Inorg. Chem. **2006**, *45*, 9907−9913

Inorganic Chemistry
Article

Lanthanide and Uranium Complexes with an SPS-Based Pincer Ligand

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Received July 21, 2006

Reactions of $Ln(BH_4)_3(THF)_n$ and $[Li(Et_2O)][SPS^{Me}]$, the lithium salt of an anionic SPS pincer ligand composed of a central hypervalent λ^4-phosphinine ring bearing two ortho-positioned diphenylphosphine sulfide sidearms, led to the monosubstituted compounds $[Ln(BH_4)_2(SPS^{Me})(THF)_2]$ [Ln = Ce (**1**), Nd (**2**)], while the homoleptic complexes $[Ln(SPS^{Me})_3]$ [Ln = Ce (**3**), Nd (**4**)] were obtained by treatment of LnX_3 (X = I, BH_4) with $[K(Et_2O)][SPS^{Me}]$. The $[UX_2(SPS^{Me})_2]$ complexes [X = Cl (**5**), BH_4 (**6**)] were isolated from reactions of UX_4 and the lithium or potassium salt of the $[SPS^{Me}]^-$ anion. The X-ray crystal structures of **1**·1.5THF, **2**·1.5THF, **3**·2THF·2Et_2O, and **5**·4py reveal that the flexible tridentate $[SPS^{Me}]^-$ anion is bound to the metal as a tertiary phosphine with electronic delocalization within the unsaturated parts of the ligand.

Introduction

The chemistry of the lanthanide and actinide complexes with phosphorus and sulfur donor ligands has witnessed significant advances during the last two decades,[1,2] and a variety of compounds including phosphide,[3−8] phospholyl,[9,10] thiolate,[11−15] sulfide,[16−18] and dithiolene[19−21] derivatives have been characterized. In addition to their challenging synthesis and their novel structural and reactivity features, these complexes deserve much attention for both their fundamental interest, with the precise knowledge of the metal−ligand bonding and the role of the f electrons,[12,19] and their applications in catalysis[2,6−8] and materials science.[15,17,18] These complexes are also attractive for the study of lanthanide(III)/actinide(III) differentiation,[12,19,22,23] an important and difficult problem in the management of nuclear wastes, which can be surmounted by the selective complexation of the trivalent 5f over 4f ions with soft ligands.[24−26] In this

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(1) Nief, F. *Coord. Chem. Rev.* **1998**, *180*, 13.
(2) Li, H. X.; Zhu, Y. J.; Cheng, M. L.; Ren, Z. G.; Lang, J. P.; Shen, Q. *Coord. Chem. Rev.* **2006**, *250*, 2059.
(3) Izod, K.; O'Shaughnessy, P.; Sheffield, J. M.; Clegg, W.; Liddle, S. T. *Inorg. Chem.* **2000**, *39*, 4741.
(4) Izod, K.; Liddle, S. T.; Clegg, W. *Chem. Commun.* **2004**, 1748.
(5) Izod, K.; Liddle, S. T.; McFarlane, W.; Clegg, W. *Organometallics* **2004**, *23*, 2734.
(6) Kawaoka, A. M.; Marks, T. J. *J. Am. Chem. Soc.* **2004**, *126*, 12764.
(7) Motta, A.; Fragala, I. L.; Marks, T. J. *Organometallics* **2005**, *24*, 4995.
(8) Zhang, L. X.; Luo, Y.; Hou, Z. *J. Am. Chem. Soc.* **2005**, *127*, 14562.
(9) Turcitu, D.; Nief, F.; Ricard, L. *Chem.*—*Eur. J.* **2003**, *9*, 4916.
(10) Cendrowski-Guillaume, S. M.; Le Gland, G.; Nierlich, M.; Ephritikhine, M. *Eur. J. Inorg. Chem.* **2003**, 1388.
(11) Arliguie, T.; Lescop, C.; Ventelon, L.; Leverd, P. C.; Thuéry, P.; Nierlich, M.; Ephritikhine, M. *Organometallics* **2001**, *20*, 3698.
(12) Roger, M.; Barros, N.; Arliguie, T.; Thuéry, P.; Maron, L.; Ephritikhine, M. *J. Am. Chem. Soc.* **2006**, *128*, 8790.
(13) Li, Y.; Pi, C.; Zhang, J.; Zhou, X.; Chen, Z.; Weng, L. *Organometallics* **2005**, *24*, 1982.
(14) Li, H. X.; Ren, Z. G.; Zhang, Y.; Zhang, W. H.; Lang, J. P.; Shen, Q. *J. Am. Chem. Soc.* **2005**, *127*, 1122.
(15) Banerjee, S.; Emge, T. J.; Brennan, J. G. *Inorg. Chem.* **2004**, *43*, 6307.
(16) Kornienko, A. Y.; Emge, T. J.; Brennan, J. G. *J. Am. Chem. Soc.* **2001**, *123*, 11933.
(17) Kornienko, A.; Emge, T. J.; Kumar, G. A.; Riman, R. E.; Brennan, J. G. *J. Am. Chem. Soc.* **2005**, *127*, 3501.
(18) Mirkovic, T.; Hines, M. A.; Nair, P. S.; Scholes, G. D. *Chem. Mater.* **2005**, *17*, 3451.
(19) Roger, M.; Belkhiri, L.; Thuéry, P.; Arliguie, T.; Fourmigué, M.; Boucekkine, A.; Ephritikhine, M. *Organometallics* **2005**, *24*, 4940.
(20) Roger, M.; Arliguie, T.; Thuéry, P.; Fourmigué, M.; Ephritikhine, M. *Inorg. Chem.* **2005**, *44*, 594.
(21) Roger, M.; Arliguie, T.; Thuéry, P.; Fourmigué, M.; Ephritikhine, M. *Inorg. Chem.* **2005**, *44*, 584.
(22) Karmazin, L.; Mazzanti, M.; Pécaut, J. *Chem. Commun.* **2002**, 654.
(23) Brennan, J. G.; Stults, S. D.; Andersen, R. A.; Zalkin, A. *Organometallics* **1988**, *7*, 1329.
(24) *Implications of Partitioning and Transmutation in Radioactive Waste Management*; IAEA-TRS 435; IAEA: Vienna, Austria, 2005.
(25) Nash, K. L. Separation chemistry for lanthanides and trivalent actinides. In *Handbook on the Physics and Chemistry of Rare Earths*; Gschneidner, K. A., Jr., Eyring, L., Choppin, G. R., Lander, G. H., Eds.; Elsevier Science: New York, 1994; Vol. 18 (121), p 197.
(26) *Actinides and Fission Products Partitioning and Transmutation. Status and Assessment Report*; NEA/OECD Report; NEA/OECD: Paris, 1999.

