Group 4 Metal Complexes of $Ph_4P_2N_4S_2R^-$ Anions: Preparation, Structure, and Reactions with Electrophiles

Tristram Chivers,* Robert W. Hilts, Masood Parvez, and Rainer Vollmerhaus

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

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The reaction of $[Li(Ph_4P_2N_4S_2R)THF]_2$ (R = Me, ${}^tBu$, Ph, CH_2PPh_2) with the metallocene dihalides MCp_2Cl_2 (M = Ti, Zr, Hf) in THF produces complexes of the type $MCp_2Cl(Ph_4P_2N_4S_2R)$ in which the $Ph_4P_2N_4S_2R^-$ anion is bonded to the metal in an η^2-N,S fashion as demonstrated by an X-ray structural determination of $ZrCp_2Cl(Ph_4P_2N_4S_2{}^tBu)$ (**2a**). Crystals of **2a** are triclinic, space group $P\bar{1}$, with $a = 12.439(4)$ Å, $b = 18.200(5)$ Å, $c = 10.370(2)$ Å, $\alpha = 100.40(2)°$, $\beta = 106.65(2)°$, $\gamma = 72.53(2)°$, $V = 2136(1)$ Å^3, and $Z = 2$. The final R and R_w values were 0.054 and 0.061, respectively. The dimensions of the three-membered ZrNS ring are d(Zr–S) = 2.634(2) Å, d(Zr–N) = 2.206(5) Å, and d(S–N) = 1.697(6) Å. The treatment of **2a** with electrophiles results in the regiospecific functionalization of the $P_2N_4S_2$ ring. The reactions of **2a** with methyl iodide or bromide produce the unsymmetrical *S,S'*-diorgano derivative $Ph_4P_2N_4(S{}^tBu)(SMe)$ and the *S*-bromo derivative $Ph_4P_2N_4(S{}^tBu)(SBr)$, respectively. By contrast, the reaction of **2a** with 2 molar equiv of HCl gas generates $[Ph_4P_2N_4S_2{}^tBuH_2]Cl$ (**4**) in which the two nitrogen atoms separated by the two-coordinate sulfur in the $Ph_4P_2N_4S_2{}^tBu^-$ anion have been protonated. Compound **4** was characterized by ^{31}P and ^1H-^{15}N HMQC NMR spectra and by X-ray crystallography which revealed that **4** exists as a hydrogen-bonded dimer in the solid state. Crystals of **4** are triclinic, space group $P\bar{1}$ with $a = 12.797(4)$ Å, $b = 14.618(3)$ Å, $c = 8.276(5)$ Å, $\alpha = 90.48(3)°$, $\beta = 105.59(3)°$, $\gamma = 81.24(2)°$, $V = 1473(1)$ Å^3, and $Z = 2$. The final R and R_w values were 0.045 and 0.033, respectively. An X-ray structural determination of $Ph_4P_2N_4(SPh)(SBr)$ (**5b**), prepared by bromination of $[Li(Ph_4P_2N_4S_2Ph)THF]_2$ or $[ZrCp_2Cl(Ph_4P_2N_4S_2Ph)]$, gave an S–Br distance of 2.573(5) Å. Crystals of **5b** are orthorhombic, space group $P2_12_12_1$ with $a = 14.534(7)$ Å, $b = 17.647(5)$ Å, $c = 11.523(5)$ Å, $V = 2955(1)$ Å^3, and $Z = 4$. The final R and R_w values were 0.063 and 0.042, respectively. Surprisingly, the complex **2a** does not react with strong nucleophiles such as $Li[Et_3BH]$ or methyllithium.

Introduction

The coordination chemistry of *N,N'*-diorgano sulfur diimides, RNSNR, was investigated extensively by Vrieze and co-workers in the 1970s[1] and, more recently, by Herberhold et al.[2] and Woollins et al.[3] The reaction of organolithium reagents with these sulfur diimides proceeds quantitatively to produce S-substituted derivatives of the type Li[RNS(R')NR][1,4] and the solid-state and solution structures of these lithium derivatives have been established recently.[5] Investigations of the ligand behavior of the anions $RNS(R')NR^-$ have been limited to electron-rich transition metals. These anions may act as bridging ligands (through N) with Cu(I) to give eight-membered rings[6] or as chelating (η^2-N,N') ligands in monometallic complexes of Rh(I)[7] and Pd(II).[8] These complexes are unstable in solution with respect to the formation of a diazene and a metal thiolate[1] and this facile decomposition has restricted studies of metal complexes of the $RNS(R')NR^-$ anions.

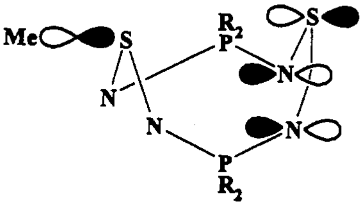

Figure 1. HOMO of the $R_4P_2N_4S_2Me^-$ anion (R = Me).

Recently, we have shown that the 1,5-diphosphadithiatetrazocine **1** (R = Ph) also reacts readily with organolithium reagents to give the adducts $Li[Ph_4P_2N_4S_2R]$ (R = alkyl, aryl), which exist as step-shaped dimers in the solid-state or in solution.[9] Nucleophilic attack on **1** by a carbanion occurs via the LUMO, an antibonding σ^*(S–S) orbital, and results in cleavage of the S–S bond.[10] The composition of the HOMO of the resulting anion $Ph_4P_2N_4S_2Me^-$, **2** (R = Me), is shown in Figure 1.[11] Significantly, this orbital is localized on the side of the ring opposite to the site of methylation and is weakly antibonding with respect to the C–S bond.[10] Thus it is reasonable to anticipate metal complexation with **2** will take place on the side of the ring remote from the SR group, and consequently, decomposition of the metal complexes to metal thiolates will not be a facile process. In addition, the presence of coordinatively saturated P(V) centers in these anionic ligands provides a convenient NMR probe of structures and fluxional processes.

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(11) To facilitate computations, the calculations were carried out on the $Me_4P_2N_4S_2Me^-$ anion.

