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Observations Concerning the Inactivity of Dimethylhafnocene as a Catalyst for the Dehydrocoupling of Phenylsilane

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Summary: Neither dimethylhafnocene nor [1,2-bis(tetrahydroindenyl)ethane]dimethylzirconium, 1, reacts at an appreciable rate with phenylsilane. In the case of the hafnium compound, this results in complete masking of catalytic activity toward dehydrocoupling of phenylsilane, while in the case of 1 activity is greatly suppressed. This behavior is governed by the low reactivity of the M–C bonds toward σ-bond metathesis with silanes. Catalysts generated by reaction of MeLi and $PhSiH_3$ with hafnocene dichloride or [1,2-bis(tetrahydroindenyl)ethane]dichlorozirconium, 2, show high activities toward $PhSiH_3$ coupling. The molecular weights of the resulting polymers are significantly higher than those of polymers derived from Cp_2TiMe_2 and Cp_2ZrMe_2 catalysts, and the hafnocene catalyst gives unusually low proportions of low molecular weight cyclic products. It is proposed that the catalyst species, probably a hydrido silyl complex, in these new systems are generated by reaction of a reactive lithium hydride, resulting from rapid reaction of MeLi with $PhSiH_3$, with the chloro complexes.

Introduction

A number of studies have reported on the unusual activity of group 4 metallocene derivatives as catalysts for the dehydrocoupling of hydrosilanes.[1-6] Our work has centered around the use of compounds of the type Cp_2MMe_2, where Cp can be η^5-cyclopentadienyl, an alkylated η^5-cyclopentadienyl, an indenyl or tetrahydroindenyl, etc.[1] Important modifications were made to our approach by Tilley et al., who have worked extensively with presynthesized silyl complexes of Zr and Hf,[2] and Corey et al., who have pioneered the in situ generation of active catalyst by the alkylation of dichlorometallocenes with butyllithium.[3]

In the course of a survey of group 4 organometallics, designed to delineate the factors influencing their activity in dehydrocoupling, we were surprised to find, given the usual trends in this group, that whereas titanocene and zirconocene dimethyls were highly active, dimethylhafnocene showed no activity under comparable reaction conditions.[1c] This anomaly was further emphasized by the subsequent report by Woo and Tilley that CpCp*Hf silyl complexes, while less active than their zirconium analogues, were nevertheless quite respectable catalysts.[2b]

In the present paper we present the results of a study of the dehydrocoupling activity of a number of group 4 metallocene complexes where the catalyst is generated in situ by reaction of the dichlorometallocene with methyllithium. These results indicate that the origin of the inactivity of dimethylhafnocene lies in the sluggishness of the reactions which convert the dimethyl derivative into the true catalyst, which is probably a silyl hydride complex, as proposed by Tilley et al.[2c]

Results and Discussion

Dichlorohafnocene System. The results of a number of reactions of undiluted phenylsilane catalyzed by in situ generated group 4 catalysts are summarized in Table I. The results for titanocene and zirconocene dichlorides are essentially the same as those obtained with the dimethylmetallocenes. The results with dichlorohafnocene are different from those obtained with dimethylhafnocene. Initially, this might seem unusual, since the standard synthesis of dimethylhafnocene is the reaction of methyllithium with dichlorohafnocene. This reaction is, however, quite slow, and an independent experiment showed that the reaction of methyllithium with phenylsilane, to give methylphenylsilane, is essentially complete in the time it takes to mix the reactants and run an NMR spectrum on the mixture. Thus, the actual reagent that is reacting with the dichlorohafnocene is most likely a lithium hydride species, rather than methyllithium itself. Since normal lithium hydride is completely insoluble in the media used for these reactions, and does not react at a significant rate in heterogeneous suspension with dichlorohafnocene, it must be concluded that the lithium hydride produced in the present reactions either is in an unusually highly divided state or is complexed in some way with one of the reactants.

The effect of the molar ratio of methyllithium to dichlorohafnocene indicates that it is necessary to replace both chlorines to get high reactivity. This conforms with the previously studied $CpCp^*Hf^{IV}$ and $CpCp^*Zr^{IV}$ systems.[2c] The inhibition observed for higher ratios of methyllithium could be due to complexation of Me on the zirconium, blocking the unoccupied coordination site that is necessary for the σ-bond metathesis mechanism.

One feature of the dichlorohafnocene system, for which we presently have no explanation, is the long induction period (see Experimental Section). It is not likely that

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(1) (a) Aitken, C. A.; Harrod, J. F.; Samuel, E. *J. Am. Chem. Soc.* 1986, *108*, 4059. (b) Aitken, C. A.; Harrod, J. F.; Samuel, E. *Can. J. Chem.* 1987, *64*, 1677. (c) Aitken, C. A.; Barry, J.-P.; Gauvin, F.; Harrod, J. F.; Malek, A.; Rousseau, D. *Organometallics* 1989, *8*, 1732. (d) Gauvin, F.; Harrod, J. F. *Can. J. Chem.* 1990, *68*, 1638. (e) Mu, Y.; Cote, B.; Aitken, C. A.; Harrod, J. F.; Samuel, E. *Can. J. Chem.* 1991, *69*, 264.

