Coordination Chemistry of Cyclic Disilylated Stannylenes and Plumbylenes to Group 4 Metallocenes

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1. INTRODUCTION

The chemistry of heavier carbone analogues has attracted the attention of both experimentally and theoretically oriented chemists over the last decades.1,2 The fundamental differences in electronic ground states, reactivities, and structures between carbenes and their heavier counterparts are certainly a major reason for this attraction. Heavy tetrylenes usually possess a singlet ground state with an increasing singlet–triplet gap with higher atomic number.3 Responsible for this ground-state preference is a progressing reluctance to form hybrid orbitals. The s-electrons of the thus preferred (ns)2(np)2 configuration remain paired. As a consequence of this, dimerization of divalent species is not necessarily a favored process. Most heavier tetrylene dimers do not feature π-bonds, as common for olefins, but rather exist as dimeric donor–acceptor adducts. Attachment of electropositive substituents to the divalent group 14 atoms forms some mixing of their s- and p-orbitals. This way the singlet–triplet gap can significantly be diminished. Sekiguchi’s distannene (Bu2MeSi)2SnSnBu2, which, despite rather bulky groups on the tin atoms, does not disassociate into monomers in solution, is a good example for this behavior.4 Descending group 14 further to lead, the reluctance to form dimeric compounds becomes even more pronounced. This is nicely illustrated by the difference between bis[tris(trimethylsilyl)]silyletin and the analogous lead compound. While both compounds exist as monomers in solution, the stannylene crystallizes as a distannene, while the plumbylene retains its monomeric structure in the solid state.5

Recently, we could show that the bidentate tetrakis-(trimethylsilyl)tetramethyltetraethylsilanylene ligand can be employed to stabilize divalent tin and lead compounds.6,7 These can be isolated either as the respective base adducts (1 and 2) or as dimers (3 and 4). The dimeric stannylene and plumbylene compounds 3 and 4 exhibit considerable structural differences. While the tin compound 3 is the result of a dimerization–rearrangement process of a disilylated stannylene and exists as an endocyclic bicyclic distannene,6 the plumbylene appears as a monomer in solution but crystallizes as a weak donor–acceptor adduct (4).7

In the present contribution we report on an extension of these studies to explore the coordination chemistry of disilylated stannylene and plumbylene compounds with early transition metals and in particular with group 4 metallocenes. Only few examples of related compounds are known so far. In a seminal study Piers and co-workers8,9 could demonstrate complexation of Lappert’s stannylene10 Sn(CH(SiMe3)2)2 to zirconocene derivatives. More recently reactions of C,N-chelated tin(II) and lead(II) compounds to zirconocene were reported by Ruzicka and co-workers.11 In the latter case the employed plumbylene decomposed to elemental lead and free ligand during the reaction, thus no compound with a Zr–Pb bond was observed.11 In this context also the formation of a hafnocene silylene complex, reported recently by Sekiguchi and co-workers, should be noted.12 That the heavier tetrylenes can display quite different bonding motifs to transition metals has been shown recently by Hahn and co-workers.13

2. RESULTS AND DISCUSSION

Synthesis. For the synthesis of group 4 metallocene plumbylene and stannylene complexes a new general approach
was sought. In the mentioned examples, the zirconocene stannylene complexes were prepared by warming Negishi zirconocene Cp2ZrCl2−2BuLi in the presence of 2 equiv of stannylene from −80 °C to room temperature, thus limiting the scope of the reaction to zirconium.8,9,11 Alternatively, we found that reductions of group 4 metallocene dichlorides with magnesium15,16 in the presence of stannylene or plumbylene phosphine adducts (1 and 2) provided smooth conversion to the desired complexes (5−10) (Scheme 1). Isolated yields after crystallization from pentane of these highly colored compounds were above 80%. The plumbylene complexes of titanocene (8), zirconocene (9), and hafnocene (10) represent the first examples of compounds with group 4 metal−lead bonds. In general it should be noted that the number of known plumbylene transition-metal complexes is quite small.17

By reaction of 1,2-dipotassiodisilanes and -digermanes with metallocene dichlorides, we recently succeeded in the synthesis of group 4 disilene and digermene complexes.18 When this reaction, however, was carried out with the respective 1,2-dipotassiodistannane, instead of the expected distannene complexes, metallacyclotetrastrannanes were isolated as the only tin containing products.18 This behavior of tin was attributed to its greater preference for the divalent state compared to its lighter congeners.18 As the distannene unit of 3 (Scheme 2) is held together by two bridging tetrasilanylene ligands, we reasoned that the dissociation to stannynes might be blocked, and thus an equimolar amount of 3 could serve as a precursor for a distannene complex. However, when Cp2HfCl2 was reduced with magnesium in the presence of an equimolar amount of 3, the only pentane soluble product was the hafnocene bis(stannylene) complex 11 (Scheme 2). Its formation is apparently facilitated by the reversible rearrangement of 3 to the exocyclic distannene isomer,6 which is the direct dimerization product of the monomeric stannylene 12 (Table 2).6 Coordination of the exocyclic distannene to the hafnocene would then favor the distannylene over the distannene complex as observed previously.18

Complex 11 was isolated in about 60% yield as thin almost black needles. Piers et al. briefly mentioned the possibility of replacing just one stannylene ligand in their zirconocene bis(stannylene) complex with PMe3, but no detailed information on this reaction was provided.9 Reaction of 11 with 2 equiv of PEt3 in fact led to selective formation of 7 and 1 (Scheme 2). Reaction of 3 with Cp2TiCl2 and magnesium yielded the titanocene bis(stannylene) complex 13 (Scheme 2), but in this case, starting material 3 was contaminated with KN(SiMe3)2 leading in addition to the formation of the trivalent titanium compound Cp2TiN(SiMe3)2 (14). The eventually obtained crystals contained 13 and 14 in a 1:1 ratio. An interesting aspect of these reactions is that attempts to react 3 with excess metallocene dichloride did not lead to monostannylene complexes but selectively to the distannylene compounds.

