sharp contrast to this, we note that the Ir–Cl(B)–Ir angle in the species $[(\eta^5\text{-}C_5Me_5)IrCl]_2(\mu\text{-}H)(\mu\text{-}Cl)$ is reduced to 72.65 (8)° as a result of the associated Ir–H(B)–Ir bonding system.[3]

(7) The X(B)–Ir–X(B′) angles, which are precisely supplementary to the Ir–X(B)–Ir′ angles (due to precise $C_i$ symmetry of each molecule), show a slight increase with increasing size of halogen—i.e., 79.55 (12)° for the chloride, 81.26 [8]° for the bromide, and 82.58 (2)° for the iodide.

(8) An unexpected, but nevertheless unambiguous, result is that the bonding of the $\eta^5\text{-}C_5Me_5$ ligand to the iridium(III) center is strongest for the chloride, intermediate for the bromide, and weakest for the iodide. There are three distinct measurements indicating this. (a) The average Ir–C(ring) distance increases from 2.132 [16] Å in the chloride to 2.148 [13] Å in the bromide and 2.172 [13] Å in the iodide. (b) The perpendicular distance from the iridium(III) ion to the pentaatomic carbocyclic ring increases from 1.7563 (4) Å in the chloride to 1.7712 [17] Å in the bromide and 1.8013 (3) Å in the iodide. (c) The iridium···methyl interactions (Ir···C(Me)) from 3.280 [33] Å in the chloride to 3.292 [23] Å in the bromide and 3.303 [23] Å in the iodide. The stronger $\eta^5\text{-}C_5Me_5 \rightarrow Ir$ bonding for the chloride is believed to be a result of the (highly electronegative) chloride ligands removing charge from the iridium atom.

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**Registry No.** $[(\eta^5\text{-}C_5Me_5)IrBr]_2(\mu\text{-}Br)_2$, 55971-89-6; $[(\eta^5\text{-}C_5Me_5)IrI]_2(\mu\text{-}I)_2$, 33040-12-9.

**Supplementary Material Available:** A table of data-processing formulas, Table III, and two listings of structure factor amplitudes (27 pages). Ordering information is given on any current masthead page.

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# Chloro-, Methyl-, and (Tetrahydroborato)tris((hexamethyldisilyl)amido)thorium(IV) and -uranium(IV). Crystal Structure of (Tetrahydroborato)tris((hexamethyldisilyl)amido)thorium(IV)

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Reaction of sodium (hexamethyldisilyl)amide with thorium tetrachloride or uranium tetrachloride yields chlorotris((hexamethyldisilyl)amido)thorium(IV) or -uranium(IV), respectively. The chloroamides of thorium or uranium react with dimethylmagnesium or methyllithium yielding the methyl derivatives $MeTh[N(SiMe_3)_2]_3$ or $MeU[N(SiMe_3)_2]_3$, respectively. The chloro compounds yield $BH_4M[N(SiMe_3)_2]_3$ upon reaction with lithium tetrahydroborate, where M is thorium or uranium. Infrared spectra of the tetrahydroborate derivatives suggest that $BH_4^-$ is bonded in a tridentate fashion in both compounds, the metal atoms being six-coordinate. Single-crystal X-ray analysis of the thorium borohydride confirms the infrared result. The white $BH_4Th[N(Si(CH_3))_2]_3$ crystals are rhombohedral with cell dimensions $a_r = 11.137$ Å and $\alpha_r = 113.61°$; the triply primitive hexagonal cell has $a_h = 18.640$ (3) Å, $c_h = 8.604$ (1) Å, $V = 2489$ Å$^3$, $Z = 3$, and $D_x = 1.40$ g/cm$^3$, space group $R3m$. The structure was refined by full-matrix least squares to a conventional $R$ factor of 0.031 for 1014 data. The Th atom is on a threefold axis 2.32 Å from three nitrogen atoms and 2.61 Å from the boron atom, a distance which represents a triple bridge bond between Th and B. The three (dimethylsilyl)amide ligands are disordered by a mirror plane parallel to the threefold axis. $CH_3Th[N(Si(CH_3)_3)_2]_3$ is isomorphous with $BH_4Th[N(Si(CH_3)_3)_2]_3$ with cell dimensions $a_h = 18.68$ (1) Å and $c_h = 8.537$ (6) Å. The diffraction data yielded $f'' = 12.16 \pm 0.33$ e for the imaginary scattering term for Th with Cu K$\alpha$ radiation.

