in ref 6, has been also carried out in benzene: Calderazzo, F.; Ferri, I.; Pampaloni, G.; Troyanov, S. *J. Organomet. Chem.* **1996**, *518*, 189.

(20) Bochmann, M.; Karger, G.; Jaggar, A. J. *J. Chem. Soc., Chem. Commun.* **1990**, 1038.

(21) Pellecchia, C.; Grassi, A.; Immirzi, A. *J. Am. Chem. Soc.* **1993**, *115*, 1160.

(22) Gillis, D. J.; Quyoum, R.; Tudoret, M.-J.; Wang, Q.; Jeremic, D.; Roszak, A. W.; Baird, M. C. *Organometallics* **1996**, *15*, 3600 and references therein.

(23) The assignment made in our previous communication (ref 6) is incorrect, since the resonance at 2.55 ppm was assigned to **3** rather that to **4**, due to the low intensity of the resonance at 2.40 ppm.

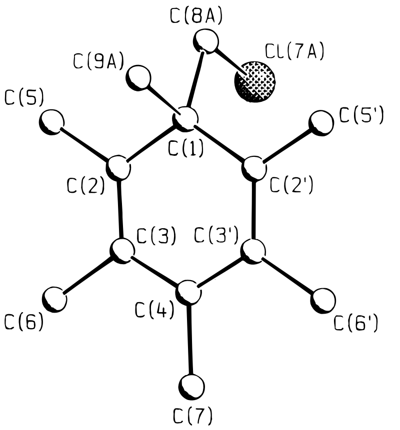
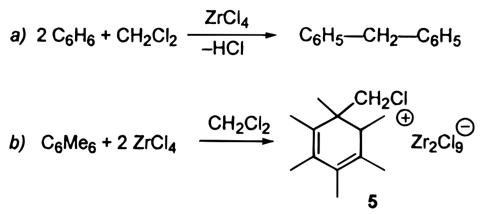


Figure 2. SCHAKAL drawing of the cation in **5**. Disorder is omitted for clarity. Prime denotes a transformation of *x*, 0.5 − *y*, *z*.

Scheme 3



for **4** the formulation of an ionic species similar to that reported in the case of titanium[24] and hafnium,[19] *i.e.*, $[(\eta^6\text{-}C_6Me_6)ZrCl_3]^+[Zr_2Cl_9]^-$, though we do not have significant support for that. We should mention, however, that, when $AlCl_3$ is added to a solution of **3** in CD_2Cl_2, the ^1H NMR spectrum shows exclusively the singlet at 2.55 ppm, though we and others[19] have isolated exclusively **3** from the same solution.

The solubilization of $ZrCl_4$ was achieved using methylbenzenes as carriers and was a function of the arene and the solvent. The use of benzene, toluene, and xylenes as either solvents or carriers was not appropriate. The solubilization of $ZrCl_4$ occurs only under conditions using halogenated solvents, such as CH_2Cl_2, $CHCl_3$, 1,2-$Cl_2C_2H_4$, and *o*-$Cl_2C_6H_4$, the best one being CH_2Cl_2 with a reasonably basic arene. On the down side, the use of CH_2Cl_2 is inconvenient in that $ZrCl_4$ can assist, in secondary reactions, the Friedel−Craft alkylation of the arene by the solvent. Scheme 3, reaction a, shows the formation of insoluble diphenylmethane derivatives in the case of benzene or other low methylated benzenes. The reaction proceeds via the preliminary addition of the $[CH_2Cl]^+$ carbocation to the arene ring. This was supported by the isolation and structural characterization of **5** derived from the alkylation of C_6Me_6.