Under very similar conditions, employing magnesium reduction of hafnocene dichloride in the presence of 2 equiv of 4 even the hafnocene bis(plumbylene) complex 15 could be obtained in moderate yield (Scheme 3). Again, addition of PEt3 to 15 led to the selective formation of plumbylene phosphine adduct 2 and hafnocene complex 10. Due to the very high

Scheme 1. Formation of Group 4 Metallocene Stannylene and Plumbylene Complexes

Scheme 2. Formation of Hafnocene and Titanocene Bis(stannylene) Complexes 11 and 13
solubility in pentane of both 11 and 15, they were difficult to isolate, and unfortunately only rather low-quality crystals could be obtained and used for X-ray diffraction experiments.

A reaction of Cp₂ZrCl₂ and magnesium with a substoichiometric amount of 4 (Scheme 4) was carried out to check whether the preference for the formation of ditetrylene complexes extends to lead. The formation of the zirconocene plumbylene complex 16, where the vacant coordination site at zirconium is occupied by a THF molecule, showed this not to be the case.

In order to assess the general applicability of this simple access to group 4 metal tetrylenes, we reacted TaCl₅ as a group 5 compound with magnesium in the presence of stannylene adduct 1 (Scheme 5). The successful formation of a stannylene complex of TaCl₅, 17, was confirmed by NMR spectroscopy, and a low-quality crystal structure, which revealed a distorted octahedral coordination geometry around tantalum with two trans-oriented PE₃ ligands.

**NMR Spectroscopy.** Distannene 3 exhibits a typical distannene ¹¹⁹Sn NMR shift of 545 ppm, strongly indicating the persistence of the Sn=Sn double bond in solution. Further proof for the retained Sn–Sn bond in solution is the presence of ¹¹⁷Sn satellites in the ¹¹⁹Sn NMR spectrum of 3. The coupling constant of ¹¹⁷J(¹¹⁷Sn/¹¹⁹Sn) = 1240 Hz is relatively small compared to a value of 2930 Hz found for Masamune’s tetraaryldistannene, suggesting only weak bonding of donor–acceptor type. By coordination of a phosphine ligand to the stannylene (1), electron octet configuration is achieved. Therefore, chemical shifts far uphill from those expected for the free stannylene 12 are observed. In 1 the ¹¹⁹Sn resonance was found at -224 ppm, consistent with the very recent report by Escudié and co-workers for the NHC adduct of bis[(trimethylsilyl)silyl]tin (δ = -197 ppm). The ¹¹⁹Sn NMR signal of 1 is split into a doublet by the adjacent ³¹P nucleus with a coupling constant of 2220 Hz. The group 4 metalocene stannylene complexes 5–7 display downfield shifted ¹¹⁹Sn resonances compared to 1. The chemical shift of titanocene complex 5 was found to be 1635 ppm with the signal being a doublet with ²¹J(¹¹⁹Sn/³¹P) = 276 Hz coupling to phosphorus. The respective zirconocene and hafnocene complexes 6 and 7 exhibit their ¹¹⁹Sn signals at considerably higher field at 1263 ppm (6, ²¹J(¹¹⁹Sn/³¹P) = 132 Hz) and 1080 ppm (7, ²¹J(¹¹⁹Sn/³¹P) = 92 Hz) with smaller coupling constants. The same trend can also be observed in the ³¹P spectra of these complexes, as the chemical shift ranges from 50.2 ppm in the titanocene complex down to 38.5 ppm for zirconium (6) to finally 34.8 ppm in the hafnium case (7) (Table 1). NMR spectroscopy thus clearly suggests an increasing degree of π-back-donation when descending group 4.

For the hafnium bis(stannylene) complex 11 the ¹¹⁹Sn NMR resonance was found at a much lower field at 1785 ppm. This is in good agreement with the value of 1677 ppm observed by Piers and co-workers for their zirconocene bis(stannylene) complex. The zirconocene bis(stannylene) complex published by Ruzicka and co-workers for the NHC adduct of bis[tris(trimethylsilyl)silyl]tin (δ = -197 ppm). The ¹¹⁹Sn NMR signal of 1 is split into a doublet by the adjacent ³¹P nucleus with a coupling constant of 2220 Hz. The group 4 metalocene stannylene complexes 5–7 display downfield shifted ¹¹⁹Sn resonances compared to 1. The chemical shift of titanocene complex 5 was found to be 1635 ppm with the signal being a doublet with ²¹J(¹¹⁹Sn/³¹P) = 276 Hz coupling to phosphorus. The respective zirconocene and hafnocene complexes 6 and 7 exhibit their ¹¹⁹Sn signals at considerably higher field at 1263 ppm (6, ²¹J(¹¹⁹Sn/³¹P) = 132 Hz) and 1080 ppm (7, ²¹J(¹¹⁹Sn/³¹P) = 92 Hz) with smaller coupling constants. The same trend can also be observed in the ³¹P spectra of these complexes, as the chemical shift ranges from 50.2 ppm in the titanocene complex down to 38.5 ppm for zirconium (6) to finally 34.8 ppm in the hafnium case (7) (Table 1). NMR spectroscopy thus clearly suggests an increasing degree of π-back-donation when descending group 4.

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region. The associated downfield shift compared to $\delta = 1080$ ppm found for $7$, which contains also a third row transition metal and a phosphine ligand, is likely caused by a combination of several factors. Together with the fact that compound $17$ is a 14 electron complex, the electrongative chloride substituents further diminish electron density at the metal. This certainly affects the ability of the tantalum atom to engage in back-donation.