## Introduction

Tris((hexamethyldisilyl)amido)metal compounds have been described for a large group of p-, d-, and 4f-block metal atoms.[1-3] In contrast, only four silylamido compounds have been described for the 5f-block series, $ClTh[N(SiMe_3)_2]_3$,[4] $O_2U[N(SiMe_3)_2]_2(THF)_2$, $OU[N(SiMe_3)_2]_3$, and $U[N(SiMe_3)_2]_3$.[5] This paper describes the series $XM[N(SiMe_3)_2]_3$, where M is thorium or uranium and X is chloro, methyl, or tetrahydroborate. The crystal structure of one of these compounds, $(BH_4)Th[N(SiMe_3)_2]_3$, is also described.

## Results and Discussion

Sodium (hexamethyldisilyl)amide reacts with thorium or uranium tetrachloride affording chlorotris((hexamethyldisilyl)amido)thorium or -uranium, respectively. The air- and moisture-sensitive, monomeric (by mass spectrometry) amides are readily soluble in pentane from which they may be crystallized. Physical properties of the compounds are shown in Table I.

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**Table I.** Physical Properties of the Series $XM[N(SiMe_3)_2]_3$

| | | $^1H$ NMR[b] | | infrared[c] | | |
|---|---|---|---|---|---|---|
| compd | $\mu_B$[a] | M–Me | M–N(SiMe$_3$)$_2$ | M–N | M–Cl | M–BH$_4$ |
| $ClTh[N(SiMe_3)_2]_3$ | diamag | | 0.50 | 385 s | 270 m | |
| $ClU[N(SiMe_3)_2]_3$ | 2.8 | | −2.22 | 385 s | 272 m | |
| $MeTh[N(SiMe_3)_2]_3$ | diamag | 0.85 | 0.57 | 385 s | | |
| $MeU[N(SiMe_3)_2]_3$ | 2.7 | −224 | −1.49 | 385 s | | |
| $BH_4Th[N(SiMe_3)_2]_3$ | diamag | | 0.58 | 385 s | | 2500 s, 2345 w, 2240 s, 2180 m |
| $BH_4U[N(SiMe_3)_2]_3$ | 2.6 | | −1.87 | 390 s | | 2500 s, 2335 w, 2240 s, 2170 m |

[a] Benzene solution at 25 °C; Evans' method.[12] Units are Bohr magnetons. [b] Benzene solution at 25 °C; δ units (positive value, high frequency), relative to $Me_4Si$. [c] Nujol mulls; $cm^{-1}$.

