Communications

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

Eric J. Hawrelak and Paul A. Deck*

Department of Chemistry, Virginia Tech, Blacksburg, Virginia 24061-0212

Summary: NMR-scale reactions of several group 4 met-allocene dimethyls with either trityl chloride or benzyl bromide gave the corresponding $L_2M(Me)X$ complexes selectively. Five reactions, including syntheses of Cp_2-$Zr(Me)Cl$ 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 $[L_2MMe]^+[MeMAO]^-$.[3] However, the fate of the halide upon activation and its subsequent role during olefin polymerization catalysis are not yet fully known.[4−18] As part of our ongoing study of metallocene activation using C_6F_5-substituted Cp ligands as ^{19}F NMR spectroscopic probes,[19] we needed to prepare

$(C_6F_5Cp)_2Zr(Me)Cl$, $(C_6F_5Cp)CpZr(Me)Cl$, and $(C_6F_5$-$Cp)_2Hf(Me)Cl$, 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[1,2,20−24] 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[19,25−30] 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

$$L_2MMe_2 + Ph_3CCl =$$
$$L_2M(Me)Cl (+L_2MCl_2) + Ph_3CCH_3 \quad (1)$$
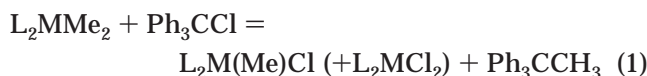
Ph_3CCl on the basis of its reactivity and ready availability. NMR-scale reactions enabled us to follow the course of each reaction and thereby optimize both the reaction time and the selectivity for $L_2M(Me)Cl$. The results are presented in Table 1.

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[a]

entry	substrate	reagent	reacn conditions			product, mol %[b]		
			solvent	T, °C	time	MMe_2	$M(Me)X$[c,d]	MX_2[d]
1	Cp_2ZrMe_2	Ph_3CCl	C_6D_6	60	18 h	0	95 (80)	5
2	Cp_2ZrMe_2	$PhCH_2Br$	tol-d_8	95	15 h	6	86	8
3	Cp_2ZrMe_2	$0.5\ PbCl_2$	tol-d_8	90	2 days	65	5	30
4	Ind_2ZrMe_2	Ph_3CCl	tol-d_8	90	18 h	0	98 (78)	2
5	$(C_6F_5Cp)_2ZrMe_2$	Ph_3CCl	C_6D_6	60	18 h	0	96 (85)	4
6	$(C_6F_5Cp)_2ZrMe_2$	Ph_3SiCl	C_6D_6	70	23 h	100	0	0
7	$(C_6F_5Cp)_2ZrMe_2$	CD_2Cl_2	CD_2Cl_2	25	26 h	100	0	0
8	$(C_6F_5Cp)CpZrMe_2$	Ph_3CCl	C_6D_6	60	18 h	3	96 (88)	1
9	$(C_6F_5Cp)_2HfMe_2$	Ph_3CCl	C_6D_6	60	18 h	0	98 (64)	2
10	$(Me_3SiCp)_2ZrMe_2$	Ph_3CCl	C_6D_6	60	15 h	2	98	0
11	$(Me_3SiCp)_2ZrMe_2$	$PhCH_2Br$	tol-d_8	90	60 days	3	97	0
12	$(Me_5Cp)CpZrMe_2$	Ph_3CCl	tol-d_8	95	18 h	0	95	5
13	$(Me_5Cp)CpHfMe_2$	Ph_3CCl	tol-d_8	95	2 days	3	95	2
14	$(C_6F_5Cp)(Me_5Cp)ZrMe_2$	Ph_3CCl	C_6D_6	60	2 days	10	85	5
15	*rac*-$C_2H_4(Ind)_2ZrMe_2$	Ph_3CCl	tol-d_8	25	6 h	2	89	9
16	*rac*-$C_2H_4(Ind)_2ZrMe_2$	$PhCH_2Br$	C_6D_6	70	5 days	0	95	5
17	$[(Me_4C_5)SiMe_2N^tBu]ZrMe_2$	Ph_3CCl	C_6D_6	25	5 min	2	91	7
18	$[(Me_4C_5)SiMe_2N^tBu]ZrMe_2$	$PhCH_2Br$[e]	tol-d_8	95	2 days	2	98	0

[a] 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. [b] Relative amounts were determined by either ^{1}H NMR or ^{19}F NMR integration. [c] Quantities in parentheses are isolated yields from analogous preparative-scale reactions. [d] Where reagent = Ph_3CCl, $PbCl_2$, X = Cl; where reagent = $PhCH_2Br$, X = Br. [e] An excess (10 equiv) of $PhCH_2Br$ 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 $L_2M(Me)Cl$ products were also formed selectively but were too soluble in hexane to be isolated efficiently from the byproducts (see below) by crystallization. Ph_3SiCl did not react under similar conditions (entry 6). Our failure using $PbCl_2$ was surprising, considering the success reported previously by Wailes et al.[23] However, the reaction is heterogeneous and Wailes's procedure indicated "vigorous stirring"; thus, perhaps we did not agitate our reactions enough.