Four signals in the $^{29}$Si NMR spectrum of complex $11$ indicate the equivalence of both five-membered rings in the complex. However, the two faces of each ring are not equivalent as two signals for the four SiMe$_3$ groups were observed. The same molecular symmetry was also derived from the respective $^1$H and $^{13}$C NMR spectra. This face differentiation suggests hindered rotation around the $Zr$--Sn bond in compound $11$.

The $^{207}$Pb NMR spectroscopic results for the plumbylene complexes $8$--$10$ show a similar trend as observed for their stannylene counterparts ($5$--$7$). A steady decrease in the chemical shift value descending group $4$ was found: titanocene plumbylene complex $8$ resonates at $\delta = 5299$ ppm, zirconocene complex $9$ at $\delta = 4165$ ppm, and finally hafnocene plumbylene $10$ at $\delta = 3462$ ppm. The expected splitting into doublets caused by coupling to the $^{31}$P nucleus of the phosphine ligand was not observed. The weaker bonds between Pb and the respective metal, compared to the analogous stannylene complexes, in addition to the fact that the $^{207}$Pb signals are comparably broad [values for full width at half-maximum (fwhm) range from $130$ to $220$ Hz] seem to impede the observation of the $^3J_{\mathrm{PbP}}$ coupling. $^{31}$P NMR spectroscopic results for compounds $8$--$10$ parallel the behavior observed for their lighter tin congeners. The $^{31}$P NMR shifts are $\delta = 57.6$, $46.3$, and $45.5$ ppm for $8$--$10$, respectively. The observed trend points again to a higher degree of back-bonding between the group $4$ metal and Pb in Zr and Hf compounds $9$ and $10$ compared to titancene complex $8$. The dependence of the M--E back-bonding from the additional phosphine ligands can be estimated from a comparison of the $^{207}$Pb NMR chemical shifts of the plumbylene zirconocene $9$ ($\delta = 4165$ ppm) with the respective THF adduct $16$ ($\delta = 5770$). A downfield shift of ca. $\Delta \delta^{207}\text{Pb} = 1600$ ppm illustrates the superior electron-donating ability of the phosphine compared to THF.

Compared to a $^{207}$Pb NMR chemical shift of $\delta = 3587$ ppm reported for $[\text{Fe(CO)}_3]_2\text{Pb}$, the strongly downfield shifted resonances between $\delta = 3462$--$5770$ ppm for compounds $8$--$10$ and $16$ seem to indicate a marked plumbylene character. However, these chemical shifts have to be seen in the context of the free plumbylene, $18$, for which an extremely downfield shifted $^{207}$Pb resonance at $\delta = 19516$ ppm was found. Compared to this, the plumbylene character of $8$--$10$ and $16$ seems to be not so pronounced.

The increasing electronic saturation of the Pb atom also can be observed in the $^{29}$Si NMR spectra. In $8$ the central silicon atoms resonate at $\delta = -16$ ppm. With stronger $\pi$-back-bonding from the $d^2$ transition metal to the plumbylene, this resonance shifts upfield to $\delta = -42$ and $-54$ ppm for $9$ and $10$, respectively. Consistent with this argumentation, the comparison of $9$ and $16$ revealed a downfield shift of the $^{29}$Si resonance of the silicon attached to Pb from $\delta = -42$ ppm for $9$ to $\delta = -37$ ppm for $16$. The $^{29}$Si signals for the more remote silicon atoms in $8$--$10$ are found at almost identical positions, suggesting a very similar chemical environment. For $8$--$10$ two different resonances for the trimethylsilyl groups were observed indicating hindered rotation around the metal--Pb bond and also no dissociation of phosphines. In contrast to this, only one SiMe$_3$ signal was observed for $16$, which suggests dissociation of THF, which can also be concluded from broadened signals in the respective $^1$H spectrum. For hafnocene bis(plumbylene) complex $15$ only $^1$H, $^{13}$C, and $^{29}$Si NMR data could be obtained. The spectra for these nuclei are very similar to those of $11$ and consistent with the proposed structure.

**X-ray Crystallography.** As all six phosphine tetrylene complexes ($5$--$10$) are isostructural, only one example of each group is shown [Figure 1: $7$ and Figure 2: $10$; depictions of the others ($5$, $6$, $8$, and $9$) are available in the Supporting Information (Figures S1--S4)]. Compounds $5$--$10$ feature planar geometries around the tetrel(II) center and short transition-metal tetrel(II) bond lengths. The sums of bond angles around tin or lead in all six examples match $360^\circ$ almost exactly with a maximum deviation of $0.5^\circ$. The group $4$--$E$ ($E = $ Sn or Pb) bond lengths are significantly shorter than the sum of tabulated covalent radii$^{22,23}$ or respective single bonds in the case of tin (Table $1$). For lead this comparison cannot be made, as compounds containing Ti, Zr, or Hf bonds to Pb have not been reported so far. The X-ray crystallographic study strongly supports the conclusions drawn from the NMR observations with respect to the extent of bond order between the group $4$ transition metals and tin or lead. Interesting in this respect is also the $P$ transition-metal--$E$ ($E = $ Sn or Pb) angle of $90^\circ$ in all compounds that ensures non-disturbance of the transition-metal interaction by the orthogonally coordinated phosphine ligand.

The crystals obtained of hafnocene bis(stannylene) $11$ and hafnocene bis(plumbylene) $15$ were not of high enough quality to permit a detailed structural discussion, therefore no metrical data can be given. But these structures (Figures S5 and S6, Supporting Information) still serve as proof for the atom connectivity and therefore validate the assignments made based...
on NMR spectroscopy. The crystals containing titanocene bis(stannylene) 13 (Figure 3) together with Cp2TiN(SiMe3)2 (14, Figure 4) in a 1:1 ratio were of much better quality. The bond lengths of Ti−Sn in 13, with 2.71 and 2.72 Å, reflect the diminished degree of back-bonding compared to 5 (2.69 Å). The structure of compound 14 is also interesting as it represents a rare example of a structurally characterized titanocene amide with Ti in the oxidation state +3.

