# Facile and reversible displacement of $\eta$-$C_5H_5$ from Zr by organolithiums; formation of ($\eta^5$-cyclopentadienyl)trialkylzirconiums and their reactions with electrophiles and alkenes

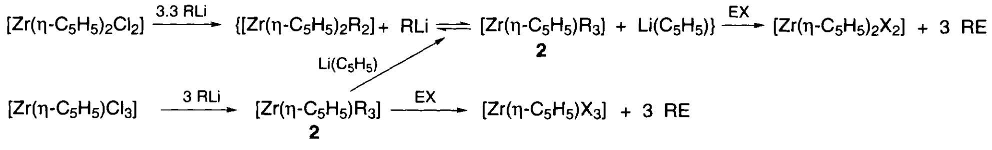
**Denis Kondakov and Ei-ichi Negishi***

*Department of Chemistry, Purdue University, West Lafayette, Indiana 47907, USA*

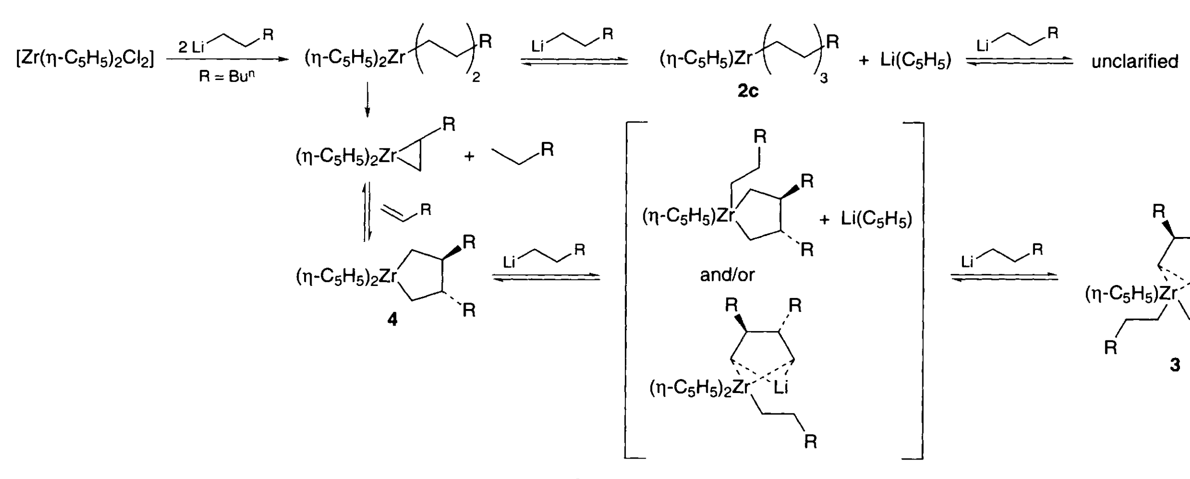
**Treatment of $[Zr(\eta\text{-}C_5H_5)_2Cl_2]$ with 3 equiv. of $Bu^nLi$ gives a 1:1 mixture of $[Zr(\eta\text{-}C_5H_5)Bu^n_3]$ and $Li(C_5H_5)$, which reacts with HCl or $I_2$ to give *n*-butane and $[Zr(\eta\text{-}C_5H_5)_2Cl_2]$ or $Bu^nI$ and $[Zr(\eta\text{-}C_5H_5)_2I_2]$, respectively, while the reaction of $[Zr(\eta\text{-}C_5H_5)_2Cl_2]$ with 3.3 equiv. of $C_6H_{12}Li$ and hex-1-ene provides a novel zirconate best represented by 3.**