10.1021/ic061364g CCC: $33.50

context, it seemed interesting to us to introduce into f-element chemistry the novel SPS-based pincer ligand, featuring a central λ^4-phosphinine unit and two pendant phosphinosulfide groups, which was used for the synthesis of a variety of d transition metal complexes exhibiting attractive structures and reactions.[27−33] While the softness of both the phosphorus and sulfur centers would appear to be an unfavorable factor at first glance, we reasoned that the flexibility and negative charge of the system would allow the coordination to the large lanthanide and actinide ions. Here, we present the syntheses and crystal structures of such compounds of cerium(III), neodymium(III), and uranium(IV).

Experimental Section

All reactions were carried out under argon (<5 ppm oxygen or water) using standard Schlenk-vessel and vacuum-line techniques or in a glovebox. Solvents were dried by standard methods and distilled immediately before use. The ^{1}H and ^{31}P NMR spectra were recorded on a Bruker DPX 200 or DRX 300 instruments; the ^{1}H NMR spectra are referenced internally using the residual proton solvent resonances relative to tetramethylsilane (δ 0), and the ^{31}P NMR chemical shifts are given relative to an 85% H_3PO_4 external reference. Elemental analyses were performed by Analytische Laboratorien at Lindlar (Germany).

Syntheses. The precursors $Nd(BH_4)_3(THF)_2$,[34] $Ce(BH_4)_3(THF)_3$,[21] UCl_4,[35] and $U(BH_4)_4$[36] were prepared by published methods. Li[SPS^{Me}] was synthesized from 2,6-bis(diphenylphosphine sulfide)-3,5-diphenylphosphinine[31] using a procedure similar to that already published,[32] but crystallization from diethyl ether afforded [Li(Et_2O)][SPS^{Me}] isolated in an 85% yield; [K(Et_2O)][SPS^{Me}] was obtained by reacting [Li(Et_2O)][SPS^{Me}] with KO*t*Bu in diethyl ether and isolated in an 88% yield.

[Ce(BH$_4$)$_2$(SPS^{Me})(THF)$_2$] (1). A flask was charged with Ce(BH$_4$)$_3$(THF)$_3$ (50 mg, 0.125 mmol) and [K(Et_2O)][SPS^{Me}] (101.1 mg, 0.125 mmol), and THF (30 mL) was condensed into it. The reaction mixture was stirred for 2 h at 20 °C, and the THF was evaporated off overnight. The orange residue was extracted in THF (30 mL); the bright orange solution was filtered and evaporated to dryness, leaving an orange powder of [Ce(BH$_4$)$_2$(SPS^{Me})(THF)$_2$]. Yield: 109 mg (86%). Anal. Calcd for $C_{50}H_{58}B_2O_2P_3S_2Ce$: C, 59.47; H, 5.79; P 9.20; S, 6.35. Found: C, 59.29; H, 5.70; P 9.04; S, 6.25. ^{1}H NMR (200 MHz, THF-*d*$_8$, 23 °C): δ 5.15 (t, ^4J(H−P$_L$) = 3.9 Hz, 1 H, H$_4$), 6.68−6.05 (m, 24 H, Ph), 7.21 (s, $w_{1/2}$ = 7.0 Hz, 3 H, Me), 7.40 (t, *J* = 7.3 Hz, 4 H, Ph), 7.72 (t, *J* = 7.3 Hz, 2 H, Ph), 50.0 (broad s, $w_{1/2}$ = 300 Hz, 8 H, BH$_4$). ^{31}P NMR (81 MHz, THF-*d*$_8$, 23 °C): δ 15.7 (s, $w_{1/2}$ = 180 Hz, P$_L$Ph$_2$), 517 (broad s, $w_{1/2}$ = 426 Hz, P$_C$Me).

[Nd(BH$_4$)$_2$(SPS^{Me})(THF)$_2$] (2). A flask was charged with Nd(BH$_4$)$_3$(THF)$_2$ (51 mg, 0.153 mmol) and [K(Et_2O)][SPS^{Me}] (123.8 mg, 0.153 mmol), and THF (30 mL) was condensed into it. The reaction mixture was stirred for 2 h at 20 °C, and THF was evaporated off overnight. The orange residue was extracted in THF (30 mL); the bright orange solution was filtered and evaporated to dryness, leaving an orange powder of [Nd(BH$_4$)$_2$(SPS^{Me})(THF)$_2$]·1.5THF. Yield: 158 mg (92%). Anal. Calcd for $C_{56}H_{70}B_2O_{3.5}P_3S_2Nd$: C, 59.94; H, 6.29; S, 5.71. Found: C, 59.92; H, 6.32; S, 5.44. ^{1}H NMR (200 MHz, THF-*d*$_8$, 23 °C): δ 5.42 (t, ^4J(H−P$_L$) = 3.9 Hz, 1 H, H$_4$), 5.93 (m, 4 H, Ph), 7.0−6.50 (m, 20 H, Ph), 7.77 (m, 4 H, Ph), 7.95 (t, *J* = 6.6 Hz, 2 H, Ph), 8.27 (s, 3 H, Me), 113.2 (broad s, $w_{1/2}$ = 400 Hz, 8 H, BH$_4$). ^{31}P NMR (81 MHz, THF-*d*$_8$, 23 °C): δ −8.63 (s, $w_{1/2}$ = 70 Hz, P$_L$Ph$_2$), 2210 (broad s $w_{1/2}$ = 800 Hz, P$_C$Me).

[Ce(SPS^{Me})$_3$] (3). Method a. A flask was charged with Ce(BH$_4$)$_3$(THF)$_3$ (119 mg, 0.297 mmol) and [K(Et_2O)][SPS^{Me}] (720.8 mg, 0.891 mmol), and THF (30 mL) was condensed into it. The reaction mixture was stirred for 2 h at 20 °C, and THF was evaporated off overnight. The orange residue was extracted in THF (30 mL) leaving a white precipitate of KBH$_4$; the bright orange solution was filtered and evaporated to dryness, leaving an orange powder of [Ce(SPS^{Me})$_3$]. Yield: 516 mg (78%). Anal. Calcd for $C_{126}H_{102}P_9S_6Ce$: C, 67.94; H, 4.61; S, 8.64. Found C, 68.00; H, 4.78; S, 8.50. ^{1}H NMR (200 MHz, THF-*d*$_8$, 23 °C): δ 2.75 (d, ^2J(H−P$_C$) = 9.0 Hz, 9 H, Me), 5.68 [t, ^4J(H−P$_L$) = 4.8 Hz, 3 H, H$_4$], 6.65−8.21 (m, 90 H, Ph). ^{31}P NMR (81 MHz, THF-*d*$_8$, 23 °C): δ 15.1 (d, ^2J(P$_C$-P$_L$) = 141 Hz, P$_L$Ph$_2$], 444.5 [t, *J*(P$_C$-P$_L$) = 141 Hz, P$_C$Me].

Method b. The same procedure starting from CeI$_3$ (30 mg, 0.058 mmol) and [K(Et_2O)][SPS^{Me}] (139.8 mg, 0.173 mmol) gave **3**. Yield: 104 mg (80%).

An NMR tube was charged with CeI$_3$ (6.0 mg, 0.012 mmol) and [Li(Et_2O)][SPS^{Me}] (28 mg, 0.036 mmol) and THF-*d*$_8$ (0.4 mL) was added. After 1 h at 20 °C, the spectrum showed the quantitative formation of **3**.