Theoretical Studies. Optimizations of the molecular structures of the free tetrylenes 12 and 18, the group 4 element mono(tetrylene) complexes 5−10, and the metalloccenes bis(tetrylene) complexes 11, 13, 15, and 19−21 at the density functional M06-2X/SDD (Sn, Pb, Ti, Zr, Hf) and 6-31G(d) (P, Si, C, H) level of theory result in structural parameters which are very close to those found by X-ray diffraction methods for some of these compounds. Data which are important for the discussion are summarized in Table 2. For the tetrylenes 12 and 18 for which no experimental structural data are available, half-chair conformations of the metalacyclopentasilane rings were predicted with the heavy group 14 element and the two neighboring silicon atoms spanning the ortho positions.
Table 2. Selected Experimental and Calculated [in parentheses, at M06-2X/SDD (M,E), 6-31G(d) (Si,C,H)] Structural Parameter, WBI, Molecular Orbital Energy Differences $\Delta E$ and Experimental Element NMR Chemical Shifts for Tetrylenes 12, 18, Monotetrylene Complexes 5–10, and Bis-tetrylene Complexes of Group 4 Metalloccenes 11, 13, 15, 19–21.

| compd M–E | $d$(M–E) [pm] | $d$(E–Si) [pm] | $\alpha$(M–E) [$^\circ$] | $\alpha$(E–Si) [$^\circ$] | WBI (ME) | $\Delta E(d_{z^2}/\pi)$ [eV] | $\Delta E(p_x/\pi^*)$ [eV] | $\delta$ $^{3\text{rd}}$E expt | $\text{BDE}$ (ME) [kJ mol$^{-1}$] | $\text{BDE}^\text{B3LYP}$ (ME) [kJ mol$^{-1}$] | $\text{BDE}^\text{NCl}$ (ME) [kJ mol$^{-1}$] |
|----------|----------------|----------------|--------------------------|--------------------------|----------|---------------------------|---------------------------|------------------------|--------------------------|--------------------------|--------------------------|
| 5        | Ti–Sn          | 269.4(265.3)   | 264.7(267.5)             | 89.5 (91.1)              | 99.1 (98.3) | 1.23                       | 0.27                       | 1.21                   | 5.20                     | 1635$^a$                 | 151                       | 70                       | 81                       |
| 6        | Zr–Sn          | 279.4(278.0)   | 263.6(265.9)             | 90.8 (92.0)              | 99.3 (98.8) | 1.52                       | 0.60                       | 1.42                   | 5.45                     | 1263$^a$                 | 249                       | 162                      | 87                       |
| 7        | Hf–Sn          | 275.9(278.3)   | 262.4(265.2)             | 90.5 (92.0)              | 99.4 (99.1) | 1.58                       | 0.66                       | 1.55                   | 5.57                     | 1080$^a$                 | 270                       | 180                      | 90                       |
| 8        | Ti–Pb          | 272.7(275.4)   | 271.1(274.1)             | 90.2 (90.6)              | 97.8 (95.9) | 1.07                       | 0.34                       | 0.96                   | 5.04                     | 5209$^{b,c}$             | 118                       | 58                       | 60                       |
| 9        | Zr–Pb          | 282.1(284.3)   | 270.8(272.4)             | 90.1 (92.2)              | 98.0 (97.5) | 1.38                       | 0.62                       | 1.25                   | 5.40                     | 4165$^{c,d}$             | 215                       | 145                      | 70                       |
| 10       | Hf–Pb          | 279.3(284.2)   | 269.7(271.7)             | 90.1 (92.2)              | 98.2 (97.2) | 1.44                       | 0.67                       | 1.40                   | 5.83                     | 3462$^{d,e}$             | 234                       | 161                      | 73                       |
| 11       | Sn             | (267.4)        | (91.7)                    | (90.5)                   | 98.4 (97.6) | 1.07                       | 2172$^e$                  | 153$^e$                 | 60$^e$                    | 93                       |
| 12       | Pb             | (275.1)        | (267.1)                  | 89.0 (86.1)              | 98.4 (97.6) | 1.07                       | 19516$^{f}$               | 222$^e$                 | 133$^f$                   | 89                       |
| 13       | Ti–Sn          | 271.4(269.3)   | 264.8(267.1)             | 89.0 (86.1)              | 98.4 (97.6) | 1.07                       | 2172$^e$                  | 153$^e$                 | 60$^e$                    | 93                       |
| 14       | Zr–Sn          | (285.3)        | (267.3)                  | (90.1)                   | (97.6)       | 1.19                       | 1785$^f$                  | 239$^e$                 | 151$^g$                   | 88                       |
| 15       | Hf–Sn          | (286.1)        | (267.1)                  | (90.2)                   | (97.7)       | 1.22                       | 120$^f$                   | 47$^e$                  | 73                       |
| 16       | Ti–Pb          | (280.0)        | (274.6)                  | (87.5)                   | (95.9)       | 0.93                       | 193$^f$                   | 116$^g$                 | 77                       |
| 17       | Zr–Pb          | (291.6)        | (273.8)                  | (89.1)                   | (96.5)       | 1.15                       | 209$^{f,g}$               | 132$^f$                 | 77                       |