The structure of **5** contains independent $[Zr_2Cl_9]^-$ anions,[19,25] $(C_{13}H_{20}Cl)^+$ cations, and dichlorobenzene solvent molecules of crystallization in the stoichiometric molar ratio of 1:1:1. Figure 2 shows a picture of the cation, while the figure and structural parameters of the anion are available as Supporting Information. The cation possess a crystallographically imposed mirror plane running through the C1, C4 *p*-carbon atoms though the methyl (C9) and chloromethyl (C8, Cl7) groups on C1. In spite of disorder affecting the substituents and influencing the accuracy of the crystal structure analysis, bond distances and angles involving the C1 carbon atom are consistent with an sp^3 character. The bonding sequence shown for **5** is in agreement with the C−C bond distances [C1−C8A, 1.46(3); C1−C9A, 1.76(3); C2−C3, 1.355(13); C3−C4, 1.396(12); and C1−C2, 1.501(12) Å].

As far as the solubilization of $ZrCl_4$ is concerned, we can summarize that durene and mesitylene are probably the best carriers when used in CH_2Cl_2, though such a solvent may, to a limited extent, show secondary reactions involving the hydrocarbon. The *o*-$Cl_2C_6H_4$ does not produce any secondary reaction but is much less efficient as a solvent for the arene−$ZrCl_4$ entities. The use of other halogenated solvents, such as $ClCH_2CH_2Cl$ and $CHCl_3$, has disadvantages similar to those of CH_2Cl_2, namely the metal-assisted Friedel−Craft reaction. We can conclude that the solubilization of the polymeric form of $ZrCl_4$ is associated with the occurrence of the reactions in Scheme 2 and with the presence of species like **3** and **4**. This requires the use of a basic arene and a halogenated solvent.

Methyl Transfer in Methylbenzenes Promoted by $ZrCl_4$. We mentioned earlier that, during the arene-assisted solubilization of $ZrCl_4$ and the isolation of the η^6-arene complexes of zirconium, we observed a large extent of methyl transfer in the methylbenzenes employed. This type of activity is a unique property of $ZrCl_4$ and has never been observed with the few other η^6−arene zirconium(IV) complexes so far identified.[20−22] Further, we found that the activity of $ZrCl_4$ in promoting the rearrangement of methylbenzenes is a function of the reaction solvent, a issue which is discussed here. As we mentioned above, $ZrCl_4$ dissolves very well in CH_2Cl_2 in a few hours upon addition of an equimolar amount of durene. When we examined the solution after 24 h, we found that the molar ratio between the methylbenzenes $C_6Me_3H_3$, $C_6Me_4H_2$, C_6Me_5H, and C_6Me_6 was 1:6.5:4:0.7. When the solution was kept standing for a longer time (2 months), we observed a significant increase in the polymethylated forms ($C_6Me_4H_2/C_6Me_5H/C_6Me_6$ = 1:2.5:2). The isomeric distribution of the tri- and tetramethylbenzenes is not considered here as being relevant. The quantitative determination of the hydrocarbon ratios has been carried out by reacting the hydrocarbon solution with THF and then removing $ZrCl_4(thf)_2$ and analyzing the THF solution. The same kind of rearrangement was observed using mesitylene or pentamethylbenzene (see the Experimental Section). In this kind of analysis, it was rather intriguing to get a consistent balance of the methyl groups, since we found essentially the polymethylated form but not the corresponding demethylated forms in the expected amounts. This is due to the hardly definible amount of oligomeric methylene-bridged arenes forming from the demethylated forms reacting with CH_2Cl_2 in the presence of $ZrCl_4$. As a matter of fact, running the same reaction in the presence of benzene, toluene, or xylenes, we discovered the formation of dimeric/oligomeric diphenylmethane derivatives, as reported in Scheme 3 (reaction *a*), and it is this that is responsible for the absence of the appropriate demethylated forms in the analyzed solution.