[Nd(SPS^{Me})$_3$] (4). Method a. A flask was charged with Nd(BH$_4$)$_3$(THF)$_2$ (37 mg, 0.111 mmol) and [K(Et_2O)][SPS^{Me}] (269.4 mg, 0.333 mmol), and THF (30 mL) was condensed into it. The reaction mixture was stirred for 2 h at 20 °C, and THF was evaporated off overnight to precipitate KBH$_4$. The orange residue was extracted in THF (30 mL) leaving a white precipitate of KBH$_4$; the bright orange solution was filtered and evaporated to dryness, leaving an orange powder of [Nd(SPS^{Me})$_3$]. Yield: 183 mg (74%). Anal. Calcd for $C_{126}H_{102}P_9S_6Nd$: C, 67.82; H, 4.61; S, 8.62. Found: C, 67.18; H, 4.52; S, 8.46. ^{1}H NMR (200 MHz, THF-*d*$_8$, 23 °C): δ 5.99−7.39 (8 m, 34 H, CH of Ph, H$_4$ and Me). ^{31}P NMR (81 MHz, THF-*d*$_8$, 23 °C): δ −6.37 (s, $w_{1/2}$ = 90 Hz, P$_L$Ph$_2$), 1859 (broad s, $w_{1/2}$ = 1080 Hz, P$_C$Me).

Method b. The same procedure starting from NdI$_3$ (32 mg, 0.061 mmol) and [K(Et_2O)][SPS^{Me}] (147.9 mg, 0.183 mmol) gave **4**. Yield: 107 mg (79%).

An NMR tube was charged with NdI$_3$ (6.0 mg, 0.011 mmol) and [Li(Et_2O)][SPS^{Me}] (25 mg, 0.033 mmol), and THF-*d*$_8$ (0.4 mL) was added. After 1 h at 20 °C, the spectrum showed the quantitative formation of **4**.

[UCl$_2$(SPS^{Me})$_2$] (5). A flask was charged with UCl$_4$ (60 mg, 0.158 mmol) and [K(Et_2O)][SPS^{Me}] (255.6 mg, 0.316 mmol), and THF (30 mL) was condensed into it. A white precipitate of KCl was formed after the mixture was stirred for 4 h at 20 °C. The solution was filtered and evaporated to dryness, leaving an orange powder. The latter was then extracted in THF (30 mL). After filtration, the solution was concentrated to ∼5 mL, and upon the addition of diethyl ether (30 mL), the mixture was left standing

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(27) Doux, M.; Ricard, L.; Le Floch, P.; Jean, Y. *Organometallics* **2005**, *24*, 1608.

(28) Doux, M.; Mézailles, N.; Ricard, L.; Le Floch, P. *Organometallics* **2003**, *22*, 4624.

(29) Doux, M.; Le Floch, P.; Jean, Y. *Theor. Chem.* **2005**, *724*, 73.

(30) Doux, M.; Mézailles, N.; Melaimi, M.; Ricard, L.; Le Floch, P. *Chem. Commun.* **2002**, 1566.

(31) Doux, M.; Bouet, C.; Mézailles, N.; Ricard, L.; Le Floch, P. *Organometallics* **2002**, *21*, 2785.

(32) Doux, M.; Mézailles, N.; Ricard, L.; Le Floch, P. *Eur. J. Inorg. Chem.* **2003**, 3878.

(33) Doux, M.; Ricard, L.; Le Floch, P.; Mézailles, N. *Dalton Trans.* **2004**, 2593.

(34) Mirsaidov, U.; Rotenberg, T. G.; Dymova, D. T. N. *Akad. Nauk. SSSR* **1976**, *19*, 30.

(35) Hermann, J. A.; Suttle, J. F. *Inorg. Synth.* **1957**, *5*, 143.

(36) Volkov, V. V.; Myakishev, K. G. *Radiokhimiya* **1980**, *22*, 745.

Table 1. Crystal Data and Structure Refinement Details

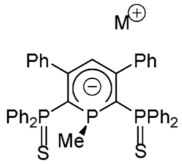
	1·1.5THF	**2**·1.5THF	**3**·2THF·2Et$_2$O	**5**·4py
empirical formula	$C_{56}H_{70}B_2CeO_{3.5}P_3S_2$	$C_{56}H_{70}B_2NdO_{3.5}P_3S_2$	$C_{142}H_{138}CeO_4P_9S_6$	$C_{104}H_{88}Cl_2N_4P_6S_4U$
M (g mol^{-1})	1117.89	1122.01	2519.73	2016.77
cryst syst	triclinic	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	10.3250(4)	10.3078(6)	16.311(3)	12.2300(4)
b (Å)	22.8023(14)	22.7922(17)	16.7552(18)	16.1054(7)
c (Å)	23.9332(14)	23.8918(15)	24.037(4)	23.8636(7)
α (deg)	95.174(3)	95.051(4)	95.421(9)	104.816(3)
β (deg)	91.414(3)	91.311(4)	100.691(6)	95.565(3)
γ (deg)	98.993(4)	99.068(4)	103.437(8)	91.068(2)
V (Å^3)	5538.4(5)	5517.6(6)	6213.1(17)	4518.1(3)
Z	4	4	2	2
D_{calcd} (g cm^{-3})	1.341	1.351	1.347	1.482
μ(Mo Kα) (mm^{-1})	1.026	1.146	0.638	2.106
F(000)	2316	2324	2622	2040
reflns collected	37 405	122 258	39 503	145 793
indep reflns	19 245	20 937	21 126	17 131
obsd reflns [$I > 2\sigma(I)$]	12 267	15 463	8404	12 476
R_{int}	0.064	0.083	0.087	0.091
params refined	1218	1218	1466	1092
R1	0.072	0.055	0.091	0.044
wR2	0.174	0.143	0.203	0.066
S	1.035	1.024	0.938	0.965
$\Delta\rho_{min}$ (e Å^{-3})	−1.22	−1.11	−0.76	−0.84
$\Delta\rho_{max}$ (e Å^{-3})	1.68	1.36	0.63	0.86

for 24 h, after which red crystals were deposited. The crystals were filtered off and dried under vacuum, leading to an orange powder. Yield: 255 mg (95%). Anal. Calcd for $C_{84}H_{68}Cl_2P_6S_4U$: C, 59.33; H, 4.03; P 10.93; S, 7.54. Found: C, 59.09; H, 4.07; P 10.61; S, 7.41. ^{31}P NMR (81 MHz, THF-d_8, 23 °C): major signals δ −265 (s, $w_{1/2}$ = 175 Hz), 2018 (broad s, $w_{1/2}$ = 1100 Hz).