$^a$BDE of the ME bonds calculated using the M06-2X functional are given as BDE(ME). For comparison, the BDE computed applying the B3LYP functional, here denoted as BDE$^\text{B3LYP}$(ME), is summarized as well. Finally, the noncovalent contributions to the BDE, BDE$^\text{NCl}$(ME), calculated from the difference between BDE(ME) and BDE$^\text{B3LYP}$(ME) are listed. $^b$For definition see Figure 5. $^{119}$Sn NMR, $^{207}$Pb NMR. $^c$Mean value computed from the dissociation of the complex into a Cp,M fragment and two tetrylenes.
central plane. A common feature of all optimized molecular structures of the mono(tetrylene) (5–10) and of the metalloocene bis(tetrylene) complexes 11, 13, 15, and 19–21 are trigonal planar coordinated Sn or Pb atoms (sum of the bond angles ω around the element atom, Σω(E) = 358–360°) embedded in a half-chair metallacyclopentasilane ring of local C2 symmetry. The computational results indicate no significant influence of the complexation on the molecular structure of the tetrylene. The most obvious structural modification is a widening of the endocyclic SiESi bond angle α(SiESi) by 5.4–7.4° (see Table 2). In accordance with the available experimental structures, the results of the computation predict that the tetrylene units are oriented mostly perpendicular to the central E–M–P plane in tetrylene complexes 5–10 (dihedral angle β = 82–84°), while in the metalloocene bis(tetrylene) complexes 11, 13, 15, and 19–21, the equivalent dihedral angle is somewhat smaller (β = 65–74°). This specific arrangement allows for an efficient back-bonding from metal d-orbitals to the formally empty p-orbital at the tetryl atom. The calculated M–E(II) bond lengths, which are summarized in Table 2, show the expected trends. That is, for a given tetrylene the E–M distances increase along the series E–Ti < E–Zr ~ E–Hf, and the Sn–M separations are always smaller than the corresponding Pb–M distances. The calculated M–E(II) bond lengths as well as those determined experimentally (see Table 2) are all smaller than standard values for E–M single bonds (Sn–M: 276 pm (Ti), 294 pm (Zr), 292 pm (Hf); Pb–M: 280 pm (Ti), 298 pm (Zr), 296 pm (Hf)), in no case, however, the values predicted for σ2σ* E=–M double bonds are reached (Sn=–M: 247 pm (Ti), 257 pm (Zr), 258 pm (Hf); Pb=–M: 252 pm (Ti), 262 pm (Zr), 263 pm (Hf)). In agreement with these structural criteria also, the results of a natural bond orbital (NBO) analysis indicate the multiple-bond character for the M–E(II) linkage in mono- and bis(tetrylene) complexes 5–10, 11, 13, 15, 19–21 (see Table 2). In detail, all calculated Wiberg bond indices (WBI) are significantly larger than computed for the respective metalloocene–ditetrayl compound (Cp2M(EMe3)2)(E = Sn: 0.83 (Ti), 0.93 (Zr), 0.94 (Hf); E = Pb: 0.79 (Ti), 0.91 (Zr), 0.92 (Hf)]. As it is expected, the WBI for the M–E(II) bond for stannylene complexes are always larger than computed for the corresponding plumbylene complex, and the calculated bond orders for the M–E(II) bond, as expressed by the WBIs, increase for a given tetrel element in the order Ti < Zr ≤ Hf. In addition the calculated bond order is for each M–E pair larger for the mono(tetrylene) complex than for the metalloocene bis(tetrylene). These trends are also reflected by the computed bond dissociation energies for the M–E(II) bond BDE(Me) for the tetrylene complexes (see Table 2). The E–Ti bonds are significantly less stable than the E–Zr bonds [by 97 (5/6) and 98 kJ mol−1 (8/9) in the case of the mono(tetrylene) complexes and by 68 (13/19) and 72 kJ mol−1 (20/21) for the bis(tetrylene) complexes], and there is a second although smaller increase predicted for the BDE of the E–Hf bonds (by 17–21 kJ mol−1). The Pb–M bonds are for all calculated metalloocene complexes 29–36 kJ mol−1 weaker than the corresponding Sn–M linkages. The BDE values for the Ti–E bonds in mono(tetrylene) (5, 8) and bis(tetrylene) complexes 13, 20 are very similar (see Table 2). The situation differs, however, for the hafnocene and zirconocene complexes for which the computed BDEs of the M–E(II) bond are smaller in bis(tetrylene) complexes than in their mono(tetrylene) counterparts by 18–31 kJ mol−1.

The bonding between the zirconium and the tin atoms in the mono(tetrylene) complex 6 is rationalized by the orbital interaction diagram shown in Figure 5. This orbital interaction diagram is also valid qualitatively for all investigated metalloocene mono(tetrylene) complexes 5–10. Plots of the surface diagrams for frontier molecular orbitals (FMOs) of compound 6 can be found in the Supporting Information. The M–E(II) bond in complexes 5–10 is best described by the conventional σ-bonding/(d/p) π-back-bonding scheme for carbene complexes. In the framework of perturbation theory, the relative extent of back-bonding in the metalloocene tetrylene complexes can be estimated by the evaluation of the calculated orbital stabilization energy ΔE(dπ/σ) and the corresponding destabilization

Figure 5. FMO interaction scheme for monotetrylene complex 6, derived from M06-2X/SDD (Zr, Sn), 6-31G(d) (Si, P, C, H) calculations. This MO scheme is qualitatively valid for all investigated monometaenyl complexes 5–10.
energy $\Delta E(\pi^*/p_x)$ (see Figure 5 and Table 2). Both energy differences increase for both kinds of metallocene mono-(tetrylene) complexes along the series Ti < Zr < Hf. This suggests that the $d_{zx} \rightarrow p_x$ $\pi$-back-bonding is smallest for the titanium complexes (5–8) and largest for the hafnium compounds (7, 10).

The analysis also indicates that for each group 4 metallocene, the lowering of the $\pi$-orbital as expressed by $\Delta E(d_{zx}/\pi)$ is slightly smaller in the stannylene complexes (5–7) than in the corresponding plumbylene complexes (8–10, by 0.07 eV (Ti), 0.02 eV (Zr), 0.01 eV (Hf)). On the other hand, the effect of the tetrylene on the $\pi^*$ level is more significant, as the destabilization energy $\Delta E(\pi^*/p_x)$ is markedly larger for the stannylene complexes (5–7) than for the corresponding plumbylene complexes (8–10, by 0.25 eV (Ti), 0.17 eV (Zr), 0.15 eV (Hf)).

