FLUORINATED BENZAMIDINATE LIGANDS AND THEIR TIN(II), LEAD(II), AND ZIRCONIUM(IV) COMPLEXES

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Abstract

The preparation of a new benzamidinate ligand containing the nonafluoromesityl substituent is reported. Li[$R_FC(N$-*c*-$C_6H_{11})_2$] (**1b**) is prepared by addition of R_FLi to N,N'-dicyclohexylcarbodiimide (R_F = nonafluoromesityl). Treatment of $ZrCl_4$ with two equivalents of **1b** results in the formation of the zirconium dichloride derivative [$R_FC(N$-*c*-$C_6H_{11})_2]_2ZrCl_2$ (**2**). The related ligand Li[$R_FC(NSiMe_3)_2$] (**1a**) has been used to prepare the corresponding tin(II) and lead(II) derivatives. The complexes [$R_FC(NSiMe_3)_2]_2M$ (**3**: M = Sn, **4**: M = Pb) have been synthesized and spectroscopically characterized.

Introduction

In recent years the 2,4,6-tris(trifluoromethyl)phenyl substituent (= nonafluoromesityl, abbreviated R_F) has been extensively used to stabilize unusual low-coordinated main group element derivatives.[1-4] The stabilizing effect of nonafluoromesityl is based on a combination of steric and electronic characteristics. Especially important in many cases is the formation of metal-fluorine interactions between the central atoms and fluorine atoms of the *ortho*-CF_3 groups. Among the most remarkable species containing the nonafluoromesityl substituent were the stable diarylstannylene derivative $(R_F)_2Sn$ [5] as well as the first diarylplumbylene, $(R_F)_2Pb$.[6] The nonafluoromesityl ligand has also been successfully employed in the synthesis of very bulky heteroallylic ligands. Bulky heteroallylic ligands such as the benzamidinate anions $[RC_6H_4C(NSiMe_3)_2]^-$ have recently been shown to be highly versatile building blocks in main group and coordination chemistry.[7,8] The sterically most demanding ligand of this type was found to be $[(CF_3)_3C_6H_2C(NSiMe_3)_2]^-$ based on nonafluoromesityl.[9] We describe here the preparation of a related N-alkylated ligand as well as the use of these ligands in the synthesis of zirconium(IV), tin(II), and lead(II) complexes.

Results and Discussion

All syntheses of nonafluoromesityl compounds generally start with the lithiation of nonafluoromesitylene by *n*-butyllithium which produces the intermediate aryllithium derivative R_FLi.[1,2] The latter can be isolated in the solid state as a diethylether adduct, although is has been found very convenient to prepare R_FLi *in situ* and use the resulting solutions in diethylether directly for further reactions. This procedure is especially recommended as the pure organolithium compound is potentially explosive.[2] The lithium salt Li[$R_FC(NSiMe_3)_2$] (**1a**) has been prepared earlier by reacting freshly prepared R_FLi with N,N'-bis(trimethylsilyl)carbodiimide in a 1:1 molar ratio according to Equation (1).[9] We have now found that the reaction can also be extended to N-alkylated carbodiimide derivatives such as N,N'-dicyclohexylcarbodiimide:

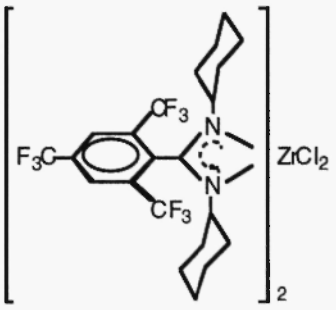
$$R_FLi + R'\text{-}N{=}C{=}N\text{-}R' \longrightarrow Li[R_FC(NR')_2] \qquad (1)$$