The reactions of $Zr(\eta\text{-}C_5H_5)_2$ derivatives have been dominated by those in which the $Zr(\eta\text{-}C_5H_5)_2$ moiety remains intact,[1,2] the photoinduced chlorination[3] of $[Zr(\eta\text{-}C_5H_5)_2Cl_2]$ to give $[Zr(\eta\text{-}C_5H_5)Cl_3]$ being a significant exception to the above generalization. We have recently noted that treatment of dialkylzirconocenes, *e.g.* $[Zr(\eta\text{-}C_5H_5)_2Me_2]$, with Grignard reagents can lead to displacement of the alkyl groups *via* transmetallation without seemingly affecting the $Zr(\eta\text{-}C_5H_5)_2$ moiety.[4] Similar observations have also been made in the reaction of zirconacyclopentane derivatives with Grignard reagents.[5,6] We now report that, in marked contrast with alkylmagnesiums, alkyllithiums react with $Zr(\eta\text{-}C_5H_5)_2$ derivatives to induce a facile displacement of a $C_5H_5$ group to produce monocyclopentadienylzirconium $[Zr(\eta\text{-}C_5H_5)]$ derivatives (Scheme 1). We additionally report some intricate and dynamic processes that $Zr(\eta\text{-}C_5H_5)$ derivatives undergo (Schemes 1 and 2).

We have previously reported that treatment of $[Zr(\eta\text{-}C_5H_5)_2Cl_2]$ with 2 equiv. of $Bu^nLi$ gives thermally unstable $[Zr(\eta\text{-}C_5H_5)_2Bu^n_2]$ which readily decomposes to give $[Zr(\eta\text{-}C_5H_5)_2(CH{=}CHEt)]$ as a '$Zr(\eta\text{-}C_5H_5)_2$' equivalent.[1,7] With the hope of obtaining an 18-electron zirconate, *i.e.* $Li[Zr(\eta\text{-}C_5H_5)_2Bu^n_3]$ **1**, we treated $[Zr(\eta\text{-}C_5H_5)_2Cl_2]$ with 3 equiv. of $Bu^nLi$ and obtained a thermally stable product to which we tentatively and erroneously assigned **1**.[8] Indeed, similar 'ate' complexes represented by $Li[Zr(\eta\text{-}C_5H_5)_2R_2(R')]$, where R and R′ were Me and/or Ph, have previously been claimed as the products of a similar reaction of $[Zr(\eta\text{-}C_5H_5)_2R_2]$ with R′Li in $Et_2O$.[9] Even less plausible $Zr^{III}$ species, such as $[Zr(\eta\text{-}C_5H_5)R(R')]$ and $Li[(\eta\text{-}C_5H_5)RR'_2]$, were also claimed in the same paper.[9] Reexamination of the reaction of $[Zr(\eta\text{-}C_5H_5)_2Cl_2]$ with 3.3 equiv. of $Bu^nLi$ in thf (−78 to 25 °C) has now revealed that it actually gives in essentially quantitative yield $[Zr(\eta\text{-}C_5H_5)Bu^n_3]$ **2a**: $^1H$ NMR ($C_6D_6$–thf, $SiMe_4$) $\delta$ 0.0–0.15 (m, 6 H), 0.6–0.8 (m, 9 H), 0.9–1.1 (m, 6 H), 1.3–1.5 (m, 6 H), 5.75 (s, 5 H); $^{13}C$ NMR ($C_6D_6$–thf, $SiMe_4$) $\delta$ 14.37 ($CH_3$, 3 C), 31.70 ($CH_2$, 3 C), 35.53 ($CH_2$, 3 C), 53.47 ($CH_2$, 3 C), 108.87 (CH, 5 C). Also formed in 98% yield was $Li(C_5H_5)$ [$^1H$ NMR $\delta$ 5.60 (s); $^{13}C$ NMR $\delta$ 103.34]. Although many attempts to isolate and purify **2a** from this reaction mixture have led only to its decomposition, the assigned structure has been amply supported. Thus, treatment of commercial $[Zr(\eta\text{-}C_5H_5)Cl_3]$ with 3 equiv. of $Bu^nLi$ provided **2a** in 56% yield, which exhibited $^1H$ and $^{13}C$ NMR spectra that are indistinguishable from those listed above except for the singlet for $Li(C_5H_5)$. Furthermore, the NMR spectra of a mixture of the two samples did not show any sign of splitting or additional signals. The results not only support the structural assignment but also indicate the absence of detectable complexation between **2a** and



