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Article

Stability and Reactivity of Phenylstrontium Compounds in Solution

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Fragmentation of tetrahydrofuran (thf) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda) by PhSrI leads to the formation of the new organostrontium compounds [(tmeda)Sr(I)(μ-Ph)$_2$-{μ-N(Me)CH$_2$CH$_2$NMe$_2$)Sr(tmeda)], [(tmeda)Sr(I)(μ-Ph)(μ-I){μ-N(Me)CH$_2$CH$_2$NMe$_2$)Sr(tmeda)], and [{(tmeda)Sr}$_4$(μ_4-O)(μ-I)$_4$(μ-Ph)$_2$].

Indroduction

In general, organostrontium compounds have received far less attention than the organic derivatives of the lighter alkaline earth metals magnesium and calcium. Nevertheless, their enhanced reactivity when compared with that of these lighter homologues makes them interesting subjects for further investigations. Different routes to organostrontium compounds have been reported. For instance, alkylstrontium compounds can be isolated from the reaction of SrI$_2$ with a potassium alkyl if bulky triorganylsilyl groups from the potassium alkyl protect the reactive Sr−C bond or if the nucleophilicity of the carbanion is reduced by delocalization of the anionic charge. Thus [(thf)$_3$Sr{CH(SiMe$_3$)$_2$}$_2$][1] and [(thf)Sr{C(SiMe$_3$)$_2$(SiMe$_2$OMe)}$_2$][2] were prepared. In addition, the reaction of a benzylpotassium derivative with anhydrous SrI$_2$ was used in the preparation of [(thf)$_2$Sr{CH-(SiMe$_3$)(C$_6$H$_4$-2-NMe$_2$)}$_2$] with hexacoordinate strontium atoms.[3] The reduction of 2,3-dimethyl-1,4-diphenylbutadiene with strontium in thf yielded deep red (thf)$_4$Sr(C$_4$H$_2$-2,3-Me$_2$-1,4-Ph$_2$).[4] Niemeyer and co-workers employed an organomercury compound to transfer a C$_6$F$_5$ group to strontium, using a shielding triazenide ligand to stabilize the resulting F$_5$C$_6$Sr derivative.[5] In some cases the extremely high reactivity of organostrontium compounds impedes the synthesis of such derivatives, and ether cleavage products are isolated instead.[6,7]

However, the possibility of the straightforward synthesis of organostrontium compounds in analogy to the Grignard reaction is of special interest. The direct reaction of strontium metal, activated with mercury, with iodobenzene in thf to yield phenylstrontium iodide was already published by Kocheshkov et al. in 1973.[8] This reaction proceeded smoothly in diethyl ether or benzene only after addition of thf.[9] The same approach was employed in the preparation of other ArSrI (Ar = tolyl, naphthyl, and 2-thienyl) compounds.[10] Treatment of thf solutions of phenylstrontium iodide with *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda) yielded PhSrI·0.5tmeda.[11] A recent reinvestigation of phenylstrontium iodide in THF showed two sets of NMR resonances, which indicates that there is a Schlenk equilibrium between PhSrI and SrPh$_2$ + SrI$_2$ in solution.[12] However, little is known about the reactivity and structures of arylstrontium derivatives in solution and solid state.

Results and Discussion

Activated strontium metal as well as organostrontium compounds show a much higher reactivity than homologous magnesium and calcium derivatives. Therefore, the direct reaction of activated strontium with iodobenzene was performed in THF at 0 °C under an argon atmosphere, and the reaction mixture was always kept at temperatures below 0 °C. A solvent change to diethyl ether led to drastically lower yields. Initial attempts to isolate arylstrontium compounds from those reaction mixtures failed. The precipitate, obtained at −90 °C, consisted mainly of [(thf)$_5$SrI$_2$] and contained only about 10% of aryl strontium derivatives. Due to the fact that a Schlenk-type equilibrium between PhSrI and Ph$_2$Sr/SrI$_2$ (eq 1)[12] obviously favored the homoleptic