[U(BH$_4$)$_2$(SPS^{Me})$_2$] (6). A flask was charged with U(BH$_4$)$_4$ (109 mg, 0.366 mmol) and [Li(Et$_2$O)][SPS^{Me}] (569.5 mg, 0.733 mmol), and THF (30 mL) was condensed into it. The reaction mixture was stirred for 2 h at 20 °C. The compound precipitated as an orange microcrystalline powder, which was filtered off, washed with THF (2 × 20 mL), and dried under vacuum. Yield: 596 mg (98%). Anal. Calcd for $C_{84}H_{76}B_2P_6S_4U$: C, 60.80; H, 4.62; B 1.30; S, 7.73. Found: C, 60.62; H, 4.77; B 1.38; S, 7.61. The insolubility of **6** prevented the collection of NMR spectra.

Crystallographic Data Collection and Structure Determination. The data were collected at 100(2) K on a Nonius Kappa-CCD area detector diffractometer[37] using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The crystals were introduced in glass capillaries with a protective Paratone-N oil (Hampton Research) coating. The unit cell parameters were determined from 10 frames, and they were then refined on all data. The data (φ- or φ- and ω-scans with 2° steps) were processed with HKL2000.[38] The structures were solved by direct methods or by Patterson map interpretation with SHELXS-97 and subsequent Fourier-difference synthesis and refined by full-matrix least-squares on F^2 with SHELXL-97.[39] Absorption effects were corrected empirically with the program DELABS in PLATON.[40] All non-hydrogen atoms were refined with anisotropic displacement parameters, with some restraints on bond lengths and/or displacement parameters for some badly behaving atoms, particularly in the solvent molecules. The hydrogen atoms of the borohydride groups in the two isomorphous compounds **1**·1.5THF and **2**·1.5THF were found on Fourier difference maps. All the other hydrogen atoms were introduced at calculated positions, and all were treated as riding atoms with an isotropic displacement parameter equal to 1.2 (BH$_4$, CH, CH$_2$) or 1.5 (CH$_3$) times that of the parent atom. Crystal data and structure refinement details are given in Table 1. The molecular plots were drawn with SHELXTL.[41]

Scheme 1. Alkali Metal Salt of the SPS^{Me} Ligand



Results and Discussion

Lanthanide Complexes. Reactions of Ln(BH$_4$)$_3$(THF)$_n$ (Ln = Ce, n = 3; Ln = Nd, n = 2) with 1 mol equiv of the lithium or potassium salt of the SPS^{Me} ligand, represented in Scheme 1, led to the formation of [Ce(BH$_4$)$_2$(SPS^{Me})(THF)$_2$] (**1**) and [Nd(BH$_4$)$_2$(SPS^{Me})(THF)$_2$]·1.5THF (**2**·1.5THF), which were isolated as orange powders in 86 and 92% yields, respectively (Scheme 2).

The ^{1}H NMR spectra of **1** and **2** display, in addition to the resonances attributed to the hydrogen atoms of the phenyl rings, signals corresponding to the central hydrogen atom of the phosphinine moiety, the methyl group, and the two borohydride ligands. The ^{31}P NMR spectra exhibit two broad signals for the AX$_2$ spin-system pattern, with the resonances of the central P$_C$ atom visible at much higher field than those of the P$_L$ atoms of the pendant arms.

One may note that complexes **1** and **2** were the sole products even when [Li(Et$_2$O)][SPS^{Me}] was used in excess. However, the tris(SPS^{Me}) lanthanide compounds [Ln-

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(37) Nonius *Kappa-CCD Software*; Nonius BV: Delft, The Netherlands, 1998.

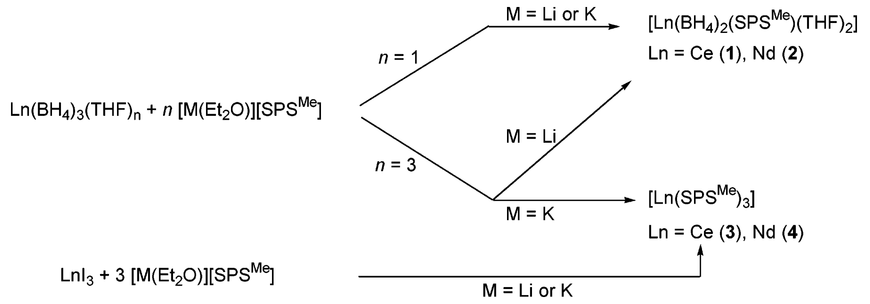
(38) Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276*, 307.

(39) Sheldrick, G. M. *SHELXS-97* and *SHELXL-97*; University of Göttingen: Göttingen, Germany, 1997.

(40) Spek, A. L. *PLATON*; University of Utrecht: Utrecht, The Netherlands, 2000.

(41) Sheldrick, G. M. *SHELXTL*, version 5.1; Bruker AXS Inc.: Madison, WI, 1999.

Scheme 2. Syntheses of the Lanthanide Complexes **1**−**4**



$(SPS^{Me})_3]$ [Ln = Ce (**3**), Nd (**4**)] were synthesized by treatment of $Ln(BH_4)_3(THF)_n$ with 3 mol equiv of $[K(Et_2O)]$-$[SPS^{Me}]$ in THF (Scheme 2); this difference is obviously related to the distinct solubilities of $LiBH_4$ and KBH_4, the byproducts of the reaction. The bright orange powders of the homoleptic compounds **3** and **4** were isolated in 78 and 74% yields, respectively. These complexes were alternatively prepared in an 80% yield by reaction of LnI_3 with either the lithium or potassium salt of the SPS^{Me} ligand; the nature of the iodide ion, which is a good leaving group, associated with the lower solubility of LiI versus $LiBH_4$, permitted the reaction to go to completion.

The ^1H and ^{31}P NMR spectra of **3** and **4** demonstrate the chemical equivalence of the three SPS^{Me} ligands and the high symmetry of the complexes in solution, in agreement with the approximate D_{3h} symmetry found in the solid state (vide infra). While the ^1H NMR spectrum of Nd compound **4** shows eight overlapping multiplets between δ 5.99 and 7.39, the characteristic signals of the central hydrogen atom of the phosphinine ligand and of the methyl group are easily identified at δ 5.68 and 2.75, respectively, in the spectrum of the Ce congener **3**. The ^{31}P NMR spectrum of **3** exhibits a triplet and a doublet corresponding to the P_C and P_L atoms, respectively, but the multiplicity is not observable in the spectrum of **4** which shows two broad signals; as in the case of **1** and **2**, the resonances of the central P_C atom appear at higher field.

Crystals of **1**·1.5THF and **2**·1.5THF, obtained by crystallization of **1** and **2** in THF, are isomorphous; a view of **1** is shown in Figure 1, while selected bond lengths and angles are listed in Table 2. The asymmetric unit in **1**·1.5THF contains two independent but nearly identical complex molecules, denoted A and B, and three THF molecules. The mean plane defined by the atoms Ce, B(1), B(2), and P(1) (rms deviations 0.019 and 0.009 Å for molecules A and B, respectively) is a plane of pseudosymmetry for the complex. The metal is seven-coordinate in a pentagonal bipyramidal environment, with the two BH_4 groups in apical positions. The short Ce···B distances, which average 2.684(19) and 2.681(12) Å in molecules A and B, respectively, can be compared with the mean U···B distances of 2.65(3) and 2.68(4) Å in $U(BH_4)_3(THF)_3$[42] and $[U(BH_4)_3(Me_2PCH_2CH_2PMe_2)_2]$,[43] respectively, and indicate a tridentate ligation mode of the BH_4 ligands, in keeping with the positions found for the hydrogen atoms. These distances are significantly shorter than that of 2.93(2) Å in the BH_4-bridged dimer $[Ce(1,3\text{-}^tBuC_5H_3)_2(\mu\text{-}BH_4)]_2$,[44] the only other cerium borohydride to have been crystallographically characterized.

