Practical and Selective Method for Preparation of Cp_2HfRCl and Cp_2HfRR'

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Practical method for preparation of Cp_2HfRCl and Cp_2HfRR' has been investigated. Mono(alkyl)hafnocene chloride complexes were selectively prepared by the following methods; (i) a reaction of $Cp_2HfR(OMe)$ with MeCOCl and (ii) a reaction of Cp_2HfCl_2 with an excess of R_3Al. Treatment of Cp_2HfRCl with R'_3Al led to an alkyl exchange reaction to form $Cp_2HfR'Cl$. Mono(alkyl)hafnocene complexes prepared by (ii) reacted with one equiv of R'Li to give Cp_2HfRR' ($R \neq R'$) with a high selectivity.

Recently we have reported the highly selective catalytic and stoichiometric reactions of zirconocene-ethylene complexes with alkenes.[2] In these reactions dialkylzirconocene derivatives played a very important role for the high selectivities.[2] In order to investigate the origin of the selectivity, selective preparation of dialkylzirconocenes is necessary. However, the usual dialkylzirconocenes were unstable at room temperature and it was difficult to prepare in situ the usual dialkylzirconocenes which have different two alkyl groups with a high purity.[3] Therefore we turned our attention from dialkylzirconocene to more stable dialkylhafnocene. Surprisingly, however, there is no practical and selective preparation method reported so far for useful Cp_2HfRCl (**1**) and Cp_2HfRR' (**2**). Although some papers have shown the formation of **1** or **2**,[4] the desired complexes have been formed either as a mixture of several complexes or with special bulky alkyl groups or in low yields. In this paper we would like to report some practical and selective preparation methods of **1** and **2**.

$$\mathbf{Cp_2HfR_2} \xrightarrow{\text{excess MeOH}} \underset{\mathbf{3:\ >99\%}}{\mathbf{Cp_2HfR(OMe)}} \xrightarrow{\text{MeCOCl}} \underset{\mathbf{1:\ 80\%}}{\mathbf{Cp_2HfRCl}} \qquad (1)$$

Recently we reported quantitative formation of mono(alkyl)-alkoxyhafnocene complexes $Cp_2HfR(OMe)$ (**3**) by the reaction of Cp_2HfR_2 with an excess of MeOH.[5] Since the yield of this complex was excellent, we tried to convert this complex into **1**. When **3** (R = Bu^n) was treated with 1 equiv of MeCOCl at room temperature, **1** (R = Bu^n) was formed in 80% yield. Zirconocene analog $Cp_2ZrBu^n(OMe)$ did not afford the corresponding complex Cp_2ZrBu^nCl cleanly.

It is well known that treatment of Cp_2ZrCl_2 with Et_3Al gives ethylene bridged di-zirconium complex, $[Cp_2Zr(ClAlEt_2Cl)]_2(\mu\text{-}CH_2CH_2)$.[6] Interestingly, in contrast, the reaction of Cp_2HfCl_2 with an excess of Et_3Al in hexane selectively afforded $Cp_2HfEtCl$ in 89% yield. No formation of an ethylene bridged di-hafnium complex was detected. This method could be used for complexes containing other n-alkyl groups such as Pr and Bu^n groups.[7] These mono(alkyl)hafnocene chlorides **1** were cleanly obtained in 76-89% yields (by NMR). It is noteworthy that Cp_2HfRCl (R = Et, Pr^n, or Bu^n) were inert toward another equiv of R_3Al. This inertness is very attractive to prepare mono(alkyl)hafnocene compounds selectively. The formation of dialkylhafnocene Cp_2HfR_2 was not observed. The complexes **1** (R = Et, Pr^n, or Bu^n) were precipitated as micro crystals at -40°C in hexane. Filtration provided pure compounds in 73, 65, and 55% yields for Et, Pr^n, and Bu^n, respectively.

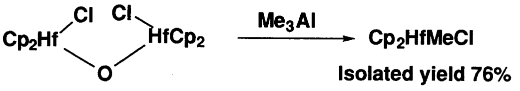
$$\mathbf{Cp_2HfCl_2} \xrightarrow{\mathbf{R_3Al}} \underset{\mathbf{1}}{\mathbf{Cp_2HfRCl}} \overset{\mathbf{R_3Al}}{\not\longrightarrow} \mathbf{Cp_2HfR_2} \qquad (2)$$

R = Et: 89%(73%); Pr-n: 76%(65%); Bu-n: 89%(55%)