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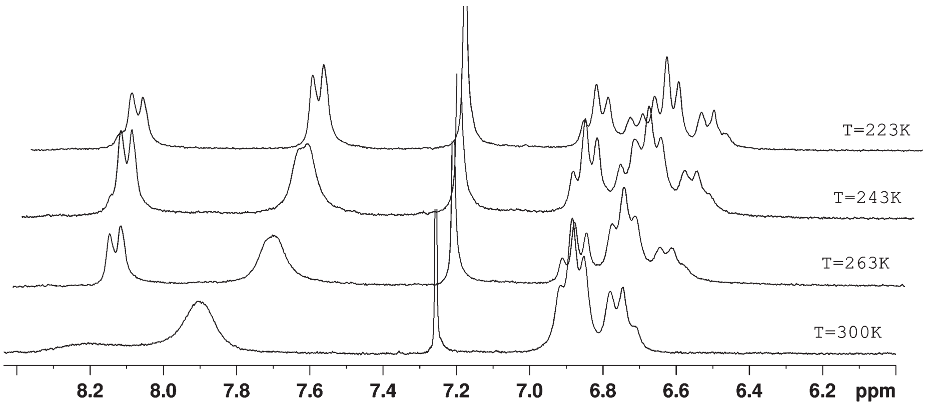


Figure 1. Temperature dependence of the ^{1}H NMR spectrum of "[$(thf)_5Sr(Ph)I$]" in d_8-THF.

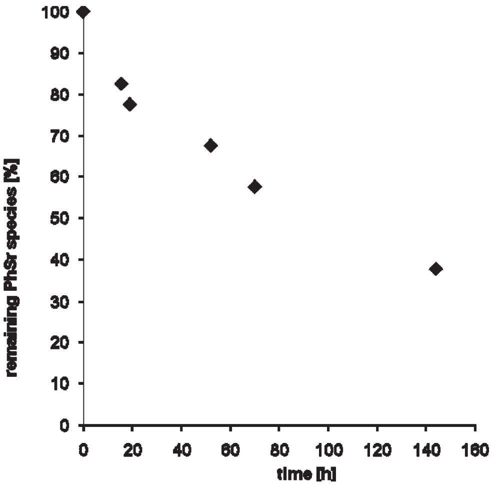
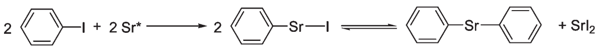


Figure 2. Decomposition of "[$(thf)_5Sr(Ph)I$]" in d_8-THF.

compounds and, additionally, arylstrontium compounds exhibit an even greater solubility in THF than arylcalcium complexes,[13] it was necessary to increase the concentration of the reaction solution to enable the isolation of arylstrontium-richer reaction products. Following this strategy we were able to nearly meet the expected formula of a post-Grignard reagent, and a composition of the isolated product of [$(thf)_5Sr(Ph)_{0.96}I_{1.04}$] was determined. However, the content of arylstrontium species varies between different crops, indicating that the composition given above is only an empirical one and the white powder obtained may consist of different complexes. A saturated solution in d_8-THF shows only one signal set for metal-bound phenyl groups in the ^{1}H NMR spectrum, but the broadened doublet of the *o*-CH groups at δ 8.04 indicates fluxional behavior. Dilution and cooling lead to the observation of two different signal sets for the strontium-coordinated phenyl groups (see Figure 1), and two different doublets at δ 8.20 and 7.70 were now observed for the *o*-CH groups. These results can be interpreted with respect to the above-mentioned Schlenk-type equilibrium. However, the observation of an additional shoulder at δ 8.25 at −50 °C indicates that this interpretation is simplified. Obviously, there are more species participating in that equilibrium.