$R_F = 2,4,6\text{-}(CF_3)_3C_6H_2$
1a: R = $SiMe_3$
1b: R = *c*-C_6H_{11}

The new lithium salt **1b** was isolated in low yield (11%) in the form of yellow-orange crystals, which are highly soluble in common organic solvents including pentane and hexane. The low yield is due to the formation of significant amounts of oily by-products. However, the reaction can be carried out on a fairly large scale and the product is readily isolated and purified by recrystallization from hexane. The characterization of **1b** by spectroscopic methods is straightforward and unambiguous. Just like the known N-trimethylsilyl derivative **1a**,[7] crystalline **1b** is unsolvated. Bulky heteroallylic ligands such as the anions in **1a** and **1b** are interesting precursors for catalytically active titanium and zirconium complexes.[10-13] This is due to the fact that such heteroallylic ligands may act as steric cyclopentadienyl equivalents.[8,14] Thus disubstituted titanium(IV) or zirconium(IV) complexes containing these ligands often resemble the corresponding metallocenes. Treatment of anhydrous $ZrCl_4$ with two equivalents of **1b** according to Equation (2) afforded the zirconium dichloride derivative **2**:

$$ZrCl_4 + 2\,\underset{\textbf{1 b}}{Li[R_FC(N\text{-}c\text{-}C_6H_{11})_2]} \xrightarrow{THF} \underset{\textbf{2}}{[R_FC(N\text{-}c\text{-}C_6H_{11})_2]_2ZrCl_2} + 2\,LiCl \qquad (2)$$

The exclusive formation of the disubstitution product is a result of the very high steric demand of the new benzamidinate ligand, which is comparable in size with pentamethylcyclopentadienyl. Similar results have been obtained earlier in actinide chemistry, where $[R_FC(NSiMe_3)_2]_2AnCl_2$ (An = Th,U) are the only products regardless of the stoichiometry, when $ThCl_4$ or UCl_4 are reacted with $Li[R_FC(NSiMe_3)_2]$.[14)] Metallocene analogs like **2** are of current interest as new types of polymerization catalysts. It has been shown that in many cases catalytic activity is retained if one or both cyclopentadienyl ligands in Group 4 metallocenes are replaced by bulky heteroallylic ligands.[15)]



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The fluorinated benzamidinate anions are useful ligands for main group elements as well. This has been demonstrated by the formation of tin(II) and lead(II) derivatives according to Equation (3):

$$MCl_2 + 2\,Li[R_FC(NSiMe_3)_2] \xrightarrow{THF} [R_FC(NSiMe_3)_2]_2M + 2\,LiCl \qquad (3)$$

3: M = Sn
4: M = Pb

Both complexes **3** and **4** were isolated in moderate yield and characterized by elemental analyses and spectroscopic methods. The two metal(II) benzamidinates are readily soluble even in non-polar organic solvents such as toluene, pentane, or hexane. The results show that very bulky heteroallylic ligands are readily accessible from nonafluoromesitylene and that these ligands are suitable to form coordination compounds with main group elements and transition metals as well.

Experimental Section

All reactions were carried out under dry, purified nitrogen. Solvents were dried with Na/benzophenone and freshly distilled under N_2 prior to use. IR spectra: Bio-Rad FTS 7 and (Nujol/KBr). NMR spectra: Bruker 250 AM. Elemental analyses: Analytical laboratories of the Department of Inorganic Chemistry at the University of Göttingen and the Department of Chemistry at Magdeburg. The starting materials nonafluoromesitylene [16)] and R_FLi [1)] were prepared according to literature procedures. N,N'-Dicyclohexylcarbodiimide as well as anhydrous $ZrCl_4$, $SnCl_2$, and $PbCl_2$ were purchased and used as received.

*Lithium-N,N'-dicyclohexyl-2,4,6-tris(trifluoromethyl)benzamidinate (**1b**)*
6.81 g (106.3 mmol) *n*-butyllithium in 98.4 ml hexane are added dropwise at 0 °C to a stirred solution of 30.00 g (106.3 mmol) nonafluoromesitylene in 200 ml diethylether. After stirring at room temperature for 12 h the reaction mixture is transferred by syringe into a dropping funnel and added slowly to a stirred solution of 21.94 g (106.3 mmol) of N,N'-dicyclohexylcarbodiimide in 200 ml diethylether. The mixture is stirred at room temperature for an additional 24 h. Evaporation to dryness furnishes an oily red residue, which is recrystallized from hot hexane (*ca.* 60 ml) to give 5.53 g (11%) of yellow-orange crystals, which decompose above 115 °C.