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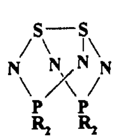
Table 1. Selected NMR Data for the Complexes $[MCp_2Cl(Ph_4P_2N_4S_2R)]$ (M = Ti, Zr, Hf; R = ${}^tBu$, Me, Ph, CH_2PPh_2)

compd	M	R	X	$\delta(^{31}P)^a$	$\delta(^1H)^b$	$\delta(^{13}C)^b$
2a	Zr	${}^tBu$	Cl	45.3 (s, PPh_2) 36.3 (s, PPh_2)	1.10 (s, 9H, $C(CH_3)_3$) 5.46 (s, 5H, C_5H_5) 6.48 (s, 5H, C_5H_5)	57.8 (t, $C(CH_3)_3$, $^3J(PC)$ = 15 Hz) 22.9 (s, $C(CH_3)_3$) 112.0 (s, C_5H_5) 114.9 (s, C_5H_5)
2b	Zr	Me	Cl	44.1 (s, PPh_2) 35.1 (s, PPh_2)	2.61 (s, 3H, CH_3) 5.49 (s, 5H, C_5H_5) 6.48 (s, 5H, C_5H_5)	47.0 (t, CH_3, $^3J(PC)$ = 20 Hz) 112.1 (s, C_5H_5) 114.9 (s, C_5H_5)
2c	Zr	Ph	Cl	46.9 (s, PPh_2) 37.2 (s, PPh_2)	5.52 (s, 5H, C_5H_5) 6.52 (s, 5H, C_5H_5)	
2d	Zr	CH_2PPh_2	Cl	43.8 (s, PPh_2) 34.8 (s, PPh_2) −28.5 (s, CH_2PPh_2)	3.88 (dd, 1H, $CHHPPh_2$, $^2J(PH)$ < 1 Hz, $^2J(HH)$ = 13 Hz) 3.74 (dd, 1 H, $CHHPPh_2$, $^2J(PH)$ = 2 Hz, $^2J(HH)$ = 13 Hz) 5.47 (s, 5H, C_5H_5) 6.46 (s, 5H, C_5H_5)	62.0 (dt, CH_2PPh_2, $^1J(PC)$ = $^3J(PC)$ = 24 Hz) 111.2 (s, C_5H_5) 114.1 (s, C_5H_5)
2e	Hf	${}^tBu$	Cl	45.5 (s, PPh_2) 37.2 (s, PPh_2)	1.12 (s, 9H, $C(CH_3)_3$) 5.43 (s, 5H, C_5H_5) 6.48 (s, 5H, C_5H_5)	22.9 (s, $C(CH_3)_3$) 110.9 (s, C_5H_5) 113.6 (s, C_5H_5)
2f	Hf	Me	Cl	44.4 (d, PPh_2, $^4J(PP)$ = 3 Hz) 36.1 (d, PPh_2, $^4J(PP)$ = 3 Hz)	2.56 (s, 3H, CH_3) 5.39 (s, 5H, C_5H_5) 6.42 (s, 5H, C_5H_5)	47.1 (t, CH_3, $^3J(PC)$ = 21 Hz) 111.0 (s, C_5H_5) 113.6 (s, C_5H_5)
2g	Hf	Ph	Cl	47.1 (d, PPh_2, $^4J(PP)$ = 3 Hz) 38.1 (d, PPh_2, $^4J(PP)$ = 3 Hz)	5.42 (s, 5H, C_5H_5) 6.46 (s, 5H, C_5H_5)	
2h	Ti	${}^tBu$	Cl	50.3 (s, PPh_2) 35.7 (s, PPh_2)	1.13 (s, 9H, $C(CH_3)_3$) 5.10 (s, 5H, C_5H_5) 6.38 (s, 5H, C_5H_5)	
2i	Ti	Me	Cl	49.8 (s, PPh_2) 34.6 (s, PPh_2)	2.58 (s, 3H, CH_3) 5.29 (s, 5H, C_5H_5) 6.33 (s, 5H, C_5H_5)	
2j	Ti	Ph	Cl	52.2 (s, PPh_2) 36.5 (s, PPh_2)	5.13 (s, 5H, C_5H_5) 6.39 (s, 5H, C_5H_5)	

[a] Phosphorus-31 chemical shifts are quoted in ppm relative to 85% H_3PO_4; s = singlet, and d = doublet. [b] Proton and carbon-13 chemical shifts are quoted in ppm relative to $SiMe_4$; s = singlet, t = triplet, dd = doublet of doublets, and dt = doublet of triplets.

Our first studies of metal complexes of **2** involved the preparation and structural characterization of η^1-S-bonded complexes of Pt(II) and Pd(II) of the type **3**.[12] The anions **2** are potentially versatile ligands in view of the availability of multiple hard (N) and soft (S) coordination sites, and the early transition metals are particularly interesting candidates for probing main group element interactions with metals. Specifically, the composition of the HOMO of $R_4P_2N_4S_2Me^-$ (Figure 1) suggests that bonding modes other than η^1-S should be possible. In a preliminary communication we reported that zirconium binds to **2** in an η^2-N,S fashion and that such derivatives are useful for the regiospecific functionalization of the $P_2N_4S_2$ ring by reactions with electrophiles.[13] In this article, we provide a full account of the preparation and characterization of Ti, Zr, and Hf derivatives of the anions **2** (R = Me, ${}^tBu$, Ph) and the X-ray structure and investigations of the reactions of the zirconium compound $ZrCp_2Cl(Ph_4P_2N_4S_2{}^tBu)$ with electrophiles and nucleophiles. The X-ray structural determinations of $[Ph_4P_2N_4S_2{}^tBuH_2]Cl$ and $Ph_4P_2N_4(SPh)(SBr)$ are also reported.