Attempts to obtain suitable crystals of an organostrontium compound from these solutions in THF failed not only due to the unfavorable Schlenk equilibrium but also as a result of the reactivity of those species toward THF. The initial step of the degradation reaction is the α-deprotonation of THF by the heavy Grignard reagent. The degradation reaction was monitored in d_8-THF, which is more stable than THF due to a direct isotope effect and slows the decomposition of the organostrontium species (see Figure 2). The main products observed via NMR measurement are benzene and ethene. Additional signals detected may belong to a strontium ethenolate complex, but this assignment remained uncertain because of the very low concentration of this species in solution. During decomposition, colorless crystals deposited that were identified as [$(thf)_5SrI_2$] by X-ray diffraction experiments.

The solid initially obtained from THF was used for further investigations in various solvents. It was found that the Schlenk equilibrium is operative in all ether solvents tested. Different solvent adducts of SrI_2 were isolated upon cooling of these solutions. Depending on the solvent used, the compounds [$(thf)_5SrI_2$] (pure THF; see also ref 14), [$(thf)_5SrI_2$]·toluene (**1**) (thf/toluene mixture), [$(thf)_3(dme)SrI_2$] (**2**), [$(thf)_2(dme)_2SrI_2$] (**3**) (mixtures of THF and 1,2-dimethoxyethane (dme)), and [$(dme)_3SrI_2$] (pure dme or dme/diethyl ether mixture; see also ref 15) were obtained (see Supporting Information). However, no crystalline arylstrontium compounds could be isolated from those solutions, even after removal of SrI_2 and further concentration.



(1)

Recently, we found that arylcalcium compounds are less soluble in tmeda than in ethers, which enabled the crystallization of [$(tmeda)Ca(Ph)(\mu\text{-}Ph)]_2$.[13] Therefore tmeda was employed as solvent, too. While the starting material was soluble in the solvent mixtures mentioned above, it only partially dissolved in tmeda. Assuming that the arylstrontium compounds were more soluble than the strontium iodides, the solution was further investigated. Crystals of a heavy dinuclear Grignard reagent of strontium were obtained from this solution by cooling to −40 °C (Chart 1).

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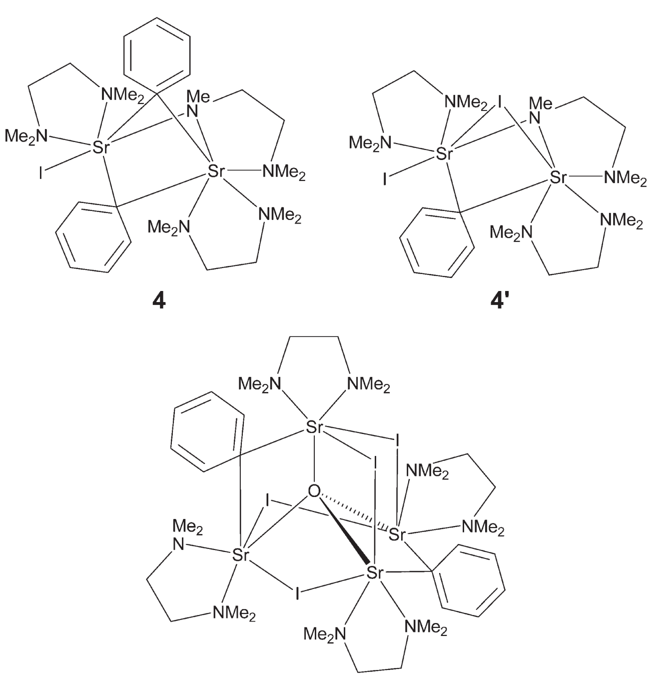
Chart 1. Schematic Representation of 4, 4′, and 5



