Inorg. Chem. **1995,** *34,* 1681−1687

Group 4 Metal Complexes of the Tetradentate (η^4-N,N′,S,S′) $Ph_4P_2N_4S_2^{2-}$ and $Ph_4P_2N_4S_2R^-$ Anions. X-ray Structures of $\{Cp^*HfCl_2[Ph_4P_2N_3(NH)S_2]\}_2$, $Cp^*ZrCl_2[Ph_4P_2N_4S(SMe)]$, and $[Me_3PNPPh_2NSMeNPPh_2NH_2]Cl$

Tristram Chivers,* Xiaoliang Gao, and Masood Parvez

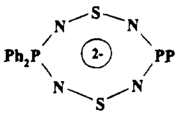
Department of Chemistry, The University of Calgary, Calgary, Alberta, Canada T2N 1N4

Received September 30, 1994®

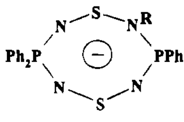
The reaction of Cp^*MCl_3 (M = Zr, Hf) with $Na_2[Ph_4P_2N_4S_2]$ in THF produces the complexes $Na[Cp^*MCl_2(Ph_4P_2N_4S_2)]$ (**3a**, M = Hf; **3b**, M = Zr), which were characterized by ^{23}Na and ^{31}P NMR spectroscopy and by the preparation of the protonated derivatives $\{Cp^*MCl_2(Ph_4P_2N_3(NH)S_2)\}_2$ (**4a**, M = Hf; **4b**, M = Zr). Complex **4a** was shown by X-ray crystallography to be a hydrogen-bonded dimer in which the $P_2N_4S_2$ ring is bonded to the metal in a tetradentate (η^4-N,N′,S,S′) fashion and the proton is attached to nitrogen. The Hf−N bond lengths in **4a** are 2.227(10) and 2.241(8) Å and the Hf−S distances are 2.859(3) and 2.911(3) Å. Crystals of **4a** are monoclinic, space group $P2_1/n$, with a = 11.046(2) Å, b = 18.962(4) Å, c = 17.548(3) Å, β = 99.55(2)°, V = 3624(1) Å^3, and Z = 4. The final R and R_w values were 0.039 and 0.033, respectively. The methylation of **3a** or **3b** with methyl triflate or methyl iodide generates the S-methylated derivatives $Cp^*MCl_2[Ph_4P_2N_4S(SMe)]$ (**6a**, M = Hf; **6b**, M = Zr) via the corresponding N-methylated isomers. Complexes **6a** and **6b** are more conveniently prepared in >90% yields from Cp^*MCl_3 and $\{Li[Ph_4P_2N_4S(SMe)]\}_2$. An X-ray structural determination shows that the $Ph_4P_2N_4S(SMe)^-$ ligand in **6b** adopts a tetradentate (η^4-N,N′,S,S′) bonding mode. Crystals of **6b** are orthorhombic, space group $P2_12_12_1$, with a = 19.255(4) Å, b = 22.839(3) Å, c = 8.296(3) Å, V = 3648(1) Å^3, and Z = 4. The final R and R_w values were 0.071 and 0.072, respectively. The reaction of **6b** with an excess of Me_3P, followed by hydrolysis, yields the open-chain compound $[Me_3PNPPh_2NSMeNPPh_2NH_2]Cl$ (**8**) which was characterized by ^1H and ^{31}P NMR spectroscopy and by X-ray crystallography. Crystals of **8** are triclinic, space group $P\bar{1}$, with a = 10.551(3) Å, b = 16.572(3) Å, c = 9.879(2) Å, α = 99.90(2)°, β = 105.59(2)°, γ = 104.70(2)°, V = 1555.0(8) Å^3, and Z = 2. The final R and R_w values were 0.045 and 0.025, respectively.

Introduction

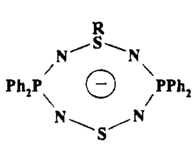
The combination of main group element and group 4 metal chemistry is an area of increasing activity.[1] Such complexes are of interest in providing unusual coordination environments and/or reactivity at the metal center as well as convenient reagents for the functionalization of main group element substrates. We recently discovered that alkali metal derivatives of the dianion $Ph_4P_2N_4S_2^{2-}$ (**1**) are readily prepared by the reaction of 1,5-$Ph_4P_2N_4S_2$ with 2 molar equiv of $M[BEt_3H]$ (M = Li, Na, K).[2,3] This dianion behaves as a bidentate (η^2-S,S′)[2,4] or tridentate (η^3-N,S,S′)[3] ligand in mononuclear complexes with late transition metals. It also acts as a bridging tridentate (η^2-N,S-μ,η^1-S′)[4,5] or tetradentate (η^3-N,N′,S-μ,η^1-S)[6] ligand in dinuclear complexes.



1



2a



2b

The dianion **1** offers interesting possibilities for providing early transition metals with unique surroundings in the coordination sphere. Recently we reported that the related monoanion $Ph_4P_2N_4S(SR)^-$ (**2b**), which forms monodentate (η^1-S) complexes with Pt(II) or Pd(II),[7] adopts a bidentate (η^2-N,S) coordination mode in complexes of the type $Cp_2MCl[Ph_4P_2N_4S(SR)]$ (M = Zr, Hf).[8] These early transition metal complexes are useful for preparing functionalized derivatives of the $P_2N_4S_2$ ring by reactions with electrophiles.

We now describe an investigation of the preparation and spectroscopic characterization of group 4 metal complexes of the dianion **1** which, upon protonation, yield complexes of the N-protonated ring system **2a** (R = H) in which the monoanionic ligand adopts the novel tetradentate (η^4-N,N′,S,S′) bonding mode. A similar bonding mode is also observed for group 4 metal complexes of the S-methylated ligand **2b** (R = Me), which are obtained from the methylation of the corresponding complexes of **1** or, more directly, by treatment of Cp^*MCl_3 (M =

® Abstract published in *Advance ACS Abstracts,* March 1, 1995.

(1) See, for example: (a) Boutonnet, F.; Zablocka, M.; Igau, A.; Majoral, J.-P.; Raynaud, B.; Jaud, J. *J. Chem. Soc., Chem. Commun.* **1993**, 1866. (b) Fryzuk, M. D.; Mylvaganam, M.; Zaworotko, M. J.; MacGillivray, L. R. *J. Am. Chem. Soc.* **1993**, *115*, 10360. (c) Le Flach, P.; Ricard, L.; Mathey, F. *J. Chem. Soc., Chem. Commun.* **1993**, 789. (d) Igau, A.; Dufour, N.; Mahieu, A.; Majoral, J.-P. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 95.

(2) Chivers, T.; Cowie, M.; Edwards, M.; Hilts, R. W. *Inorg. Chem.* **1992**, *31*, 3349.

(3) Chivers, T.; Edwards, M.; Gao, X.; Hilts, R. W.; Parvez, M.; Vollmerhaus, R. *Inorg. Chem.*, to be submitted for publication.

(4) Chivers, T.; Edwards, M.; Meetsma, A.; van de Grampel, J. C.; van der Lee, A. *Inorg. Chem.* **1992**, *31*, 2156.

(5) Chivers, T.; Edwards, M.; Kapoor, P. N.; Meetsma, A.; van de Grampel, J. C.; van der Lee, A. *Inorg. Chem.* **1990**, *29*, 3068..

(6) Chivers, T.; Hilts, R. W.; Parvez, M.; Ristic-Petrovic, D.; Hoffman, K. *J. Organomet. Chem.* **1994**, *480*, C4.

(7) (a) Chivers, T.; Edwards, M.; Hilts, R. W.; Meetsma, A.; van de Grampel, J. C. *J. Chem. Soc., Dalton Trans.* **1992**, 3053. (b) Chivers, T.; Edwards, M.; Hilts, R. W.; Parvez, M.; Vollmerhaus, R. *Inorg. Chem.* **1994**, *33*, 1440.

(8) (a) Chivers, T.; Hilts, R. W.; Parvez, M. *Inorg. Chem.* **1994**, *33*, 997. (b) Chivers, T.; Hilts, R. W.; Parvez, M.; Vollmerhaus, R. *Inorg. Chem.* **1994**, *33*, 3459.