The poor ability of the titanocene to engage in $\pi$-bonding is mostly due to the poor spatial and energetic match between the 3$d_{xz}$ orbital of titanium and the 5$p_x$ orbital of the tin ($\Delta E(d_{zx}/p_x) = 2.65$ vs 2.08 eV for Zr or 1.88 eV for Hf) or $p_\sigma$ of lead atom ($\Delta E(d_{zx}/p_x) = 2.80$ vs 2.22 eV for Zr or 2.03 eV for Hf).

NMR chemical shifts of group 14 carbone analogs are always extremely large due to a dominant paramagnetic contribution, which arises from the efficient interaction of the applied magnetic field with the filled $sp^2$-type MO and the orthogonal empty $p$-type orbital at the dicordinated tetrel element.29 The paramagnetic shift is very large for small energy differences $\Delta E_{\pi\pi}^{para}$ between these two magnetically active orbitals.29 In the mono(tetrylene) complexes the $sp_3$ orbital is transformed to the $\sigma$-orbital of the M–E(II) bond, and the $p_z$ orbital can be associated with the $\pi^*$-orbital (Figure 5). Therefore, the $^{119}\text{Sn}$ NMR chemical shift of the stannylene complexes 5–7 and the $^{207}\text{Pb}$ NMR chemical shift of the metallocene plumbylene complexes 8–10 are determined mainly by the energy difference between these two molecular orbitals, $\Delta E_{\pi\pi}^{para}$ (see Figure 5).

While the energy of the $\sigma$-orbital remains nearly constant for a given tetrel element along the series of group 4 metals ($E(\sigma) = -6.09$ eV (5), $-6.13$ eV (6), $-6.12$ eV (7)), the $\pi^*$-level is significantly altered by the different extent of back-bonding ($E(\pi^*) = -0.90$ eV (5), $-0.68$ eV (6), $-0.55$ eV (7)).30 Consequently, the changes in $\Delta E_{\pi\pi}^{para}$, summarized in Table 2, are mostly due to the different extent of back-bonding in that sense as the larger $\Delta E_{\pi\pi}^{para}$, the higher the multiple-bond character of the M–E(II) bond. Therefore the experimental $^{119}\text{Sn}$ NMR chemical shift of stannylene compounds 5–7 and the experimental $^{207}\text{Pb}$ NMR shift of the metallocene plumbylene complexes 8–10 can be used as a tool to estimate the degree of multiple bonding in these complexes. Increasing multiple-bond character of the M–E(II) bond leads to increasing energy differences $\Delta E_{\pi\pi}^{para}$, which becomes manifest in an upfield shift of the element resonance in NMR spectroscopy. These relations become obvious by analyzing the data summarized in Table 2, and although only a very limited set of data is used, by the correlations between the reciprocal calculated $\Delta E_{\pi\pi}^{para}$ and the experimental chemical shifts $\delta^{119}\text{Sn}$ (5–7) and $\delta^{207}\text{Pb}$ (8–10) shown in Figure 6.

The bonding in bis(stannylene) zirconocenes was treated principally already by Piers.9 In agreement with that earlier investigation we found that multicenter interactions are important for the understanding of the bonding in bis-(tetrylene) complexes 11, 13, 15, and 19–21. The FMO interaction diagram of the bis(stannylene) zirconocene 19 is shown in Figure 7. Qualitatively, it is also valid for the investigated bis(tetrylene) complexes 11, 13, 15, 20, and 21. The analysis reveals that the ME(II)2 group is built up by two $\sigma$-type orbitals and the $\pi$-type HOMO, each delocalized across all three constituent atoms (see Figures 7 and 8 for surface diagrams of the respective MOs). The delocalization of the $\pi$-type HOMO across all three atoms helps to rationalize the smaller bond order and the weaker M–E(II) bond in group 4 metallocene bis(tetrylene) complexes compared to their mono(tetrylene) counterparts. In addition, inspection of the HOMO of compound 19 indicates some degree of bonding interaction between the two distant Sn atoms, although their separation, d(SnSn), approaches the sum of the van der Waals radii, $\Sigma vdWR$ (d(SnSn) 403.8 pm, $\Sigma vdWR$ 434 pm).31 The computed WBI index between this pair of atoms differs significantly from zero; it is however only 22% of the bond index computed at the same theoretical level for the central Sn–Sn single bond in (H3Si)6Sn2 (19: WBI(SnSn) = 0.20; (H3Si)3Sn2: WBI(SnSn) = 0.92, d(SnSn) 283.7 pm). Similar small WBIs were computed for the bis-(tetrylene) complexes 11, 13, 15, 20, and 21 (WBIs range from 0.15 (PbPb in complex 20) to 0.23 (SnSn in compound 11)). These computational data suggest that in the continuum of possible bonding modes for group 4 metallocene bis(tetrylene) complexes, beginning with the ditetren complex A, passing the metallacyclopropane B and ending at the delocalized bis(tetrylene) structure C, the here investigated complexes 11, 13, 15 and , 19–21 are best described by canonical structure C with only minor contribution from structure B (Scheme 6).

The large and polarizable substituents which are present in all investigated metallocene complexes suggest that attractive dispersion energy contributions to the overall binding energy of the complexes might be a decisive factor. The here applied M06-2X functional32 properly accounts for dispersion forces, while the most prominent deficit of the popular B3LYP functional is the nearly complete negligence of noncovalent van der Waals interactions. Therefore, the difference in the calculated bond dissociation energies (BDEs) using these two functionals allows estimating the contribution of noncovalent bonding in metallocene complexes 5–11, 13, 15, and 19–21.33–35 The contribution of noncovalent interactions, BDE\text{NCI} to the overall BDE, which is calculated as the difference between the BDE obtained at the M06-2X level and the reduced BDE\text{B3LYP} obtained at the B3LYP level (see Table 2), is
substantial in all cases. In the case of the titanium complexes it accounts for 60% of the overall BDE and even in the hafnium complexes it amounts to 30%.