4 **4'** **5**

The X-ray structure determination and NMR spectroscopic investigations showed that the crystal consists of dinuclear [(tmeda)Sr(I)(μ-Ph)$_2${μ-N(Me)CH$_2$CH$_2$NMe$_2$)Sr-(tmeda)] (**4**) as the major component (85%) (see Figure 3). However, one of the bridging phenyl groups can also be exchanged by a bridging iodide anion, leading to [(tmeda)-Sr(I)(μ-Ph)(μ-I){μ-N(Me)CH$_2$CH$_2$NMe$_2$)Sr(tmeda)] (**4′**), which was found to occupy 15% of the lattice sites. Both structures contain two hexacoordinate strontium atoms. In these molecules the phenyl groups occupy bridging positions, whereas the iodide anion is also bound terminally. Due to the bridging position of the phenyl groups, rather large Sr−C bond lengths (average Sr−C 2.84 Å) are observed. The terminally bound iodide anion shows a Sr1−I1 distance of 3.2608(9) Å, which is comparable to those of [(thf)$_5$SrI$_2$] (3.230(2) Å).[14] The unsymmetrical iodide bridge shows Sr1−I2 and Sr2−I2 bond lengths of 3.441(9) and 3.240(8) Å, respectively. The asymmetry of the bridge is reflected in the amide coordination, with Sr1−N3 and Sr2−N3 values of 2.632(7) and 2.529(7) Å. In contrast to these bridges the phenyl groups exhibit only small deviations from a symmetric bonding situation. In solution, only one set each of signals for the phenyl groups and for the amide ligand was found, indicative of a fluxional behavior of **4**/**4′** in thf.

The origin of the unexpected bridging amide ligand can be ascribed to the fragmentation of tmeda by these extremely reactive organostrontium reagents. GC-MS examination of the used tmeda solvent did not show any sign of the presence of *N*,*N*,*N*′-trimethylethylenediamine as an alternative source of the observed ligand. However, such α-elimination reactions are well known in organolithium chemistry. For instance, Ziegler and Gellert showed that the fragmentation of dimethyl ether follows this reaction pathway.[16] Here the initial step is the metalation of a CH$_3$ group of the ether molecule by an alkyllithium. The related lithiation of tmeda by alkyllithum compounds is well known.[17−20] In addition, the methylene transfer from *N*-lithiomethyl-*N*,*N*′,*N*″,*N*″-tetramethyldiethylenetriamine to epoxides and oxetanes resulting in the formation of the corresponding lithium amide was reported by Klumpp and co-workers.[21]

