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gaps.[14] By mixing thiophene and isothianaphthothiophene we arrive at poly(isonaphthothiophene–thiophene), PINTT, as shown in Figure 4. In this polymer the two repeat units are connected by a CC bond of intermediate strength, and the calculated gap is expected to be rather small.

We have to note that there are several factors neglected in the above model which can increase the real energy gap: steric effects which may cuase nonplanarity, short conjugated segments due to cross-links, randomly coiled segments, etc. Last but not least, electron–electron interactions and correlation effects may influence the band gap. Nevertheless, the parametrization of our model has been quite successful for several related systems (cf. Table I), which leads us to conclude that the present estimations for the band gaps of PBITNM (0.7 eV) and PINTT (0.5 eV) are not far from reality. Even though the reduced alternation of $\delta r_{av} = 0.044$ Å along the main chain for PBITNM would predict a gap of 1.5 eV × (0.044/0.090) = 0.73 eV if one based the gap solely on the alternation of the C–C–C–C carbon skeleton, this agreement with the theoretical prediction of 0.69 eV is completely fortuitous. Orbital interpretation of the small gap is in concordance with earlier results.[3,6,8] The frontier orbitals are delocalized over the main chain as well as the side rings and heteroatoms. Although these two materials have not been synthesized yet, syntheses of similar polymers[15a,b] and oligomers[15c] have been reported recently.

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**Supplementary Material Available:** Parameters used in the present study (4 pages). Ordering information is given on any current masthead page.

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## Synthesis and Reactivity of Bis-Stannylene Adducts of Zirconocene and (1,1′-Dimethyl)zirconocene. X-ray Crystal Structure of $(C_5H_4CH_3)_2Zr\{Sn[CH(SiMe_3)_2]_2\}_2$

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The formation and transformation of transition metal to main group element bonds are important steps in a variety of processes including metal mediated hydrometalation cycles,[1] dehydrogenative polymerizations,[2] and semiconductor growth.[3] New methods for generating such bonds are thus of interest, particularly in cases where existing synthetic procedures do not work efficiently. For example, although group 4–silicon compounds have found extensive application in some of the above-mentioned processes,[2,4] group 4–tin derivatives remain virtually unknown,[5] primarily due to a lack of synthetic technology.[6] Herein we report the synthesis of a new Zr–Sn complex via a route that takes advantage of zirconium's strong Lewis acidity and the propensity of two carbene-like fragments to couple. The resulting metal–metal bonds are stabilized by a significant $\pi$ component as indicated by a short Zr–Sn distance.

In situ generated "zirconocene"[7] was trapped while warming a THF solution of $Cp'_2Zr(n\text{-}Bu)_2$[8] ($Cp' = C_5H_5$ (**a**), $C_5H_4CH_3$ (**b**)) to room temperature from −78 °C in the presence of 2 equiv of Lappert's monomeric stannylene $Sn[CH(SiMe_3)_2]_2$[9] (Scheme I). During warming, a slow darkening of the reaction mixture was observed. Upon stirring at room temperature for 1 h, removal of the THF followed by extraction with hexanes yielded a deep blue filtrate from which red-purple microcrystals of $Cp'_2Zr\{Sn[CH(SiMe_3)_2]_2\}_2$ (**1a** and **1b**) could be isolated in 40–55% yield. Although the reaction proceeded in better than 80% yield based on crude product returns, isolated yields were lower owing to the high solubility of both **1a** and **1b** even in hydrocarbon solvents.[10]

The $^1H$ and $^{13}C\{^1H\}$ NMR spectral data obtained for **1a** and **1b** (supplementary material) indicated that 2 equiv of stannylene were incorporated into the products. Originally it was anticipated that the bulky nature of the stannylene would prevent coordination of the second equivalent; nevertheless, when the reaction was performed with 1 equiv of stannylene, only lower yields of **1a** were obtained. An X-ray diffraction analysis[11,12] on crystals of **1b** confirmed that the formally Zr(II) center had accommodated two stannylene donors and possesses pseudo-tetrahedral geometry with a 2-fold axis bisecting the Cp–Zr–Cp and Sn–Zr–Sn′ angles. The $CH(SiMe_3)_2$ groups on tin are positioned above and below the plane defined by Sn–Zr–Sn′, an orientation which aligns the empty p-orbitals on the two Sn atoms for maximum $\pi$ overlap with the filled $1a_1$ orbital of the $Cp_2Zr^{II}$ fragment.[13] Additionally, the alkyl groups are bent back slightly (9.67°) from the Zr–Sn vector, i.e., the Sn atom sits 0.155 Å above the plane defined by Zr, C(7), and C(8). Though these structural features favor a $\sigma$ interaction between the two tin p-orbitals (I, Scheme I), it appears that steric interaction between the alkyl groups has arrested Sn–Sn bond formation in this complex; the large separation of 4.236 Å indicates that any Sn–Sn interaction is weak.[14]

The most interesting datum is the Zr–Sn distance of 2.8715 (11) Å. A handful of group 4 metal–tin complexes have been structurally characterized[5c,f] and typically the M–Sn bond is long

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(12) Selected bond distances (Å) and angles (deg) with estimated standard deviations in parentheses: Zr–Sn, 2.8715 (11); Zr–$Cp_{cent}$, 2.196 (8); Sn–Sn′, 4.236 (2); Sn–Zr–Sn′, 95.06 (4); $Cp_{cent}$–Zr–$Cp_{cent}'$, 131.5 (3); C(7)–Sn–C(8), 102.4 (2); C(7)–Sn–Zr, 135.9 (2); C(8)–Sn–Zr, 120.5 (2).