3. CONCLUSION

The present study demonstrates that stannylene and plumbylene complexes of all three group 4 metallocenes are synthetically accessible by magnesium reduction of the corresponding metallocene dichlorides in the presence of the phosphine-stabilized tetrylenes \( \text{SnR}_2 \) or \( \text{Pb} \)-tetrylene. Significant \( \pi \)-back-bonding from the transition metal to the heavy main group atom was shown by NMR spectroscopy and confirmed by X-ray structure analyses of all six complexes \( \text{SnR}_2 \). The stannylene complexes \( \text{SnR}_2 \) and \( \text{Pb} \)-tetrylene are the first stannylene complexes of titanium and hafnium to be reported, whereas \( \text{SnR}_2 \) and \( \text{Pb} \)-tetrylene are the first compounds to feature group 4–lead bonds at all. Using the base-free compounds \( \text{SnR}_2 \) and \( \text{Pb} \)-tetrylene, \( \text{SnR}_2 \) and \( \text{Pb} \)-tetrylene complexes, \( \text{SnR}_2 \) and \( \text{Pb} \)-tetrylene, could be prepared. In these complexes the extent of \( \pi \)-back-bonding is substantial in all cases. In the case of the titanium complexes it accounts for 60% of the overall BDE and even in the hafnium complexes it amounts to 30%.
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4. EXPERIMENTAL SECTION

General Remarks. All reactions involving air-sensitive compounds were carried out under a nitrogen atmosphere using Schlenk techniques or a glovebox. All solvents were dried using column-based solvent purification systems. Chemicals were obtained from different suppliers and used without further purification.

General Spectroscopic Data. NMR spectra were recorded on a Varian INOVA 300 spectrometer. If not noted otherwise for all samples, CD2Cl2 was used as solvent. To compensate for the low isotopic abundance of 29Si, the INEPT pulse sequence was used for the amplification of the signal. Elemental analyses were carried out using a Heraeus VARIO ELEMENTAR instrument. For the NMR spectra, attempts to obtain elemental analysis data gave consistently low values for C and H.

X-ray Structure Determination. For X-ray structure analyses, the crystals were mounted onto the tip of glass fibers, and data collection was performed with a Bruker-AXS SMART APEX CCD diffractometer using graphite-monochromated Mo Kα radiation (0.71073 Å). The data were reduced to F^2 and corrected for absorption effects with SADABS respectively. The structures were solved by direct methods and refined by full-matrix least-squares method (SHELXL97) . If not noted otherwise, all non-hydrogen atoms were refined with anisotropic displacement parameter. All hydrogen atoms were located in calculated positions to correspond to standard bond lengths and angles. All diagrams were drawn with 30% probability thermal ellipsoids, and all hydrogen atoms were omitted for clarity. Unfortunately the obtained crystal quality of some substances was poor. This fact is reflected by quite high R and low χ values.

Crystallographic data (excluding structure factors) for the structures of compounds 5–10 and 13–15 reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-831742 (5), 831743 (6), 831744 (7), 831751 (8), 831748 (9), 831745 (10), 855936 (11), 855938 (13 and 14), and 855937 (15). Copies of data can be obtained free of charge at: http://www.ccdc.cam.ac.uk/products/csd/request/.

General Procedure. For group 4 metallocones monotereylene complexes 5–10: An equimolar (0.5 mmol each) mixture of group 4 metalocene dichloride, magnesium turnings, and 1 or 2 was stirred in THF (5 mL) for 3 h. During this time deeply colored solutions formed. The THF was removed under reduced pressure, and the remaining solid was extracted with pentane (3×5 mL each). The filtrate was concentrated to 6 mL and stored at −60 °C for 16 h. Crystals could be isolated by decantation. Typical yield: about 80%.

Titanocene Stannylene Phosphine Complex (5). Dark-blue crystals (yield: 81%). "H NMR (δ in ppm): 5.24 (s, 10H, Cp), 1.05 (m, 9H, P(CH2)3(CH3)), 0.88 (m, 6H, P(CH2)3(CH3)), 0.58 (s, 18H, SiMe2), 0.54 (s, 18H, SiMe2), 0.48 (s, 6H, SiMe2), 0.43 (s, 6H, SiMe2). "C NMR (δ in ppm): 69.3 (Cp), 22.7 (P(CH2)3(CH3)), 9.4 (P(CH2)3(CH3)), 5.6 (SiMe2), 5.4 (SiMe2), 0.3 (SiMe2). "Si NMR (δ in ppm): −41.4 (SiMe2), −50.6 (SiMe2), −20.1 (SiMe2), −101.4 (quart. Si). "P NMR (δ in ppm): 50.2 (δP/"C76H110P=92Hz=232Hz266Hz). "Sn NMR(δ in ppm): 1635 (δSn/"C76H110P=92Hz), 1478 (δSn/"C76H110P=92Hz), 1108 (δSn/"C76H110P=92Hz). Anal. calcd for C32H73P2Si8Sn: C, 41.62; H, 7.97. Found: C, 40.96; H, 8.05.