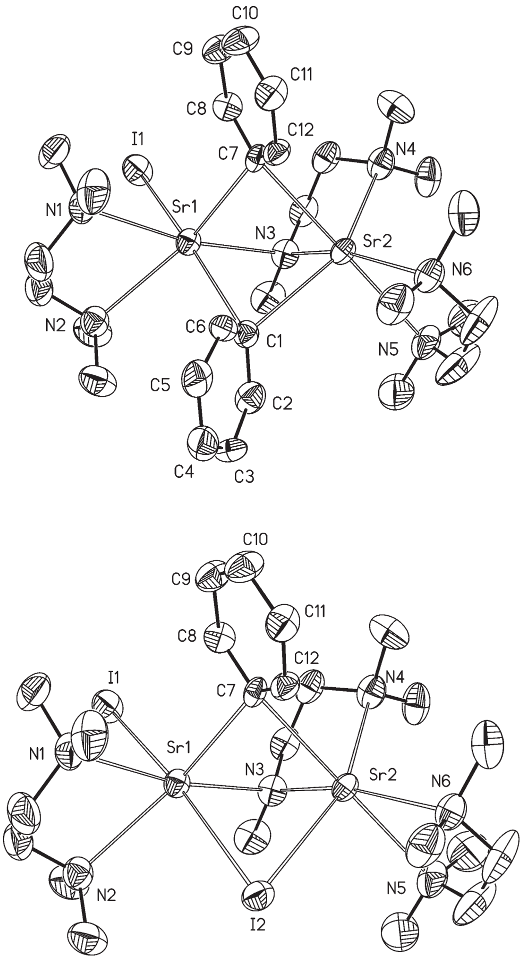


Figure 3. Molecular structures and numbering schemes of **4** (top) and **4′** (bottom). The thermal ellipsoids represent a probability of 40%; H atoms are neglected for clarity reasons. Selected bond lengths (Å) and angles (deg): **4**: Sr1−C1 2.827(14), Sr1−C7 2.830(8), Sr1−N3 2.632(7), Sr1−I1 3.2608(9), Sr2−C1 2.848(14), Sr2−C7 2.854(7), Sr2−N3 2.529(7), Sr2−N4 2.731(7), Sr1−C1−Sr2 75.6(3), C2−C1−C6 113.8(14), Sr1−C7−Sr2 75.5(2), C8−C7−C12 116.3(7), Sr1−N3−Sr2 84.7(2), I1−Sr1−C1 165.5(3), N4−Sr2−C1 150.8(3); **4′**: Sr1−I2 3.441(9), Sr2−I2 3.240(8), Sr1−I2−Sr2 62.69(15).

Another derivative, [{(tmeda)Sr}$_4$(μ_4-O)(μ-I)$_4$(μ-Ph)$_2$] (**5**), could be crystallized from the mother liquor. These crystals diffract only weakly due to an extremely large lattice constant (c = 72.9560(13) Å). Therefore only the atom connectivity can be given (Figure 4).

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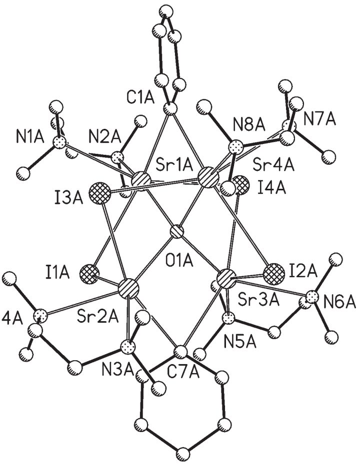

Figure 4. Structural representation and numbering scheme of **5**.

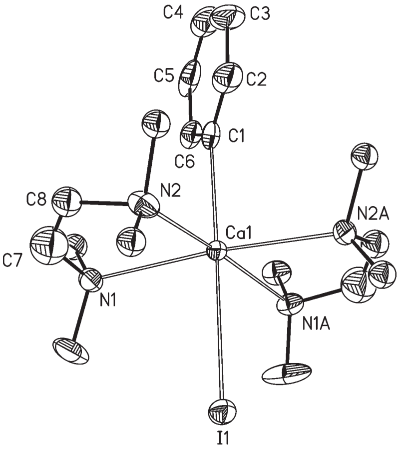

Figure 5. Molecular structure and numbering scheme of **6**. The thermal ellipsoids represent a probability of 40%; H atoms are omitted for clarity reasons. Selected bond lengths (Å) and angles (deg): Ca1−C1 2.658(9), Ca1−N1 2.590(5), Ca1−N2 2.575(5), Ca1−I1 3.302(1); N1−Ca1−N2 74.0(2), C1−Ca1−I1 177.6(2), C1−Ca1−N1 93.9(2), C1−Ca1−N2 94.2(2), N1−Ca1−I1 84.7(1), N2−Ca1−I1 87.3(1), C2−C1−C6 115.9(11), Ca1−C1−C2 121.3(8), Ca1−C1−C6 122.9(7).

The strontium tetrahedron is centered by an oxygen atom that stems from THF cleavage. Interstitial oxygen atoms are well known for strontium cages, as, for example, in square $Sr_5(\mu_5\text{-}O)$ pyramids and in $Sr_4(\mu_4\text{-}O)$ tetrahedra.[22,23] All Sr···Sr edges of the Sr_4 tetrahedron of **5** are bridged by monovalent anions. Two opposite edges are bridged by phenyl groups; all other edges by iodide anions. Each strontium atom also binds to a tmeda ligand in order to complete the coordination sphere, leading to hexacoordinate metal atoms.