$C_{22}H_{24}F_9LiN_2$ (494.37). Calcd.: C 53.5, H 4.9, N 5.7; found: C 53.1, H 4.3, N 5.3%. IR: 1635 m, 1522 m, 1360 m, 1303 m, 1281 s, 1202 s, 1151 s, 1109 m, 1057 m, 1029 m, 985 m, 915 m, 890 w, 845 w, 806 m, 685 m, 660 w, 602 w, 560 w, 429 w cm^{-1}. EI-MS (70 eV): *m/z* 488 [$(CF_3)_3C_6H_2C(NC_6H_{11})_2^+$, 5%], 419 [$(CF_3)_2C_6H_2C(NC_6H_{11})_2^+$, 84%], 325 [$(CF_3)_3C_6H_2C(NH_2)_2^+$, 87%], 104 [$C_6H_5CNH^+$, 100%], 83 [$C_6H_{11}^+$, 36%]. ^1H NMR (THF-d_8, 250 MHz): δ 8.20 (s, 2 H, C_6H_2), 2.20 (m, 2 H, $C\mathit{H}C_5H_{10}$), 0.85-1.80 (m, 20 H, $CHC_5\mathit{H}_{10}$) ppm.

Dichloro-bis[N,N'-dicyclohexyl-2,4,6-tris(trifluoromethyl)benzamidinato]zirconium(IV) (**2**)

A solution of 9.07 g (18.3 mmol) **1b** in 10 ml THF is added dropwise over a period of 15 min to a stirred suspension of 3.47 g (9.2 mmol) $ZrCl_4(THF)_2$ in 130 ml THF and the reaction mixture is stirred for 12 h at room temperature. The resulting solution is evaporated to dryness, the residue is extracted with 80 ml of boiling toluene and filtered while hot through a thin layer of Celite filter aid. The solvent is removed *in vacuo* and the residue is washed with 20 ml of hexane and dried under vacuum (12 h) to afford 2.46 g (24%) of a cream-colored solid. M.p. 161 °C (dec.).
$C_{44}H_{48}Cl_2F_{18}N_4Zr$ (1136.99). Calcd.: C 46.5, H 4.3, N 4.9; found: C 45.9, H 4.0, N 4.3%. IR (Nujol): 2122 w, 1652 m, 1605 w, 1583 w, 1411 m, 1301 m, 1281 m, 1204 m, 1152 s, 912 w, 891 w, 870 w, 685 w, 538 w, 465 w cm^{-1}. EI-MS: *m/z* 488 [$(CF_3)_3C_6H_2$-$C(NC_6H_{11})_2^+$, 10%], 419 [$(CF_3)_2C_6H_2$-$C(NC_6H_{11})_2^+$, 10%], 325 [$(CF_3)_3C_6H_2$-$C(NH_2)_2^+$, 71%], 83 [$C_6H_{11}^+$, 12%]. ^1H NMR (THF-d_8, 250 MHz): δ 8.59 (s, 4 H, C_6H_2), 4.62 (m, 2 H, $C\mathit{H}C_5H_{10}$), 2.85 (m, 2 H, $C\mathit{H}C_5H_{10}$), 0.91 - 2.25 (m, 40 H, $CHC_5\mathit{H}_{10}$) ppm. ^{13}C NMR (THF-d_8): δ 155.2 [s, $(CF_3)_3C_6H_2\mathit{C}(NC_6H_{11})_2$], 140.0 [s, $(CF_3)_3\mathit{C}_6H_2$, C_{ipso}], 135.5 (q, *p*-C_6H_2, $^2J_{C\text{-}F}$ = 32.4 Hz), 132.3 (q, *o*-C_6H_2, $^2J_{C\text{-}F}$ = 32.4 Hz), 129.9 (q, *m*-C_6H_2, $^3J_{C\text{-}F}$ = 6.8 Hz), 123.7 (q, CF_3, $^1J_{C\text{-}F}$ = 274.5 Hz), 58.8 (s, $\mathit{C}HC_5H_{10}$), 54.0 (s, $\mathit{C}HC_5H_{10}$), 32.1 (s, $CH\mathit{C}_5H_{10}$), 26.3 (s, $CH\mathit{C}_5H_{10}$), 25.9, (s, $CH\mathit{C}_5H_{10}$) ppm. ^{19}F NMR (THF-d_8, 235.32 MHz): δ -57.5 Hz (s, 12 F, *o*-CF_3), -63.3 Hz (s, 6 F, *p*-CF_3) ppm.