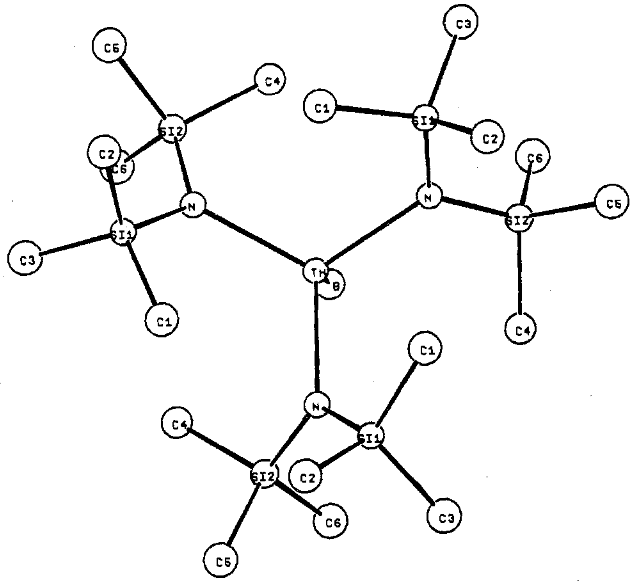

**Figure 1.** View of the $Th[N(Si(CH_3)_2)]_3BH_4$ molecule as viewed down, but slightly off, the *c* axis.

**Table II.** Positional and Thermal Parameters with Estimated Standard Deviations[a]

| atom | *x* | *y* | *z* | *B*, Å$^2$ |
|---|---|---|---|---|
| Th | 0.0 | 0.0 | 0.0 | *b* |
| B | 0.0 | 0.0 | −0.303 (3) | 4.4 (4) |
| H | 0.0 | 0.0 | −0.43 (2) | 4.4[c] |
| N[d] | 0.1014 (7) | 0.1351 (7) | 0.055 (1) | 3.3 (2) |
| Si(1) | 0.0886 (4) | 0.1915 (2) | 0.2023 (4) | 3.4 (1) |
| Si(2) | 0.1901 (3) | 0.1790 (3) | −0.0605 (5) | 3.9 (1) |
| C(1) | −0.015 (1) | 0.129 (1) | 0.293 (2) | 5.5 (4) |
| C(2) | 0.165 (1) | 0.219 (1) | 0.366 (2) | 5.7 (4) |
| C(3) | 0.100 (1) | 0.289 (1) | 0.128 (2) | 6.0 (4) |
| C(4) | 0.210 (1) | 0.096 (2) | −0.138 (2) | 4.9 (4) |
| C(5) | 0.286 (1) | 0.255 (1) | 0.045 (2) | 5.9 (4) |
| C(6) | 0.180 (1) | 0.236 (1) | −0.230 (2) | 6.0 (4) |

[a] Here and in the following tables the number in parentheses is the estimated standard deviation in the least significant digit. [b] The anisotropic temperature factor for thorium has the form $\exp(-0.25(B_{11}h^2a^{*2} + 2B_{12}hka^*b^* + \ldots))$, where $B_{11} = 2.98$ (2), $B_{22} = 2.98$, $B_{33} = 3.30$ (2), $B_{12} = 1.49$, $B_{13} = B_{23} = 0$. [c] The thermal parameter for hydrogen was restrained to equal that for boron. [d] The N, Si, and C atoms are all disordered.

**Table III.** Selected Interatomic Distances (Å)

| | | | |
|---|---|---|---|
| Th–B | 2.61 (3) | Si(1)–C(3) | 1.84 (2) |
| Th–3N | 2.32 (2) | Si(2)–C(4) | 1.89 (2) |
| N–Si(1) | 1.74 (2) | Si(2)–C(5) | 1.87 (2) |
| N–Si(2) | 1.74 (2) | Si(2)–C(6) | 1.87 (2) |
| Si(1)–C(1) | 1.86 (2) | B–H | 1.1 (2) |
| Si(1)–C(2) | 1.88 (2) | | |

**Table IV.** Selected Angles (deg)

| | | | |
|---|---|---|---|
| N–Th–N | 115.9 (2) | C(1)–Si(1)–C(3) | 110 (1) |
| Si(1)–N–Th | 122 (1) | C(2)–Si(1)–C(3) | 107 (1) |
| Si(2)–N–Th | 117 (1) | C(4)–Si(2)–N | 110 (1) |
| Si(1)–N–Si(2) | 121 (1) | C(5)–Si(2)–N | 114 (1) |
| C(1)–Si(1)–N | 110 (1) | C(6)–Si(2)–N | 112 (1) |
| C(2)–Si(1)–N | 113 (1) | C(4)–Si(2)–C(5) | 106 (1) |
| C(3)–Si(1)–N | 111 (1) | C(4)–Si(2)–C(6) | 108 (1) |
| C(1)–Si(1)–C(2) | 105 (1) | C(5)–Si(2)–C(6) | 106 (1) |