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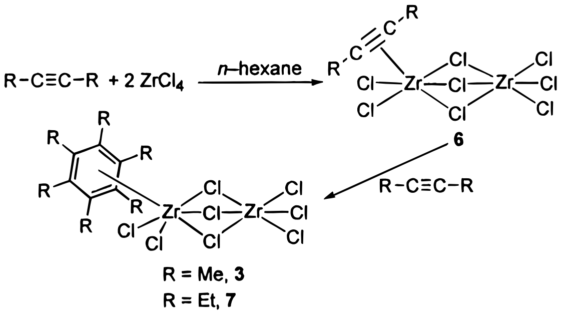
The same rearrangement reactions, carried out in other solvents, though slower, do not show any alkylation of the hydrocarbon, *i.e.*, the formation of diphenylmethanes. Therefore, the balance of the methyl groups was rather correct in the rearrangement of durene carried out, *i.e.*, in CCl_4. Other solvents are involved in the formation of byproducts. In $CHCl_3$ and $ClCH_2CH_2Cl$, we observed the same kind of methylbenzene distribution as we found in CH_2Cl_2, except for the appearance in both cases of significant amounts of C_6Me_5Et (see Experimental Section). The genesis of the ethyl substituent from the solvent can be easily understood in the latter case, while a more complex hypothesis is required for the reaction carried out in $CHCl_3$. *o*-$Cl_2C_6H_4$ seems to be the most innocent solvent in the rearrangement reactions, but it is the last efficient in assisting the reaction. In the latter case, though under severe conditions (100 °C, days) the only byproducts formed in the reaction between $ZrCl_4$ and durene were small amounts of methyldichlorobenzene derivatives. The use of a chlorinated solvent seems to be almost compulsory, as attempts to move to aliphatic hydrocarbon solutions were very ineffective.

The experiments mentioned above were carried out with the alkylated benzenes and $ZrCl_4$, in the 1:1 or 2:1 molar ratio. However, we are left with some unanswered questions concerning the methyl transfer reaction: What is the correct mass balance of the methyl groups? Is the methyl transfer an equilibrium reaction, in the absence of byproducts? Can $ZrCl_4$ function as a catalyst for the methyl transfer reaction?

Answers to these questions have been obtained by running the methyl redistribution reaction in the presence of $ZrCl_4$ added to neat methylbenzenes. In such cases, we obtained a correct balance of the methyl groups distributed over all the methylbenzenes present. The reaction rate, which is usually rather slow, was increased by increasing the temperature to 90 °C (see the Experimental Section). Second, the reaction in neat hydrocarbons reaches the equilibrium of the methyl distribution products (see the Experimental Section) in the absence of any irreversible byproduct. This has been proved using either durene or isodurene, or an equimolar amount of mesitylene and pentamethylbenzene, or equimolar amounts of mesitylene, durene, and pentamethylbenzene. In these experiments, we obtained the same equilibrium composition. Such experiments have also been investigated under catalytic conditions. The reaction, in fact, has been performed using a $ZrCl_4$/durene 1:1 molar ratio, followed by continuous addition of durene until a 1:100 ratio was reached, and the system still continued to reach the equilibrium. In another experiment, we ran the reaction at a $ZrCl_4$/durene ratio of 1:20 and showed that the isolated zirconium adduct was still able to catalyze the rearrangement of durene.

A rather intriguing question concerns the mechanism of the zirconium-assisted catalytic methyl transfer with methylbenzenes. We should mention that the intramolecular methyl transfer with durene was observed previously by action of concentrated sulfuric acid, the so-called Jacobsen reaction.[26,27a] Contrary to our results, in the alkylation and dealkylation reactions promoted either by H_2SO_4 or Lewis acids, such as H^+, BF_3, and AlX_3, the methyl migration occurs almost exclusively in an intramolecular fashion.[27b] Such reactions are believed to proceed via a carbocation intermediate, as is the case in alkylbenzene rearrangements promoted by the $TaCl_5-CH_2Cl_2$[28a] system and in alkane isomerization assisted by $CX_4{\cdot}AlX_3$.[28b] Unlike these cases, we believe that, in our reaction, a methyl group is transferred intermolecularly from a methyl-donor free arene to a methyl-accepting metal-bonded arene via the intermediacy of a charge-transfer complex between an electron-poor and an electron-rich arene. In addition, rearrangement of methylbenzenes carried out in hydrocarbons implies that the active species is most likely the neutral arene complex **3** or **4**. When the reaction was performed at 100 °C in 1,2-$Cl_2C_6H_4$ with C_6Me_6, which cannot rearrange, the formation of pentamethylbenzene and monomethyl-1,2-dichlorobenzenes was observed.

