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EXCHANGE REACTIONS BETWEEN DIALKYLZIRCONOCENE AND ALKYLALUMINIUM COMPOUNDS

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Abstract—The dimethylmetallocenes $Cp_2Zr(^{13}CH_3)_2$, $(Me_5Cp)_2Zr(^{13}CH_3)_2$, $(indenyl)_2Zr(^{13}CH_3)_2$, $Me_2Si(C_5H_4)_2Zr(^{13}CH_3)_2$ and $Cp_2Hf(^{13}CH_3)_2$ undergo degenerate methyl exchange with the methyl-acceptor materials Me_6Al_2, $(MeAlO)_x$ and MeAl(2,6-di-t-butyl-4-methylphenoxy)$_2$. Free energies, enthalpies and entropies of activation for these processes have been obtained in two solvents by ^{13}C NMR. Increased steric hindrance at zirconium increases the free energy of activation. There appears not to be a correlation with electronic effects as assessed by gas phase appearance potentials for the $(P-CH_3)^+$ ions.

The role of cationic, coordinatively unsaturated zirconium(IV) compounds, as the active species in the catalytic polymerization of ethylene, has recently received considerable attention.[1,2] The cation $Cp_2ZrCH_3^+$ is of special interest. In fluid solution, it may be generated by oxidation or protonation of Cp_2ZrMe_2 but it has been characterized only in solvated form, for example, as $Cp_2ZrMe(S)^+$ ($S = CH_3CN$ or THF).[1a] In the gas phase, successive detachment of methyl groups occurs upon electron impact ionization to afford Cp_2ZrMe^+ and Cp_2Zr^+.[3] It is open to question whether Cp_2ZrMe^+ is stable in solution in the absence of coordinating solvents and if it is, whether it might not exhibit an agnostic Zr—H—CH_2 interaction involving the α-hydrogen on the methyl group.[4] Previously, we reported that Cp_2ZrMe_2 readily exchanges methyl groups with Me_6Al_2 and that it reacts with $(Me_2AlEt)_2$ in neat Me_6Al_2 to form $Cp_2Zr(\mu\text{-}CH_3)(\mu\text{-}1,2\text{-}CH_2CH_2)AlMe_2$.[5] We surmise that methyl exchange may proceed via an ionic intermediate as shown conceptually (i.e. complexation by solvent or by Al_2Me_6 is neglected) in eq. (1):

$$Cp_2ZrMe_2 + Me_3Al \rightleftharpoons Cp_2ZrMe^+AlMe_4^- . \quad (1)$$

This equilibrium lies far to the left. In principle, eq. (1) is generally applicable to any Lewis acid capable of (formally) accepting a CH_3^- group. In order to gain further understanding of the interaction of Cp_2ZrMe_2 with such Lewis acids, we have undertaken a study of methyl exchange reactions with dimethylzirconocene and related compounds with a series of methylaluminium reagents.

RESULTS AND DISCUSSION

Rates of methyl exchange in the systems reported here were studied in two ways; $Cp_2Zr(^{13}CH_3)_2$ was combined with the methylaluminium compound in toluene and diminution of the Zr—CH_3 signal was followed as a function of time by ^{13}C NMR spectroscopy. In some cases, equilibrium was reached in too short a time (< 5 min) for this technique to be useful. In these situations, rates usually could be obtained by total line-shape analysis of the Zr—CH_3 resonance which was exchange-broadened. The methylaluminium compounds were used in large excess, typically 10–20 fold (cf. Experimental), so that kinetics of the exchange reactions are pseudo-first order with respect to the zirconium compound. Toluene was selected as the least interactive solvent capable of producing requisite concentrations of the reactants notwithstanding that it may weakly solvate three-coordinate aluminium(III) (*vide infra*). In the context of eq. (1), we refer to Cp_2ZrMe_2 and its congeners as methyl *donors*, and to Me_3Al and its congeners as methyl *acceptors*. This allows one to view methyl transfer processes in the framework of more generalized acid–base chemistry. The reactions studied are fully reversible and, in the kinetic experiments, no new products are detectable by NMR.