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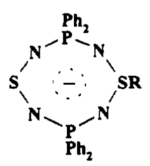

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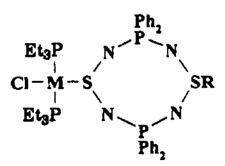

3 (M = Pd, Pt)

Previous studies of the coordination of group 4 metals to inorganic S–N ligands include (a) complexes in which the metal is part of an S–N ring system, e.g. $Cp_2TiS_3N_4$,[14] $Cp_2TiS_3N_2$,[14] and $Cp_2Zr(NSN)_2ZrCp_2$,[15] (b) the acyclic complexes $Cp_2Ti(NSO)_2$,[16,17] $Cp_2Ti(NSNSiMe_3)_2$,[16b] and $ZrCpCp^*(NSO)_2$,[18] and (c) the N-bonded adduct $[Cp_2Ti(S_4N_4)][AsF_6]_2$.[19]

Experimental Section

Reagents and General Procedures. All solvents were dried, distilled and purged with argon before use. All reactions and the manipulation of products were carried out under an atmosphere of argon by using Schlenk techniques. The compounds $Ph_4P_2N_4S_2$,[20] $[Li(Ph_4P_2N_4S_2R)THF]_2$ (R = Me, ${}^tBu$, Ph)[9] and $[LiCH_2PPh_2{\cdot}TMEDA]$[21] were prepared by literature methods. Organolithium reagents, MCp_2Cl_2 (M = Ti, Zr, Hf), bromine, iodomethane, and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were purchased from Aldrich and used as received. HCl gas (Union Carbide) was used directly from the cylinder.

Instrumentation. ^1H and ^{13}C NMR spectra were recorded in THF-d_8 or toluene-d_8 by using either a Bruker AM-400 or a Bruker AM-200 spectrometer locked to the solvent deuterium resonance. ^{31}P NMR spectra were obtained on the Bruker AM-400 instrument with a D_2O insert serving as the lock material. The 2D ^1H–^{15}N-HMQC (heteronuclear multiple quantum coherence) spectra were obtained on a Bruker AMX-500 spectrometer by using a standard four-pulse sequence.[22] Electron impact mass spectra were recorded by using a Kratos MS80RFA instrument set at 70 eV. Elemental analyses were performed by the microanalytical service within the Chemistry Department at The University of Calgary.

Preparation of Complexes 2a–j. All of the group 4 metal complexes of the anions $Ph_4P_2N_4S_2R^-$, except **2d**, were prepared and purified by

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procedures similar to those described in detail below for **2a**. Consequently, only yields and the results of elemental analyses for **2b**, **2c** and **2e–j** are reported below. The NMR data for **2a–j** are summarized in Table 1.

Preparation of $[ZrCp_2Cl(Ph_4P_2N_4S_2{}^tBu)]$ (2a). A pale yellow solution of $[Li(Ph_4P_2N_4S_2Bu^t)THF]_2$ (0.256 g, 0.204 mmol) in tetrahydrofuran (20 mL) at −78 °C was added dropwise, over 10 min, to a rapidly stirred, colorless solution of $[ZrCp_2Cl_2]$ (0.119 g, 0.408 mmol) in tetrahydrofuran (20 mL) at −78 °C. The pale yellow reaction mixture was warmed to 23 °C with a water bath, and stirring was continued at room temperature for 1 h. The solvent was removed under vacuum, and the yellow residue was dissolved in toluene (30 mL). The resulting cloudy solution was filtered to remove the precipitated lithium chloride, and the clear filtrate was evaporated to dryness under vacuum. Recrystallization of the pale yellow product from tetrahydrofuran–diethyl ether (1:1) at 0 °C furnished colorless crystals of $[ZrCp_2Cl(Ph_4P_2N_4S_2Bu^t)]$ (0.128 g, 0.159 mmol) in 39% yield. Anal. Calcd for $C_{38}H_{39}N_4ClP_2S_2Zr$: C, 56.73; H, 4.89; N, 6.97. Found: C, 56.24; H, 4.76; N, 7.19.

Preparation of $[ZrCp_2Cl(Ph_4P_2N_4S_2CH_2PPR_2)]$ (2d). A yellow solution of $LiCH_2PPh_2{\cdot}TMEDA$ (0.177 g, 0.550 mmol) in tetrahydrofuran (15 mL) at −78 °C was added via a transfer needle to a solution of 0.270 g of 1,5-$Ph_4P_2N_4S_2$ in tetrahydrofuran (15 mL) at −78 °C. The resulting pale yellow solution was warmed to 23 °C, stirred for 30 min, recooled to −78 °C, and then added dropwise, via cannula, to a colorless solution of $ZrCp_2Cl_2$ (0.161 g, 0.550 mmol) in tetrahydrofuran (10 mL) at −78 °C. At the end of the addition, the reaction mixture was allowed to warm slowly to room temperature, and stirring was continued at this temperature for 1 h. The solvent was removed under vacuum and toluene (30 mL) was added to give a cloudy yellow solution, which was immediately filtered to remove the precipitated LiCl. The clear yellow toluene filtrate was then taken to dryness under vacuum to yield a sticky yellow solid. Recrystallization of this solid from a 1:1 tetrahydrofuran-diethyl ether mixture at 0 °C gave $[ZrCp_2Cl(Ph_4P_2N_4S_2CH_2PPh_2)]$ (0.214 g, 0.226 mmol) as a yellow powder in 41% yield. Anal. Calcd for $C_{47}H_{42}ClN_4P_3S_2Zr$: C, 59.64; H, 4.47; N, 5.92. Found: C, 58.51; H, 4.82; N, 5.72.

$[ZrCp_2Cl(Ph_4P_2N_4S_2Me)]$ (2b) was obtained as a colorless crystalline solid. Yield: 53%. Anal. Calcd for $C_{35}H_{33}N_4ClP_2S_2Zr$: C, 55.14; H, 4.36; N, 7.35. Found: C, 54.75; H, 4.84; N, 6.84.

$[ZrCp_2Cl(Ph_4P_2N_4S_2Ph)]$ (2c) was obtained as a colorless crystalline solid. Yield: 69%. Anal. Calcd for $C_{40}H_{35}N_4ClP_2S_2Zr$: C, 58.27; H, 4.28; N, 6.80. Found: C, 59.01; H, 4.60; N, 7.12.

$[HfCp_2Cl(Ph_4P_2N_4S_2Bu^t)]$ (2e) was obtained as a colorless crystalline solid. Yield: 55%. Anal. Calcd for $C_{38}H_{39}N_4ClHfP_2S_2$: C, 51.18; H, 4.41; N, 6.28. Found: C, 51.17; H, 4.65; N, 6.23.