Scheme 4

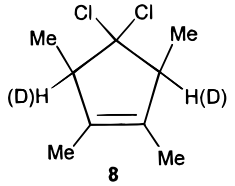


We must emphasize at this stage the unique property of $ZrCl_4$, which, via a quite rare C−C bond activation and cleavage process, assists intra- and intermolecular methyl transfers.

Trimerization of Internal Alkynes. Keeping in mind the unexpected high stability of an η^6-arene-zirconium(IV) complex like **3**, we examined the reaction of $ZrCl_4$ in an innocent solvent, *i.e.*, *n*-hexane, with the internal alkynes 2-butyne and 3-hexyne. The reactions, displayed in Scheme 4, led quantitatively to the corresponding zirconium(IV)-arene complexes **3** and **7**.

For the occurrence of the reaction, we believe that an interaction of the carbon−carbon triple bond with the polymeric $ZrCl_4$ would free the Zr_2Cl_8 dimer, like in **6** (Scheme 4), which promotes the cycloaddition of the bound to the free alkyne.

The coupling between two alkynes preceeding the formation of the arene ring has been shown by the interception of **8** when the reaction of $ZrCl_4$ with 2-butyne was carried out in CH_2Cl_2 or CD_2Cl_2.



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The cyclooligomerization reaction proceeds by a very small extent behind the formation of hexamethylbenzene, with the obtention of very small amounts of octamethylcyclooctatetraene. The reactions in Scheme 4, which are stoichoimetric, are driven by the formation of stable η^6-arene complexes.

Rare examples of metal halide-promoted cycloologomerization of internal acetylenes, *i.e.*, but-2-yne, have been observed, making use of $AlCl_3$,[29] $NbCl_5$, and $TaCl_5$.[30] In spite of the impressive number of proposed mechanisms for acetylene cyclooligomerization, many of them are inappropriate in our case.[31] They involve the following: (i) changes to the oxidation state of the metal (oxidative addition, reductive elimination); (ii) preliminary insertion of the C−C triple bond into the M−Cl bond, a mechanism we ruled out in a detailed study of the reaction between $TiCl_4$ and isocyanides concerning the Passerini reaction;[32] and (iii) the intermediate formation of a metalloalkylidene or -alkylidyne.

Conclusions

The discovery that $ZrCl_4$ forms labile η^6-arene complexes in noncoordinating halogenated solvents has led to a source of soluble $ZrCl_4$ available for synthetic purposes. In the meantime, it has been observed that such η^6-arene−zirconium complexes function as catalysts both in halogenated solvents and in neat hydrocarbons for the rearrangement of polymethylbenzenes assisting intra- and intermolecular methyl transfer, in the Jacobsen-type reaction[26,27] but under very mild conditions. The particularly high stability of the zirconium(IV)−arene complexes is the driving force in assisting the $ZrCl_4$-induced trimerization of internal alkyne to the corresponding hexaalkylbenzenes.

Acknowledgment. We thank the Fonds National Suisse de la Recherche Scientifique (Bern, Switzerland, Grant No. 20-46’590.96) and Ciba Specialty Chemicals (Basle, Switzerland) for financial support.

Supporting Information Available: ORTEP drawings; tables of experimental details associated with data collection and structure refinement, atomic coordinates, hydrogen atom coordinates, thermal parameters, and bond distances and angles for **2**, **3**, and **5**; X-ray crystallography for **2**; and description of the structure for **5** (12 pages). Ordering information is given on any current masthead page.

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