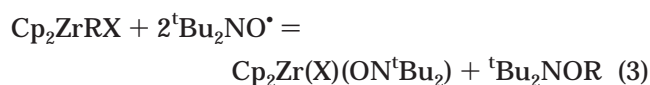We then tried using benzyl bromide for a few reactions (eq 2, results in Table 1). We selected two

$$L_2M(Me)_2 + PhCH_2Br =$$
$$L_2M(Me)Br\ (+L_2MBr_2) + PhCH_2Me \quad (2)$$
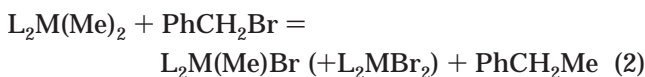
substrates for which reactions with Ph_3CCl were rapid but unselective (Table 1, entries 15 and 17). Generally the reactions with benzyl bromide were more selective but also rather slow (especially entries 11 and 16).

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 (δ_{Me} 2.03 ppm), significant quantities of Ph_3CH (δ_{CH} 5.50 ppm) and $Ph_2(4\text{-Me-}C_6H_4)CCH_3$ (δ_{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_2Ph, Me and X = CH_2Ph, Me, Cl, Br) was found to proceed by

an S_H2 radical substitution (eqs 4 and 5).[31,32]

$$Cp_2ZrRX + 2^tBu_2NO^{\bullet} =$$
$$Cp_2Zr(X)(ON^tBu_2) + {}^tBu_2NOR \quad (3)$$

$${}^tBu_2NO^{\bullet} + Cp_2ZrRX = Cp_2Zr(X)(ON^tBu_2) + R^{\bullet} \quad (4)$$

$$R^{\bullet} + {}^tBu_2NO^{\bullet} = {}^tBu_2NOR \quad (5)$$

Interestingly, Cp_2ZrMe_2 reacted much more rapidly than $Cp_2Zr(Me)Cl$, foreshadowing the selectivity reported here. The analogous process using Ph_3CCl would require thermal initiation (not photochemical—our reactions were run in the dark) followed by substitution (eqs 6–8).

$$Ph_3CCl = Ph_3C^{\bullet} + Cl^{\bullet} \ \text{(initiation)} \quad (6)$$

$$Cp_2ZrMe_2 + Cl^{\bullet} = Cp_2Zr(Me)Cl + Me^{\bullet} \quad (7)$$

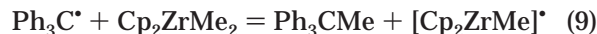$$Me^{\bullet} + Ph_3C^{\bullet} = Ph_3CMe \quad (8)$$

However, in contrast to eq 5, where the nitroxyl radical is present in stoichiometric quantities, eq 6 requires thermal dissociation of Ph_3CCl first. Assuming $E_{a(6)} \approx D_{C-Cl} \approx 70$ kcal mol^{-1} and a reasonable preexponential factor ($A \approx 10^{11}$ s^{-1}), the rate of dissociation at 100 °C would be too slow ($k_6 \approx 10^{-30}$ 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.[33,34]

$$Ph_3C^\bullet + Cp_2ZrMe_2 = Ph_3CMe + [Cp_2ZrMe]^\bullet \quad (9)$$

$$[Cp_2ZrMe]^\bullet + Ph_3CCl = Cp_2Zr(Me)Cl + Ph_3C^\bullet \quad (10)$$

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 $L_2M(Me)Cl$. 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.

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(33) The mixed alkyl complex $Cp_2Zr(CH=CHPh)(CH_2Ph)$ reacts with $PhCH_2Cl$ under photolysis conditions to give $Cp_2Zr(CH=CHPh)(Cl)$ and $PhCH_2CH_2Ph$. Photolysis of Cp_2ZrMe_2 affords Cp_2ZrMe, which may be trapped as the $P(OMe)_3$ adduct and characterized by EPR, supporting the proposition of a Cp_2ZrMe 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 Ind_2TiMe_2 to $Ind_2Ti(Me)Cl$ using $SiCl_4$ (4 equiv, toluene solvent, 50 °C, 6 h) and of Ind_2ZrMe_2 to $Ind_2Zr(Me)Cl$ using $FeCl_3$ (1 equiv, CH_2Cl_2 solvent, 40 °C, 6 h).[36]

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 Ph_3CCl or $PhCH_2Br$, 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 ^1H NMR (400 MHz) and, where appropriate, ^{19}F NMR (376 MHz). (b) In a representative preparative-scale experiment, a mixture of Cp_2ZrMe_2 (188 mg, 0.749 mmol), Ph_3-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 $Cp_2Zr(Me)Cl$ as pale yellow crystals. ^1H NMR (C_6D_6) δ 5.73 (s, 10 H, Cp), 0.439 (s, 3 H, ZrMe).

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