Methyl-analog $Cp_2HfMeCl$ was not cleanly formed by this method using Me_3Al. However, reaction of **1** with a different alkylaluminum R'_3Al led to an alkyl exchange reaction to form $Cp_2HfR'Cl$. Therefore the reaction of Cp_2HfRCl with Me_3Al could provide $Cp_2HfMeCl$. In fact the reaction of $Cp_2HfEtCl$ with an excess (5 equiv) of Me_3Al gave $Cp_2HfMeCl$ in 85% isolated yield. When $Cp_2HfEtCl$ was treated with one equiv of Me_3Al in C_6D_6 and hexane, a mixture of $Cp_2HfMeCl$ and $Cp_2HfEtCl$ was obtained in a ratio of 1.6:1. Similar alkyl group exchange of dialkyl-hafnocene with trialkylaluminum has been reported.[4d]

$$\mathbf{Cp_2HfEtCl} \xrightarrow{\text{5 eq. } Me_3Al} \underset{\text{85\% isolated yield}}{\mathbf{Cp_2HfMeCl}} \qquad (3)$$

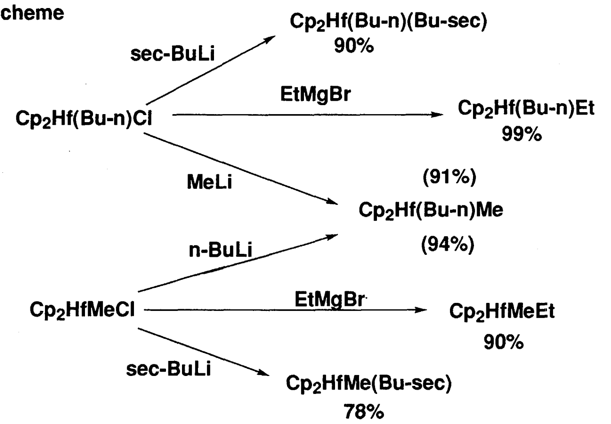
$Cp_2HfMeCl$ obtained by this alkyl exchange method from $Cp_2HfEtCl$ contained 2% of $Cp_2HfEtCl$ as an impurity after crystallization at -40°C. In order to prepare the pure $Cp_2HfMeCl$, we tried the reaction of oxo-bridged complex with Me_3Al as reported for a zirconium case.[8] This reaction smoothly proceeded to give pure $Cp_2HfMeCl$ in 76% isolated yield.[9] Interestingly, this method did not give **1** (R = Et, Pr, or Bu^n) cleanly, when other alkylaluminum compounds such as Et_3Al, Pr_3Al and Bu^n_3Al were used.



(4)

Thus mono(alkyl)hafnocene chlorides **1** were selectively obtained. Mono(alkyl)hafnocene chlorides reacted with one equiv of R'Li to give Cp_2HfRR' ($R \neq R'$)[10] selectively as shown in the scheme.

Scheme



Dialkylhafnocene complexes **2** such as Cp_2HfBu^nEt thus prepared were very pure. The ^{13}C NMR spectrum of Cp_2HfBu^nEt prepared *in situ* is shown in Figure. This spectrum was taken in C_6D_6 just after evaporation of the solvent without any purification. The complex Cp_2HfBu^nEt obtained here was stable in THF at room temperature. Disproportionation to produce $Cp_2HfBu^n{}_2$ or Cp_2HfEt_2 was not observed.

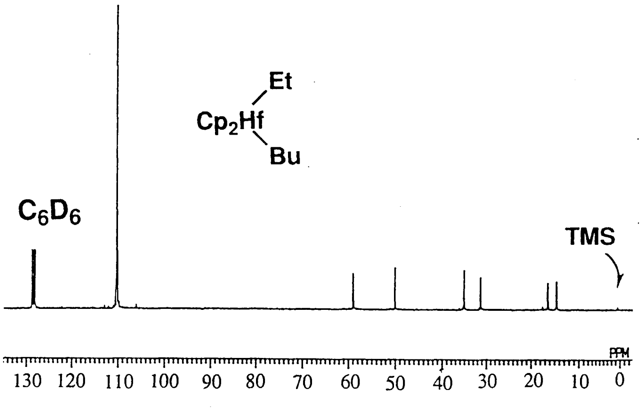


Figure. ^{13}C NMR spectrum of Cp_2HfBu^nEt prepared *in situ*.

