

# Communications

## Selective Halodemethylation Reactions of Metallocene Dimethyls with Triphenylmethyl Chloride and Benzyl Bromide

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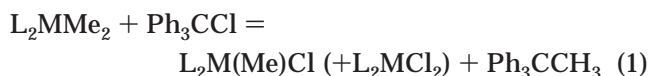
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**Summary:** NMR-scale reactions of several group 4 metallocene dimethyls with either trityl chloride or benzyl bromide gave the corresponding  $L_2M(Me)X$  complexes selectively. Five reactions, including syntheses of  $Cp_2Zr(Me)Cl$  and  $Ind_2Zr(Me)Cl$ , were conducted on a preparative scale to afford useful isolated yields of  $L_2M(Me)Cl$  complexes.

Activation of group 4 metallocene dichlorides ( $L_2MCl_2$ ) toward olefin polymerization using methylalumoxane (MAO) is believed to proceed by initial halodemethylation to form  $L_2M(Me)Cl$ , followed by chloride abstraction to afford ionic-like species formulated as  $[L_2MMe]^+ [ClMAO]^-$  and  $[L_2MMe]^+ [MeMAO]^-$ .<sup>3</sup> However, the fate of the halide upon activation and its subsequent role during olefin polymerization catalysis are not yet fully known.<sup>4–18</sup> As part of our ongoing study of metallocene activation using  $C_6F_5$ -substituted Cp ligands as  $^{19}F$  NMR spectroscopic probes,<sup>19</sup> we needed to prepare

$(C_6F_5Cp)_2Zr(Me)Cl$ ,  $(C_6F_5Cp)CpZr(Me)Cl$ , and  $(C_6F_5Cp)_2Hf(Me)Cl$ , first to assign these species conclusively in spectra of complex reaction mixtures and second to study their reactivity toward alkylaluminum species, including MAO. Established routes<sup>1,2,20–24</sup> to  $Cp_2Zr(Me)Cl$  did not afford the target compounds selectively. Because alkyl halides are known to react with transition-metal alkyls or hydrides to form the corresponding metal halides, we surmised that the wide range of reactivity among readily available alkyl halides might allow us to find generally selective reagents and reaction conditions for the monohalodemethylation of metallocene dimethyls.

Metallocene dimethyls<sup>19,25–30</sup> were treated with 1 equiv of triphenylmethyl chloride ( $Ph_3CCl$ ) in either benzene- $d_6$  or toluene- $d_8$  according to eq 1, where L = Cp (or congener) and M is a group 4 metal. We chose



$Ph_3CCl$  on the basis of its reactivity and ready availability. NMR-scale reactions enabled us to follow the course of each reaction and thereby optimize both the reaction time and the selectivity for  $L_2M(Me)Cl$ . The results are presented in Table 1.

An NMR-scale reaction was considered a promising candidate for scale-up if no more than 5% of  $L_2ZrMe_2$  remained and no more than 5% of  $L_2MCl_2$  had formed

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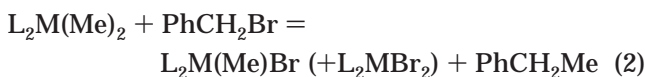
**Table 1.** Halodemethylation Reactions of Dimethylmetallocenes<sup>a</sup>