0020-1669/95/1334-1681$09.00/0

Zr, Hf) with $\{Li[Ph_4P_2N_4S(SMe)]THF\}_2$. The reaction of the complex $\{Cp^*ZrCl_2[Ph_4P_2N_4S(SMe)]\}$, obtained in this manner, with trimethylphosphine is also described.

Experimental Section

Reagents and General Procedures. All reactions and the manipulation of air- and moisture-sensitive compounds were carried out under an atmosphere of dry N_2 by using Schlenk techniques or a Vacuum Atmospheres drybox.

The following reagents were prepared by literature procedures: $\{Li[Ph_4P_2N_4S(SMe)]THF\}_2$,[7] Cp*H,[9a] Cp^*MCl_3 (M = Zr, Hf).[9b] The commercially available compounds HCl gas (Linde), methyl trifluoromethanesulfonate (Aldrich), Me_3P (Strem), and methyllithium in diethyl ether (Aldrich) were used as received.

Instrumentation. ^1H and ^{13}C NMR spectra were obtained on a Bruker ACE 200 MHz spectrometer, and chemical shifts are reported in ppm relative to Me_4Si. ^{23}Na and ^{31}P NMR spectra were determined on a Bruker AM 400 MHz spectrometer with saturated NaCl in D_2O and 85% H_3PO_4, respectively, as the external references.

Preparation of $Na[Cp^*HfCl_2(Ph_4P_2N_4S_2)]$ (3a). To a slurry of $Na_2[Ph_4P_2N_4S_2]$ (0.516 mmol), prepared from 1,5-$Ph_4P_2N_4S_2$ (0.253 g, 0.516 mmol) and $Na[Et_3BH]$ (1.14 mmol in THF), in THF (15 mL) at −78 °C in a Schlenk vessel equipped with a J-Young valve was added a solution of Cp^*HfCl_3 (0.217 g, 0.516 mmol) in THF (15 mL). After 1 h at 23 °C, the reaction mixture was filtered to remove NaCl, and the filtrate was reduced in volume to 10 mL. Colorless crystals of $[Na(THF)_3]$ $[Cp^*HfCl_2(Ph_4P_2N_4S_2)]$ deposited at 0 °C overnight. Concentration of the mother liquor to 2 mL produced more crystals. The combined yield was 85%. ^1H NMR ($CDCl_3$): δ 7.0−8.0 (m, 20H, C_6H_5), 3.67 (m, 12H, C_4H_8O, α-*H*), 2.19 (s, 15H, CH_3), 1.89 (m, 12H, C_4H_8O, β-*H*); $^{31}P\{^1H\}$ NMR (THF): δ 77.8 (s). The crystals of $[Na(THF)_3][Cp^*HfCl_2(Ph_4P_2N_4S_2)]$ desolvate readily, and recrystallization from dimethoxyethane also gave the unsolvated product $Na[Cp^*HfCl_2(Ph_4P_2N_4S_2)]$ as determined by ^1H NMR. Anal. Calcd for $C_{34}H_{35}Cl_2NaHfN_4P_2S_2$: C, 45.46; H, 3.92; N, 6.23. Found: C, 45.60; H, 4.07; N, 6.62. ^{23}Na NMR (DME): δ −3.8 (s).

Preparation of $Na[Cp^*ZrCl_2(Ph_4P_2N_4S_2)]$ (3b). The zirconium complex was prepared from Cp^*ZrCl_3 and $Na_2[Ph_4P_2N_4S_2]$ in a manner similar to that described for the Hf analogue. The yield after recrystallization from CH_2Cl_2/diethyl ether was 92%. Anal. Calcd for $C_{34}H_{35}Cl_2NaN_4P_2S_2Zr$: C, 50.36; H, 4.35; N, 6.91. Found: C, 50.70; H, 4.66; N, 7.31. ^1H NMR (CD_2Cl_2): δ 7.1−8.1 (m, 20H, C_6H_5), 2.09 (s, 15H, CH_3). $^{31}P\{^1H\}$ NMR (THF): δ 76.8 (s). ^{23}Na NMR (THF): δ −3.0 (s).

Reaction of $Na[Cp^*HfCl_2(Ph_4P_2N_4S_2)]$ with HCl Gas. To a solution of $Na[Cp^*HfCl_2(Ph_4P_2N_4S_2)]$ (0.343 g, 0.382 mmol) in THF (30 mL) at −78 °C was added HCl gas (9.3 mL, 0.382 mmol) from a gastight syringe. The solution was allowed to reach 23 °C in 1 h with vigorous stirring. The precipitate of NaCl was removed by filtration, and solvent was removed from the filtrate under vacuum. Recrystallization of the product from DME/diethyl ether gave $\{Cp^*HfCl_2[Ph_4P_2N_3(NH)S_2]\}_2$, **4a** (0.271 g, 0.309 mmol, 90% yield). Anal. Calcd for $C_{34}H_{36}Cl_2HfN_4P_2S_2$: C, 46.61; H, 4.14; N, 6.39. Found: C, 46.92; H, 4.31; N, 6.58. ^1H NMR (CD_2Cl_2): δ 12.03 (s, br, 1H, N*H*), 7.0−8.2 (m, 20H, C_6H_5), 2.17 (s, 15H, CH_3), $^{31}P\{^1H\}$ NMR (THF): δ 66.4 (s).

Reaction of $Na[Cp^*ZrCl_2(Ph_4P_2N_4S_2)]$ with HCl Gas. This reaction was carried out at −100 °C in a manner similar to that described for the Hf analogue to give $\{Cp^*ZrCl_2(Ph_4P_2N_4S_2H)\ (THF)\}_2$, **4b**·2THF, in 87% yield after recrystallization from THF. Anal. Calcd for $C_{38}H_{44}Cl_2ON_4P_2S_2Zr$: C, 53.01; H, 5.15; N, 6.51. Found: C, 52.43; H, 5.03; N, 6.65. ^1H NMR (CD_2Cl_2): δ 11.8 (s, br, 1H, N*H*), 7.0−8.0 (m, *20H*, C_6H_5), 3.70 (m, 4H, C_4H_8O, α-*H*), 2.09 (s, 15H, CH_3), 1.83 (m, 4H, C_4H_8O, β-*H*). $^{31}P\{^1H\}$ NMR (THF): δ 76.3 (s).

Preparation of $\{Cp^*HfCl_2[Ph_4P_2N_4S(SMe)]\}$ (6a). (a) From $Na[Cp^*HfCl_2(Ph_4P_2N_4S_2)]$ and $CH_3SO_3CF_3$ or CH_3I. Neat $CH_3SO_3CF_3$ (47.3 μL, 0.418 mmol) was added to a stirred solution of $Na[Cp^*HfCl_2(Ph_4P_2N_4S_2)]$ (0.375 g, 0.418 mmol) in THF (30 mL) at −78 °C. The reaction mixture was allowed to reach 23 °C to give a pale yellow solution after 2 h. Solvent was removed under vacuum, the residue was dissolved in toluene, and the resulting solution was filtered. Removal of solvent from the filtrate under vacuum gave a colorless residue which was recrystallized from DME/diethyl ether to give colorless crystals of $\{Cp^*HfCl_2[Ph_4P_2N_4S(SMe)]\}$ (**6a**) (0.249 g, 0.280 mmol, 67% yield). Anal. Calcd for $C_{35}H_{38}Cl_2HfN_4P_2S_2$: C, 47.22; H, 4.30; N, 6.29. Found: C, 46.82; H, 4.33; N, 6.36. ^1H NMR ($CDCl_3$): 7.2−8.0 (m, 20H, C_6H_5), 3.28 (s, 3H, SCH_3), 2.17 (s, 15H, Cp*-CH_3). ^{31}P NMR (THF): δ 68.4 (s).

A large excess of methyl iodide (0.1 mL) was added to a solution of $Na[Cp^*HfCl_2(Ph_4P_2N_4S_2)]$ (0.359 g, 0.400 mmol) in DME (30 mL). After 10 h the ^{31}P NMR spectrum of the reaction mixture exhibited resonances (δ, ppm) at 82.2 (d, J = 22.9 Hz), 77.5 (s), 74.5 (d, J = 22.9 Hz), and 68.4 (s). After 2 days the ^{31}P NMR spectrum showed only the singlet at 68.4 ppm attributable to **6a**.