Table 2. Selected Distances (Å) and Angles (deg) for Complexes **1**·1.5THF and **2**·1.5THF

	Ln = Ce (**1**·1.5THF)		Ln = Nd (**2**·1.5THF)	
	molecule A	molecule B	molecule A	molecule B
Ln−S(1)	2.992(2)	2.959(2)	2.9623(14)	2.9308(14)
Ln−S(2)	2.947(2)	2.984(2)	2.9162(15)	2.9487(14)
Ln···B(1)	2.665(10)	2.668(11)	2.620(7)	2.629(7)
Ln···B(2)	2.703(10)	2.693(11)	2.654(6)	2.656(8)
Ln−P(1)	3.020(2)	3.064(2)	2.9797(14)	3.0248(15)
Ln−O(1)	2.548(5)	2.594(6)	2.533(4)	2.566(4)
Ln−O(2)	2.574(6)	2.585(6)	2.550(4)	2.554(4)
P(2)−S(1)	2.007(3)	2.009(3)	2.0066(19)	2.007(2)
P(3)−S(2)	2.007(3)	2.008(3)	2.0086(19)	2.011(2)
P(1)−C(1)	1.818(7)	1.800(8)	1.801(5)	1.791(5)
P(1)−C(5)	1.788(8)	1.807(8)	1.785(5)	1.806(5)
P(2)−C(1)	1.769(8)	1.764(7)	1.780(6)	1.773(6)
P(3)−C(5)	1.764(8)	1.765(8)	1.773(5)	1.771(5)
S(1)−Ln−S(2)	134.75(6)	133.47(6)	135.85(4)	134.63(4)
B(1)···Ln···B(2)	177.5(3)	177.5(3)	178.4(2)	177.7(2)
P(1)−C(1)−P(2)	115.0(4)	116.0(4)	114.8(3)	115.7(3)
P(1)−C(5)−P(3)	117.3(4)	114.8(4)	116.7(3)	114.6(3)
O(1)−Ln−O(2)	71.27(19)	72.5(2)	71.51(13)	72.19(13)

The Ce−S bond lengths of 2.992(2), 2.947(2) Å and 2.959(2), 2.984(2) Å in the two independent molecules of **1**·1.5THF are similar to the average values of 2.994, 2.991, and 2.969 Å measured in $[Ce(C_5H_5)_2\{N(SPPh_2)_2\}]$,[45] $[\{Ce(Me_2PS_2)_4\}\{AsPh_4\}]$,[46] and $[\{Ce((MeO)_2PS_2)_4\}\{AsPh_4\}]$,[47] respectively. The S(1)−Ce−S(2) bite angles are 134.75(6) and 133.47(6)° in molecules A and B, respectively. The Ce−P

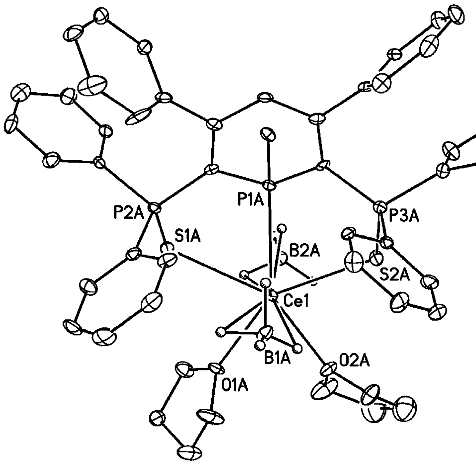


Figure 1. View of one of the two independent molecules in complex **1**·1.5THF. The hydrogen atoms (except those of the borohydride groups) and solvent molecules have been omitted. Displacement ellipsoids are drawn at the 30% probability level.

distances of 3.020(2) and 3.064(2) Å in the two independent molecules are slightly shorter than those observed in the only other two compounds containing a Ce−P bond which have been crystallographically characterized, 3.072(4) Å in [Ce(C_5H_4Me)$_3$(PMe_3)][48] and 3.086(3) Å in [Ce(C_5H_4Me)$_3$(P(OCH_2)$_3$CEt)].[23] From these data it is difficult to establish whether the ligand behaves as an anionic λ^4-phosphinine (form A in Scheme 4) or as a classical tertiary phosphine (form B). This particular point will be discussed later for all the compounds, by consideration of the geometrical parameters of the SPS^{Me} ligand.

The structures of **1** and **2** can be compared with that of the only other lanthanide compound with an SPS-type ligand to have been crystallographically characterized, [$NHEt_3$][Sm{PhP(C_6H_3S-2-R)$_2$}$_2$(py)$_2$].[49] In this compound, the dianionic pincer ligand is trihaptocoordinated with Sm−S bond lengths of 2.835(2)−2.883(2) Å and Sm−P distances of 2.974(2) and 2.980(2) Å. From the variation in the ionic radii of octacoordinate samarium(III) and heptacoordinate cerium(III),[50] the corresponding metal−ligand distances should be shorter in **1** than in the samarium anion, by ∼0.1 Å. This is obviously not the case since the inverse trend is observed. This feature should be related to the fact that, in the samarium compound, the SPS pincer is a dianionic ligand with smaller bite angles of 105.00(5) and 103.78(5)°.

The average Nd−S distance of 2.94(2) Å in **2** is larger than that of 2.85(2) Å in the thiolate compound [Ln(SC_6F_5)$_2$(DME)$_3$]$_2$[Hg_2(SC_6F_5)$_6$][15] and is similar to that of 2.953(9) Å in [{Nd((O^{i}Pr)$_2$$PS_2$)$_4$}{$AsPh_4$}][47] or 2.93(1) Å in [Nd{(O^{i}Pr)$_2$$PS_2$}$_3${Ph($NH_2$)CO}$_2$].[47] The Nd−P distances of 2.9797(14) and 3.0248(15) Å in molecules A and B, respectively, are significantly shorter than those in the hexacoordinate tertiary phosphine complex [Nd(OC^t$Bu_2$$CH_2$$PMe_2$)$_3$][51] (average 3.154(2) Å), although apparently larger than in the tris(phosphido) compound [Nd(P{SiMe}$_2$)$_3$(THF)$_2$][52] (average 2.80(4) Å). Actually, they are not so different when the distinct coordination numbers of the complexes[50] are taken into account: seven in **2** and five in the phosphido compound. From these data, an anionic λ^4-phosphinine coordination mode for the SPS^{Me} ligand is still to be considered. The borohydride hydrogen atom positions experimentally determined indicate a tridentate ligation mode in both molecules A and B; the average Nd···B distance of 2.64(2) Å for the two independent molecules can be compared with that of 2.664(25) Å in [Nd($C_5H_4CH_2CH_2$OMe)$_2$(BH_4)][53] and 2.68(2) and 2.74(3) Å in [(THF)(BH_4)$_2$Nd(μ-η^7:$\eta^7$$C_7H_7$)Nd($BH_4$)(THF)$_3$].[54] As expected from the variation in the ionic radii of neodymium(III) and cerium(III),[50] the corresponding metal−ligand distances are shorter in **2** than in **1** by ∼0.03 Å.