Bis[N,N'-bis(trimethylsilyl)-2,4,6-tris(trifluoromethyl)benzamidinato]tin(II) (**3**)

A mixture of 3.80 g (8.0 mmol) **1a** and 0.76 g (4.0 mmol) $SnCl_2$ in 60 ml THF is stirred for 48 h at room temperature and the resulting solution is evaporated to dryness. Extraction of the residue with 40 ml of toluene followed by filtration through Celite and evaporation of the filtrate afforded 1.32 g (30%) of a colorless, microcrystalline solid. M.p. 166 °C (dec.).
$C_{32}H_{40}F_{18}N_4Si_4Sn$ (1053.8). Calcd.: C 36.2, H 3.8, N 5.3; found: C 35.2, H 4.3, N 4.4%. IR (Nujol): 1685 w, 1653 s, 1589 s, 1305 w, 1276 vs, 1260 s, 1243 s, 1206 s, 1151 s, 976 s, 916 s, 870 vs, 844 s cm^{-1}. EI-MS: *m/z* 429 [$R_FC(NSiMe_3)_2^+$-2F-2H, 2%], 307 [$R_FC(NSiMe_3)_2H^+$, 100%], 263 [R_F^+-F, 18%], 73 [$SiMe_3^+$, 42%]. ^1H NMR (C_6D_6, 250 MHz): δ 7.78 (s, 4 H, C_6H_2), -0.13 (s, 36 H, $SiMe_3$) ppm. ^{19}F NMR (C_6D_6): δ -59.0 (s, 6 F, *o*-CF_3), -63.2 (s, 3 F, *p*-CF_3) ppm. ^{19}F NMR (THF-d_8, 235.32 MHz): δ -57.0 (s, 6 F, o-CF_3), -62.7 (s, 3 F, p-CF_3) ppm.

Bis[N,N'-bis(trimethylsilyl)-2,4,6-tris(trifluoromethyl)benzamidinato]lead(II) (**4**)

In a similar manner the reaction of 3.80 g (8.0 mmol) **1a** with 1.11 g (4.0 mmol) $PbCl_2$ affords 1.46 g (32%) **4** as a yellow crystalline solid. M.p. 203 °C (dec.).
$C_{32}H_{40}F_{18}N_4PbSi_4$ (1145.7). Calcd.: C 33.5, H 3.5, N 3.5; found: C 31.7, H 3.7, N 3.5%. IR (Nujol): 1676 s, 1630 s, 1586 vs, 1496 s, 1402 s, 1305 s, 1280 vs, 1261 vs, 1250 s, 1204 s, 1150 vs, 962 s, 911 vs, 868 s, 838 s cm^{-1}. EI-MS: *m/z* 849 [M^+-R_F-CH_3. 2%], 429 [$R_FC(NSiMe_3)_2^+$-2F-2H, 41%], 263 [R_F^+-F, 100%], 243 [R_F^+-2F, 20%], 73 [$SiMe_3^+$, 48%]. ^1H NMR (C_6D_6, 250 MHz): δ 7.90 (s, 4 H, C_6H_2), -0.09 (s, 36 H, $SiMe_3$) ppm. ^{19}F NMR (C_6D_6): δ -59.0 (s, 6 F, *o*-CF_3), -63.0 (s, 3 F, *p*-CF_3) ppm.

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