References and Notes

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7 R = Et: ^1H NMR (C_6D_6, Me_4Si) δ 0.86 (q, *J* = 8Hz, 2H) 1.64 (t, J = 8Hz, 3H) 5.74 (s, 10H); ^{13}C NMR (C_6D_6, Me_4Si) δ 17.90, 46.68, 111.66. Anal. Calcd.for $C_{12}H_{15}ClHf$ C:38.62, H:4.06, Cl:9.50. Found C:38.28, H:3.90, Cl:9.68.; R = Pr: ^1H NMR (C_6D_6, Me_4Si) δ 0.79-0.82 (m, 2H), 1.11 (t, *J* = 7Hz, 3H), 1.59-1.73 (m, 2H), 5.73 (s, 10H). ^{13}C NMR (C_6D_6, Me_4Si) δ 22.66, 27.51, 58.71, 111.61. Anal. Calcd.for $C_{13}H_{17}ClHf$ C:40.32, H:4.43, Cl:9.15. Found C:40.25, H:4.38, Cl:9.00.; R = Bu^n: ^1H NMR (C_6D_6, Me_4Si) δ 0.81-0.87 (m, 2H), 1.04 (t, *J* = 7Hz, 3H), 1.41 (tq, J = 7Hz, 7Hz, 2H), 1.57-1.69 (m, 2H), 5.73 (s, 10H). ^{13}C NMR (C_6D_6, Me_4Si) δ 14.20, 30.76, 36.42, 55.35, 111.64. Anal. Calcd. for $C_{14}H_{19}ClHf$ C:41.90, H:4.78, Cl:8.83. Found C:41.73, H:4.67, Cl:8.98.

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9 ^1H NMR (C_6D_6, Me_4Si) δ 0.26(s, 3H), 5.68 (s, 10H); ^{13}C NMR (C_6D_6, Me_4Si) δ 33.84, 111.70. Anal. Calcd. for $C_{11}H_{13}ClHf$ C:36.78, H:3.66, Cl:9.87. Found C:36.70, H:3.69, Cl:9.79.

10 $Cp_2Hf(Bu\text{-}n)Et$: ^1H NMR (C_6D_6, Me_4Si) δ: 0.10-0.18 (m, 4H), 1.03 (t, *J* = 7 Hz, 3H), 1.46 (t, *J* = 8 Hz, 2H), 1.34-1.49 (m, 4H), 5.66 (s, 10H). ^{13}C NMR (C_6D_6, Me_4Si) δ: 14.20, 16.06, 31.07, 34.82, 49.76, 58.69, 109.88.; $Cp_2Hf(Bu\text{-}n)(Bu\text{-}sec)$:$^1H$ NMR (C_6D_6, Me_4Si) δ: 0.12-0.17 (m, 2H), 0.48-0.62 (m, 1H), 0.97 (t, *J* = 7 Hz, 3H), 1.00 (t, *J* = 7 Hz, 3H), 1.17 (d, *J* = 7 Hz, 3H), 1.23-1.43 (m, 6H), 5.66 (s, 5H), 5.67 (s, 5H). ^{13}C NMR (C_6D_6, Me_4Si) δ: 14.18, 16.56, 19.66, 30.64, 31.04, 34.74, 58.82, 62.92, 109.87, 109.92.; $Cp_2Hf(Bu\text{-}n)Me$:^1H NMR (C_6D_6, Me_4Si) δ: -0.34 (s, 3H), 0.12-0.17 (m, 2H), 1.01 (t, *J* =7 Hz, 3H), 1.29-1.37 (m, 2H), 1.40-1.50 (m, 2H), 5.66 (s, 10H). ^{13}C NMR (C_6D_6, Me_4Si) δ: 14.20, 30.91, 34.86, 36.93, 58.11, 109.79.; $Cp_2HfMeEt$: ^1H NMR (C_6D_6, Me_4Si) δ: -0.32 (s, 3H), 0.13 (q, *J* = 8 Hz, 2H), 1.46 (t, *J* = 8 Hz, 3H), 5.65 (s, 10H). ^{13}C NMR (C_6D_6, Me_4Si) δ: 16.15, 36.89, 49.18, 109.86.; $Cp_2HfMe(Bu\text{-}sec)$:^1H NMR (C_6D_6, Me_4Si) δ: -0.31 (s, 3H), 0.61-0.66 (m, 1H), 0.98 (t, *J* =7 Hz, 3H), 1.18 (d, *J* = 7 Hz, 3H), 1.21-1.34 (m, 2H), 5.65 (s, 5H), 5.66 (s, 5H). ^{13}C NMR (C_6D_6, Me_4Si) δ: 16.46, 19.69, 30.78, 37.36, 62.57, 109.88, 109.92. Some signals assinged to Cp or alkyl carbons of Cp_2HfRR' appeared at almost the same chemical shifts as those of Cp_2HfR_2 or $Cp_2HfR'_2$ in their ^{13}C NMR spectra. However, their ^1H NMR spectra indicated that Cp signals were different between them in all cases.