(b) From Cp^*HfCl_3 and $\{Li[Ph_4P_2N_4S(SMe)THF]\}_2$. The lithium reagent $\{Li[Ph_4P_2N_4S(SMe)]THF\}_2$ was prepared by the addition of a solution of methyllithium in diethyl ether (0.618 mmol) to an equimolar amount of 1,5-$Ph_4P_2N_4S_2$ in THF (30 mL) at −78 °C followed by warming to 23 °C with stirring for 2 h.[7] This reagent was then cooled to −78 °C, and a solution of Cp^*HfCl_3 (0.260 g, 0.618 mmol) in THF (30 mL) at −30 °C was added to it. The reaction mixture was allowed to reach 23 °C and was stirred for 2 h. After removal of the solvent under vacuum, the residue was dissolved in toluene, and the solution was filtered to remove LiCl. Removal of the solvent under vacuum gave a colorless residue which was recrystallized from DME/diethyl ether to give $\{Cp^*HfCl_2[Ph_4P_2N_4S(SMe)]\}$ (**6a**) (0.500 g, 0.562 mmol, 91% yield) identified by comparison of spectroscopic data with those of an authentic sample prepared from $Na[Cp^*HfCl_2(Ph_4P_2N_4S_2)]$ and methyl triflate.

Preparation of $\{Cp^*ZrCl_2[Ph_4P_2N_4S(SMe)]\}$ (6b). The Zr complex **6b** was obtained in 90% yield, after recrystallization from DME/diethyl ether, from the reaction of $\{Li[Ph_4P_2N_4S(SMe)]THF\}_2$ with Cp^*ZrCl_3 in a manner similar to that described for the hafnium analogue. Anal. Calcd for $C_{35}H_{38}Cl_2N_4P_2S_2Zr$: C, 52.35; H, 4.77; N, 6.98. Found: C, 51.92; H, 4.82; N, 6.97. ^1H NMR (CD_2Cl_2): δ 7.2−7.9 (m, 20H, C_6H_5), 3.18 (s, 3H, SCH_3), 2.07 (s, 15H, Cp*-CH_3). ^{31}P NMR (THF): 68.0(s).

Preparation of $[Me_3PNPPh_2NSMeNPPh_2NH_2]Cl$. An excess of Me_3P (0.3 mL) was added to a slurry of $\{Cp^*ZrCl_2[Ph_4P_2N_4S(SMe)]\}$ (0.613 g, 0.764 mmol) in toluene (20 mL). The solid dissolved in *ca.* 15 min to give a colorless solution which was stirred for an additional 1.5 h. The ^{31}P NMR spectrum of the reaction mixture showed four singlets at 27.8, 23.1, 9.6, and −4.4 ppm, in addition to the resonance at −62.0 ppm for unreacted Me_3P. Hexanes were then added to the toluene solution until it was slightly turbid, and the mixture was kept at −20 °C for 24 h. A white precipitate deposited and was recrystallized from THF to give colorless crystals of $[Me_3PNPPh_2NSMeNPPh_2NH_2]Cl$ (0.130 g, 0.221 mmol, 29% yield). Anal. Calcd for $C_{28}H_{34}ClN_4P_3S$: C, 57.28; H, 5.84; N, 9.54. Found: C, 56.93; H, 5.62; N, 9.54. ^1H NMR (CD_2Cl_2): δ 7.2−7.9 (m, 20H, C_6H_5), 5.16 (s, br, 2H, N*H*), 2.89 (d, 3H, SCH_3, $^4J(^1H-^{31}P)$ = 0.84 Hz), 1.53 (d, 9H, PCH_3, $^2J(^1H-^{31}P)$ = 13.1 Hz). ^{31}P NMR (CD_2Cl_2): δ 25.7 (s), 23.7 (s), 13.3 (s).

X-ray Structure Determinations. Crystallographic data for **4a**, **6b**, and **8** are summarized in Table 1. All measurements were made on a Rigaku AFC6S diffractometer with graphite-monochromated Mo Kα radiation. A colorless needle of **4a** (0.45 × 0.20 × 0.10 mm) obtained by recrystallization from DME/ether was mounted in a glass capillary. Accurate cell dimensions and a crystal orientation matrix were determined by a least-squares fit of the setting angles of 19 reflections in the range $36.53 < 2\theta < 39.88°$. Intensity data were collected by the $\omega/2\theta$ method using a scan speed of 4.0°/min and scan width of $(1.15 + 0.34 \tan \theta)°$ to a maximum 2θ value of 50.1°. The intensities of 6634 reflections were measured, of which 3229 had $I > 3\sigma(I)$. The structure was solved and expanded by using Fourier techniques.[10] The

---

(9) (a) Threlkel, R. S.; Bercaw, J. E.; Seidler, P. F.; Stryker, J. M.; Bergman, R. G. *Org. Synth.* **1987**, *65*, 42. (b) Blenkers, J.; Hessen, B.; Bolhuis, F. V.; Wagner, A. J.; Teuben, J. H. *Organometallics* **1987**, *6*, 459.

(10) DIRDIF92: Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. Technical report; Crystallography Laboratory, University of Nijmegen: Nijmegen, The Netherlands, 1992.

Table 1. Crystallographic Data for $\{Cp^*HfCl_2[Ph_4P_2N_3(NH)S_2]\}_2$ (**4a**), $\{Cp^*ZrCl_2[Ph_4P_2N_4S(SMe)]\}$ (**6b**), and $[Me_3PNPPh_2NSMeNPPh_2NH_2]Cl$ (**8**)

	4a	**6b**	**8**
formula	$C_{34}H_{36}N_4P_2S_2Cl_2Hf$	$C_{35}H_{38}N_4Cl_2P_2S_2Zr$	$C_{28}H_{34}N_4P_3SCl$
fw	876.15	802.91	587.04
crystal system	monoclinic	orthorhombic	triclinic
space group	$P2_1/n$ (No. 14)	$P2_12_12_1$ (No. 19)	$P\bar{1}$ (No. 2)
a, Å	11.046(2)	19.255(4)	10.551(3)
b, Å	18.962(4)	22.839(3)	16.572(3)
c, Å	17.548(3)	8.296(3)	9.879(2)
α, deg			99.90(2)
β, deg	99.55(2)		105.59(2)
γ, deg			104.70(2)
Z	4	4	2
V, Å3	3624(1)	3648(1)	1555.0(8)
ϱ_{calcd}, g cm^{-3}	1.605	1.462	1.254
$F(000)$	1744	1648	616
μ, mm^{-1}	3.254	0.681	0.368
radiation (λ, Å)	Mo Kα (0.710 69)	Mo Kα (0.710 69)	Mo Kα (0.710 69)
T, °C	23.0	23.0	23.0
R^a	0.039	0.071	0.045
R_w^b	0.033	0.072	0.025

^{a} $R = \Sigma(||F_o - F_c||)/\Sigma|F_o|$. ^{b} $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. Refinement converged with $R = 0.039$ and $R_w = 0.033$.

A colorless needle of **6b** (0.60 × 0.20 × 0.12 mm) obtained by layering diethyl ether onto a THF solution at 23 °C was mounted in a glass capillary. Conditions: 16 reflections in the range $20.56 < 2\theta < 31.76°$; scan speed 4.0°/min, scan width $(1.00 + 0.34 \tan\theta)°$ to a maximum 2θ value of 60.1°; 5985 reflections of which 1583 had $I > 3\sigma(I)$. The structure was solved and expanded by using Fourier techniques.[10] The non-hydrogen atoms except phenyl carbon atoms were refined anisotropically; the latter were allowed to refine as regular hexagons with overall isotropic temperature factors. Hydrogen atoms were included at geometrically idealized positions. Refinement converged at $R = 0.071$ and $R_w = 0.072$.

A colorless prism of **8** (0.32 × 0.20 × 0.10 mm) obtained by recrystallization from THF was mounted in a glass capillary. Conditions: 25 reflections in the range $20.0 < 2\theta < 30.0°$; scan speed 4.0°/min, scan width $(0.94 + 0.34 \tan\theta)°$ to a maximum 2θ value of 50.1°; 5520 reflections of which 1140 had $I > 3\sigma(I)$. The structure was solved by direct methods[11] and expanded using Fourier techniques.[10] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at geometrically idealized positions but were not allowed to refine. Refinement converged at $R = 0.045$ and $R_w = 0.025$.