The higher reactivity of phenylstrontium iodide is best shown in comparison to the reaction of phenylcalcium iodide with tmeda. Phenylcalcium iodide, prepared according to a literature procedure,[24] was treated with tmeda under similar conditions (eq 2). The isolated product was $[(tmeda)_2Ca(Ph)I]$ (**6**). Thus cleavage of tmeda had not occurred. The molecular structure of **6** is shown in Figure 5. The hexacoordinate calcium atom lies in a distorted octahedral environment with the anionic ligands in trans-positions. The Ca−C and Ca−N bond lengths of 2.658(9) and 2.575(5)/2.590(5) Å, respectively, lie in expected ranges.

$$[(thf)_4Ca(Ph)I] + 2tmeda \rightarrow [(tmeda)_2Ca(Ph)I] + 4THF \tag{2}$$

Conclusion

Tmeda molecules are able to completely displace the thf ligands of the coordination spheres of the heavy alkaline earth metal compounds. The enhanced reactivity of the arylstrontium iodides leads to tmeda degradation, whereas a similar reaction was not observed for arylcalcium iodides. In conclusion we have shown that phenylstrontium compounds show excellent solubility in THF and dme even at low temperature probably due to the Schlenk equilibrium that is occurring. In tmeda their solubility is considerably lower, which allows isolation of two rare, structurally characterized examples of arylstrontium compounds. Those products arise from solvent fragmentation and underline the higher reactivity of the strontium derivatives in comparison to their calcium analogues. It is also noteworthy that phenyl groups favor bridging positions in organostrontium compounds (leading to multinuclear derivatives), whereas in organocalcium chemistry terminally bound phenyl groups are common, which facilitates the isolation of mononuclear phenylcalcium compounds.

Experimental Section

General Remarks. All manipulations were carried out under an argon atmosphere using standard Schlenk techniques. The solvents were dried according to common procedures and distilled under argon; deuterated solvents were dried over sodium, degassed, and saturated with argon. The yields given are not optimized. The ^1H and $^{13}C\{^1H\}$ NMR spectra were obtained on a Bruker AC 200 or 400 MHz spectrometer. Metal content was determined by complexometric titration with 0.05 M EDTA (indicator: Eriochrome Black T).

Tmeda was dried over sodium/benzophenone and distilled before use. $[(thf)_4Ca(Ph)I]$ was prepared according to a known procedure.[24]

Detection of *N*,*N*,*N*′-trimethylethylendiamine in the used tmeda was attempted by GC-MS analysis. A Thermo Finnigan Trace GC-MS with a EI/CI combi source was used. Benzene (t_R = 4.08 min) and toluene (t_R = 5.51 min) were the only detectable impurities in tmeda (t_R = 6.05 min). Instrument conditions: gas chromatograph: RTX-5 Amine capillary column (30 m × 0.25 mm, 1 μm film); injector 250 °C, surge pressure 3 kPa, oven program 60 °C for 0.2 min, 10 °C/min to 150 °C, 25 °C/min to 250 °C, hold for 2.8 min. Mass spectrometer: ionization mode EI+, scan range 61−379 amu, 3 scans per second, detector voltage 500.0 V, source temperature 120 °C, GC interface temperature 200 °C.

Synthesis of "PhSrI". A suspension of strontium metal (1.57 g, 17.9 mmol, activated with ammonia), together with glass balls, in THF (40 mL) was cooled to −40 °C. Iodobenzene (2.53 g, 12.4 mmol) was added at this temperature, and the resulting

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Table 1. Crystal Data and Refinement Details for the X-ray Structure Determinations