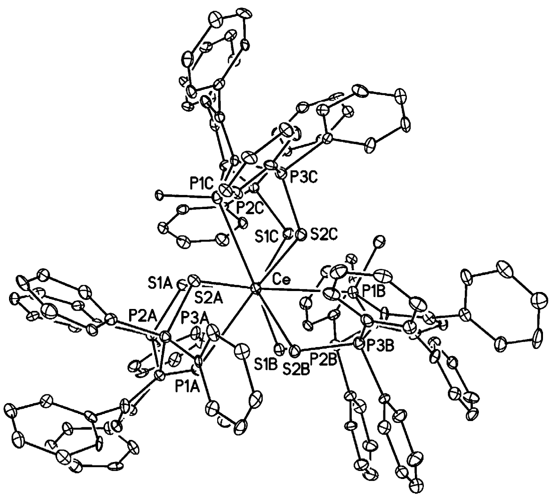


Figure 2. View of complex **3**. The hydrogen atoms and solvent molecules have been omitted. Displacement ellipsoids are drawn at the 20% probability level.

Table 3. Selected Bond Distances (Å) and Angles (deg) for Complex **3**·2THF·2Et_2O

	ligand A	ligand B	ligand C
Ce−S(1)	2.964(3)	2.943(3)	2.966(3)
Ce−S(2)	2.947(3)	2.995(3)	2.917(3)
Ce−P(1)	3.152(3)	3.086(3)	3.113(3)
P(2)−S(1)	1.992(4)	1.996(4)	1.997(4)
P(3)−S(2)	1.993(4)	1.998(4)	1.983(4)
P(1)−C(1)	1.794(11)	1.823(11)	1.829(10)
P(1)−C(5)	1.822(10)	1.780(10)	1.805(11)
P(2)−C(1)	1.771(11)	1.792(11)	1.762(11)
P(3)−C(5)	1.773(11)	1.758(10)	1.740(10)
S(1)−Ce−S(2)	87.37(8)	85.18(9)	88.54(8)
S(1)−Ce−P(1)	67.13(8)	70.68(8)	66.86(8)
S(2)−Ce−P(1)	68.54(8)	68.10(8)	69.28(8)

After the Rh(II) and (III) compounds [Rh(SPS^{Me})$_2$]$^{0,+}$,[55] **3** is a new example of homoleptic complex with a SPS-based pincer ligand. Crystals of the solvate **3**·2THF·2Et_2O were obtained by slow diffusion of diethyl ether into a THF solution of **3**. A view of **3** is shown in Figure 2, and selected bond lengths and angles are listed in Table 3. Despite its bulkiness, the SPS^{Me} ligand still adopts the trihaptocoordination mode. The metal is nine-coordinate in a quite perfect mer tricapped trigonal prismatic configuration which is classical for complexes of general formula [M(tridentate ligand)$_3$].[56] The two trigonal bases are defined by the atoms S(1A), S(1B), S(1C) and S(2A), S(2B), S(2C), forming a dihedral angle of 1.34(14)°, and they are almost parallel to the plane containing the three atoms P(1A), P(1B), and

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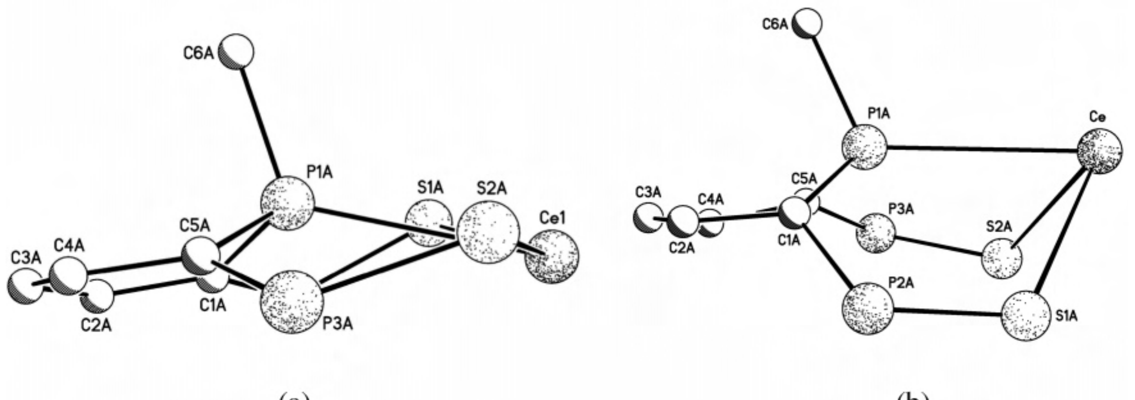
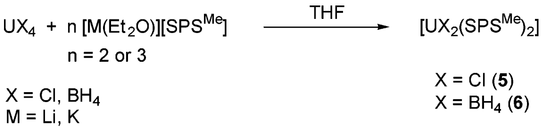
(42) Männ, D.; Nöth, H. *Z. Anorg. Allg. Chem.* **1986**, *543*, 66.
(43) Brennan, J.; Shinomoto, R.; Zalkin, A.; Edelstein, N. *Inorg. Chem.* **1984**, *23*, 4143.
(44) Gun'ko, Y. K.; Bulychev, B. M.; Soloveichik, G. L.; Belsky, V. K. *J. Organomet. Chem.* **1992**, *424*, 289.
(45) Sekar, P.; Ibers, J. A. *Inorg. Chim. Acta* **2006**, *359*, 2751.
(46) Spiliadis, S.; Pinkerton, A. A.; Schwarzenbach, D. *J. Chem. Soc., Dalton Trans.* **1982**, 1809.
(47) Spiliadis, S.; Pinkerton, A. A.; Schwarzenbach, D. *Inorg. Chim. Acta* **1983**, *75*, 115.
(48) Stults, S.; Zalkin, A. *Acta Crystallogr., Sect. C* **1987**, *43*, 430.
(49) Froelich, N.; Hitchcock, P. B.; Hu, J.; Lappert, M. F.; Dilworth, J. R. *J. Chem. Soc., Dalton Trans.* **1996**, 1941.
(50) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *32*, 751.
(51) Hitchcock, P. B.; Lappert, M. F.; Mackinnon, I. A. *J. Chem. Soc., Chem. Commun.* **1988**, 1557.
(52) Rabe, G. W.; Ziller, J. W. *Inorg. Chem.* **1995**, *34*, 5378.
(53) Deng, D. L.; Zheng, X. F.; Qian, C. T.; Sun, J.; Zhang, L. *J. Organomet. Chem.* **1994**, *466*, 95.
(54) Arliguie, T.; Lance, M.; Nierlich, M.; Ephritikhine, M. *J. Chem. Soc., Dalton Trans.* **1997**, 2501.
(55) Doux, M.; Mézailles, N.; Ricard, L.; Le Floch, P.; Adkine, P.; Berclaz, T.; Geoffroy, M. *Inorg. Chem.* **2005**, *44*, 1147.
(56) Kepert, D. L. *Inorganic Stereochemistry*; Inorganic Chemistry Concepts, Vol. 6; Springer-Verlag: Berlin, 1982.