For all three structures the data were corrected for Lorentz and polarization effects, and an empirical absorption correction using the program DIFABS[12] was applied. Scattering factors were those of Cromer and Waber,[13] and allowance was made for anomalous dispersion.[14]

All calculations for **4a**, **6b**, and **8** were performed using the TEXSAN[15] crystallographic software package. The positional parameters for **4a**, **6b**, and **8** are given in Tables 2–4, respectively.

Table 2. Final Fractional Coordinates and Equivalent Isotropic Temperatujre Factors (B_{eq}) with Esd's in Parentheses for $\{Cp^*HfCl_2[Ph_4P_2N_3(NH)S_2]\}$

atom	x	y	z	B_{eq},^{a} Å^2
Hf(1)	0.11310(5)	0.23330(3)	−0.08100(3)	2.72(1)
Cl(1)	0.2369(3)	0.2324(2)	0.0488(2)	4.05(8)
Cl(2)	0.2720(3)	0.1667(2)	−0.1321(2)	3.91(10)
S(1)	−0.1438(3)	0.2033(2)	−0.1146(2)	3.12(8)
S(2)	0.1079(3)	0.0891(2)	−0.0247(2)	2.94(8)
P(1)	−0.0252(3)	0.0879(2)	−0.1752(2)	2.99(9)
P(2)	−0.0733(3)	0.1678(2)	0.0428(2)	2.59(8)
N(1)	−0.0285(9)	0.1739(5)	−0.1612(5)	3.0(3)
N(2)	−0.0546(8)	0.2231(5)	−0.0254(4)	2.5(2)
N(3)	0.022(8)	0.0936(5)	0.0367(5)	2.8(3)
N(4)	0.0395(9)	0.0428(5)	−0.1007(5)	3.0(3)
C(1)	0.02481(15)	0.3566(6)	−0.1032(9)	4.1(4)
C(2)	0.1476(16)	0.3640(7)	−0.0633(9)	5.4(5)
C(3)	0.2298(14)	0.3422(8)	−0.1099(8)	4.6(4)
C(4)	0.1636(12)	0.3214(7)	−0.1803(8)	3.5(4)
C(5)	0.0385(15)	0.3299(6)	−0.1780(7)	3.9(4)
C(6)	−0.0951(15)	0.3784(7)	−0.0774(8)	5.7(5)
C(7)	0.1733(17)	0.3959(7)	0.0156(9)	7.3(6)
C(8)	0.3658(14)	0.3450(8)	−0.0862(8)	6.2(5)
C(9)	0.2121(12)	0.3044(7)	−0.2518(7)	4.6(4)
C(10)	−0.0664(13)	0.3199(6)	−0.2462(8)	4.8(4)
C(11)	0.0573(12)	0.0753(7)	−0.2559(7)	3.4(4)
C(12)	0.0390(13)	0.1220(6)	−0.3181(8)	4.4(4)
C(13)	0.1017(17)	0.1117(10)	−0.3776(9)	7.0(6)
C(14)	0.1825(17)	0.0596(10)	−0.3781(10)	7.1(6)
C(15)	0.2006(15)	0.0126(8)	−0.3179(10)	6.0(5)
C(16)	0.1403(13)	0.0210(8)	−0.2570(8)	5.0(4)
C(17)	−0.1773(12)	0.0552(6)	−0.2023(7)	3.0(3)
C(18)	−0.2442(14)	0.0567(7)	−0.2763(8)	5.1(4)
C(19)	−0.3656(15)	0.0337(8)	−0.2900(9)	5.7(5)
C(20)	−0.4249(15)	0.0101(8)	−0.2316(10)	6.1(5)
C(21)	−0.3624(15)	0.0092(9)	−0.1587(10)	6.5(5)
C(22)	−0.2393(13)	0.0292(7)	−0.1448(8)	4.8(4)
C(23)	−0.2353(10)	0.1481(6)	0.0410(6)	2.5(3)
C(24)	−0.3235(12)	0.1990(6)	0.0217(8)	4.0(4)
C(25)	−0.4436(12)	0.1839(8)	0.0199(9)	5.5(5)
C(26)	−0.4776(11)	0.1181(8)	0.0385(8)	4.2(4)
C(27)	−0.3923(12)	0.0649(7)	0.0577(8)	4.3(4)
C(28)	−0.2730(12)	0.0794(6)	0.0581(7)	3.5(4)
C(29)	−0.0216(11)	0.2084(7)	0.1338(7)	2.7(3)
C(30)	0.0515(12)	0.1754(8)	0.1940(9)	5.1(4)
C(31)	0.0826(13)	0.2103(9)	0.2661(8)	5.9(5)
C(32)	0.0389(15)	0.2768(11)	0.2751(10)	7.5(6)
C(33)	−0.0337(15)	0.3101(7)	0.2179(10)	5.4(5)
C(34)	−0.0639(12)	0.2781(9)	0.1467(7)	5.1(4)

^{a} $B_{eq} = {}^8/_3\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos\gamma + 2U_{13}aa^*cc^* \cos\beta + 2U_{23}bb^*cc^* \cos\alpha)$.

Results and Discussion

Preparation and Protonation of $Na[Cp^*MCl_2(Ph_4P_2N_4S_2)]$ (3a, M = Hf; 3b, M = Zr). The reaction of $Na_2[Ph_4P_2N_4S_2]$ with Cp^*MCl_3 (M = Zr, Hf) in THF results in the replacement of one chloride by the $Ph_4P_2N_4S_2{}^{2-}$ ligand to give complexes of the type $[Na(THF)_3][Cp^*MCl_2(Ph_4P_2N_4S_2)]$ in 85–90% yields as colorless crystals which readily desolvate to give opaque white powders.

$$Na_2[Ph_4P_2N_4S_2] + Cp^*MCl_3 \rightarrow Na[Cp^*MCl_2(Ph_4P_2N_4S_2)] + NaCl \quad (1)$$

3a, M = Hf
3b,M = Zr

The ^{31}P NMR spectra of **3a** and **3b** exhibit singlets at 77–78 ppm, indicating that the $P_2N_4S_2$ ligand is bonded symmetrically to both the group 4 metal and the sodium atom (see Scheme 1). However, the facile loss of solvent from crystals of **3a** and **3b** has prevented an X-ray structural determination. Consequently, these sodium salts were converted to the proto-

---

(11) SAPI91: Fan, Hai-Fu. Structure Analysis Programs with Intelligent Control; Rigaku Corp: Tokyo, Japan, 1991.

(12) DIFABS: Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158. An empirical absorption correction program.

(13) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV, Table 2.2A, pp 71–98.

(14) Creagh, D. C.; McAuley, W. J. *International Tables for Crystallography*; Wilson, A, J. C., Ed.; Kluwer Academic Publishers: Boston, MA, 1992; Vol. C, Table 4.2.6.8, pp 219–222.

(15) teXsan: Crystal Structure Analysis Package, Molecular Structure Corp., 1985 and 1992.

Table 3. Final Fractional Coordinates and Equivalent Isotropic Temperatujre Factors (B_{eq}) with Esd's in Parentheses for $\{Cp^*ZrCl_2[Ph_4P_2N_4S(SMe)]\}$