	1	**2**	**3**	**4/4′**	**5**	**6**
formula	$C_{27}H_{48}I_2O_5Sr$	$C_{16}H_{34}I_2O_5Sr$	$C_{16}H_{36}I_2O_6Sr$	$[0.85\,(C_{29}H_{55}IN_6Sr_2)\cdot 0.15(C_{23}H_{50}I_2N_6Sr_2)\cdot 0.5(C_6H_{16}N_2)]$	$C_{36}H_{74}I_4N_8OSr_4$	$C_{18}H_{37}CaIN_4$
fw/g·mol^{-1}	794.07	647.85	665.87	855.50	1493.11	476.50
T/°C	−90(2)	−90(2)	−90(2)	−90(2)	−90(2)	−90(2)
cryst syst	monoclinic	monoclinic	monoclinic	orthorhombic	tetragonal	orthorhombic
space group	$C2/c$	$P2_1/c$	$C2/c$	$Pbca$	$I\bar{4}2d$	$Cmc21$
a/Å	21.7972(7)	17.1871(4)	15.0594(11)	12.7937(4)	25.1714(4)	13.2520(5)
b/Å	13.9236(6)	8.9208(4)	10.0303(7)	18.8424(4)	25.1714(4)	11.3612(7)
c/Å	13.8943(3)	16.1756(6)	16.9646(15)	33.4870(11)	72.9560(13)	15.6074(9)
α/deg	90	90	90	90	90	90.00
β/deg	126.763(2)	99.600(2)	106.462(4)	90	90	90.00
γ/deg	90	90	90	90	90	90.00
V/Å^3	3378.2(2)	2445.35(15)	2457.5(3)	8072.5(4)	46224.9(13)	2349.8(2)
Z	4	4	4	8	24	4
ρ/g·cm^{-3}	1.559	1.760	1.800	1.408	1.287	1.347
μ/cm^{-1}	34.53	47.48	47.3	35.5	43.8	15.88
measd data	11 859	16 065	7755	48 714	89 646	7850
data with $I > 2\sigma(I)$	2636	4047	1773	4402	9149	2120
unique data/R_{int}	3876/0.0327	5531/0.0447	2790/0.0707	8791/0.1141	25550/0.2280	2559/0.0518
wR_2 (all data, on F^2)^a	0.0894	0.0909	0.0914	0.1821	0.3130	0.0807
R_1 ($I > 2\sigma(I)$)^a	0.0349	0.0369	0.0432	0.0742	0.1112	0.0359
S^b	1.010	1.014	0.928	1.016	1.044	1.014
res dens/e·Å^{-3}	0.338/−0.860	0.575/−1.030	1.088/−0.775	0.684/−0.752	1.491/−1.613	0.506/−0.550
absorpt method	none	none	none	none	none	none
CCDC no.	738735	739481	739482	738736	motif	743858

[a] Definition of the R indices: $R_1 = (\sum||F_o| - |F_c||)/\sum|F_o|$; $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$; $P = [2F_c^2 + \mathrm{Max}(F_o^2)]/3$. [b] $S = \{\sum[w(F_o^2 - F_c^2)^2]/(N_o - N_p)\}^{1/2}$.

mixture was allowed to warm to 0 °C and was kept at this temperature for 4.5 h. During this procedure the reaction flask was shaken. The resulting brown solution was filtered, and the solid residue was discarded. The solution (79% yield of organostrontium compounds, as determined by titration with 0.1 M HCl of a hydrolyzed aliquot) was stored at −90 °C for 3 days. Afterward the crystalline solid that had formed was collected on a cooled Schlenk frit and dried in vacuo. Yield: 2.70 g (33%, 96% of the expected alkalinity of [(thf)$_5$Sr(Ph)I] determined by titration with 0.1 M HCl of a hydrolyzed aliquot). Two signal sets for strontium-bound phenyl groups were observed in the NMR spectra. ^{1}H NMR (200 MHz, d_8-THF, 300 K): δ 6.65−7.0 (m, p-CH + m-CH Ph + Ph*), 7.91 (br, o-CH Ph), 8.2 (v br, o-CH Ph*). ^{13}C NMR (50.33 MHz, d_8-THF): δ 125.1 (p-CH Ph), 125.2 (p-CH Ph*), 126.4 (m-CH Ph), 126.6 (m-CH Ph*), 141.8 (o-CH Ph*), 142.3 (o-CH Ph), 193.0 (i-C Ph*), 194.5 (i-C Ph).