The chloro silylamide of uranium reacts with methyllithium yielding the monomethyl derivative $MeU[N(SiMe_3)_2]_3$. In contrast methyllithium displaces a (hexamethyldisilyl)amide group from the coordination sphere of $ClTh[N(SiMe_3)_2]_3$, lithium (hexamethyldisilyl)amide being the only product isolated. The monomethylthorium compound, however, can be isolated by using dimethylmagnesium as alkylating agent. The four-coordinate monomethyl derivatives are soluble in hydrocarbon solvents and are rather air and moisture sensitive. This sensitivity is to be contrasted with that of the air and moisture stability of the zirconium and hafnium analogues.[5] This is doubtless a kinetic effect and must be related to the larger ionic radii of the 5f-block metal atoms.

The $^1H$ NMR spectra of the alkyl derivatives are temperature independent to −65 °C. Again, this is to be contrasted with those of the hafnium analogue which are temperature dependent. The hafnium analogue shows two equal-area resonances due to trimethylsilyl groups, the coalescence temperature being ca. −25 °C. This latter observation has been previously described.[5] The diamagnetic thorium compounds have been further characterized by $^{13}C\{^1H\}$ NMR spectroscopy. $ClTh[N(SiMe_3)_2]_3$ shows a single resonance at δ 3.98 due to the carbon atoms of the $Me_3Si$ group, and $MeTh[N(SiMe_3)_2]_3$ shows two single absorptions at δ 4.17 and 1.28 due to the carbon atoms of the $Me_3Si$ and Me groups, respectively.

The chloro amides of thorium or uranium yield hydrocarbon-soluble tetrahydroborate derivatives upon reaction with lithium tetrahydroborate. The infrared spectra, which are essentially identical, strongly suggest that the tetrahydroborate is bonded in a tridentate fashion, with one absorption in the terminal and two absorptions in the bridging B–H stretching frequency region.[6] This has been confirmed by a single-crystal X-ray analysis (see below).

The $^1H$ NMR spectrum of $(BH_4)Th[N(SiMe_3)_2]_3$ shows a 1:1:1:1 quartet at δ 4.34, $J_{^1H-^{11}B}$ = 81 Hz, and a singlet at δ 0.58 in an area ratio of 4:54. The paramagnetic ($f^2$) uranium analogue shows a 1:1:1:1 quartet centered at δ 101, $J_{^1H-^{11}B}$ = 79 Hz, and a singlet at δ 1.87 in an area ratio of 4:54. Lowering the temperature to −80 °C only results in slight line broadening. Thus these are fluxional molecules even at this temperature.

The crystal structure has disorder consisting of two possible orientations of the molecule. A picture of the ordered molecule is shown in Figure 1. Atomic parameters, distances, and angles for $BH_4Th[N(SiMe_3)_2]_3$ are listed in Tables II–IV.

The thorium atom is on a threefold axis and lies 0.47 Å below the plane of the three nitrogen atoms. The shape and dimensions of the tris[bis(trimethylsilyl)amido]thorium part of this structure are similar to the geometry found in the molecule $M[N(Si(CH_3)_3)_2]_3$ where M = Eu,[7] Yb,[8] Sc,[7] and Nd;[9] in all these compounds the metal atom is out of the plane of the nitrogen atoms.

All of the atoms with the exception of thorium, boron, and the terminal hydrogen atom on the boron atom are disordered. The nature of the disorder is such that the atoms are on one side or the other of a mirror plane that runs parallel to the *z* axis. It is not possible with these data to distinguish a random disorder from twinning; our description is that of a random disorder.