The aluminium-containing methyl acceptors employed in this work are Me_6Al_2, MeAl(BHT)$_2$

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(BHT = 2,6-di-t-butyl-4-methylphenoxy) and $(MeAlO)_x$. The first of these, Me_6Al_2, exists primarily as a methyl-bridged dimer. Nevertheless, the energetics of bridge–terminal methyl exchange in the dimer are quite solvent-dependent, differing significantly even between cyclopentane and toluene. It is thought that toluene may behave as a π-base toward $AlMe_3$ and thus lead to higher steady-state concentrations of solvated monomer.[6] We believe that it is with monomeric, i.e. solvated, Me_3Al that methyl exchange occurs and that the presence of three-coordinate aluminium is necessary for this reaction (*vide infra*). For this reason, we refer below to Me_3Al and express aluminium concentrations in terms of this monomer. Methylaluminoxane, $(MeAlO)_x$, is a substance produced by the controlled hydrolysis of Me_6Al_2. It is difficult to purify and characterize. Even today, its nature remains an enigma; it is not established whether it is a single substance or whether it has a static or a dynamic structure. However, acting with Cp_2ZrMe_2, it is a powerful if not unique, co-catalyst for the polymerization of ethylene.[7] Its inclusion in this study is warranted on technological grounds alone. Methylaluminoxane represents a special case of methyl acceptor molecules in two regards. First, its reaction with Cp_2ZrMe_2 in toluene leads to slow phase separation; a denser, orange layer contains all the $(MeAlO)_x$. A kinetic study in such a heterogeneous system is fraught with difficulty. Of the compounds studied, only Cp_2HfMe_2 remained homogeneous in toluene in the presence of $(MeAlO)_x$. Methyl exchange chemistry involving $(MeAlO)_x$ was, therefore, examined in dichloromethane. This choice of solvent limits the accessible temperature range so that only free energy data are available (*vide supra* and Experimental). Second, $(MeAlO)_x$ (unlike other organoaluminium compounds studied) and Cp_2ZrMe_2 undergo a *non*-equilibrium reaction that is much slower than the methyl exchange chemistry and which, therefore, does not affect the kinetic results. This reaction is still under investigation and will be described in detail elsewhere. Midway between Me_3Al and $(MeAlO)_x$ is $MeAl(BHT)_2$. The steric effects of the BHT groups prevent dimerization and this compound has been shown to be monomeric by X-ray crystallography (in the solid state)[8] and ^{27}Al NMR spectroscopy (in solution).[9] It is an uncommon and unambiguous example of a material containing three-coordinate aluminium for which reason it has been studied here. We consider, notwithstanding the ability of aryloxy groups to π-backbond, that it may be a heuristically useful model for $(MeAlO)_x$ for it features a MeAl moiety bonded to two oxygen atoms.

The dimethylmetallocene compounds employed include $Cp_2Zr(^{13}CH_3)_2$, $(Me_5Cp)_2Zr(^{13}CH_3)_2$, $(indenyl)_2Zr(^{13}CH_3)_2$, $Me_2Si(C_5H_4)_2Zr(^{13}CH_3)_2$, $(Me_3SiCp)_2Zr(^{13}CH_3)_2$ and $Cp_2Hf(^{13}CH_3)_2$. Using dimethylzirconocene as a reference point, the pentamethylcyclopentadienyl analogue is expected to be considerably more sterically hindered. Also, X-ray photoelectron spectroscopic studies indicate that the metal centre is much more electron-rich in this compound, perhaps approaching zirconium(III).[10] The η^5-indenyl ligand *can*, optionally, "slip" or move laterally so that C_9H_7 becomes a four-electron donor but in a $\leqslant$16-electron system, it is more probable that the η^5 structure is more stable and that the annelated benzo ring will be electron-withdrawing.[11] On the basis of a curious shielding of the C_1 (*ipso*) carbon atom in $Me_2Si(C_5H_4)_2ZrCl_2$ (this shielding is also seen in the $ZrMe_2$ analogue) as well as cyclic voltammetry results, it was concluded that the bridging Me_2Si group is electron-withdrawing.[12] Chemical and structural studies on $[Me_2Si(Me_4C_5)_2ThH_2]_2$ indicate that Me_2Si ring chelation significantly opens the thorium coordination sphere and is associated with enhanced reactivity of Th—H and Th—C σ bonds lying in the equatorial girdle.[13] Thus, the structural modifications to Cp_2ZrMe_2 available in the series under study here can alter relative reactivity through either steric or electronic effects. We shall argue below that the former is more important. It is difficult to predict with confidence the relative reactivity of Cp_2ZrMe_2 and Cp_2HfMe_2 towards a methyl acceptor. It has been noted that the metal–carbon σ bonds in the latter are short[14] and perhaps, therefore, more stable than in the zirconium analogue.