$[HfCp_2Cl(Ph_4P_2N_4S_2Me)]$ (2f) was obtained as a colorless crystalline solid. Yield: 55%. Anal. Calcd for $C_{35}H_{33}N_4ClHfP_2S_2$: C, 49.47; H, 3.91; N, 6.60. Found: C, 49.33; H, 3.99; N, 5.96.

$[HfCp_2Cl(Ph_4P_2N_4S_2Ph)]$ (2g) was obtained as a colorless crystalline solid. Yield: 40%. Anal. Calcd for $C_{40}H_{35}N_4ClHfP_2S_2$: C, 52.69; H, 3.87; N, 6.15. Found: C, 52.02; H, 4.29; N, 5.90.

$[TiCp_2Cl(Ph_4P_2N_4S_2Bu^t)]$ (2h) was obtained as an orange-red solid. Yield: 58%. Anal. Calcd for $C_{38}H_{39}N_4ClP_2S_2Ti$: C, 59.96; H, 5.16; N, 7.36. Found: C, 61.02; H, 5.30; N, 7.03.

$[TiCp_2Cl(Ph_4P_2N_4S_2Me)]{\cdot}THF$ (2i) was obtained as an orange-red solid. Yield: 67%. Anal. Calcd for $C_{39}H_{41}N_4ClOP_2S_2Ti$: C, 59.20; H, 5.22; N, 7.08. Found: C, 59.70; H, 4.98; N, 7.86.

$[TiCp_2Cl(Ph_4P_2N_4S_2Ph)]$ (2j) was obtained as an orange-red solid. Yield: 42%. Anal. Calcd for $C_{40}H_{35}N_4ClP_2S_2Ti$: C, 61.50; H, 4.52; N, 7.17. Found: C, 62.22; H, 4.88; N, 7.73.

Preparation of $[Ph_4P_2N_4S_2{}^tBuH_2]Cl$ (4). HCl gas (14 mL, *ca.* 0.625 mmol) in a gastight syringe was injected into a cold solution (−78 °C) of $ZrCp_2Cl(Ph_4P_2N_4S_2Bu^t)$ (0.246 g, 0.306 mmol) in 20 mL of tetrahydrofuran. The resulting pale yellow mixture was stirred for 1 h, and the solvent was removed under vacuum. The yellow residue was dissolved in dichloromethane to give a cloudy yellow solution, which was filtered to remove the precipitated LiCl. The solvent was again removed under vacuum and the residue was washed with toluene (3 × 10 mL) to give an off-white solid. Recrystallization from CH_2Cl_2–Et_2O (1:5) at 23 °C gave colorless crystals of $[Ph_4P_2N_4S_2Bu^tH_2]Cl$ (0.042 g, 0.072 mmol) in 23% yield. Anal. Calcd for $C_{28}H_{31}P_2N_4S_2Cl$: C, 57.48; H, 5.34; N, 9.58. Found: C, 56.88; H, 5.25; N, 9.47. ^1H NMR (CH_2Cl_2, 23 °C): δ 1.19 (s, 9H, $C(CH_3)_3$), 7.15–7.95 (m, 20H, C_6H_5), 10.3 (d, 2H, NH, ^2J(PH) = 21 Hz). ^{13}C NMR (CD_2Cl_2, 23 °C): δ 21.36 (s, $C(CH_3)_3$), 58.11 (t, $C(CH_3)_3$, ^3J(PC) = 15 Hz), 133.3–127.6 (m, C_6H_5). ^1H–^{15}N-HMQC (CH_2Cl, 23°C): δ (^{15}N) = −309 ppm, ^1J(NH) = 86 Hz. ^{31}P NMR (CH_2Cl_2, 23 °C): δ 39.70 (s).

Preparation of $Ph_4P_2N_4(S^tBu)(SBr)$ (5a). Liquid bromine (42 μL, 0.816 mmol) was added dropwise, over 5 min, to a rapidly stirred pale yellow solution of $ZrCp_2Cl(Ph_4P_2N_4S_2Bu^t)$ (0.656 g, 0.816 mmol) in tetrahydrofuran (30 mL) at −78 °C. The resulting orange mixture was allowed to warm up to 23 °C and stirred for 1 h, and then the solvent was removed under vacuum. Toluene (30 mL) was added to give a cloudy yellow solution, which was filtered to remove the precipitated LiCl. The solvent volume of the orange filtrate was reduced to *ca.* 5 mL under vacuum, and the concentrated solution was stored at −18 °C for 8 h. Colorless crystals of $ZrCp_2ClBr$ formed on the bottom of the flask, and the supernatant was decanted. Addition of hexane (20 mL) caused the immediate precipitation of $Ph_4P_2N_4(SBu^t)(SBr)$ (0.344 g, 0.548 mmol) as a yellow-orange solid. Yield: 67%. Satisfactory C, H, and N analysis could not be obtained for this compound due to its acute sensitivity to moisture. ^{31}P NMR (THF, 23 °C, D_2O lock): δ 14.1(s). ^1H NMR (C_6D_6, 23°C): δ 1.18 (s, 9H, $C(CH_3)_3$), 6.95–8.15 (m, 20H, C_6H_5).

Preparation of $Ph_4P_2N_4(SPh)(SBr)$ (5b). (a) From $[Li(Ph_4P_2N_4S_2Ph)THF]_2$. Liquid bromine (53 μL, 1.00 mmol) was added rapidly to a pale yellow solution of $[Li(Ph_4P_2N_4S_2Ph)THF]_2$ (1.0 mmol) in tetrahydrofuran (25 mL) at 23 °C. After 10 min solvent was removed under vacuum, and then the addition of dichloromethane (10 mL) produced a cloudy orange solution, which was filtered to remove LiBr. The addition of pentane (30 mL) to the filtrate yielded $Ph_4P_2N_4(SPh)(SBr)$ (0.49 g, 0.76 mmol, 74%) as a highly moisture-sensitive orange solid. ^{31}P NMR (THF, 23 °C, D_2O lock): δ 13.2 (s). Crystals of **5b** suitable for an X-ray structure determination were obtained by recrystallization from dichloromethane–hexane.

(b) From $[ZrCp_2Cl(Ph_4P_2N_4S_2Ph)]$. Compound **5b** was also obtained in essentially quantitative yield by the treatment of $[ZrCp_2Cl(Ph_4P_2N_4S_2Ph)]$ with 1 molar equiv of liquid bromine in THF at 23 °C.