entry	substrate	reagent	reacn conditions			product, mol % <sup>b</sup>		
			solvent	T, °C	time	MMe <sub>2</sub>	M(Me)X <sup>c,d</sup>	MX <sub>2</sub> <sup>d</sup>
1	Cp <sub>2</sub> ZrMe <sub>2</sub>	Ph <sub>3</sub> CCl	C <sub>6</sub> D <sub>6</sub>	60	18 h	0	95 (80)	5
2	Cp <sub>2</sub> ZrMe <sub>2</sub>	PhCH <sub>2</sub> Br	tol- <i>d</i> <sub>8</sub>	95	15 h	6	86	8
3	Cp <sub>2</sub> ZrMe <sub>2</sub>	0.5 PbCl <sub>2</sub>	tol- <i>d</i> <sub>8</sub>	90	2 days	65	5	30
4	Ind <sub>2</sub> ZrMe <sub>2</sub>	Ph <sub>3</sub> CCl	tol- <i>d</i> <sub>8</sub>	90	18 h	0	98 (78)	2
5	(C <sub>6</sub> F <sub>5</sub> Cp) <sub>2</sub> ZrMe <sub>2</sub>	Ph <sub>3</sub> CCl	C <sub>6</sub> D <sub>6</sub>	60	18 h	0	96 (85)	4
6	(C <sub>6</sub> F <sub>5</sub> Cp) <sub>2</sub> ZrMe <sub>2</sub>	Ph <sub>3</sub> SiCl	C <sub>6</sub> D <sub>6</sub>	70	23 h	100	0	0
7	(C <sub>6</sub> F <sub>5</sub> Cp) <sub>2</sub> ZrMe <sub>2</sub>	CD <sub>2</sub> Cl <sub>2</sub>	CD <sub>2</sub> Cl <sub>2</sub>	25	26 h	100	0	0
8	(C <sub>6</sub> F <sub>5</sub> Cp)CpZrMe <sub>2</sub>	Ph <sub>3</sub> CCl	C <sub>6</sub> D <sub>6</sub>	60	18 h	3	96 (88)	1
9	(C <sub>6</sub> F <sub>5</sub> Cp) <sub>2</sub> HfMe <sub>2</sub>	Ph <sub>3</sub> CCl	C <sub>6</sub> D <sub>6</sub>	60	18 h	0	98 (64)	2
10	(Me <sub>3</sub> SiCp) <sub>2</sub> ZrMe <sub>2</sub>	Ph <sub>3</sub> CCl	C <sub>6</sub> D <sub>6</sub>	60	15 h	2	98	0
11	(Me <sub>3</sub> SiCp) <sub>2</sub> ZrMe <sub>2</sub>	PhCH <sub>2</sub> Br	tol- <i>d</i> <sub>8</sub>	90	60 days	3	97	0
12	(Me <sub>3</sub> Cp)CpZrMe <sub>2</sub>	Ph <sub>3</sub> CCl	tol- <i>d</i> <sub>8</sub>	95	18 h	0	95	5
13	(Me <sub>3</sub> Cp)CpHfMe <sub>2</sub>	Ph <sub>3</sub> CCl	tol- <i>d</i> <sub>8</sub>	95	2 days	3	95	2
14	(C <sub>6</sub> F <sub>5</sub> Cp)(Me <sub>3</sub> Cp)ZrMe <sub>2</sub>	Ph <sub>3</sub> CCl	C <sub>6</sub> D <sub>6</sub>	60	2 days	10	85	5
15	<i>rac</i> -C <sub>2</sub> H <sub>4</sub> (Ind) <sub>2</sub> ZrMe <sub>2</sub>	Ph <sub>3</sub> CCl	tol- <i>d</i> <sub>8</sub>	25	6 h	2	89	9
16	<i>rac</i> -C <sub>2</sub> H <sub>4</sub> (Ind) <sub>2</sub> ZrMe <sub>2</sub>	PhCH <sub>2</sub> Br	C <sub>6</sub> D <sub>6</sub>	70	5 days	0	95	5
17	[(Me <sub>4</sub> C <sub>5</sub> )SiMe <sub>2</sub> N <sup>t</sup> Bu]ZrMe <sub>2</sub>	Ph <sub>3</sub> CCl	C <sub>6</sub> D <sub>6</sub>	25	5 min	2	91	7
18	[(Me <sub>4</sub> C <sub>5</sub> )SiMe <sub>2</sub> N <sup>t</sup> Bu]ZrMe <sub>2</sub>	PhCH <sub>2</sub> Br <sup>e</sup>	tol- <i>d</i> <sub>8</sub>	95	2 days	2	98	0