From an analogy with the distances in the $U(BH_4)_4$[10] structure, one can deduce how the borohydride group is bonded to the thorium atom. In $U(BH_4)_4$, the borohydride is bonded to the uranium atom by triple hydrogen bridge bonds and by double hydrogen bridge bonds with resulting U–B distances of 2.5 and 2.9 Å, respectively. In $Th[N(SiMe_3)_2]_3$, the Th–B distance is 2.6 Å and represents a triply bridged hydrogen bond. The terminal hydrogen atom was found in the Fourier maps and refined, but the three bridging hydrogen bonds are disordered and were not found. Thorium has six nearest neighbors, three nitrogen and three hydrogen atoms. Similar reasoning was used by Bird and Churchill[11] to determine the structure of $Zr(BH_4)_4$.

## Experimental Section

Analyses were done by the microanalytical laboratory of this department. Solution magnetic susceptibilities were measured on a Varian T-60 machine operating at 25 °C by Evans' method.[12] The $^1H$ NMR spectra were measured on a modified Bruker WH 1180 machine operating at 180 MHz in toluene-$d_8$. The $^{13}C\{^1H\}$ NMR spectra were recorded on a Nicolet TT-23 instrument operating at 25.14 MHz in benzene-$d_6$. All operations were performed under nitrogen.

**Chlorotris((hexamethyldisilyl)amido)thorium(IV).** This compound was previously described in a note without experimental details.[4] Sodium (hexamethyldisilyl)amide (10.0 g, 0.0545 mol) in tetrahydrofuran (100 mL) was added to thorium tetrachloride (6.80 g, 0.0182 mol) in tetrahydrofuran (200 mL). The mixture was stirred for 72 h. The tetrahydrofuran was filtered, and the filtrate was evaporated to ca. 60 mL under vacuum. Pentane (200 mL) was added, and the solution was cooled (−10 °C). The white needles were collected and dried under vacuum: mp 210–212 °C; yield 10.2 g (75%).

**Chlorotris((hexamethyldisilyl)amido)uranium(IV).** Sodium (hexamethyldisilyl)amide (14 g, 0.076 mol) in tetrahydrofuran (100 mL) was added to uranium tetrachloride (9.7 g, 0.026 mol) in tetrahydrofuran (200 mL). The mixture was stirred for 24 h and was filtered. The residue was extracted with tetrahydrofuran (150 mL), and the combined extracts were concentrated to ca. 100 mL. Pentane (200 mL) was added, and the solution was cooled (−10 °C). The tan needles were collected and dried under vacuum: mp 178–180 °C; yield 13 g (70%). Anal. Calcd for $C_{18}H_{54}ClN_3Si_6U$: C, 28.7; H, 7.17; Cl, 4.70; N, 5.57. Found: C, 28.5; H, 6.93; Cl, 4.50; N, 5.54.

**Methyltris((hexamethyldisilyl)amido)thorium(IV).** Dimethylmagnesium (1.3 mL of a 1.0 M diethyl ether solution, 0.0013 mol) was added to a solution of chlorotris((hexamethyldisilyl)amido)thorium (2.0 g, 0.0027 mol) in diethyl ether (50 mL) at 0 °C. The mixture was stirred for 20 h (0 °C). The diethyl ether was removed under vacuum, and the residue was extracted with pentane (50 mL). The pentane extract was filtered and concentrated to ca. 30 mL. Cooling (−78 °C) afforded white needles: mp 133–135 °C; yield 1.5 g (78%). Anal. Calcd for $C_{19}H_{57}N_3Si_6Th$: C, 31.4; H, 7.84; N, 5.78. Found: C, 31.0; H, 7.88; N, 5.80.

**Methyltris((hexamethyldisilyl)amido)uranium(IV).** Methyllithium (2.3 mL of a 0.88 M diethyl ether solution, 0.0020 mol) was added to chlorotris((hexamethyldisilyl)amido)uranium (1.5 g, 0.0020 mol) in diethyl ether (50 mL) at 0 °C. The mixture was stirred for 15 h at 0 °C. The diethyl ether was removed under vacuum, and the residue was extracted with pentane (50 mL). The extract was concentrated to ca. 30 mL and cooled (−10 °C). The light brown needles were collected and dried under vacuum: mp 130–132 °C; yield 1.2 g (80%). Anal. Calcd for $C_{19}H_{57}N_3Si_6U$: C, 31.1; H, 7.72; N, 5.70. Found: C, 30.6; H, 7.69; N, 5.68.