Preparation of $Ph_4P_2N_4(S^tBu)(SMe)$ (6). Iodomethane (25 μL, 0.408 mmol) was added by syringe to a pale yellow solution of $ZrCp_2Cl(Ph_4P_2N_4S_2Bu^t)$ (0.328 g, 0.408 mmol) in 20 mL of tetrahydrofuran at 23 °C. During the next 2 h the solution gradually changed from pale yellow to dark yellow. The solvent was removed under vacuum, toluene (20 mL) was added, and the resulting cloudy yellow mixture was filtered to remove the precipitated LiCl. The solvent was again removed under vacuum and the resulting yellow solid was washed with diethyl ether (3 × 10 mL) to remove $ZrCp_2ClI$. Recrystallization of the beige residue from a 1:1 mixture of hexane–dichloromethane at −18 °C afforded colorless crystals of $[Ph_4P_2N_4(SMe)(SBu^t)]{\cdot}{}^1/_4CH_2Cl_2$ (0.087 g, 0.149 mmol) in 37% yield. Anal. Calcd for $C_{29.25}H_{32.5}Cl_{0.5}N_4P_2S_2$: C, 60.17; H, 5.61; N, 9.60. Found: C, 59.53; H, 5.31; N, 9.52. ^1H NMR ($CDCl_3$, 23 °C): δ 1.24 (s, 9H, $C(CH_3)_3$), 2.84 (s, 3H, CH_3), 5.34 (s, 0.5H, CH_2Cl_2), 7.30–7.95 (m, 20H, C_6H_5). ^{13}C NMR ($CDCl_3$, 23 °C): δ 22.8 (s, $C(CH_3)_3$), 56.28 (t, $C(CH_3)_3$, ^3J(PC) = 15 Hz), 45.34 (t, CH_3, ^3J(PC) = 21 Hz), 127.6–131.9 (m, C_6H_5). ^{31}P NMR (CH_2Cl_2, 23 °C): δ 26.6 (s). MS: 562 (M^+, 0.3%), 547 ($M^+ - CH_3$, 10%), 505 ($M^+ - C(CH_3)_3$, 100%), 490 ($M^+ - CH_3 - C(CH_3)_3$, 31%).

X-ray Analyses. Crystallographic data for **2a**, **4**, and **5b** are summarized in Table 2. All measurements were made on a Rigaku AFC6S diffractometer with graphite monochromated Mo Kα radiation.

2a. A colorless prismatic crystal (0.30 × 0.35 × 0.40 mm) obtained by recrystallization from THF–diethyl ether was mounted on a glass fiber. Accurate cell dimensions and a crystal orientation matrix were determined by a least-squares fit of the setting angles of 24 reflections in the range $41.19 < 2\theta < 49.12°$. Intensity data were collected by the $\omega/2\theta$ method using a scan speed of 8.0°/min and a scan width of $(1.31 + 0.34 \tan \theta)°$ to a maximum 2θ value of 50.1°. The intensities of 7579 reflections were measured, of which 4223 had $I > 3\sigma(I)$. The structure was solved by the heavy-atom method and expanded using Fourier techniques.[23,24] Non-hydrogen atoms of the Zr complex were refined anisotropically, while those of diethyl ether were refined isotropically. Hydrogen atoms were included but not refined. Refinement converged with $R = 0.054$ and $R_w = 0.061$.

4. A colorless platelike crystal (0.20 × 0.20 × 0.06 mm) obtained by recrystallization from dichloromethane–diethyl ether was mounted on a glass fiber. A total of 25 reflections were measured in the range $21.96 < 2\theta < 31.09°$. Scan speed was 4.0°/min; scan width was $(0.94 + 0.34 \tan \theta)°$ to a maximum 2θ value of 50.3°. A total of 5231 unique reflections

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Table 2. Crystallographic Data for $[ZrCp_2Cl(Ph_4P_2N_4S_2{}^tBu)]$, (**2a**), $[Ph_4P_2N_4S_2{}^tBuH_2]Cl$, (**4**), and $Ph_4P_2N_4(SPh)(SBr)$, (**5b**)

	2a·$0.5Et_2O$	**4**	**5b**
formula	$C_{40}H_{42}N_4ClP_2S_2ZrO_{0.50}$	$C_{28}H_{31}N_4P_2S_2Cl$	$C_{30}H_{25}P_2N_4S_2Br$
fw	839.54	585.10	647.53
crystal system	triclinic	triclinic	orthorhombic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_12_12_1$ (No. 19)
a, Å	12.439(4)	12.797(4)	14.534(7)
b, Å	18.220(5)	14.618(3)	17.647(5)
c, Å	10.370(2)	8.276(5)	11.523(5)
α, deg	100.40(2)	90.48(3)	
β, deg	106.65(2)	105.59(3)	
γ, deg	72.53(2)	81.24(2)	
Z	2	2	4
V, Å^3	2136(1)	1472.9(10)	2955(1)
ρ_{calcd}, g cm^{-3}	1.305	1.319	1.455
$F(000)$	866	612	1320
μ, cm^{-1}	5.25	4.05	16.72
radiation (λ, Å)	Mo Kα (0.710 69)	Mo Kα (0.710 69)	Mo Kα (0.710 69)
T, °C	−73	−73	−123
R^a	0.054	0.045	0.063
$R_w{}^b$	0.061	0.033	0.042