Formation of 4/4′ and 5. Phenylstrontium iodide (650 mg) prepared as described above was suspended in tmeda (20 mL) at room temperature and stirred for 20 min. The remaining solid was removed by filtration, and the mother liquor was concentrated to 16 mL in vacuo. Then the solution was stored for 3 weeks at −40 °C. Afterward the irregularly shaped, pale yellow crystals of **4/4′** that had formed were isolated by decantation of the supernatant solution. Yield: 180 mg. ^{1}H NMR (200 MHz, d_8-THF): δ 2.0−2.2 (br, 36H, CH$_3$ tmeda + 2 × NCH$_3$), 2.30 (s, 10H, CH$_2$ tmeda), 2.59 (br, 2H, CH$_2$N), 2.90 (br s, 3H, NCH$_3$), 3.06 (br, 2H, NCH$_2$), 6.86 (m, 2H, p-CH Ph), 7.01 (m, 4H, m-CH Ph), 8.09 (m, 4H, o-CH Ph). ^{13}C NMR (50.3 MHz, d_8-THF): δ 43.0 (NCH$_3$), 45.9 (2 × NCH$_3$), 46.2 (10 × NCH$_3$ tmeda), 57.1 (NCH$_2$), 58.8 (5 × NCH$_2$ tmeda), 62.3 (NCH$_2$), 124.6 (2 × p-CH Ph), 126.6 (4 × m-CH Ph), 141.7 (4 × o-CH Ph), 194.4.0 (2 × i-C Ph). The mother liquor was filtered to remove a small amount of amorphous precipitate, concentrated to approximately 5 mL, and stored again for 3 weeks at −40 °C, resulting in the formation of approximately 10 mg of crystalline **5**.

Synthesis of [(tmeda)$_2$Ca(Ph)I] (6). [(thf)$_4$Ca(Ph)I] (450 mg, 0.85 mmol) was suspended in tmeda (20 mL) at room temperature and stirred for 1 h. The solvent was removed under reduced pressure, and the residual solid was dried in vacuo. Yield: 390 mg, 0.82 mmol, 97% (crude product). Suitable crystals of **6** for X-ray diffraction experiments were obtained by cooling a saturated solution in tmeda from rt to −40 °C. These crystals were used for NMR measurement and elemental analysis. Anal. Calcd for $C_{18}H_{37}CaIN_4$: Ca, 8.41. Found: Ca, 8.7. ^{1}H NMR (400 MHz, d_8-THF): δ 2.16 (s, 24H, CH$_3$ tmeda), 2.31 (s, 8H, CH$_2$ tmeda), 6.70 (m, 1H, p-CH Ph), 6.81 (m, 2H, m-CH Ph), 7.66 (m, 2H, o-CH Ph). ^{13}C NMR (100.65 MHz, d_8-THF): δ 46.2 (8 × NCH$_3$ tmeda), 58.8 (4 × NCH$_2$ tmeda), 122.7 (p-CH Ph), 125.4 (2 × m-CH Ph), 141.1 (2 × o-CH Ph), 189.9 (i-C Ph). A second signal set of low intensity for the phenyl group was observed. The values are similar to the one reported for [(tmeda)Ca(Ph)(μ-Ph)]$_2$,[13] indicative of an active Schlenk equilibrium in solution. ^{13}C NMR: δ 125.9 (p-CH Ph*), 126.4 (m-CH Ph*), 144.3 (o-CH Ph*), 185.2 (i-C Ph*).

Crystal Structure Determinations. The intensity data for the compounds were collected on a Nonius KappaCCD diffractometer using graphite-monochromated Mo Kα radiation. Data were corrected for Lorentz and polarization effects but not for absorption effects.[25,26] The structures were solved by direct methods (SHELXS)[27] and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97) (Table 1).[28] All hydrogen atoms were included at calculated positions with fixed thermal parameters. All nondisordered non-hydrogen atoms were refined anisotropically.[28]

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Supporting Information Available: Crystallographic data of the new compounds and CIF files giving data collection and refinement details as well as positional coordinates of all atoms. This material is available free of charge via the Internet at http://pubs.acs.org. In addition, crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC-738735 for **1**, -739481 for **2**, -739482 for **3**, -738736 for **4**, and -743858 for **6**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [e-mail: deposit@ccdc.cam.ac.uk].