The free energies, enthalpies and entropies of activation of reversible methyl exchange between these materials and Me_3Al (*vide supra*) and $MeAl(BHT)_2$ in toluene are shown in Table 1. All of the reactions exhibit large, negative entropies of activation. This indicates that the transition state has a substantial loss of translational and rotational freedom, consistent with the bimolecular nature of the reaction.

The trends in free energies of activation reveal several correlations between reactivity and structure. First, the relative order of strength of methyl acceptors decreases in the order $(MeAlO)_x > Me_3Al > MeAl(BHT)_2$. This is in agreement with the expectation that two adjacent, electronegative oxygen atoms will increase Lewis acidity, and with the finding that, based on ^1H NMR chemical shifts and changes in ν_{CN} in benzonitrile complexes, that $(Me_2Al)_2O$ is a stronger Lewis acid than Me_3Al.[15] The alkoxide derivative MeAl

Table 1. Free energies,[a] enthalpies and entropies of activation of methyl exchange in toluene[b]

Methyl donor	Methyl acceptor Me_6Al_2	 $MeAl(BHT)_2$
Cp_2ZrMe_2	$\Delta G^\ddagger$ 16.7 $\Delta H^\ddagger$ 11 $\Delta S^\ddagger$ −21	$\Delta G^\ddagger$ 22.4 $\Delta H^\ddagger$ 5 $\Delta S^\ddagger$ −59
$(Me_5Cp)_2ZrMe_2$	$\Delta G^\ddagger$ 22.3 $\Delta H^\ddagger$ 9 $\Delta S^\ddagger$ −46	No exchange $\leqslant$80°C
$Me_2Si(C_5H_4)_2ZrMe_2$	$\Delta G^\ddagger$ 14.3 $\Delta H^\ddagger$ 8 $\Delta S^\ddagger$ −22	$\Delta G^\ddagger$ 21.5 at 22°C
$(indenyl)_2ZrMe_2$	[c]	$\Delta G^\ddagger$ 27.7 at 81°C
$(Me_3SiCp)_2ZrMe_2$	No exchange $\leqslant$81°	$\Delta G^\ddagger$ 27.7 at 81°C
Cp_2HfMe_2	$\Delta G^\ddagger$ 20.4 $\Delta H^\ddagger$ 12 $\Delta S^\ddagger$ −30	No exchange

[a] At 22°C.

[b] Free energies and enthalpies in kcal mol^{-1}, entropies in cal K^{-1} mol^{-1}.

[c] Too slow for DNMR, too fast for kinetics; $\Delta G^\ddagger$ = 17–19 kcal mol^{-1} at 22°C.

$(BHT)_2$ is especially interesting. $\Delta S^\ddagger$ for methyl exchange is unusually large, −59 e.u., but $\Delta H^\ddagger$, 5 kcal mol^{-1}, is quite small. We interpret these data as meaning that a large fraction of the free energy of activation goes towards twisting the 2,6-di-t-butyl-4-methylphenoxy groups so that the peripheral alkyl groups do not, as the transition state is approached, block access to aluminium. This aluminium atom, being three-coordinate, is expected to be a powerful Lewis acid and accordingly, the activation enthalpy for transfer of a methyl group to it should be, and is, very low.

Again using free energies of activation to illustrate trends, methyl donor strength decreases in the order $Me_2Si(C_5H_4)_2ZrMe_2$ > $(indenyl)_2ZrMe_2$ > Cp_2HfMe_2 > $(Me_5Cp)_2ZrMe_2$.

Free energies of activation at 22°C for methyl exchange between some dimethylmetallocenes and $(MeAlO)_x$ in dichloromethane are shown in Table 2. In contrast to data for Me_3Al in toluene, they are very similar, ranging from 13 to 15 kcal mol^{-1}. We interpret this as a levelling effect; that is, the tendency of a very strong Lewis acid to make all bases appear to be of equal strength. This phenomenon has been long recognized in proton donors and acceptors.[16]