(a) (b)

Figure 3. Distinct coordination modes of the SPS^{Me} ligand: almost planar in **1** (a) and facial in **3** (b).

Scheme 3. Syntheses of the Uranium Complexes **5** and **6**



UX_4 + n $[M(Et_2O)][SPS^{Me}]$ $\xrightarrow{THF}$ $[UX_2(SPS^{Me})_2]$

n = 2 or 3

X = Cl, BH_4
M = Li, K

X = Cl (**5**)
X = BH_4 (**6**)

P(1C), which occupy the capping positions, with dihedral angles of 0.16(12) and 1.40(12)°, respectively. The Ce−S distances range from 2.917(3) to 2.995(3) Å and are similar to those measured in **1**. In contrast, the Ce−P(1) distances are 0.1 Å larger, with a mean value of 3.12(3) Å, and the S(1)−Ce−S(2) bite angles which average 87(1)° are much smaller than in **1**. These differences are associated with a conformation change of the ligand which can adopt either an almost planar or a facial coordination mode, as shown in Figure 3a and b. In all cases, the five carbon atoms defining the central ring of the ligand are planar, with rms deviations smaller than 0.07 Å. However, whereas the sulfur atoms in **1** are close to this mean plane, with out-of-plane displacements of 0.08(2)−0.48(2) Å, they are much more displaced in **3**, by 0.93(2)−1.54(2) Å. The atoms P(2) and P(3) are also more displaced from the mean plane in **3** (0.51(2)−1.20(2) Å) than in **1** (0.247(10)−0.695(11) Å). To summarize, while Ce and P(1) remain on the same side of the C_5 mean plane, P(2), P(3), S(1), and S(2) adopt a boatlike conformation in **3** and a chairlike conformation in **1**. Such a variation in the geometry of the flexible tridentate ligand is reminiscent of that observed between the rhodium complex $[Rh(SPS^{Me})(PPh_3)]$ and its monoadducts with CO, CO_2, or CS_2.[28]

Uranium Complexes. Treatment of UX_4 (X = Cl, BH_4) with $[M(Et_2O)][SPS^{Me}]$ in THF afforded, regardless of the quantity (2 or 3 mol equiv) and nature of the alkali metal salt (M = Li or K), the disubstituted compounds $[UX_2(SPS^{Me})_2]$ [X = Cl (**5**), BH_4 (**6**)], according to Scheme 3. Crystals of chloride derivative **5** were slowly deposited from the THF solution, whereas the borohydride congener **6** readily precipitated from the very beginning of the reaction; after the usual workup, **5** and **6** were isolated as red and orange microcrystalline powders in 95 and 98% yields, respectively.

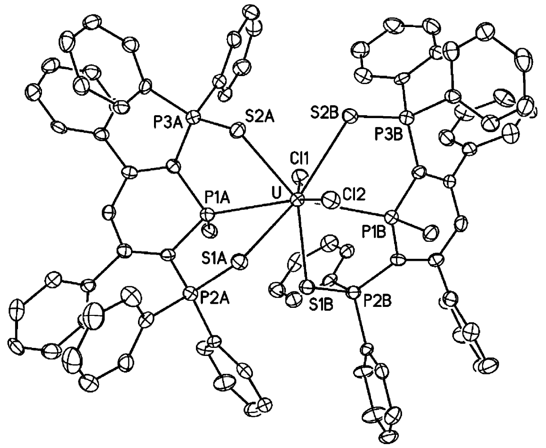


Figure 4. View of complex **5**. The hydrogen atoms and solvent molecules have been omitted. The displacement ellipsoids are drawn at the 50% probability level.

Table 4. Selected Bond Distances (Å) and Angles (deg) for Complex **5**·4py

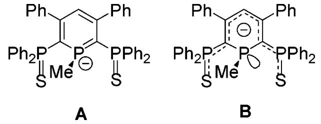
U−S(1A)	2.9892(12)	P(3A)−S(2A)	2.0184(16)
U−S(2A)	2.8326(9)	P(3B)−S(2B)	1.9995(15)
U−S(1B)	2.7799(10)	P(1A)−C(1A)	1.813(4)
U−S(2B)	2.9091(11)	P(1B)−C(1B)	1.797(4)
U−Cl(1)	2.6087(11)	P(1A)−C(5A)	1.791(4)
U−Cl(2)	2.6087(11)	P(1B)−C(5B)	1.813(4)
U−P(1A)	3.0001(12)	P(2A)−C(1A)	1.780(4)
U−P(1B)	2.9508(11)	P(2B)−C(1B)	1.750(4)
P(2A)−S(1A)	2.0098(16)	P(3A)−C(5A)	1.758(4)
P(2B)−S(1B)	2.0242(14)	P(3B)−C(5B)	1.788(4)
S(1A)−U−S(2A)	82.50(3)	Cl(1)−U−Cl(2)	152.64(4)
S(1B)−U−S(2B)	139.53(3)		

The poor solubility of **6** in organic solvents prevented recording of the NMR spectra. The ^1H and ^{31}P NMR spectra of **5** in THF or pyridine are complicated, indicating that the compound would retain in solution the dissymmetric structure found in the crystalline form (vide infra); the spectra also reveal the presence of free SPS^{Me} ligand likely resulting from partial decomposition of the complex.