atom	x	y	z	B_{eq}/B_{iso},[a] Å^2
Zr(1)	0.0490(1)	0.1164(1)	0.022(2)	2.55(8)
Cl(1)	0.0086(3)	0.1847(2)	0.2324(8)	4.8(3)
Cl(2)	0.0658(3)	0.0409(3)	0.2345(7)	4.0(3)
S(1)	−0.0155(3)	0.0980(2)	−0.2773(6)	3.0(3)
S(2)	−0.0913(3)	0.0778(2)	0.1031(6)	2.9(3)
P(1)	−0.1134(3)	0.1681(2)	−0.0987(7)	3.0(3)
P(2)	−0.0451(3)	−0.0054(2)	−0.0998(6)	3.0(2)
N(1)	−0.0293(9)	0.1544(6)	−0.1538(18)	2.9(8)
N(2)	0.0129(9)	0.0429(7)	−0.1428(21)	3.3(8)
N(3)	−0.1046(8)	0.0130(7)	0.0173(18)	3.2(8)
N(4)	−0.1471(7)	0.1262(8)	0.0468(19)	3.1(9)
C(1)	−0.1182(8)	0.2414(5)	−0.0352(18)	4.5
C(2)	−0.0724(6)	0.2833(6)	−0.0951(15)	4.5
C(3)	−0.0785(6)	0.3416(6)	−0.0469(16)	4.5
C(4)	−0.1305(7)	0.3579(5)	0.0613(16)	4.5
C(5)	−0.1764(6)	0.3159(7)	0.1212(14)	4.5
C(6)	−0.1702(7)	0.2577(6)	0.0730(17)	4.5
C(7)	−0.1704(6)	0.1638(7)	−0.2736(14)	4.4
C(8)	−0.1758(7)	0.2113(5)	−0.3785(18)	4.4
C(9)	−0.2197(7)	0.2082(5)	−0.5119(15)	4.4
C(10)	−0.2582(6)	0.1575(6)	−0.5404(13)	4.4
C(11)	−0.2528(7)	0.1099(5)	−0.4355(17)	4.4
C(12)	−0.2089(7)	0.1131(6)	−0.3021(15)	4.4
C(13)	−0.0859(8)	−0.0290(6)	−0.2842(13)	4.4
C(14)	−0.1563(7)	−0.0434(6)	−0.2913(13)	4.4
C(15)	−0.1836(5)	−0.0690(6)	−0.4302(17)	4.4
C(16)	−0.1406(7)	−0.0801(6)	−0.5620(13)	4.4
C(17)	−0.0703(7)	−0.0657(6)	−0.5549(13)	4.4
C(18)	−0.0429(5)	−0.0401(6)	−0.4160(17)	4.4
C(19)	−0.0022(7)	−0.0691(5)	−0.0364(14)	4.3
C(20)	0.0690(6)	−0.0772(5)	−0.0579(15)	4.3
C(21)	0.1000(5)	−0.1298(6)	−0.018(15)	4.3
C(22)	0.0598(7)	−0.1743(5)	0.0558(14)	4.3
C(23)	−0.0114(6)	−0.1662(5)	0.0773(14)	4.3
C(24)	−0.0424(5)	−0.1136(6)	0.0312(15)	4.3
C(25)	−0.1163(13)	0.0731(12)	0.301(2)	5(1)
C(26)	0.1298(12)	0.1717(9)	−0.176(3)	4(1)
C(27)	0.1406(10)	0.1945(9)	0.004(4)	6(1)
C(28)	0.1721(11)	0.1520(11)	0.081(2)	3(1)
C(29)	0.1745(9)	0.0973(10)	−0.013(3)	5(1)
C(30)	0.1515(11)	0.1151(12)	−0.175(2)	4(1)
C(31)	0.1085(13)	0.2035(13)	−0.326(4)	7(2)
C(32)	0.1322(12)	0.2574(11)	0.035(3)	6(1)
C(33)	0.1939(12)	0.1516(16)	0.257(3)	8(2)
C(34)	0.2127(12)	0.0411(13)	0.011(4)	7(2)
C(35)	0.1581(14)	0.0710(12)	−0.310(3)	6(2)

[a] $B_{eq} = {}^8/_3\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos \gamma + 2U_{13}aa^*cc^* \cos \beta + 2U_{23}bb^*cc^* \cos \alpha)$.

nated derivatives $\{Cp^*MCl_2[Ph_4P_2N_3(NH)S_2]\}_2$ (**4a**, M = Hf; **4b**, M = Zr) by treatment of a THF solution at -78 °C with 1 molar equiv of HCl. The ^{1}H NMR spectra of **4a** and **4b** exhibit broad singlets at δ 12.0 and 11.8, respectively, which can be attributed to an NH group. Surprisingly, however, the ^{31}P NMR spectra of **4a** and **4b** each consist of a singlet at 66.4 and 76.3 ppm, respectively. In order (a) to determine the mode of coordination of the $P_2N_4S_2$ ligand to the early transition metal in these complexes and (b) to confirm the site of protonation, an X-ray structural determination of **4a** was carried out.

X-ray Structure of $\{Cp^*HfCl_2[Ph_4P_2N_3(NH)S_2]\}_2$. An ORTEP drawing of **4a** with the atomic numbering scheme is shown in Figure 1. Selected bond distances and bond angles are given in Table 5. The X-ray structural determination reveals that the heterocyclic ligand in **4a** is connected to hafnium in a tetradentate (η^4-N,N′,S,S′) fashion to give a formally nine-coordinate metal atom and confirms that the proton is attached to a nitrogen atom. Thus the ligand is formally $Ph_4P_2N_3(NH)S_2^-$ (**2a**, R = H), the N-protonated derivative of **1**. Complex **4a** exists as a hydrogen-bonded dimer with d(N−H−N) = 2.89(1) Å in the solid state (see Figure 2). The observation of a singlet in the ^{31}P NMR spectrum of **4a** within the temperature range −90 to +25 °C is only consistent with the retention of a dimeric structure in solution if the NH protons connecting two $P_2N_4S_2$ rings exchange rapidly between equivalent positions. Alternatively, a monomeric structure in solution in which the proton undergoes a rapid 1,3-nitrogen shift (across a sulfur atom) could account for the singlet in the ^{31}P NMR spectrum.

Table 4. Final Fractional Coordinates and Equivalent Isotropic Temperatujre Factors (B_{eq}) with Esd's in Parentheses for $[Me_3PNPPh_2NSMeNPPh_2NH_2]Cl$

atom	x	y	z	B_{eq},[a] Å^2
Cl(1)	0.9580(3)	0.1243(2)	0.3582(4)	5.0(1)
S(1)	0.4657(4)	0.2352(2)	0.6007(4)	4.0(1)
P(1)	0.3029(4)	0.1346(2)	0.7270(4)	3.8(1)
P(2)	0.6997(4)	0.3779(3)	0.7581(4)	4.2(1)
P(3)	0.8559(4)	0.2717(3)	0.6627(4)	5.0(1)
N(1)	0.1876(9)	0.0611(6)	0.5824(9)	4.1(3)
N(2)	0.3580(9)	0.2247(6)	0.6908(10)	4.0(3)
N(3)	0.5464(9)	0.3361(6)	0.6372(10)	3.9(3)
N(4)	0.8043(10)	0.3237(6)	0.7726(10)	4.5(3)
C(1)	0.2365(14)	0.1621(10)	0.8719(13)	3.4(4)
C(2)	0.2807(14)	0.2452(10)	0.9614(18)	5.6(5)
C(3)	0.2221(18)	0.2613(9)	1.0705(15)	5.6(5)
C(4)	0.1208(17)	0.1985(12)	1.0888(16)	6.0(6)
C(5)	0.0774(14)	0.1164(9)	0.9970(17)	4.7(5)
C(6)	0.1302(16)	0.0990(9)	0.8887(15)	4.8(5)
C(7)	0.4319(13)	0.0848(10)	0.7902(20)	4.1(5)
C(8)	0.5224(20)	0.1138(9)	0.9300(21)	6.2(6)
C(9)	0.6312(25)	0.0822(15)	0.9787(28)	9.0(9)
C(10)	0.6499(27)	0.0224(17)	0.8847(34)	10(1)
C(11)	0.5600(24)	−0.0100(13)	0.7444(26)	9.2(9)
C(12)	0.4520(17)	0.0215(12)	0.6948(18)	6.9(6)
C(13)	0.6857(14)	0.4038(11)	0.9363(14)	4.9(5)
C(14)	0.6757(17)	0.4820(13)	0.9942(19)	7.6(7)
C(15)	0.6524(20)	0.5002(13)	1.1276(24)	9.6(8)
C(16)	0.6429(24)	0.4346(17)	1.1997(22)	11.1(8)
C(17)	0.6528(22)	0.3571(14)	1.1462(23)	9.7(7)
C(18)	0.6802(15)	0.3418(10)	1.0152(20)	7.4(6)
C(19)	0.7705(15)	0.4775(8)	0.7155(15)	3.8(4)
C(20)	0.9056(16)	0.5280(11)	0.7916(18)	7.5(6)
C(21)	0.9573(18)	0.6011(13)	0.7503(24)	9.8(9)
C(22)	0.8824(21)	0.6288(11)	0.6431(23)	7.6(7)
C(23)	0.7510(19)	0.5792(10)	0.5711(15)	6.4(6)
C(24)	0.6941(13)	0.5050(9)	0.6061(15)	4.7(4)
C(25)	0.8283(14)	0.1637(9)	0.6781(14)	8.0(6)
C(26)	0.7803(13)	0.2661(9)	0.4762(13)	7.4(5)
C(27)	1.0363(13)	0.3154(9)	0.7015(14)	8.2(5)
C(28)	0.3536(12)	0.2206(8)	0.4251(12)	5.5(4)

[a] $B_{eq} = {}^8/_3\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos \gamma + 2U_{13}aa^*cc^* \cos \beta + 2U_{23}bb^*cc^* \cos \alpha)$.