With a weak methyl acceptor, solvent effects are manifest. It would be expected that going from toluene to the more polar solvent dichloromethane should accelerate methyl transfer between Cp_2ZrMe_2 and $MeAl(BHT)_2$ if the transition state involved appreciable charge separation; otherwise, the solvent change should have minimal effect. In fact, the exchange rate in CH_2Cl_2 is immeasurably slow. We suggest that this striking change is due to weak complexation between $MeAl(BHT)_2$ and the lone electron pairs on chlorine in CH_2Cl_2. Organometallic complexes containing halocarbon donors are now well known.[17] Solvent effects exhibited by the stronger methyl acceptor $(MeAlO)_x$ are much less pronounced. For Cp_2HfMe_2, $\Delta G^\ddagger$ at 22°C is 15.3 kcal mol^{-1} ($\Delta H^\ddagger$ = 7 kcal mol^{-1}, $\Delta S^\ddagger$ = −29 e.u.) in toluene and 15.4 kcal mol^{-1} in dichloromethane.

Table 2. Free energies of activation for methyl exchange with $(MeAlO)_x$ in dichloromethane at 22°C

Compound	$\Delta G^\ddagger$ (kcal mol^{-1})
Cp_2ZrMe_2	13.9
$(Me_5Cp)_2ZrMe_2$	13.4
$(indenyl)_2ZrMe_2$	13.8
$Me_2Si(C_5H_4)_2ZrMe_2$	13.0
Cp_2HfMe_2	15.4
$(Me_3SiCp)_2ZrMe_2$	Irreversible reaction

In order to help estimate the relative roles of steric and electronic effects in these methyl exchange processes, we have measured the gas phase appearance potentials for ions formed by loss of CH_3^- from dimethylmetallocenes as illustrated in eq. (2):

$$Cp_2ZrMe_2 \rightarrow Cp_2ZrMe^+ + CH_3^- . \qquad (2)$$

This was carried out in a mass spectrometric experiment by plotting the integral of the $(P-CH_3)^+$ ion as a function of ionizing voltage and extrapolating the linear portion of the curve to zero intensity, at which point the intercept is the appearance potential. The reaction in eq. (2) can be viewed as proceeding in several steps. These are (1) homolytic cleavage of a Zr—CH_3 bond, (2) ionization of the resulting $Cp_2ZrCH_3^{\bullet}$ radical and (3) electron capture by $CH_3^{\bullet}$. If it is assumed that, in the group of structurally similar compounds studied, the Zr—CH_3 bond dissociation energies are essentially constant, then trends in these appearance potentials reflect relative stabilities of the $(P-CH_3)^+$ ion, that is, the ability of a Cp_2ZrR group to support a positive charge. Typical data for $Me_2Si(C_5H_4)_2ZrMe_2$ are shown in Fig. 1 and appearance potentials are collected in Table 3. Their estimated uncertainties are ±0.15 eV. In the zirconium compounds, there is no apparent correlation between appearance potentials for $(P-CH_3)^+$ and free energies of activation for methyl exchange. $(Me_5Cp)_2ZrMe_2$ should, because of the electron-releasing effect of the 10 ring-methyl groups, form a more stable $(P-CH_3)^+$ ion than Cp_2ZrMe_2,[10] and this ion does have, accordingly, a 0.5 eV lower appearance potential. But in fact, $(Me_5Cp)_2ZrMe_2$ undergoes methyl exchange with both Me_3Al and $MeAl(BHT)_2$ more slowly than does Cp_2ZrMe_2. As noted above, $(Me_5Cp)_2ZrMe_2$ is sterically more hindered than Cp_2ZrMe_2 and $Me_2Si(C_5H_4)_2ZrMe_2$ less so, and this is reflected in values of $\Delta G^{\ddagger}$ for methyl exchange. Conspicuous is $(Me_3SiCp)_2ZrMe^+$ which has a quite low appearance potential, yet $(Me_3SiCp)_2ZrMe_2$, which contains two large, bulky trimethylsilyl groups, has a large $\Delta G^{\ddagger}$ for exchange with $MeAl(BHT)_2$. This raises the question of whether this ion might not be stabilized in the gas phase by intramolecular Zr—H—C agnostic interactions. We believe that the major determinant of methyl donor ability of a dimethyl zirconium metallocene is comprised of steric effects. The hafnium compound Cp_2HfMe_2 forms a $(P-CH_3)^+$ ion with a lower appearance potential than any of the zirconium compounds studied, except $(Me_3SiCp)_2ZrMe_2$, yet it exchanges more slowly. This may be associated with a higher Hf—CH_3 bond energy noted above. In qualitative agreement with this, we find that the asymmetrical and symmetrical M—CH_3 stretching frequencies in Cp_2MMe_2 are 462 and 422 cm^{-1}, respectively (M = Zr); and 470 and 441 cm^{-1} (M = Hf), cf. Table 3.