Crystals of **5**·4py were obtained by crystallization from pyridine; a view of **5** is shown in Figure 4, and selected bond lengths and angles are listed in Table 4. The structure is devoid of any element of symmetry, even approximate. The metal is eight-coordinate in a distorted dodecahedral configuration defined by the two trapezia Cl(1), Cl(2), S(1A), P(1A) and S(1B), S(2B), S(2A), P(1B) [rms deviations 0.31 and 0.11 Å, respectively] forming an angle of 88.46(2)°. The U−S distances vary from 2.7799(10) to 2.9892(12) Å with an average value of 2.88(8) Å which is identical to that of 2.85(4) Å in $[Li(dme)]_4[U(edt)_4]$ (edt = ethane-1,2-dithiolate).[57] These distances are in the range of U−S bond lengths for uranium(IV) dithiolene complexes, which lie between 2.720(3) Å in $[U(C_8H_8)(mdt)(py)_2]$ and 2.946(6) Å in $[\{U(C_8H_8)(mdt)\}_2]$ (mdt = 2H-1,3-dithiole-4,5-dithiolate).[58] The U−S distances can also be compared with that of 2.856(9) Å in $[U\{S_2PMe_2\}_2\{O(S)PMe_2\}\{\mu\text{-}O_2PMe_2\}]_2$.[59] The two U−P distances are 2.9508(11) and 3.0001(12) Å. By comparison with the $U-P_{phosphido}$ bond lengths in $[Cp^*{}_2UCl\{P(SiMe_3)_2\}]$ (2.789(4) Å)[60] or $[U\{P(CH_2CH_2PMe_2)_2\}_4]$ (2.778(2) Å),[61] and the $U-P_{phosphino}$ bond lengths in $[U\{P(CH_2CH_2PMe_2)_2\}_4]$ (2.993(2) Å),[61] $[UCl_2\{N(CH_2CH_2PEt_2)_2\}_2]_2$ (3.13(2) Å),[62] or $[U(BH_3Me)_4(Me_2PCH_2CH_2PMe_2)]$ (3.02(1) Å),[43] the U−P distances in **5** strongly suggest that the SPS^{Me} ligand is better described as containing a tertiary phosphine functionality. It is interesting to note that the SPS^{Me} ligand denoted A adopts a facial coordination mode, the S(1A) and S(2A) atoms being located 1.330(9) and 1.715(8) Å, respectively, from the plane defined by the five carbon atoms of the central ring and the S(1A)−U−S(2A) angle being equal to 82.50(3)°, whereas ligand B is closer to the planar geometry, with atoms S(1B) and S(2B) at 0.437(10) and 0.022(10) Å from the central ring and the S(1B)−U−S(2B) angle equal to 139.53(3)°. The U−S and U−P bonds are longer in ligand A than in ligand B by 0.06 and 0.05 Å, respectively.

Bonding Situation in the Complexes. The geometrical parameters of the SPS^{Me} ligand in **1**, **2**, **3,** and **5** shed light on the bonding situation in these complexes. The external P(2)−C(1) and P(3)−C(5) bond lengths, with mean values of 1.766(2), 1.774(3), 1.766(16), and 1.769(16) Å in complexes **1**, **2**, **3**, and **5**, respectively, are shorter than in the neutral λ^3-phosphinine SPS (1.826(2) and 1.835(2) Å)[32] and similar to the ones found in the anion $[Na(2.2.2)][SPS^{OMe}]$ (1.770(4) and 1.794(5) Å).[32] Concomitantly, the average P−S distances of 2.008(1), 2.008(2), 1.993(5), and 2.013(9) Å in **1**, **2**, **3**, and **5**, respectively, are larger than in SPS (1.953(1) and 1.956(1) Å) and, again, are comparable to the P−S bond lengths in the $[SPS^{OMe}]^-$ anion (1.968(2) and 1.974(2) Å). In turn, the internal P(1)−C(1) and P(1)−C(5) bond lengths, with mean values of 1.803(11), 1.791(13), 1.809(18), and 1.804(10) Å, are larger than those in SPS (1.742(2) and 1.745(5) Å) and similar to those in $[SPS^{OMe}]^-$ (1.791(5) and 1.794(5) Å); these bond lengths are typical for classical phosphine ligands.

Scheme 4. Phosphinine and Phosphine Forms of the SPS^{Me} Ligand



Overall, it appears that the bond lengths within the SPS^{Me} ligand in the complexes of Ce, Nd, and U presented here are similar to the ones found in the SPS^{OMe} anion[32] which is considered to be a phosphanyl-substituted pentadienyl anion. The relatively large internal P(1)−C(1) and P(1)−C(5) bonds indicate that the ligand has lost the ylidic structure of the phophinine upon complexation, and the relatively short external P(2)−C(1) and P(3)−C(5) bonds and the long P−S bonds point to the delocalization within the unsaturated parts of the ligand. The variations observed with the neutral SPS species result from the presence of the anionic charge. In fact, the two "Ph_2PS" moieties act as acceptors of the electron density of the pentadienyl anion via negative hyperconjugation.[63] Therefore, the best description of the ligand SPS^{Me} in our complexes, as well as in previously reported $[Pd(SPS^{Me})Cl]$[28] and $[Mn(SPS^{nBu})(CO)_3]$, is form B (Scheme 4).[64]

Conclusion

Reactions of LnX_3 (Ln = Ce, Nd; X = BH_4, I) and UCl_4 with the alkali metal salts of the $[SPS^{Me}]^-$ anion gave the first f-element complexes bearing an SPS-phosphinine-based pincer ligand. The flexibility of this tridentate ligand, which can adopt either an almost planar or facial coordination mode, permitted the formation of homoleptic tris(SPS) compounds of the lanthanide metals. The trihapto-SPS^{Me} unit led to the formation of the unique uranium complex displaying phosphorus and sulfur atoms both coordinated to the metal. The crystal structures of all the complexes indicate that the anionic $[SPS^{Me}]^-$ group is better seen as a phosphine moiety with delocalization of the charge within the unsaturated parts of the ligand for the lanthanide, as well as for the uranium, compounds. The SPS^{Me} ligand provides a fairly unique coordination environment suitable for 4f/5f comparisons; however, to be significant, this type of study needs to be performed on complexes in the same oxidation state and attempts to synthesize a uranium(III) compound with the SPS^{Me} ligand are accordingly actively pursued.

Supporting Information Available: Tables of crystal data, atomic positions, and displacement parameters, anisotropic displacement parameters, bond lengths, and bond angles in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(57) Tatsumi, K.; Matsubara, I.; Inoue, Y.; Nakamura, A.; Cramer, R. E.; Tagoshi, G. J.; Golen, J. A.; Gilje, J. W. *Inorg. Chem.* **1990**, *29*, 4928.

(58) Arliguie, T.; Thuéry, P.; Fourmigué, M.; Ephritikhine, M. *Organometallics* **2003**, *22*, 3000.

(59) Greiwing, H.; Krebs, B.; Pinkerton, A. A. *Inorg. Chim. Acta* **1995**, *234*, 127.

(60) Hall, S. W.; Huffman, J. C.; Miller, M. M.; Avens, L. R.; Burns, C. J.; Arney, D. S. J.; England, A. F.; Sattelberger, A. P. *Organometallics* **1993**, *12*, 752.

(61) Edwards, P. G.; Parry, J. S.; Read, P. W. *Organometallics* **1995**, *14*, 4, 3649.

(62) Coles, S. J.; Danopoulos, A. A.; Edwards, P. G.; Hursthouse, M. B.; Read, P. W. *J. Chem. Soc., Dalton Trans.* **1995**, 3401.

(63) Cantat, T.; Jaroschik, F.; Ricard, L.; Le Floch, P.; Nief, F.; Mézailles, N. *Organometallics* **2006**, *25*, 1329.

(64) Doux, M.; Mézailles, N.; Ricard, L.; Le Floch, P.; Vaz, P. D.; Calhorda, M. J.; Mahabiersing, T.; Hartl, F. *Inorg. Chem.* **2005**, *44*, 9213.