**(Tetrahydroborato)tris((hexamethyldisilyl)amido)thorium(IV).** Lithium tetrahydroborate (0.055 g, 0.0025 mol) in diethyl ether (20 mL) was added to chlorotris((hexamethyldisilyl)amido)thorium (1.9 g, 0.0025 mol) in tetrahydrofuran (30 mL) at 0 °C. The mixture was stirred for 20 h at 0 °C. The volatile material was removed under vacuum and the residue was extracted with pentane (50 mL). Concentration under vacuum of the extract to ca. 25 mL and cooling (−10 °C) afforded white needles: mp 168–171 °C; yield 1.5 g (82%). Anal. Calcd for $C_{18}H_{58}BN_3Si_6Th$: C, 29.7; H, 7.98; N, 5.78. Found: C, 29.0; H, 7.63; N, 5.55.

**(Tetrahydroborato)tris((hexamethyldisilyl)amido)uranium(IV).** Lithium tetrahydroborate (0.058 g, 0.0027 mol) in diethyl ether (20 mL) was added to chlorotris((hexamethyldisilyl)amido)uranium (2.0 g, 0.0027 mol) in diethyl ether (50 mL) at 0 °C. The mixture was stirred at 0 °C for 15 h. Diethyl ether was removed under vacuum and the residue was extracted with pentane (50 mL). The extract was concentrated under vacuum to ca. 20 mL. Cooling afforded light brown needles: mp 150–155 °C; yield 1.3 g (65%). Anal. Calcd for $C_{18}H_{58}BN_3Si_6U$: C, 29.5; H, 7.91; N, 5.73. Found: C, 29.0; H, 7.53; N, 5.64.

**X-ray Diffraction.** A colorless, hexagonal, needle-shaped crystal with approximate dimensions 0.06 × 0.09 × 0.23 mm was sealed inside a quartz capillary in an argon-filled drybox. Weissenberg photography showed the crystal to be rhombohedral, and rough cell dimensions were obtained. The crystal was examined on a Picker FACS-I automatic diffractometer equipped with a graphite monochromator and a Cu X-ray tube ($\lambda(K\alpha_1)$ 1.540 56 Å). $\omega$ scans of several low-angle reflections showed peaks with half-widths of 0.12–0.14°. The setting angles of 12 manually centered reflections ($94° < 2\theta < 119°$) were used to determine by least squares the dimensions of the triply primitive hexagonal cell: $a_h = 18.640$ (3) Å, $c_h = 8.604$ (1) Å, $V = 2589$ Å$^3$. For $Z = 3$ and a molecular weight of 728.05, the calculated density is 1.40 g/cm$^{-3}$. The rhombohedral cell parameters are $a_r = 11.137$ Å and $\alpha_r = 113.61°$. The structure was solved in the space group *R*3*m* by using hexagonal coordinates.

Intensity data were collected by using the $\theta$–$2\theta$ scan technique with a scan speed of 2°/min on $2\theta$. Each peak was scanned from 0.75° before the $K\alpha_1$ peak to 0.75° after the $K\alpha_2$ peak, and backgrounds were counted for 10 s at each end of the scan range, offset by 0.25°. The temperature during data collection was 22 ± 1 °C. Three standard reflections (003, 600, and $\bar{4}80$) were measured after every 200th scan. The intensity of the 003 reflection decayed about 10%, whereas the two other reflections decayed by 4%; a linear decay correction of 5% was applied uniformly to the data. The data were corrected for absorption by an analytical method[13] by using an estimated absorption coefficient of 161 cm$^{-1}$; absorption corrections varied from 2.3 to 5.1. A total of 5462 scans, not including standards, resulted in 1014 unique reflections (Friedel pairs not averaged).