<sup>a</sup> Thermolyses were carried out in NMR tubes in the dark without agitation of the solutions. Representative experiments are described in ref 35. See the Supporting Information for complete experimental details. <sup>b</sup> Relative amounts were determined by either <sup>1</sup>H NMR or <sup>19</sup>F NMR integration. <sup>c</sup> Quantities in parentheses are isolated yields from analogous preparative-scale reactions. <sup>d</sup> Where reagent = Ph<sub>3</sub>CCl, PbCl<sub>2</sub>, X = Cl; where reagent = PhCH<sub>2</sub>Br, X = Br. <sup>e</sup> An excess (10 equiv) of PhCH<sub>2</sub>Br was used.

(eq 1). Accordingly, entries 1, 4, 5, 8, and 9 also provide the isolated yields for corresponding preparative-scale reactions. For entries 10, 12, and 13, the L<sub>2</sub>M(Me)Cl products were also formed selectively but were too soluble in hexane to be isolated efficiently from the byproducts (see below) by crystallization. Ph<sub>3</sub>SiCl did not react under similar conditions (entry 6). Our failure using PbCl<sub>2</sub> was surprising, considering the success reported previously by Wailes et al.<sup>23</sup> However, the reaction is heterogeneous and Wailes's procedure indicated "vigorous stirring"; thus, perhaps we did not agitate our reactions enough.

We then tried using benzyl bromide for a few reactions (eq 2, results in Table 1). We selected two

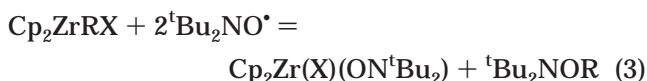


substrates for which reactions with Ph<sub>3</sub>CCl were rapid but unselective (Table 1, entries 15 and 17). Generally the reactions with benzyl bromide were more selective but also rather slow (especially entries 11 and 16).

The observation of long induction periods (up to 48 h) suggests a free-radical process. Although 1,1,1-triphenylethane is the major organic byproduct ( $\delta_{\text{Me}}$  2.03 ppm), significant quantities of Ph<sub>3</sub>CH ( $\delta_{\text{CH}}$  5.50 ppm) and Ph<sub>2</sub>(4-Me-C<sub>6</sub>H<sub>4</sub>)CCH<sub>3</sub> ( $\delta_{\text{Me}}$  2.08 and 2.15 ppm) were also observed (product assignments were confirmed by GC-MS analysis), suggesting methyl- and hydrogen-radical-transfer events. In contrast, the reactions with benzyl bromide showed ethylbenzene as the only significant organic byproduct. Ethylbenzene should be more easily separated, e.g., by evaporation or crystallization than 1,1,1-triphenylethane—a potential practical advantage.

Although we have not elucidated the mechanism of these halodemethylation reactions, a related process involving nitroxyl radicals (eq 3, where R = CH<sub>2</sub>Ph, Me and X = CH<sub>2</sub>Ph, Me, Cl, Br) was found to proceed by

an S<sub>H</sub>2 radical substitution (eqs 4 and 5).<sup>31,32</sup>



Interestingly, Cp<sub>2</sub>ZrMe<sub>2</sub> reacted much more rapidly than Cp<sub>2</sub>Zr(Me)Cl, foreshadowing the selectivity reported here. The analogous process using Ph<sub>3</sub>CCl would require thermal initiation (not photochemical—our reactions were run in the dark) followed by substitution (eqs 6–8).