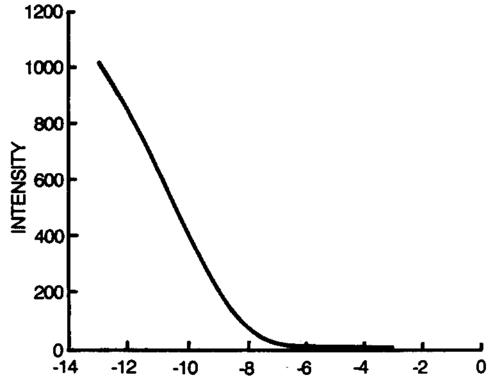

Fig. 1. Plot of integrated ion current of $(P-{}^{13}CH_3)^+$ from $({}^{12}CH_3)_2Si(C_5H_4)_2Zr({}^{13}CH_3)_2$ vs ionizing voltage.

Table 3. Gas phase appearance potentials for $(P—CH_3)^+$ ions and metal–carbon stretching frequencies

Compound (precursor)	$\nu_{M—C}$ (as) (cm^{-1})	$\nu_{M—C}$ (s) (cm^{-1})	E_{app} (eV)
Cp_2ZrMe_2	462	422	8.5±0.15
$(Me_5Cp)_2ZrMe_2$	458	427	8.0
$Me_2Si(C_5H_4)_2ZrMe_2$	458	Not resolved	8.1
$(indenyl)_2ZrMe_2$	464	439	8.1
$(Me_3SiCp)_2ZrMe_2$	462	Not resolved	6.9
Cp_2HfMe_2	470	441	6.9

What chemical and structural features of aluminium are needed to observe rapid methyl exchange? The issue of reactivity and solvation of Me_6Al_2 has been mentioned above. Aluminium compounds in which four-coordination is maintained by strong bridge bonds, e.g. $(Et_2AlOEt)_2$ and $\{[N(CH_2CH_2O)_3]Al_2Me_3\}_2$[19] are unreactive toward Cp_2ZrMe_2. In contrast, methyl exchange does occur in compounds in which aluminium participates in weak bridge bonds, e.g. $(Me_2AlCl)_2$ (Cp_2ZrCl_2 is produced) or where dissociation of an ancillary ligand is possible, e.g. $Me_2Al(BHT) \cdot PMe_3$.[8] We therefore suggest that three-coordinate aluminium acts as a methyl acceptor with Cp_2ZrMe_2 and its analogues.

Another way of assessing electronic effects, one that leads to the same general conclusions, is X-ray photoelectron spectroscopy (XPS).[10] Here, chloro- rather than methylzirconocenes were studied because the former are less volatile and less susceptible to air oxidation. We consider it probable that zirconium core levels in the two types of compounds would parallel one another. The Zr($3d_{5/2}$, $3d_{3/2}$) binding energies in Cp_2ZrCl_2, $Me_2Si(C_5H_4)_2ZrCl_2$ and $(Me_3SiCp)_2ZrCl_2$ are 182.0, 184.4; 182.7, 185.1; and 181.8, 184.1±0.1 eV, respectively. This is consistent with the NMR data which indicate that introduction of a Me_2Si bridge into Cp_2ZrCl_2 reduces electron density at the metal centre.[12] The electron-releasing effect of the Me_3Si group as assessed by XPS is almost insignificant. The Cl($2p_{3/2}$) binding energies in the same series of compounds, 199.0, 199.7 and 198.5 eV, parallel the zirconium core energies. Again, if electronic effects contributed significantly to activation energies for methyl exchange, it would be difficult to explain why $(Me_3SiCp)_2ZrMe_2$ exchanges as slowly as it does.