Because there were no observed space-group extinctions, all five point groups in the two trigonal Laue groups were considered. A careful perusal of the intensity variation of the Friedel pairs as well as certain classes of reflections did in fact strongly indicate *R*3*m* as the space group. The three-dimensional Patterson function was calculated, but it was not consistent with an ordered structure in *R*3*m*. An attempt to solve the structure in space group *R*3 indicated a disorder with a symmetry describable in *R*3*m*. Once the disorder was adopted, a series of least-squares refinements in space group *R*3*m*, in which the function $\sum w(|F_o| - |F_c|)^2/\sum wF_o^2$ was minimized, converged rapidly to the final structure. The expressions that were used in processing the data and to estimate weights are given in the supplementary material; the "ignorance factor" *p* was set to 0.05 and *q* was set to 250. Scattering factors and anomalous dispersion corrections[14] were used; for Th, $f' = -5.091$ e and $f'' = 12.330$ e. Anisotropic thermal parameters were included only for thorium. An empirical extinction correction was applied for $F_{cor} = F_o(1 + kI)$, where $k = 4.2 \times 10^{-7}$, $I$ is the raw intensity, $F_o$ is the observed structure factor, and $F_{cor}$ is the modified observed structure factor. The discrepancy indices for all 1014 data (Friedel pairs not averaged) were

$$R = \sum||F_o| - |F_c||/\sum|F_o| = 0.031$$

$$R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.037$$

The error in an observation of unit weight was 1.40. In the last cycle no parameter changed more than $0.004\sigma$.

A least-squares refinement with $f''$ of thorium as an adjustable parameter[15] confirmed that the correct absolute orientation of the structure had been chosen. The result was $f'' = 12.16 \pm 0.33$ e, in excellent agreement with the value 12.330 e calculated by Cromer and Liberman[16] for Cu K$\alpha_1$ radiation. This agreement also indicates that the specimen was substantially free of inversion twinning.

A single crystal of $Th[N(Si(CH_3)_3)_2]_3CH_3$ was examined by the X-ray diffraction method and found to be isomorphous with the $Th[N(Si(CH_3)_3)_2]_3BH_4$ complex reported here. The methyl derivative has cell dimensions $a$ = 18.68 (1) and 8.537 (6) Å. Weissenberg patterns of the two isomorphs showed intensities that were visually the same. The crystals of the methyl derivative were too poor in quality to be used for collecting a suitable set of intensity data.

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**Registry No.** $ClTh[N(SiMe_3)_2]_3$, 51700-07-3; $ClU[N(SiMe_3)_2]_3$, 69517-42-6; $MeTh[N(SiMe_3)_2]_3$, 69517-43-7; $MeU[N(SiMe_3)_2]_3$, 69517-44-8; $BH_4Th[N(SiMe_3)_2]_3$, 69532-06-5; $BH_4U[N(SiMe_3)_2]_3$, 69532-07-6; $NaN(SiMe_3)_2$, 1070-89-9; $ThCl_4$, 10026-08-1; $UCl_4$, 10026-10-5.

**Supplementary Material Available:** Data processing formulas and the listing of structure factor amplitudes (6 pages). Ordering information is given on any current masthead page.

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# Further Studies of Diphosphine- and Diarsine-Bridged Rhodium Complexes