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

Table 3. Final Fractional Coordinates (×10^4) and Equivalent Isotropic Temperature Factors U_{eq} (Å^2 × 10^3) with Esd's in Parentheses for $[ZrCp_2Cl(Ph_4P_2N_4S_2{}^tBu)]\cdot 0.5Et_2O$

atom	x	y	z	$U_{eq}{}^a$	atom	x	y	z	$U_{eq}{}^a$
Zr	830(1)	1449(1)	1847(1)	26(1)	C(18)	−1783(4)	2121(2)	6277(5)	54(5)
Cl	898(2)	159(1)	2493(2)	43(1)	C(19)	−1298(4)	1386(2)	5704(5)	58(5)
S(1)	1525(1)	2562(1)	3584(2)	28(1)	C(20)	−167(4)	1195(2)	5546(5)	47(5)
S(2)	3804(2)	2113(1)	6590(2)	35(1)	C(21)	2614(4)	546(3)	5785(5)	34(4)
P(1)	1869(1)	1550(1)	5591(2)	27(1)	C(22)	3365(4)	132(3)	4974(5)	46(5)
P(2)	3338(2)	3231(1)	4855(2)	34(1)	C(23)	4072(4)	−603(3)	5264(5)	55(6)
N(1)	1703(5)	1666(3)	4000(5)	29(3)	C(24)	4028(4)	−925(3)	6365(5)	62(6)
N(2)	2799(5)	2671(3)	3603(6)	32(3)	C(25)	3277(4)	−511(3)	7176(5)	68(7)
N(3)	3768(6)	2975(4)	6357(6)	48(4)	C(26)	2570(4)	225(3)	6885(5)	53(5)
N(4)	2511(5)	2120(4)	6696(6)	34(3)	C(27)	2372(5)	4196(3)	4998(5)	40(5)
C(1)	4624(7)	2081(7)	8384(9)	63(6)	C(28)	2088(5)	4528(3)	6220(5)	59(5)
C(2)	5813(9)	2156(10)	8428(12)	107(10)	C(29)	1333(5)	5266(3)	6302(5)	81(8)
C(3)	3987(10)	2773(8)	9219(9)	91(8)	C(30)	861(5)	5672(3)	5162(5)	69(7)
C(4)	4659(10)	1291(8)	8752(12)	95(9)	C(31)	1144(5)	5340(3)	3941(5)	63(6)
C(5)	−920(8)	2610(6)	1467(15)	70(7)	C(32)	1900(5)	4602(3)	3859(5)	52(5)
C(6)	−1026(8)	2102(9)	263(11)	77(8)	C(33)	4542(5)	3380(4)	4364(5)	37(4)
C(7)	−1213(8)	1450(7)	617(13)	66(7)	C(34)	5172(5)	3870(4)	5232(5)	71(6)
C(8)	−1249(7)	1579(7)	1915(14)	71(7)	C(35)	6111(5)	3995(4)	4907(5)	68(6)
C(9)	−1056(8)	2252(9)	2410(11)	68(7)	C(36)	6421(5)	3630(4)	3713(5)	64(6)
C(10)	2867(2)	1070(6)	1479(8)	52(5)	C(37)	5792(5)	3140(4)	2845(5)	80(8)
C(11)	2389(8)	479(6)	814(10)	62(6)	C(38)	4852(5)	3015(4)	3170(5)	59(6)
C(12)	1453(8)	761(6)	−248(8)	54(5)	O	1825(29)	4660(19)	529(33)	179(11)^b
C(13)	1376(9)	1555(7)	−251(9)	64(6)	C(39)	627(31)	4651(20)	−201(65)	326(26)^b
C(14)	2280(8)	1728(6)	874(8)	64(6)	C(40)	718(27)	3917(20)	−3(33)	113(10)^b
C(15)	480(4)	1740(2)	5961(5)	33(4)	C(41)	2858(42)	4899(24)	917(80)	304(40)^b
C(16)	−5(4)	2476(2)	6534(5)	39(4)	C(42)	3043(22)	5566(15)	1430(25)	80(7)^b
C(17)	−1137(4)	2667(2)	6692(5)	51(5)					

^{a} $U_{eq} = (U_{11} + U_{22} + U_{33})/3$. ^{b} Atoms allowed isotropic temperature factors.

were measured of which 1746 had $I > 3\sigma(I)$. The structure was solved and expanded by using Fourier techniques.[24,25] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. Refinement converged with $R = 0.045$ and $R_w = 0.033$.

5b. A yellow needle (0.20 × 0.10 × 0.50 mm) obtained by recrystallization from dichloromethane-hexane was mounted on a glass fiber. A total of 18 reflections were measured in the range $20.10 < 2\theta < 28.52°$. Scan speed was 4.0°/min; scan width was $(1.21 + 0.35 \tan \theta)°$ to a maximum 2θ value of 50.0°. A total of 2965 unique reflections were measured of which 1245 had $I > 3\sigma(I)$. Over the course of data collection, the standards increased by 0.4%. A linear correction factor was applied to account for this deviation. The structure was solved by direct methods[26] and expanded by using Fourier techniques. If all the atoms were refined anisotropically, the ratio of data to parameter would be 3.5. Consequently, only the heavy atoms were allowed to refine with anisotropic thermal parameters. The anisotropy associated with the C and N atoms at 150 K was minimal, justifying allowance of isotropic thermal motion for these atoms. Hydrogen atoms were included but not refined. Refinement converged with $R = 0.063$ and $R_w = 0.042$.

For all three structures the data were corrected for Lorentz, polarization, and absorption effects. A correction for secondary extinction was applied for **4**.[27] In the refinement cycles weights were derived from counting statistics. Scattering factors were those of Cromer and Waber[28] and allowance was made for anomalous dispersion.[29]

All calculations for **2a**, **4**, and **5b** were performed using the teXsan[30] crystallographic software package. The positional parameters for **2a**, **4**, and **5b** are given in Tables 3–5, respectively.

Results and Discussion

Preparation and Spectroscopic Characterization of $MCp_2Cl(Ph_4P_2N_4S_2R)$. The reaction of the metallocene dihalides MCp_2-

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Table 4. Final Fractional Coordinates (×10^4) and Equivalent Isotropic Temperature Factors U_{eq} (Å^2 × 10^3) with Esd's in Parentheses for $[Ph_4P_2N_4S_2{}^tBuH_2]Cl$