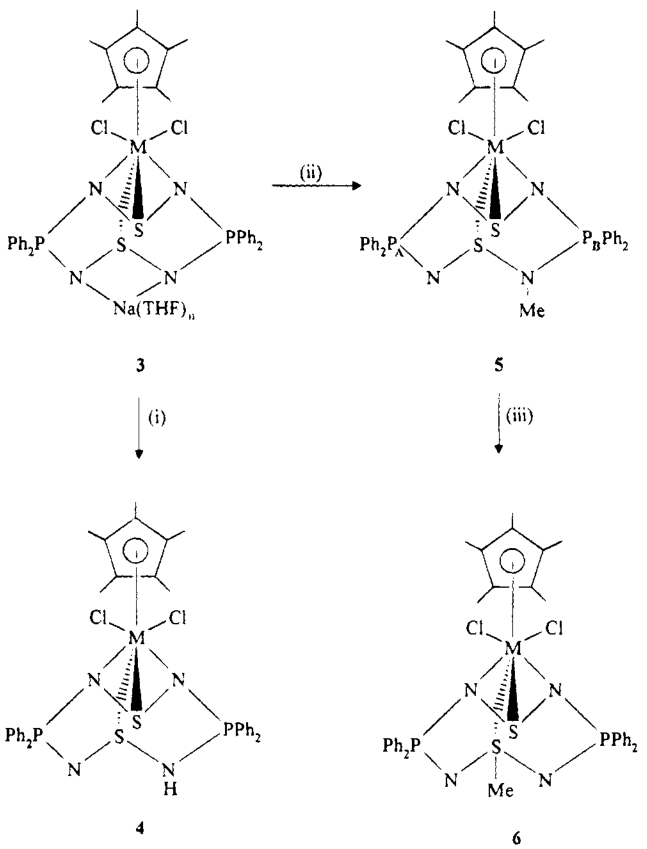
The Hf−N bond lengths in **4a** are 2.227(10) and 2.241(8) Å; *cf.* d(Hf−N) = 2.202(4) and 2.18(1) Å for η^2-aminoacyl and vinylamido derivatives of hafnocene, respectively.[16] The two sulfur atoms are less strongly bound to hafnium with d(Hf−S) = 2.859(3) and 2.911(3) Å, but we have been unable to locate literature data on comparable Hf−S bond distances. However, on the basis of a difference of *ca.* 0.30 Å between the covalent radii of nitrogen and sulfur,[17] it appears that the sulfur atoms are more weakly attached to hafnium in **4a** than the nitrogen atoms. The tetradentate coordination of the $P_2N_4S_2$ ring to hafnium has a significant effect on S−N bond lengths, which range from 1.668(9) Å for S(2)−N(4) to 1.747(8) Å for S(1)−N(2). This can be compared with an S−N distance of 1.697(6) Å for the coordinated ligand atoms in $ZrCp_2Cl(\eta^2\text{-N,S-}Ph_4P_2N_4S_2tBu)$[8] and values of 1.72(1) and 1.755(9) Å for

---

(16) Beshouri, S. M.; Chebi, D. E.; Fanwick, P. E.; Rothwell, I. P.; Huffman, J. C. *Organometallics* **1990**, *9*, 2375.

(17) Purcell, K. F.; Kotz, J. C. *Inorganic Chemistry*; W. B. Saunders Co.: Philadelphia, PA, 1977.

Scheme 1. Protonation and Methylation of $[Na(THF)_n][MCp^*Cl_2(Ph_4P_2N_4S_2)]$ (M = Zr, Hf)[a]



[a] (i) HCl, (ii) MeI or $MeSO_3CF_3$, (iii) 23 °C. For simplicity compound **4** is represented as a monomer in this scheme.

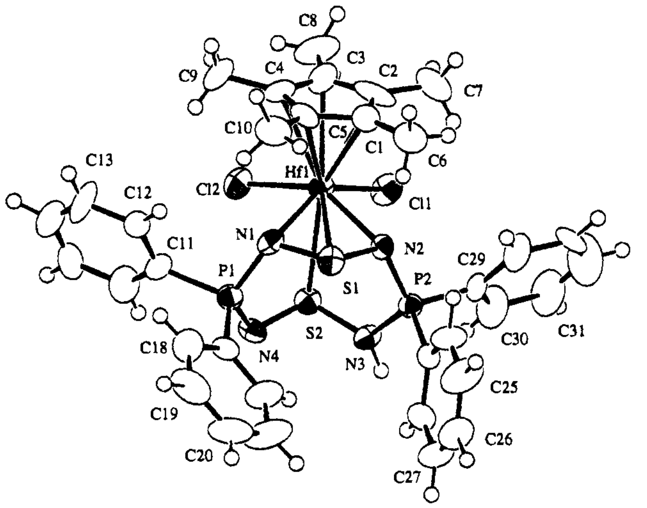


Figure 1. ORTEP diagram for $\{Cp^*HfCl_2[Ph_4P_2N_3(NH)S_2]\}_2$ showing the atomic numbering scheme. Only half of this hydrogen-bonded dimer is shown.

$[Li(Ph_4P_2N_4S_2Ph)THF]_2$, in which each lithium atom is coordinated to two nitrogen atoms of one $P_2N_4S_2$ ring and acts as a bridge to one of the nitrogen atoms of another $P_2N_4S_2$ ring.[18] The P−N bond distances in **4a** fall within the range 1.627(9)−1.651(9) Å.

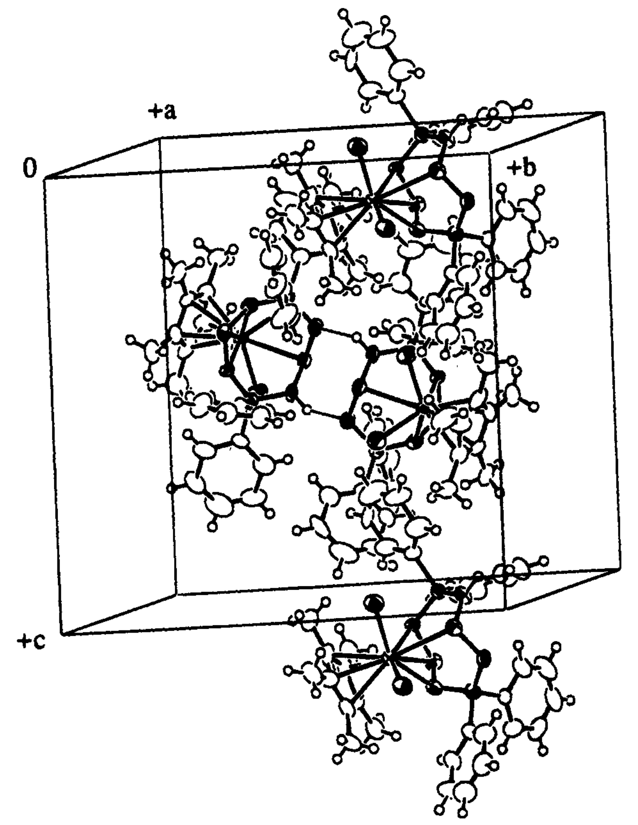


Figure 2. Unit cell diagram for $\{Cp^*HfCl_2[Ph_4P_2N_3(NH)S_2]\}_2$ showing the hydrogen-bonding interactions.