We have also investigated by NMR the reactions of Cp_2ZrMe_2 with other, potential, Group III acceptor compounds. No alkyl exchange is observed with Me_3Ga or Et_3B. Reasoning that substitution of alkyl by alkoxy on boron might increase methyl acceptor strength, Et_2BOMe was examined, but another reaction, methyl–methoxy exchange, eq. (3), supervenes. It is calculated to be exothermic by 44 kcal mol^{-1}.[18]

$$Cp_2ZrMe_2 + 2Et_2BOMe \rightarrow Cp_2Zr(OMe)_2 + 2Et_2BMe. \quad (3)$$

The product Et_2BMe may be recognized by its ^{11}B chemical shift, 86 ppm;[20] $Cp_2Zr(OMe)_2$[21] has $\delta^{13}C$ 61.3, 111.9 and $\delta^{91}Zr$ −447 ppm ($w/2$ 6500 Hz at 55°C). In neat Et_2BOMe, the kinetics of the above reaction are pseudo first-order in Cp_2ZrMe_2 and $k = 1.5 \times 10^{-4}$ min^{-1} at 22°C; $\Delta H^{\ddagger} = 15$ kcal mol^{-1} and $\Delta S^{\ddagger} = -33$ e.u. This exchange reaction involves as an intermediate $Cp_2Zr(OMe)Me$ which can be recognized by its NMR spectra: δ^1H 5.77, 3.65 (OMe), 0.23 (Zr—CH_3); $\delta^{13}C$ 111.9, 63.3 (OMe), 19.0 (Zr—Me); $\delta^{91}Zr$ −127 ($w/2$ 2500 Hz). Cleavage of B—O bonds by Cp_2ZrMe_2 appears to be a general reaction and also occurs with $(C_8H_{14}B)_2O$, $(MeBO)_3$ and $(CF_3SO_3)_3B$. It emerges that $Cp_2Zr(OMe)_2$ undergoes facile exchange of methoxy groups with Et_2BOMe. In neat Et_2BOMe, i.e. under pseudo-first order conditions, thermodynamic parameters determined by ^{13}C DNMR spectroscopy are $\Delta H^{\ddagger} = 7$ kcal mol^{-1} and $\Delta S^{\ddagger} = -21$ e.u.

Dimethylzirconium and -hafnium metallocenes are thus seen to undergo facile exchange of alkyl groups with methylaluminium reagents.[22] This exchange is general in that other (for example ethylaluminium) compounds may be used, but in this case the products are unstable because Cp_2ZrR_2, in which the R group has β-hydrogens, undergoes β-elimination to form olefin and numinous zirconium hydrides. A survey of the kinetics of degenerate methyl exchange reactions indicates that steric effects are important determinants of the free energy of activation relative to electronic effects. We suggest that, according to Hammond's postulate, the transition states in the endothermic equilibrium reactions of the type depicted in eq. (1) lie close along the reaction coordinate to the products. If we assume that a linear free energy relationship of the Brönsted type obtains (a reasonable postulate given the deliberately narrow structural range of the compounds studied), then the activation parameters for methyl exchange can provide insight into the effects of modification of the metallocene ligand set, as well as the choice of Lewis acid, on the position of the equilibrium depicted in eq. (1). This in turn may reflect the relative amounts of catalytically active metallocene cations formed in these systems.

EXPERIMENTAL

^1H, ^{11}B, ^{13}C and ^{91}Zr NMR spectra were recorded on a Varian XL-400 instrument, with a ^1H/multinuclear switchable probe, whose ^1H operating frequency is 400 MHz. External neat $BF_3 \cdot OEt_2$, $(CH_3)_4Si$ in $CDCl_3$ and 1 M Cp_2ZrBr_2 in THF were used as references with positive shifts being to lower field. Appearance potential measurements were made using a Nicolet model 2000 Fourier transform mass spectrometer and associated software. In some cases [$(Me_5Cp)_2ZrMe_2$, $Me_2Si(C_5H_4)_2ZrMe_2$] the Zr—$^{13}CH_3$ derivatives were used to ensure that ions actually derived from the loss of the Zr—Me group were observed. Integrals of the ^{90}Zr isotopomers were measured. Because no significant ion current at 1 mass unit lower was seen, one can be confident that the ions observed were not due to loss of $^{12}CH_3$ from the ^{91}Zr isotopomer. In the case of $(Me_5Cp)_2ZrMe_2$, the $(P-2CH_3)^+$ ion cluster appears to contain ions from loss of ring-methyl groups.