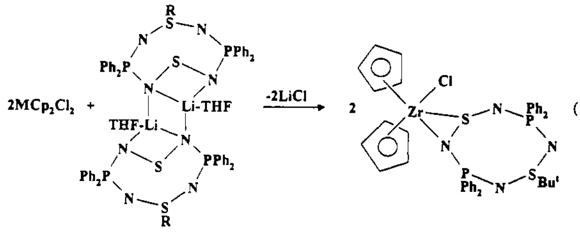
atom	*x*	*y*	*z*	$B_{eq}{}^a$
Cl(1)	0.2667(2)	−0.0220(1)	−0.1712(3)	3.18(6)
S(1)	0.3660(2)	0.2980(1)	0.3135(3)	2.79(6)
S(2)	0.4195(2)	0.1945(2)	−0.0556(3)	2.87(6)
P(1)	0.5638(2)	0.2616(2)	0.2444(3)	2.39(6)
P(2)	0.2175(2)	0.2295(2)	0.0540(3)	2.83(6)
N(1)	0.4611(5)	0.3384(4)	0.2491(8)	2.4(2)
N(2)	0.5272(4)	0.1774(4)	0.1153(7)	2.6(2)
N(3)	0.3190(5)	0.1577(4)	0.0126(8)	2.9(2)
N(4)	0.2555(5)	0.3171(4)	0.1606(8)	3.0(2)
C(1)	0.6322(6)	0.2050(6)	0.4423(10)	2.7(2)
C(2)	0.7140(7)	0.2426(6)	0.5552(11)	3.5(2)
C(3)	0.7503(8)	0.2112(7)	0.7206(12)	5.6(3)
C(4)	0.7067(10)	0.1416(8)	0.7756(12)	6.2(4)
C(5)	0.6256(9)	0.1015(6)	0.6642(13)	5.3(3)
C(6)	0.5885(7)	0.1328(6)	0.4985(11)	4.1(3)
C(7)	0.6581(7)	0.3225(6)	0.1804(10)	2.7(2)
C(8)	0.7607(6)	0.2776(5)	0.1781(10)	3.3(2)
C(9)	0.8323(7)	0.3239(6)	0.1232(11)	3.8(3)
C(10)	0.8007(8)	0.4155(7)	0.0728(11)	4.3(3)
C(11)	0.6986(8)	0.4617(6)	0.0705(12)	4.4(3)
C(12)	0.6273(6)	0.4153(6)	0.1256(10)	3.2(2)
C(13)	0.1188(6)	0.2806(6)	−0.1341(11)	2.9(2)
C(14)	0.0947(6)	0.2277(6)	−0.2742(11)	3.2(2)
C(15)	0.0177(7)	0.2662(7)	−0.4201(11)	4.3(3)
C(16)	−0.0334(7)	0.3557(7)	−0.4214(12)	4.6(3)
C(17)	−0.0070(7)	0.4093(6)	−0.2841(12)	4.4(3)
C(18)	0.0674(7)	0.3713(6)	−0.1376(11)	3.8(2)
C(19)	0.1511(7)	0.1546(5)	0.1499(10)	2.8(2)
C(20)	0.0472(7)	0.1358(6)	0.0727(11)	4.0(3)
C(21)	−0.0034(8)	0.0788(7)	0.1527(13)	5.4(3)
C(22)	0.0496(9)	0.0416(6)	0.3074(14)	5.3(3)
C(23)	0.1544(9)	0.0592(7)	0.3846(11)	5.0(3)
C(24)	0.2027(7)	0.1148(6)	0.3058(12)	4.2(3)
C(25)	0.3375(6)	0.3855(6)	0.4624(10)	3.0(2)
C(26)	0.4403(7)	0.3733(6)	0.6076(11)	5.0(3)
C(27)	0.3123(7)	0.4811(6)	0.3805(11)	4.6(3)
C(28)	0.2406(7)	0.3601(6)	0.5160(11)	5.2(3)

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

Table 5. Final Fractional Coordinates (×10^4) and Equivalent Isotropic Temperature Factors B_{eq} (Å^2 × 10^3) with Esd's in Parentheses for $Ph_4P_2N_4(SPh)(SBr)$

atom	*x*	*y*	*z*	B_{eq}
Br(1)	0.4863(2)	0.0407(1)	0.9776(2)	3.8(1)
S(1)	0.4910(4)	0.1846(2)	1.0129(4)	2.3(3)
S(2)	0.7640(4)	0.1551(3)	1.1072(5)	1.9(3)
P(1)	0.5926(4)	0.1553(3)	1.2281(5)	1.6(3)
P(2)	0.6756(4)	0.2315(3)	0.9238(4)	1.7(3)
N(1)	0.5125(11)	0.1879(7)	1.1432(11)	1.4(3)
N(2)	0.6792(11)	0.1120(9)	1.1721(13)	2.3(3)
N(3)	0.7314(10)	0.2337(7)	1.0412(12)	1.8(3)
N(4)	0.5649(10)	0.2114(8)	0.9264(13)	2.1(4)
C(1)	0.5387(13)	0.0825(10)	1.3135(16)	2.1(5)
C(2)	0.4422(14)	0.0901(11)	1.3404(17)	2.4(5)
C(3)	0.4039(14)	0.0346(13)	1.4106(17)	3.9(5)
C(4)	0.4535(15)	−0.0285(12)	1.4499(19)	3.9(6)
C(5)	0.5455(14)	−0.0302(12)	1.4244(19)	3.5(5)
C(6)	0.5903(13)	0.0231(11)	1.3563(16)	2.4(5)
C(7)	0.6186(13)	0.2360(10)	1.3233(16)	1.7(4)
C(8)	0.6606(13)	0.2206(11)	1.4299(16)	2.6(5)
C(9)	0.6847(12)	0.2836(9)	1.4994(16)	2.2(4)
C(10)	0.6611(13)	0.3554(11)	1.4641(18)	3.4(5)
C(11)	0.6155(14)	0.3699(11)	1.3602(18)	2.8(5)
C(12)	0.5946(13)	0.3076(11)	1.2870(17)	2.3(5)
C(13)	0.6814(12)	0.3259(10)	0.8697(15)	1.5(4)
C(14)	0.7514(13)	0.3747(10)	0.9082(16)	2.3(5)
C(15)	0.7581(16)	0.4482(12)	0.8626(18)	4.3(6)
C(16)	0.6912(15)	0.4729(12)	0.7871(18)	4.0(6)
C(17)	0.6230(15)	0.4290(12)	0.7522(18)	3.7(6)
C(18)	0.6171(14)	0.3523(12)	0.7942(17)	2.7(5)
C(19)	0.7228(13)	0.1729(10)	0.8153(15)	2.0(4)
C(20)	0.8110(14)	0.1828(11)	0.7759(17)	2.4(5)
C(21)	0.8431(15)	0.1346(13)	0.6877(18)	3.6(6)
C(22)	0.7938(15)	0.0830(12)	0.6377(18)	3.8(6)
C(23)	0.7043(14)	0.0709(11)	0.6709(17)	3.0(5)
C(24)	0.6663(13)	0.1170(11)	0.7595(16)	2.3(5)
C(25)	0.8343(13)	0.1948(11)	1.2217(16)	2.0(4)
C(26)	0.8715(13)	0.1422(12)	1.2997(17)	2.5(5)
C(27)	0.9239(14)	0.1693(11)	1.3922(18)	3.6(5)
C(28)	0.9356(13)	0.2461(11)	1.4017(16)	2.8(5)
C(29)	0.9035(14)	0.2974(11)	1.3266(18)	3.0(5)
C(30)	0.8468(13)	0.2750(11)	1.2333(17)	2.9(5)