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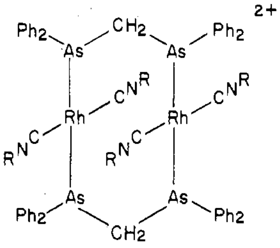
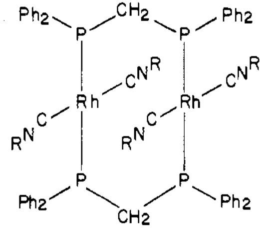
A convenient, new route to the diphosphine-bridged dimers $[Rh_2(CNR)_4(Ph_2PCH_2PPh_2)_2]^{2+}$ via the addition of the diphosphine and the isocyanide to $[(1,5\text{-cyclooctadiene})RhCl]_2$ is described. The analogous diarsine-bridged dimers $[Rh_2(CNR)_4(Ph_2AsCH_2AsPh_2)_2][BPh_4]_2$ are best prepared by adding an isocyanide to $Rh_2(CO)_2Cl_2(Ph_2AsCH_2AsPh_2)_2$ followed by precipitation of the cation with sodium tetraphenylborate. Oxidative addition of iodine to $[Rh_2(CNR)_4(Ph_2AsCH_2AsPh_2)_2]^{2+}$ produces rhodium(II) complexes, $[Rh_2I_2(CNR)_4(Ph_2AsCH_2AsPh_2)_2]^{2+}$, with direct Rh–Rh bonds. Addition of disulfides to $[Rh_2(CNR)_4(Ph_2PCH_2PPh_2)_2]^{2+}$ can produce two different products. With trifluoromethyl disulfide, rhodium(II) dimers, $[Rh_2(SCF_3)_2(CNR)_4(Ph_2PCH_2PPh_2)_2]^{2+}$, are formed while with phenyl disulfide, pentafluorophenyl disulfide, and phenyl diselenide, rhodium(III) monomers, $[Rh(SR)_2(CNR)_2(Ph_2PCH_2PPh_2)]^+$ or $[Rh(SePh)_2(CNR)_2(Ph_2PCH_2PPh_2)]^+$, are obtained. Addition of disulfides and diselenides to $Rh(CNR)_4^+$ produces six-coordinate rhodium(III) species, *trans*-$[Rh(SR)_2(CNR)_4]^+$ or *trans*-$[Rh(SePh)_2(CNR)_4]^+$.

## Introduction

Recent studies from our laboratory have been concerned with the chemical and physical properties of complexes containing two rhodium atoms.[1-4] Here we describe some additional studies in this area. The preparation of the diarsine-bridged complexes **1** and a comparison of these with their diphosphine-bridged counterparts **2**[2] are presented. Oxidation of **2** and similar dimers, including **1** as shown here, with iodine (and bromine) produces Rh(II) dimers with direct Rh–Rh bonds.[2] However the role of the ligand in promoting such transannular oxidative additions is not clear, since unbridged Rh(II) dimers, $Rh_2(CNR)_8X_2^{2+}$, may readily be prepared either by addition of halogen to $Rh(CNR)_4^+$ or by reacting $Rh(CNR)_4^+$ with $Rh(CNR)_4X_2^+$.[1] We now show that trifluoromethyl disulfide undergoes transannular oxidative addition to **1** to produce $[Rh_2(CNR)_4(Ph_2PCH_2PPh_2)_2(SCF_3)_2]^{2+}$ whereas no comparable Rh(II) species is obtained in the absence of a bridging ligand. Other aspects of the addition of disulfides to mononuclear and binuclear Rh(I) compounds are described. Previous studies have shown that disulfides can add to very reactive monomeric Rh(I) compounds to produce Rh(III) thiolate complexes.[5]



**1**



**2**

## Experimental Section

**Preparation of Compounds.** Bis(diphenylphosphino)methane and bis(diphenylarsino)methane were obtained from Strem Chemicals, and the disulfides were also obtained from commercial sources. The following compounds were obtained by established routes: $[(1,5\text{-}C_8H_{12})RhCl]_2$,[6] $Rh_2(Ph_2AsCH_2AsPh_2)_2(CO)_2Cl_2$,[7] $(C_6F_5S)_2$.[8] Only representative syntheses are reported in cases where the substituents on the isocyanides may be varied.

**$[(n\text{-}C_4H_9NC)_4Rh_2(Ph_2PCH_2PPh_2)_2][BPh_4]_2$.** *n*-Butyl isocyanide (0.31 mL, 3.2 mmol) was added dropwise to a briskly stirred slurry of 0.40 g (0.81 mmol) of $[(1,5\text{-}C_8H_{12})RhCl]_2$ and 0.63 g (1.6 mmol) of bis(diphenylphosphino)methane in 30 mL of methanol. The stirring