**Scheme 1** R = Me, $Bu^n$, $C_6H_{13}$. EX = HCl, $I_2$



**Scheme 2**

$Li(C_5H_5)$, invalidating $Li[(\eta\text{-}C_5H_5)_2R_3]$.[8,9] Secondly, treatment of **2a** prepared from $[Zr(\eta\text{-}C_5H_5)Cl_3]$ and 3 equiv. of $Bu^nLi$ with 3 mol $dm^{-3}$ HCl led to the formation of $[Zr(\eta\text{-}C_5H_5)Cl_3]$ in 68% yield and *n*-butane in 73% yield, while its treatment with $I_2$ gave $Bu^nI$ in 70% yield. Similarly, $[Zr(\eta\text{-}C_5H_5)Me_3]$ **2b**[10] [80% yield; $^1H$ NMR ($C_6D_6$–thf, $SiMe_4$) $\delta$ −0.50 (s, 9 H), 5.80 (s, 5 H); $^{13}C$ NMR ($C_6D_6$–thf, $SiMe_4$) $\delta$ 32.91, 108.52] and $[Zr(\eta\text{-}C_5H_5)(C_6H_{13})_2]$ **2c** [90% yield; $^1H$ NMR ($C_6D_6$–thf, $SiMe_4$) $\delta$ 0.0–0.15 (m, 6 H), 0.7–2.0 (m, 33 H), 5.75 (s, 5 H); $^{13}C$ NMR ($C_6D_6$–thf, $SiMe_4$) $\delta$ 14.60, 23.65, 32.66, 32.83, 38.95, 53.88, 108.82] were obtained by the reaction of $[Zr(\eta\text{-}C_5H_5)_2Cl_2]$ with RLi (R = Me, $C_6H_{13}$). Although not yet established, $[Zr(\eta\text{-}C_5H_5)R_3]$, a formal 12-electron species, must be associated with 1–3 equivalents of thf as in the case of $[Zr(\eta\text{-}C_5H_5)Cl_3]\cdot 2thf$.[3] Intriguingly, treatment of the reaction product consisting of $[Zr(\eta\text{-}C_5H_5)Bu^n{}_3]$ and $Li(C_5H_5)$ in a 1 : 1 ratio with HCl or $I_2$ produced *n*-butane and $[Zr(\eta\text{-}C_5H_5)_2Cl_2]$ or $Bu^nI$ and $[Zr(\eta\text{-}C_5H_5)_2I_2]$, respectively. These results, which were, in part, responsible for our earlier structural misassignments, can be rationalized if one assumes that a dynamic equilibrium shown in Scheme 1 exists and that $Bu^nLi$ is substantially more reactive than $Li(C_5H_5)$ towards HCl and $I_2$. In support of these assumptions, treatment of a 1 : 1 mixture of $Bu^nLi$ and $Li(C_5H_5)$ with 1 equiv. of $I_2$ indeed led to nearly exclusive conversion of $Bu^nLi$ into $Bu^nI$, and addition of 1 equiv. of $Li(C_5H_5)$ to $[Zr(\eta\text{-}C_5H_5)R_3]$ obtained from $[Zr(\eta\text{-}C_5H_5)Cl_3]$ led to a mixture which was chemically and spectroscopically identical with that obtained for $[Zr(\eta\text{-}C_5H_5)_2Cl_2]$ and RLi.