Hafnocene Stannylene Phosphine Complex (7). Dark-purple crystals (yield: 79%). "H NMR (δ in ppm): 5.29 (s, 10H, Cp), 1.13 (td, JPC = 7.6 Hz, JHH = 13.0 Hz, 9H, P(CH2)3(CH3)), 0.88 (m, 6H, P(CH2)3(CH3)), 0.62 (s, 18H, SiMe2), 0.60 (s, 6H, SiMe2), 0.52 (s, 6H, SiMe2), 0.51 (s, 18H, SiMe2). "C NMR (δ in ppm): 95.5 (Cp), 22.1 (JPC = 18.9 Hz, P(CH2)3(CH3)), 9.3 (P(CH2)3(CH3)), 5.5 (SiMe2), 5.2 (SiMe2), −0.3 (SiMe2), −0.4 (SiMe2). "Si NMR (δ in ppm): −4.4 (δPSi = 2.6 Hz, SiMe2), −5.9 (δPSi = 2.6 Hz, SiMe2), −19.0 (δPSi = 1.6 Hz, quart. Si). "P NMR (δ in ppm): 34.8 (no tin satellites observed). "Sn NMR (δ in ppm): 1079 (δSn = 92 Hz). Anal. calcd for C12H53P2Si4Sn: C, 38.02; H, 7.28. Found: C, 37.73; H, 7.25.

Titanocene Plumbenyne Phosphine Complex (8). Dark-green crystals (yield: 80%). "H NMR (δ in ppm): 5.2 (s, 10H, Cp), 1.08 (m, 9H, P(CH2)3(CH3)), 0.85 (m, 6H, P(CH2)3(CH3)), 0.62 (s, 18H, SiMe2), 0.58 (s, 18H, SiMe2), 0.52 (s, 6H, SiMe2), 0.37 (s, 6H, SiMe2). "C NMR (δ in ppm): 96.2 (Cp), 23.0 (JPC = 5.4 Hz, P(CH2)3(CH3)), 6.7 (SiMe2), 6.4 (SiMe2), 4.0 (SiMe2), 3.2 (SiMe2). "Si NMR (δ in ppm): −2.3 (δPSi = 2.7 Hz, SiMe2), −3.7 (δPSi = 3.8 Hz, SiMe2), −6.9 (δPSi = 15.6 Hz, quart. Si). "P NMR (δ in ppm): 57.5. Pb NMR (δ in ppm): 259 (fwhm: 217 Hz, #CCDC-831748).
needle-shaped crystals of Hf(Cp)2 (87 mg, 0.07 mmol, 70%) were isolated by decantation and dried in vacuo. 1H NMR (δ in ppm): 4.82 (s, 10H, Cp), 2.68 (br, 4H, THF), 1.63 (br, 4H, THF), 0.44 (s, 12H, SiMe6), 0.29 (s, 3H, H3Si). 13C NMR (δ in ppm): 95.6 (Cp), 60.6 (THF), 201 (THF), 3.5 (SiMe6), 2.0 (SiMe3). 29Si NMR (δ in ppm): -10.0 (SiMe3), -11.3 (SiMe3), -36.7 (quart. Si). 31P NMR: 5770.

Trichlorotantalum Stannylene Diphosphine Complex (17). A mixture of TaCl5 (75 mg, 0.10 mmol), magnesium turnings (17 mg, 0.5 mmol, excess), PEt3 (50 mg, 0.42 mmol), and 1 (150 mg, 0.21 mmol) were suspended in THF and subjected to ultrasonication for 2 min, during which time the suspension turned purple. The mixture was stirred for 3 h at rt, and then all volatile materials were removed in vacuo. The residue was extracted with pentane (10 mL). The purple extract was concentrated (4 mL) and stored at −60 °C for 48 h. Deep-purple crystals of 17 (107 mg, 0.10 mmol, 46%) were isolated by decantation and dried in vacuo. 1H NMR (δ in ppm): 2.17 (m, 6H, P(CH2CH3)3), 1.05 (m, 9H, P(CH2C2H5)3), 0.51 (s, 12H, SiMe6), 0.47 (s, 36H, SiMe3). 13C NMR (δ in ppm): 24.2 (P(CH2CH3)3), 9.0 (P(CH2C2H5)3), 4.5 (SiMe3), -0.9 (SiMe3). 29Si NMR (δ in ppm): 6.7 (SiMe3), -18.6 (SiMe3), -105.9 (quart. Si). 31P NMR (δ in ppm): 38.7 (δ3P = 73 Hz). 119Sn NMR (δ in ppm): 1985 (t, δ3Sn = 73 Hz). Anal. calc for C24H24Cl2P2Si8SnTa: C, 30.36; H, 7.10. Found: C, 30.17; H, 7.025.

ASSOCIATED CONTENT

Supporting Information
Plots of the molecular structures in the crystal of compounds 5, 6, 8, 9, 11, and 15, tables containing crystallographic data and information for compounds 5–10, and 13 and 14 in CIF format. Details of the calculated structures of compounds 5–13, 15, 19–21 and some additional reference compounds (22–33), and complete ref 26. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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planes in the bis(tetrylene) complexes. 

planes in the monotetrylene complexes and by the EME and SiESi given there.

\[\text{E} = \text{obtained:} \]

\[\text{Truhlar, D. G.} \]

\[\text{computations, see the Supporting Information.} \]

\[\text{Gaussian, Inc.: Wallingford, CT, 2010. For detailed description of the} \]

\[\text{see ref 6, 7.} \]

\[\text{The dihedral angle } \beta \text{ is defined by the EMP-} \]

and the SiESi planes in the monotetrylene complexes and by the EME and SiESi planes in the bis(tetrylene) complexes.

\[\text{Müller, T. J. Organomet. Chem. 2003, 686, 251–256 and refs} \]

\[\text{given there.} \]

\[\text{For the lead compounds, the following orbital energies were} \]

\[\text{obtained:} \]

\[\text{E}(\sigma) = -6.04 \text{ eV (8),} \]

\[\text{E}(\sigma^* ) = -1.00 \text{ eV (8),} \]

\[\text{E}(\pi^*) = -0.71 \text{ eV (9),} \]

\[\text{E}(\pi) = -0.56 \text{ eV (10).} \]

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