Table 5. Selected Bond Distances (Å) and Bond Angles (deg) for $\{Cp^*HfCl_2\{Ph_4P_2N_3(NH)S_2]\}_2$

Bond Distances			
Hf(1)−Cl(1)	2.454(3)	Hf(1)−Cl(2)	2.450(3)
Hf(1)−S(1)	2.859(3)	Hf(1)−S(2)	2.911(3)
Hf(1)−N(1)	2.227(10)	Hf(1)−N(2)	2.241(8)
Hf(1)−C(1)	2.54(1)	Hf(1)−C(2)	2.52(1)
Hf(1)−C(3)	2.53(1)	Hf(1)−C(4)	2.54(1)
Hf(1)−C(5)	2.54(1)	S(1)−N(1)	1.717(9)
S(1)−N(2)	1.747(8)	S(2)−N(3)	1.717(8)
S(2)−N(4)	1.668(9)	P(1)−N(1)	1.651(9)
P(1)−N(4)	1.627(9)	P(1)−C(11)	1.82(1)
P(1)−C(17)	1.78(1)	P(2)−N(2)	1.630(8)
P(2)−N(3)	1.647(9)	P(2)−C(23)	1.82(1)
P(2)−C(29)	1.78(1)		
Bond Angles			
Cl(1)−Hf(1)−Cl(2)	90.7(1)	Hf(1)−S(1)−N(2)	51.6(3)
Cl(1)−Hf(1)−S(2)	73.6(1)	Hf(1)−S(1)−N(1)	51.1(3)
Cl(1)−Hf(1)−N(2)	88.2(2)	Hf(1)−S(2)−N(3)	102.7(3)
Cl(1)−Hf(1)−S(1)	124.84(9)	Hf(1)−S(2)−N(4)	104.8(3)
Cl(1)−Hf(1)−N(1)	143.8(2)	Hf(1)−N(1)−P(1)	124.3(5)
Cl(2)−Hf(1)−S(1)	124.7(1)	Hf(1)−N(1)−S(1)	92.0(4)
Cl(2)−Hf(1)−N(1)	88.8(2)	Hf(1)−N(2)−S(1)	90.7(3)
Cl(2)−Hf(1)−S(2)	72.28(10)	Hf(1)−N(2)−P(2)	126.1(5)
Cl(2)−HF(1)−N(2)	144.0(2)	S(1)−N(1)−P(1)	115.3(5)
S(1)−Hf(1)−N(1)	36.9(2)	S(1)−N(2)−P(2)	113.4(5)
S(1)−Hf(1)−S(2)	78.92(9)	S(2)−N(3)−P(2)	119.2(5)
S(1)−Hf(1)−N(2)	37.7(2)	S(2)−N(4)−P(1)	116.5(5)
S(2)−Hf(1)−N(1)	71.8(2)	N(1)−S(1)−N(2)	98.2(5)
S(2)−Hf(1)−N(2)	73.0(2)	N(3)−S(2)−N(4)	105.3(5)
N(1)−Hf(1)−N(2)	71.8(3)	N(1)−P(1)−N(4)	114.7(5)
		N(2)−P(2)−N(3)	112.0(4)

Methylation of $Na[Cp^*MCl_2(Ph_4P_2N_4S_2)]$ (M = Hf, Zr). The methylation of the sodium derivatives **3a** and **3b** was also investigated to determine whether an electrophilic methyl group would become attached to a nitrogen or a sulfur atom of the $P_2N_4S_2$ ligand. The treatment of a THF solution of **3a** at −78 °C with an equimolar amount of methyl triflate, followed by warming to 23 °C, produced colorless crystals of $\{Cp^*HfCl_2[Ph_4P_2N_4S(SMe)]\}$, **6a**, in 67% yield. The same complex is more efficiently prepared (91% yield) by the reaction of Cp^*HfCl_3 with $\{Li[Ph_4P_2N_4S(SMe)]THF\}_2$ in THF, and the

---

(18) Chivers, T.; Edwards, M.; Hilts, R. W.; Parvez, M.; Vollmerhaus, R. *J. Chem. Soc., Chem. Commun.* **1993**, 1483.

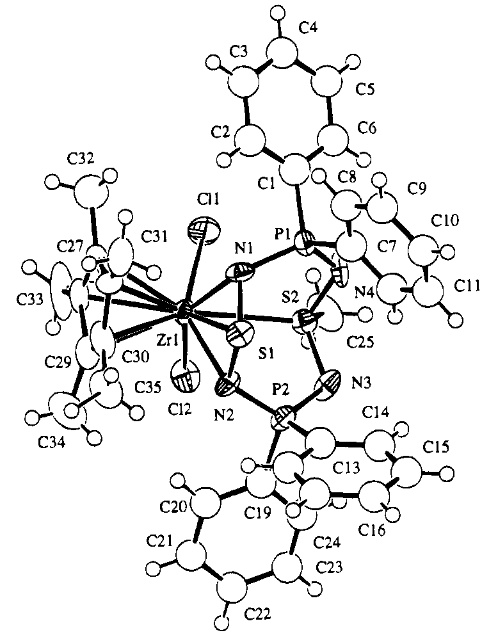


Figure 3. ORTEP diagram for Cp*ZrCl$_2$[Ph$_4$P$_2$N$_4$S(SMe)] showing the atomic numbering scheme.

Table 6. Selected Bond Distances (Å) and Bond Angles (deg) for {Cp*ZrCl$_2$[Ph$_4$P$_2$N$_4$S(SMe)]}

	Bond Distances		
Zr(1)−Cl(1)	2.465(7)	Zr(1)−Cl(2)	2.487(6)
Zr(1)−S(1)	2.810(6)	Zr(1)−S(2)	2.919(6)
Zr(1)−N(1)	2.27(2)	Zr(1)−N(2)	2.27(2)
Zr(1)−C(26)	2.59(2)	Zr(1)−C(27)	2.51(2)
Zr(1)−C(28)	2.55(2)	Zr(1)−C(29)	2.47(2)
Zr(1)−C(30)	2.57(2)	S(1)−N(1)	1.67(2)
S(1)−N(2)	1.77(2)	S(2)−N(3)	1.66(2)
S(2)−N(4)	1.61(2)	S(2)−C(25)	1.71(2)
P(1)−N(1)	1.71(2)	P(1)−N(4)	1.67(2)
P(1)−C(1)	1.76(1)	P(1)−C(7)	1.82(1)
P(2)−N(2)	1.61(2)	P(2)−N(3)	1.56(2)
P(2)−C(13)	1.80(1)	P(2)−C(19)	1.75(1)
	Bond Angles		
Cl(1)−Zr(1)−Cl(2)	88.8(2)	Cl(1)−Zr(1)−S(1)	125.5(2)
Cl(1)−Zr(1)−S(2)	74.7(2)	Cl(1)−Zr(1)−N(1)	90.3(4)
Cl(1)−Zr(1)−N(2)	142.8(5)	Cl(2)−Zr(1)−S(2)	75.4(2)
Cl(2)−Zr(1)−S(1)	125.5(2)	Cl(2)−Zr(1)−N(2)	87.3(4)
Cl(2)−Zr(1)−N(1)	143.8(4)	S(1)−Zr(1)−S(2)	75.5(2)
S(1)−Zr(1)−N(1)	36.4(4)	S(1)−Zr(1)−N(2)	39.0(4)
S(2)−Zr(1)−N(2)	68.5(4)	S(2)−Zr(1)−N(1)	69.5(4)
N(1)−Zr(1)−N(2)	72.1(6)	Zr(1)−S(1)−N(1)	53.9(6)
Zr(1)−S(1)−N(2)	54.0(6)	N(1)−S(1)−N(2)	102.1(8)
Zr(1)−S(2)−N(3)	108.3(6)	Zr(1)−S(2)−N(4)	110.0(6)
N(2)−P(2)−N(3)	117.5(9)	N(3)−S(2)−N(4)	112.6(9)
Zr(1)−N(1)−S(1)	89.8(7)	N(1)−P(1)−N(4)	117.1(8)
S(1)−N(1)−P(1)	117.1(9)	Zr(1)−N(1)−P(1)	121.7(8)
Zr(1)−N(2)−P(2)	125.8(10)	Zr(1)−N(2)−S(1)	87.1(6)
S(2)−N(3)−P(2)	113.2(10)	S(1)−N(2)−P(2)	114(1)
		S(2)−N(4)−P(1)	110.0(9)

zirconium analogue {Cp*ZrCl$_2$[Ph$_4$P$_2$N$_4$S(SMe)]}, **6b**, is obtained in *ca.* 90% yield from Cp*ZrCl$_3$ in a similar manner. Both **6a** and **6b** exhibit singlets in the ^{31}P NMR spectra at *ca.* 68 ppm, suggesting that the methyl group is attached to sulfur and the P$_2$N$_4$S$_2$ ligand is bonded symmetrically to the metal. An X-ray structural determination of **6b** has confirmed these inferences and revealed that the S-methylated ligand **2b** (R = Me) is coordinated to zirconium in a tetradentate (η^4-N,N′,S,S′) bonding mode. An ORTEP drawing of **6b** is depicted in Figure 3. Pertinent bond lengths and bond angles are summarized in Table 6. The metal−ligand bond distances are Zr(1)−N(1) = 2.27(2), Zr(1)−N(2) = 2.27(2), Zr(1)−S(1) = 2.810(6), and Zr(1)−S(2) = 2.919(6) Å, indicating moderately strong Zr−N and weak Zr−S bonding interactions as found for **4a**.