(2) (a) Woo, H. G.; Tilley, T. D. *J. Am. Chem. Soc.* 1989, *111*, 8043. (b) Woo, H. G.; Tilley, T. D. *J. Am. Chem. Soc.* 1989, *111*, 3757. (c) Tilley, T. D. *Comments Inorg. Chem.* 1990, *10*, 37. (d) Woo, H. G.; Tilley, T. D. In *Inorganic and Organometallic Oligomers and Polymers*; Laine, R. M., Harrod, J. F., Eds.; Kluwer Publishers: Amsterdam, 1991, p 3. (e) Woo, H. G.; Waltzer, J. F.; Tilley, T. D. *J. Am. Chem. Soc.* 1992, *114*, 7047.

(3) (a) Corey, J. Y.; Chang, L. S.; Corey, E. R. *Organometallics* 1987, *6*, 1596. (b) Corey, J. Y.; Chang, L. S. *Organometallics* 1989, *8*, 1885. (c) Corey, J. Y.; Zhu, X.-H.; Bedard, T. C.; Lange, L. D. *Organometallics* 1991, *10*, 924. (d) Corey, J. Y.; Zhu, X.-H. *Organometallics* 1992, *11*, 672.

(4) Brown-Wensley, K. A. *Organometallics* 1987, *6*, 1590.

(5) Campbell, W. H.; Hilty, T. K.; Yurga, L. *Organometallics* 1989, *8*, 2615.

(6) Banovetz, J. P.; Stein, K. M.; Waymouth, R. M. *Organometallics* 1991, *10*, 3430.

0276-7333/93/2312-0575$04.00/0

Table I. Molecular Weight Properties of Poly(phenylsilanes) Obtained with in Situ Generated Group 4 Metallocene Catalysts

catalyst precursor/MeLi	amt of monomer, mmol	amt of catalyst, mmol	M_w[a]	M_w/M_n	cyclics,[b] %
Cp_2TiCl_2/2 MeLi	16	0.32	1843	1.20	45
Cp_2TiCl_2/3 MeLi	8	0.16	1612	1.35	47
Cp_2TiCl_2/4 MeLi	8	0.16	1478	1.32	50
Cp_2ZrCl_2/2 MeLi	16	0.32	2296	1.33	25
Cp_2ZrCl_2/3 MeLi	8	0.16	2386	1.52	24
Cp_2ZrCl_2/4 MeLi	8	0.16	2248	1.58	23
Cp_2HfCl_2/1 MeLi[c]	4	0.08	–	–	–
Cp_2HfCl_2/2 MeLi	16	0.32	3533	1.71	15
Cp_2HfCl_2/3 MeLi[c]	4	0.08	–	–	–
Cp_2HfCl_2/4 MeLi[c]	4	0.08	–	–	–
2/2 MeLi	4	0.04	4580	1.36	42
2/3 MeLi	4	0.04	3522	1.77	21
2/4 MeLi	4	0.04	2496	2.01	25

[a] Values for higher molecular weight fraction only. [b] Estimated from chromatogram on the assumption that the low molecular weight fraction is due entirely to cyclics. [c] No reaction observed after 72 h.

Table II. Molecular Weight Properties of Poly(phenylsilanes) Made at Different Monomer Concentrations with 2/MeLi as Catalyst[a]

amt of $PhSiH_3$, mmol	amt of **2**, mmol	$PhSiH_3$/toluene (vol/vol)	M_w[b]	M_w/M_n[b]	cyclics[c]
8.0	0.04	3:1	2753	1.73	24
4.0	0.04	1:1	1779	1.56	27
4.0	0.04	1:3	820	1.34	38

[a] Reaction conditions: room temperature for 72 h. [b] Data for higher molecular weight fraction of bimodal distribution, assumed to be linear. [c] Lower molecular weight fraction of bimodal distribution, by integration of GC chromatogram.

the induction period is due to a physical effect, such as solubility, since none of the other dichlorides studied are particularly soluble in the reaction medium, yet they do not exhibit long induction periods.

Finally, we draw attention to the relatively high M_w of the poly(phenylsilane) produced with this catalyst, compared to that of poly(phenylsilanes) obtained with the other group 4 metallocene catalysts, and to the rather low proportion of low-molecular-weight cyclics. Both of these properties, together with the value for M_w/M_n, are similar to the values reported by Tilley et al. for the CpCp*Hf system.[2c]

[1,2-Bis(tetrahydroindenyl)ethane]dimethylzirconium(IV) and [1,2-Bis(tetrahydroindenyl)ethane]dichlorozirconium(IV) Systems (Compounds 1 and 2). We have studied the complex **1** to evaluate its properties as a catalyst for stereoselective polymerization of primary silanes.[1d] A notable feature of **1** is that, although it is a sluggish catalyst for the polymerization of phenylsilane, only an unmeasurably small amount of **1** is converted to active catalytic species during the course of the reaction. Since this seemed to be another case where the catalytic activity is masked by the difficulty of converting the dimethyl derivative to the true catalytic species, it was a good candidate for evaluation by the in situ generation of the catalyst by reaction of methyllithium with the dichloride. It should be noted that, although again the reaction of **2** with methyllithium is the preferred method of synthesis of **1**, the reaction is very slow, requiring many hours to go to completion.