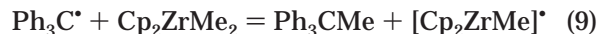


However, in contrast to eq 5, where the nitroxyl radical is present in stoichiometric quantities, eq 6 requires thermal dissociation of Ph<sub>3</sub>CCl first. Assuming  $E_{a(6)} \approx D_{\text{C-Cl}} \approx 70 \text{ kcal mol}^{-1}$  and a reasonable preexponential factor ( $A \approx 10^{11} \text{ s}^{-1}$ ), the rate of dissociation at 100 °C would be too slow ( $k_6 \approx 10^{-30} \text{ s}^{-1}$ ) to observe product formation during the intervals reported in Table 1. Furthermore, eq 8 requires efficient recombination of two dilute radicals. In the absence of kinetic evidence

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or meaningful substituent effect data, a chain process (eqs 9 and 10) seems more plausible to us.<sup>33,34</sup>



In conclusion, we find that reactions of group 4 metallocene dimethyls with either trityl chloride or benzyl bromide are generally selective for the formation of  $\text{L}_2\text{M(Me)Cl}$ . NMR-scale experiments facilitate selection of the reagent and optimization of the reaction conditions. As long as the ancillary ligands do not increase the solubility of the metallocene too much, the product may be isolated from the organic byproducts in high yield and purity by crystallization. Long induction times and minor organic byproducts suggest a free radical mechanism for halodemethylation.

(33) The mixed alkyl complex  $\text{Cp}_2\text{Zr}(\text{CH}=\text{CHPh})(\text{CH}_2\text{Ph})$  reacts with  $\text{PhCH}_2\text{Cl}$  under photolysis conditions to give  $\text{Cp}_2\text{Zr}(\text{CH}=\text{CHPh})(\text{Cl})$  and  $\text{PhCH}_2\text{CH}_2\text{Ph}$ . Photolysis of  $\text{Cp}_2\text{ZrMe}_2$  affords  $\text{Cp}_2\text{ZrMe}$ , which may be trapped as the  $\text{P(OMe)}_3$  adduct and characterized by EPR, supporting the proposition of a  $\text{Cp}_2\text{ZrMe}$  radical intermediate. See: Czisch, P.; Erker, G.; Korth, H.-G.; Sustmann, R. *Organometallics* **1984**, *3*, 945–947.

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**Note Added in Proof.** Resconi and coworkers recently reported clean conversions of  $\text{Ind}_2\text{TiMe}_2$  to  $\text{Ind}_2\text{Ti(Me)Cl}$  using  $\text{SiCl}_4$  (4 equiv, toluene solvent, 50 °C, 6 h) and of  $\text{Ind}_2\text{ZrMe}_2$  to  $\text{Ind}_2\text{Zr(Me)Cl}$  using  $\text{FeCl}_3$  (1 equiv,  $\text{CH}_2\text{Cl}_2$  solvent, 40 °C, 6 h).<sup>36</sup>

**Supporting Information Available:** Complete experimental details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(35) (a) In a typical NMR experiment, a J. Young NMR tube was charged in a nitrogen glovebox with 0.05 mmol (nominal) of the metallocene dimethyl, 1.0–1.1 equiv of either  $\text{Ph}_3\text{CCl}$  or  $\text{PhCH}_2\text{Br}$ , and about 1 mL of solvent (see Table 1). The tube was placed in an oil bath preheated to the prescribed temperature (see Table 1). At several intervals, the sample was analyzed by  $^1\text{H}$  NMR (400 MHz) and, where appropriate,  $^{19}\text{F}$  NMR (376 MHz). (b) In a representative preparative-scale experiment, a mixture of  $\text{Cp}_2\text{ZrMe}_2$  (188 mg, 0.749 mmol),  $\text{Ph}_3\text{CCl}$  (211 mg, 0.756 mmol), and benzene (15 mL) was stirred under argon at 60 °C for 18 h. The solvent was evaporated, and the residue was recrystallized from hexane under argon to afford 138 mg (0.597 mmol, 80%) of  $\text{Cp}_2\text{Zr(Me)Cl}$  as pale yellow crystals.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  5.73 (s, 10 H, Cp), 0.439 (s, 3 H, ZrMe).

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