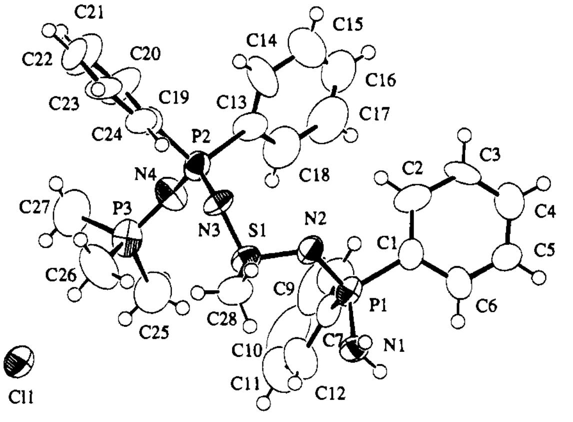
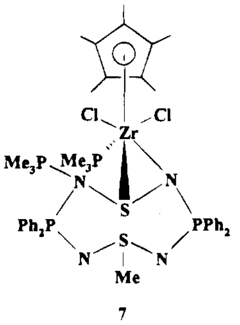


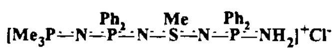
Figure 4. ORTEP diagram for [Me$_3$PNPPh$_2$NSMeNPPh$_2$H$_2$]Cl showing the atomic numbering scheme.

The methylation of **3a** with methyl iodide proceeded more slowly than the corresponding reaction of methyl triflate, thus enabling the progress of the reaction to be monitored by ^{31}P NMR spectroscopy. An intermediate was detected, which exhibits mutually coupled doublets ($^4J_{P_A-P_B}$ = 22.9 Hz) at 74.5 and 82.2 ppm, in addition to the singlet for **6a** at 68.4 ppm. After 2 days the pair of doublets and the resonance at 77.5 ppm attributable to **3a** had disappeared to give **6a** as the only product. We propose that this intermediate is the N-methylated isomer of {Cp*HfCl$_2$[Ph$_4$P$_2$N$_3$(NMe)S$_2$]} (see **5** (M = Hf) in Scheme 1).

Reaction of {Cp*ZrCl$_2$[Ph$_4$P$_2$N$_4$S(SMe)]} with Me$_3$P. In view of the apparent weakness of the metal−sulfur interactions in the tetradentate complexes {Cp*MCl$_2$[Ph$_4$P$_2$N$_4$S(SMe)]} (M = Zr, Hf), we have investigated the reaction of **6b** with an excess of trimethylphosphine. The reaction was monitored by ^{31}P NMR spectroscopy, and an intermediate, which exhibited four resonances of approximately equal intensity at 27.8, 23.1, 9.6, and −4.4 ppm, was detected. It seems reasonable to conclude that 2 equiv of Me$_3$P is taken up by **6b** to give a product with inequivalent heterocyclic PPh$_2$ groups, e.g. **7**.



7



$$[\mathrm{Me_3P{-}N{-}\overset{Ph_2}{P}{-}N{-}\overset{Me}{S}{-}N{-}\overset{Ph_2}{P}{-}NH_2}]^+\mathrm{Cl}^-$$

8

However, further characterization of this intermediate was precluded by its extreme sensitivity to traces of moisture, resulting in the formation of the acyclic compound **8**, which was identified by X-ray crystallography (*vide infra*). The deliberate addition of water to the reaction mixture also produced **8**, which was detected by ^{31}P NMR. Apparently one of the Me$_3$P ligands abstracts a sulfur atom from the P$_2$N$_4$S$_2$ ring while the other serves as a chain-terminating group for the acyclic fragment so formed.

X-ray Structure of [Me$_3$PNPPh$_2$NSMeNPPh$_2$NH$_2$]Cl (7). An ORTEP drawing of 7 with the atomic numbering scheme is shown in Figure 4. Selected bond distances and bond angles are given in Table 7. The P−N and S−N bond distances along

Table 7. Selected Bond Distances (Å) and Bond Angles (deg) for [$Me_3PNPPh_2NSMeNPPh_2NH_2$]Cl

Bond Distances			
S(1)−N(2)	1.616(9)	S(1)−N(3)	1.598(9)
S(1)−C(28)	1.75(1)	P(1)−N(1)	1.649(9)
P(1)−N(2)	1.597(9)	P(1)−C(1)	1.80(1)
P(1)−C(7)	1.79(1)	P(2)−N(3)	1.622(9)
P(2)−N(4)	1.584(9)	P(2)−C(13)	1.79(1)
P(2)−C(19)	1.80(1)	P(3)−N(4)	1.57(1)
P(3)−C(25)	1.78(1)	P(3)−C(26)	1.78(1)
P(3)−C(27)	1.76(1)		
Bond Angles			
N(2)−S(1)−N(3)	107.0(5)	N(2)−S(1)−C(28)	101.0(5)
N(3)−S(1)−C(28)	99.4(5)	N(1)−P(1)−N(2)	111.7(5)
N(1)−P(1)−C(1)	114.2(6)	N(1)−P(1)−C(7)	104.1(7)
N(2)−P(1)−C(1)	103.5(6)	N(2)−P(1)−C(7)	115.6(6)
C(1)−P(1)−C(7)	107.9(7)	N(3)−P(2)−N(4)	119.4(5)
N(3)−P(2)−C(13)	110.0(6)	N(3)−P(2)−C(19)	103.8(6)
N(4)−P(2)−C(13)	104.4(7)	N(4)−P(2)−C(19)	111.0(6)
C(13)−P(2)−C(19)	108.1(7)	N(4)−P(3)−C(25)	110.7(6)
N(4)−P(3)−C(26)	116.3(6)	N(4)−P(3)−C(27)	111.3(7)
C(25)−P(3)−C(26)	107.1(7)	C(25)−P(3)−C(27)	105.2(6)
C(26)−P(3)−C(27)	105.6(6)	S(1)−N(2)−P(1)	119.5(6)
S(1)−N(3)−P(2)	120.4(6)	P(2)−N(4)−P(3)	134.5(7)

the eight-atom chain follow the sequence 1.57(1), 1.584(9), 1.622(9), 1.598(9), 1.616(9), 1.597(9), 1.649(9) Å, suggesting extensive delocalization of the positive charge along the entire chain.

Conclusions. One of the chloride ligands in Cp^*MCl_3 (M = Zr, Hf) can be replaced by the dianion $Ph_4P_2N_4S_2^{2-}$ to give complexes of the type Na[$Cp^*MCl_2(Ph_4P_2N_4S_2)$]. The protonation of these sodium salts produces the N-protonated derivatives $\{Cp^*MCl_2[Ph_4P_2N_3(NH)S_2]\}_2$, which exist as hydrogen-bonded dimers in the solid state, whereas methylation yields the S-methylated complexes $\{Cp^*MCl_2[Ph_4P_2N_4S(SMe)]\}$ via their N-methylated isomers. In both the N-protonated and S-methylated complexes the $Ph_4P_2N_4S_2R^-$ ligand is coordinated to the group 4 metal in a tetradentate (η^4-N,N′,S,S′) bonding mode, thus providing further evidence of the adaptability of these heterocyclic ligands to the electronic requirements of the metal center. This mode of coordination activates the opening of the $P_2N_4S_2$ ring in the reaction with Me_3P.

Acknowledgment. We thank the NSERC (Canada) for financial support. We also acknowledge the contributions of Dr. R. W. Hilts for carrying out some preliminary experiments and Ian Krouse for assistance with the X-ray structure determination of **6b**.

Supplementary Material Available: Listings of crystal data, bond lengths and bond angles, anisotropic temperature factors, and torsion angles for **4a**, **6b**, and **8** (23 pages). Ordering information is given on any current masthead page.

IC941130+