Compound **2** in combination with methyllithium proved to be a very active catalyst for phenylsilane polymerization. The observed activity is not a good indicator of the activity of the true catalyst, since it is well established that much of the added metal may be tied up in the form of inactive dimeric species.[1a,b] However, it is quite clear that, although σ-bond metathesis reactions of the dimethyl compound **1** with silanes are very slow, the reactive intermediates, once generated, are highly active. The same is apparently true for the dimethylhafnocene case, and this observation is in accord with the well-established greater reactivity of *silyl* group 4 complexes to σ-bond metathesis reactions relative to the *methyl* compounds.[2c]

The molecular weight of the polymer produced by bulk polymerization of phenylsilane with the MeLi/**2** catalyst is the highest we have ever observed, and it compares to the highest values reported for the $CpCp^*Hf^{IV}$ catalyst system.[2c] Dilution of the monomer with toluene leads to a reduction in the molecular weight of the polymer and to a modest increase in the amount of cyclics. This pattern of behavior parallels that observed in all other analogous systems.[1e,2d]

Since the dichlorohafnocene/MeLi catalyst also gives an unusually high molecular weight product, it is tempting to adduce some connection between the sluggish reactivities of **1** and dimethylhafnocene with the silane and the formation of longer polymer chains. In fact, Tilley has already argued that greater specificity for chain elongation, as opposed to cyclization and chain-scissioning processes, may be favored by less active, but more discriminating, catalysts.[2e] This conclusion is based on the qualitative evaluation of the energies of the various transition states for the σ-bond metathesis processes leading to each reaction. The least sterically congested, and therefore the lowest energy, transition state corresponds to chain elongation by addition of monomer to a longer chain metal silyl species. The greater selectivity of the Cp_2Hf system, relative to Cp_2Zr, may be due to a combination of slightly lower intrinsic reactivity, due to an electronic effect, combined with the slightly smaller radius of Hf increasing the steric congestion at the metal center. It would then have to be argued that the low selectivity of Ti is due to the greater intrinsic activity arising from an electronic effect, overriding the greater steric factor due to the much smaller radius of Ti.

Experimental Section

General Procedures. All experiments were carried out in Schlenk tubes under argon, using standard inert-atmosphere techniques. Dried solvents were freshly distilled and degassed immediately before use. Phenylsilane was prepared by reduction of phenyltrichlorosilane with lithium aluminum hydride as previously described.[7] Titanocene, zirconocene, and hafnocene dichlorides were purchased from Alfa and used as supplied. Methyllithium was purchased from Aldrich Chemical Co. as a 1.4 M solution in diethyl ether. *rac*-[1,2-Bis(tetrahydroindenyl)ethane]dichlorozirconium was prepared according to a procedure described in the literature.[8]

Molecular weights were determined by GPC using a Varian 5000 liquid chromatograph, equipped with a 500-Å Ultrastyragel column and calibrated with polystyrene standards, as previously described.[1e]

Catalytic Polymerization Reactions. A typical procedure for the dichlorohafnocene reaction was as follows. A sample of dichlorohafnocene (121.8 mg; 0.32 mmol) was placed in a Schlenk

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(7) Benkeser, R. A.; Landesman, H.; Foster, D. *J. Am. Chem. Soc.* 1952, *74*, 648.

(8) Collins, S.; Kunz, B.; Naylor, N. J.; Ward, D. G. *J. Organomet. Chem.* 1988, *342*, 21.

tube equipped with a rubber septum and a magnetic stirrer. After the tube was purged with argon, methyllithium (0.46 mL of a 1.4 M solution in ether; 0.64 mmol) was added to the stirred solid crystals of hafnocene dichloride. The slurry was stirred for 2 min, and then phenylsilane (2.0 mL; 16.0 mmol) was added. Stirring was continued for 2–4 h, during which time no observable reaction occurred. After this induction period, the solution turned yellow and a gentle evolution of hydrogen commenced. At the end of a further 2 h, the mixture was too viscous for stirring. The reaction was left for a further 72 h, by which time all monomer had reacted and no further changes occurred. The polymer was isolated and analyzed by previously described methods.[1e]

When reactions were carried out with titanocene dichloride under the same conditions, no induction period was observed. There was an immediate color change from yellow to dark blue on adding the phenylsilane, with accompanying hydrogen evolution. The mixture became too viscous for stirring after about 6–8 h. There was no induction period with the zirconocene dichloride reaction, and the rate was much higher than for the Ti and Hf reactions. The gas evolution was violent, and the mixture became too viscous to stir after about 20 min. [Bis(tetrahydroindenyl)ethane]zirconium dichloride exhibited no induction period, and the rate of dehydrocoupling was similar to that of the titanocene dichloride system.

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