Even more intriguing is the reaction of the mixture obtained by the treatment of $[Zr(\eta\text{-}C_5H_5)_2Cl_2]$ with 3.3 equiv. of $C_6H_{13}Li$ with hex-1-ene (1 equiv.). After 3 h at 22 °C, quenching of the reaction mixture with 10% DCl gave DL-5,6-bis(monodeuteriomethyl)decane (80% yield, ≥95% D). Although the organometallic product before quenching has not been fully identified, analysis by NMR indicated the formation of a 1 : 1 mixture of $Li(C_5H_5)$ and a single Zr-containing species in 84% yield based on a quantitative analysis of the cyclopentadienyl signals [$^1H$ NMR ($C_6D_6$–thf, $SiMe_4$) $\delta$ −0.12 (t, *J* 10 Hz, 2 H), 0.05– 0.20 (m, 4 H), 0.6–1.0 (m, 14 H), 1.0–2.1 (m, 30 H), 5.68 (s, 5 H); $^{13}C$ NMR ($C_6D_6$–thf, $SiMe_4$) $\delta$ 14.57 ($CH_3$, 2 C), 14.77 ($CH_3$, 2 C), 23.52 ($CH_2$, 2 C), 24.15 ($CH_2$, 2 C), 30.47 ($CH_2$, 1 C), 30.68 ($CH_2$, 2 C), 30.96 ($CH_2$, 1 C), 32.63 ($CH_2$, 2 C) 37.97 ($CH_2$, 1 C), 38.03 ($CH_2$, 1 C), 40.15 ($CH_2$, 2 C), 51.34 (CH, 2 C), 52.08 ($CH_2$, 1 C), 52.92 ($CH_2$, 1 C), 61.60 ($CH_2$, 2 C), 107.96 (CH, 5 C)]. These spectroscopic data clearly indicate that it contains one $Zr(\eta\text{-}C_5H_5)$ moiety and two NMR-nonequivalent *n*-hexyl groups as well as one DL-5,6-dimethyldecamethylene moiety in which the two halves are NMR-equivalent (2 CH groups at $\delta$ 51.34). These data also require the presence of one Li. Although all attempts to obtain its crystals have been unsuccessful, one likely structure consistent with the available data is **3**, in which not only the cyclopentadienyl but also the DL-5,6-dimethyldecamethylene moiety are fluxional. Time-averaging of the two halves of the DL-5,6-dimethyldecamethylene moiety may involve its rapid rotation *via* transmetallation. It is important to note that neither $[Zr(\eta\text{-}C_5H_5)(C_6H_{13})_3]$ prepared from $[Zr(\eta\text{-}C_5H_5)Cl_3]$ nor a mixture obtained by treatment $[Zr(\eta\text{-}C_5H_5)_2Cl_2]$ with 4 equiv. of $C_6H_{13}Li$ reacts with hex-1-ene to induce alkyl–alkene coupling. However, the formation of **3** was observed by (*i*) the reaction of $[Zr(\eta\text{-}C_5H_5)_2Cl_2]$ with 3.3 equiv. of $C_6H_{13}Li$ and hex-1-ene (1 equiv.) as stated above, (*ii*) the reaction of preformed **4** (generated *in situ* in 69% yield) with 2 equiv. of $C_6H_{13}Li$ (86% yield by NMR), and (*iii*) addition of 0.18 equiv. of $[Zr(\eta\text{-}C_5H_5)_2(C_6H_{13})_2]$ to the inert mixture obtained from $[Zr(\eta\text{-}C_5H_5)_2Cl_2]$, 4 equiv. of $C_6H_{13}Li$ and hex-1-ene (64% yield by NMR).

These results strongly suggest the transformations shown in Scheme 2. We believe that ring opening of zirconacyclopentanes by their reactions with organometals, *e.g.* alkylithiums, and other metal-containing compounds can be facile and possibly general. Similar processes of zirconacyclopentenes have also been recently proposed by us.[11] In view of the growing synthetic significance of dialkylzirconocenes, the knowledge of the effects of an excess of alkyllithium reagents is of potential importance.

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