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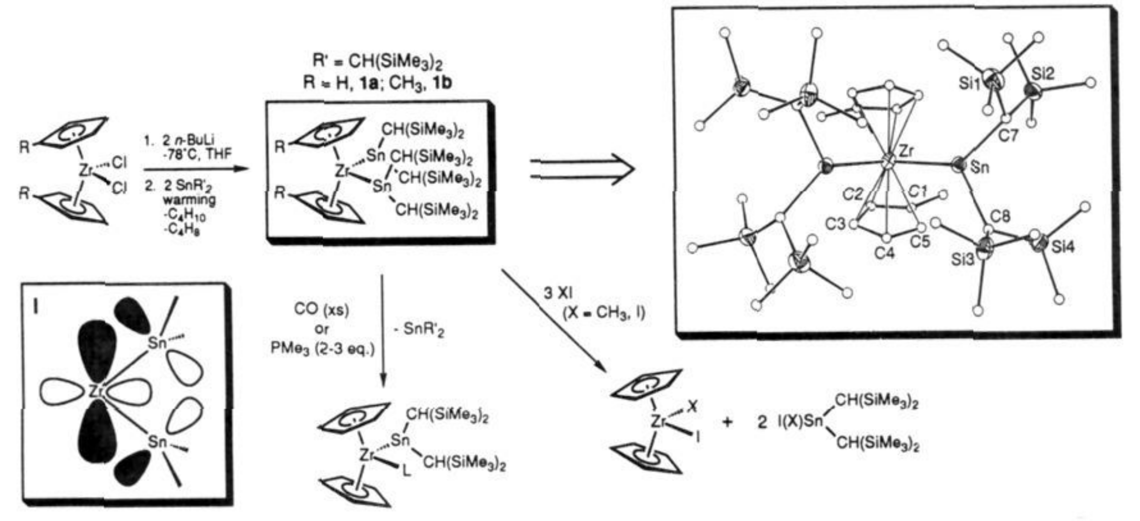
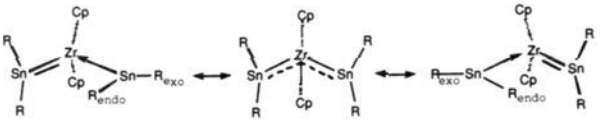
**Scheme I**



**Scheme II**



when compared to the sum of the covalent radii. This has been attributed in part to the absence of $\pi$ back-bonding in these (mostly) $d^0$ derivatives. For **1b**, despite the steric requirements of the stannylene ligand, the Zr–Sn distance is only slightly greater than the sum of the covalent radii ($\approx$2.85 Å)[15] and is considerably shorter than the Zr–Sn distance of 3.086 (1) Å reported[5a] for $[(Ph_3Sn)_4Zr(CO)_4]^{2-}$, a comparable 8-coordinate Zr(II) species. It is clear from both the orientation of the $SnR_2$ ligands and the short Zr–Sn distance that significant $\pi$ donation from Zr to Sn is occurring in **1b**.[16]

Both **1a** and **1b** are fluxional in solution. At room temperature, an $^1H$ NMR spectrum consistent with the solid-state structure is observed. At −30 °C the resonance for the $SiMe_3$ groups broadens and splits into three singlets at 0.44, 0.37, and 0.31 ppm in a 1:1:2 ratio, respectively. We interpret these observations in terms of a rotation of one stannylene ligand into the Sn–Zr–Sn′ plane (Scheme II). In this limiting structure, $\pi$ bonding is maximized between Zr and the perpendicular stannylene ligand, while the in-plane stannylene now functions as a datively bonded Lewis base. This structure is analogous to predicted[17] and observed[18] $d^2$ metallocene–carbene complexes stabilized by a Lewis base.

We have begun to explore the reactivity of these compounds (Scheme I). Reactions with other Lewis bases ($PMe_3$, CO) proceed slowly to form composite zirconocene–Lewis base adducts. Qualitatively, the rates of these substitution reactions are comparable, suggesting a dissociative mechanism in which the rate-limiting step is loss of $SnR_2$. Reactions with electrophiles (MeI, $I_2$) yield the oxidative addition products expected upon reaction of these reagents with free $SnR_2$[19] and "zirconocene".[20] Since we are most interested in reactions which preserve the Zr–Sn linkage, we are currently exploring the reactivity of **1a** and **1b** with oxidizing agents. This approach appears promising and results will be reported in due course.

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**Supplementary Material Available:** Experimental details, spectroscopic and analytical data for **1a** and **1b**, and tables of crystal, collection, and refinement data, atomic coordinates and isotropic thermal parameters, bond lengths and angles, H atom coordinates, and anisotropic thermal parameters for **1b** (9 pages); listing of observed and calculated structure factors for **1b** (19 pages). Ordering information is given on any current masthead page.

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# Diastereoselective Additions of Chiral (*E*)-Crotylsilanes to $\alpha$-Alkoxy and $\beta$-Alkoxy Aldehydes. A One-Step, Silicon-Directed Tetrahydrofuran Synthesis

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Substituted furans occur frequently as subunits of many biologically important natural products including the structurally complex polyether[1] and nucleoside[2] antibiotics. Within the context of natural product synthesis, the construction of furans having well-defined stereochemistry remains a current challenge in organic synthesis.[3] Here we describe an operationally simple method for the assemblage of highly functionalized tetrahydrofurans from simple achiral aldehydes and chiral (*E*)-crotylsilanes, under mild

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