X-ray photoelectron spectra were obtained on a Surface Science Laboratories SSX-100-1 instrument using monochromatic Al-$K_{\alpha_{1,2}}$ radiation. For high resolution spectra, the concentric hemispherical analyser was operated at 25 eV pass energy. The binding energy scale is such that the Au($4f_{7/2}$) photoelectron line occurs at 83.96±0.1 eV and the difference between the Cu($2p_{3/2}$) and 3s photoelectron lines is 810.0±0.1 eV. The C(1s) spectra showed only one component and, for charge referencing purposes, it is assigned an energy of 285.0 eV.[23]

The solvents toluene and 1,2-dimethoxyethane, and dichloromethane were distilled under nitrogen from Na–K alloy and CaH_2, respectively. Reactants were weighed in a nitrogen-filled dry-box and combined with the solvent in NMR tubes fitted with re-sealable Teflon Young valves (Brunfeldt Co., Bartlesville, Oklahoma). Temperatures were calibrated by substitution of methanol for the analytical sample and the temperature was determined from the data of van Geet.[24] In experiments with $MeAl(BHT)_2$ in toluene-d_8, the [Al] : [Zr] ratio used (10 : 1), is limited by the solubility of the aluminium reagent. The metallocene concentrations were 0.08 M. In experiments with Me_3Al, 0.5 cm^3 2 M Me_3Al in toluene, 0.1 cm^3 C_6D_6 (to provide a ^2H lock signal) and 0.05 mmol of the metallocene were combined. Thus, [Al] : [Zr] was 20 : 1 with [Zr] = 0.083. For work with $(MeAlO)_x$, [Al] : [Zr] was 15 : 1 with [Zr] = 0.11. Kinetic runs in CH_2Cl_2 utilized 0.5 cm^3 of this solvent plus 0.1 cm^3 C_6D_6 or 0.03 cm^3 toluene. ^{13}C DNMR spectra were obtained using a 5–10 s acquisition time (for maximum possible resolution), Waltz-modulated ^1H decoupling and the optimum pulse width for maximum signal : noise. The linewidth of (internal) toluene was taken as the natural linewidth due to field inhomogeneity. [Zr—CH_3] and [Al—CH_3] were determined by weighing the reactants. Slow methyl exchange was followed by recording ^{13}C spectra as a function of time with kinetics being measured directly from integrated spectra. Relaxation times and nuclear Overhauser enhancements (nOe) were measured on equilibrated samples. Single scan spectra were obtained with continuous low-power Waltz decoupling because the nOe was necessary for adequate signal : noise. The nOe corrections were not significant. For Cp_2ZrMe_2 and $(Me_5Cp)_2Zr$ Me_2, the Zr—CH_3 nOe decreases from 2.9 at 22°C to 2.5 at 81°C. For $AlMe_3$, it decreases from 2.5 at 22°C to 1.9 at 70°C and from 2.6 to 2.5 over the same temperature range for $MeAl(BHT)_2$.

IR spectra were obtained on *ca* 1 M solutions of the organometallic compound in $CHCl_3$ (vacuum transferred from P_2O_5) on a Beckman 983 spectrometer. A 0.017 mm pathlength cell having KBr windows was employed. Assignment of M—CH_3 symmetric and asymmetric stretching bands was made by use of the M—$^{13}CH_3$ and M—CD_3 isotopomers.

$MeAl(BHT)_2$,[8] Et_2BOMe[25] and $(MeAlO)_x$[7a] were prepared by literature methods. In the synthesis of the latter, $MgCl_2 \cdot 6H_2O$ was used as the water-carrier. Residual Me_6Al_2 was removed at ⩽40°C at $<5 \times 10^{-6}$ mm. Cp_2ZrCl_2, $(Me_5Cp)_2ZrCl_2$, $Me_2Si(C_5H_4)_2ZrCl_2$[12] and $(indenyl)_2ZrCl_2$ were converted using the method of Samuel and Rausch[26] to the corresponding $Zr(^{13}CH_3)_2$ derivatives employing $^{13}CH_3Li$. We used an improved synthesis of $(C_9H_7)_2ZrCl_2$, described below.

Indenyllithium was prepared by the addition of 44 cm^3 2.5 M n-BuLi in hexane to 12.8 g redistilled indene in 100 cm^3 toluene at −78°C. The reaction mixture was stirred overnight as the cooling bath warmed up. The product was collected on a Schlenk filter, washed with hexane and vacuum dried. Yield 12.3 g (99%).

A mixture of 5.5 g C_9H_7Li (50 mmol), 5.8 g (25 mmol) $ZrCl_4$ and 100 cm^3 toluene was stirred for 2 h at room temperature and for 70 h at 90°C. This was then cooled to room temperature and filtered. The solids were *rapidly* washed with two 25 cm^3 portions of absolute ethanol, then with hexane and vacuum dried. Yield : 4.2 g (58%). It is important that the ethanol washing, which removes LiCl, is done rapidly, for otherwise the product dissolves and hydrolyses. $(C_9H_7)_2ZrCl_2$ in wet CH_3CN produces a quantitative yield of indene (^1H NMR analysis). Thus, $(C_9H_7)_2ZrCl_2$ *is* stable in organic solvents provided that they are dry.[27] (The method described in ref. 27 failed in our hands.)

$Me_2Si(C_5H_4)_2ZrMe_2$

$^{13}CH_3Li$ was prepared in diethyl ether under Ar from 2 g (14 mmol) $^{13}CH_3I$ and excess Li wire (1% Na). Ether was removed by pumping in a high vacuum line. Toluene (50 cm^3) and 1.74 g $Me_2Si(C_5H_4)_2ZrCl_2$ (5 mmol) were added. The reaction mixture was stirred for 24 h at room temperature then filtered. The filtrate was evaporated and the residue sublimed (100°C/10^{-3} mm) onto a 20°C probe. The yield of resublimed product was 0.72 g (47%). Yields using diethyl ether solvent were inferior. This is due to cleavage of the Me_2Si bridge, because when the reaction is quenched with Me_3SiCl, $(Me_3SiCp)_2ZrMe_2$ is also formed.

$(Me_3SiCp)_2ZrCl_2$[28]

Me_3SiCl (purified by fractional distillation on a vacuum line to remove HCl) (6.54 g, 60 mmol) in 20 cm^3 THF was added slowly to 60 mmol NaCp in 90 cm^3 THF at −78°C. The reaction mixture was warmed to room temperature then recooled to −78°C. n-BuLi (24 cm^3 2.5 M in hexane) was added dropwise. After stirring for 30 min at room temperature, the temperature was reduced to 0°C and $ZrCl_4$ (7 g, 30 mmol) in 40 cm^3 1,2-dimethoxyethane added dropwise. After stirring overnight, solvents were removed *in vacuo*. The residue was extracted with hexane in a Soxhlet apparatus. The extracts were concentrated to 50 cm^3 and filtered to give 9.2 g crude product. Recrystallization from boiling methylcyclohexane yielded 6.2 g (48%) pure product. Found: C, 43.7; H, 5.9. Calc. C, 44.0; H, 6.0%. Mass spectrum (11 eV): 436 (P^+), 421 ($P-Cl^+$).

New NMR data for zirconium metallocenes are listed below: $Me_2Si(C_5H_4)_2ZrMe_2$: ^{1}H: 0.17 (SiCH_3), 0.14 (ZrCH_3), 5.39 (m), 6.65 (m). ^{13}C: 120.9, 112.5 (Cp), 101.3 (C_{ipso}), 30.0 (Zr—CH_3), −5.30 (Si—CH_3). ^{91}Zr: 440 (*w*/2 8100 Hz) (toluene-d_8). $(C_9H_7)_2ZrCl_2$: ^{13}C: 127.3 ($C_{3a,7a}$), 126.7, 125.6 ($C_{4,6}$), 122.2 (C_2), 104.4 ($C_{1,3}$) (CD_2Cl_2). $(C_9H_7)_2ZrMe_2$: ^{13}C: 125.1 ($C_{4,7}$), 124.5 ($C_{5,6}$), 124.2 ($C_{3a,7a}$), 115.0 (C_2), 100.0 ($C_{1,3}$), 35.8 (ZrCH_3). ^{91}Zr: 500 (*w*/2 2500 Hz) (toluene-d_8). $(Me_3SiCp)_2ZrCl_2$: ^{1}H: 6.39, 5.94 (Cp), 0.32 (SiCH_3). ^{13}C: 126.3 (C_{ipso}), 126.0, 115.3 (Cp), 0.06 (SiCH_3). ^{91}Zr: −85 (*w*/2 · 1300 Hz) (C_6D_6). $(Me_3SiCp)_2ZrMe_2$: ^{1}H: 6.07, 5.93 (Cp), 0.18 (SiCH_3), −0.16 (ZrCH_3). ^{13}C: 119.3 (C_{ipso}), 118.2, 113.5 (Cp), 31.0 (ZrCH_3), 0.36 (SiCH_3). ^{91}Zr: 420 (*w*/2 3600 Hz) (toluene-d_8).

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