Cl_2 (M = Ti, Zr, Hf) with the lithium reagents $[Li(Ph_4P_2N_4S_2R)\text{-}THF]_2$ in deoxygenated THF produces complexes of the type $MCp_2Cl(Ph_4P_2N_4S_2R)$ cleanly and in 40–65% yields (eq 1). Attempts to replace the remaining Cl^- ligand in these complexes by a second $Ph_4P_2N_4S_2R^-$ anion were unsuccessful, presumably owing to steric restrictions.



(1)

2a, M = Zr, R = ᵗBu
2b, M = Zr, R = Me
2c, M = Zr, R = Ph
2d, M = Zr, R = CH_2PPh_2
2e, M = Hf, R = ᵗBu
2f, M = Hf, R = Me
2g, M = Hf, R = Ph
2h, M = Ti, R = ᵗBu
2i, M = Ti, R = Me
2j, M = Ti, R = Ph

The complexes **2a–j** are highly oxygen- and moisture-sensitive, and it is essential to use thoroughly dry solvents that have been purged with argon in order to avoid decomposition in solution. The Ti complexes are orange-red whereas the Zr and Hf compounds are all colorless.

Selected ^{31}P, ^{13}C, and ^1H NMR data for **2a–j** are collected in Table 1. The ^{31}P NMR spectra show two resonances in the regions 44–52 and 35–38 ppm for the heterocyclic PPh_2 groups. These resonances are both singlets with the exception of those for the Hf complexes **2f** and **2g**, which exhibit two doublets with a mutual four-bond ^{31}P–^{31}P coupling of *ca.* 3 Hz. In addition, both the ^{13}C and ^1H NMR spectra indicate that the Cp ligands in **2a–j** are in inequivalent environments. Thus the NMR data point directly to an unsymmetrical attachment of the $P_2N_4S_2$ ring to the metal in these complexes. Furthermore, the ^{31}P NMR resonances of toluene-d_8 solutions of **2a** remain sharp up to 100 °C, which would seem to preclude any fluxional behavior in solution.

X-ray Structure of $ZrCp_2Cl(Ph_4P_2N_4S_2{}^tBu)$ (2a). The bonding mode of the heterocyclic ring in **2a** has been established by X-ray crystallography. The molecular geometry and atomic numbering scheme are given in Figure 2, and pertinent bond lengths and bond angles are given in Table 6. The $Ph_4P_2N_4S_2{}^tBu^-$ ligand in **2a** is attached to zirconium via adjacent sulfur and nitrogen atoms of an NSN unit on the opposite side of the ring from the ᵗBu group. The three-membered metallacycle (zirconathiaaziridene) so formed has the dimensions *d*(Zr–S) = 2.634(2) Å, *d*(Zr–N) = 2.206(5) Å, and *d*(S–N) = 1.697(6) Å. The Zr–S distance is significantly longer than the value of 2.529(3) Å found for $ZrCp_2(PMe_3)(\eta^2\text{-}SCMeH)$.[31] The Zr–N distance is slightly longer than that reported for $CpCp^*Zr(NSO)_2$ [*d*(Zr–N) = 2.121(4) Å],[18] but falls within the range 2.105(4)–2.267(3) Å reported for Zr complexes in which an imino group is acting as

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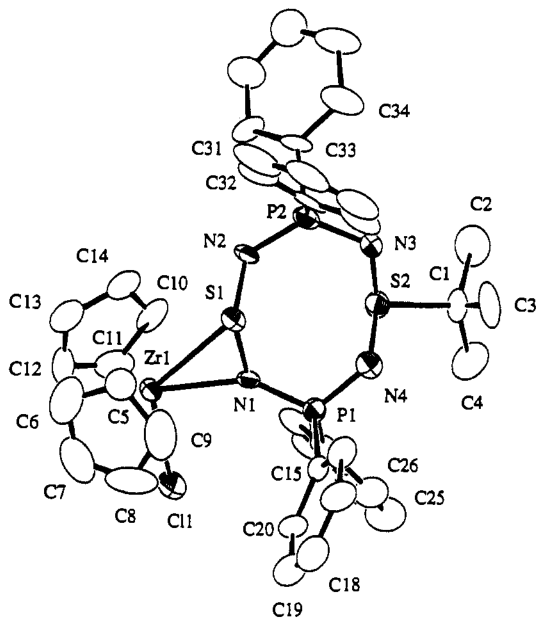

Figure 2. ORTEP drawing of $ZrCp_2Cl(Ph_4P_2N_4S_2{}^tBu)$ (**2a**) (50% probability ellipsoids). Hydrogen atoms are omitted for clarity.

Table 6. Selected Bond Distances (Å) and Bond Angles (deg) for $ZrCp_2Cl(Ph_4P_2N_4S_2{}^tBu)$ (**2a**)

	Bond Distances		
S(1)–Zr	2.634(2)	N(1)–P(1)	1.648(5)
N(1)–Zr	2.206(5)	N(4)–P(1)	1.603(6)
N(1)–S(1)	1.697(6)	N(2)–P(2)	1.615(6)
N(2)–S(1)	1.650(5)	N(3)–P(2)	1.600(7)
N(3)–S(2)	1.618(7)	Cl–Zr	2.530(2)
N(4)–S(2)	1.640(5)		
	Bond Angles		
N(1)–S(1)–Zr	56.4(2)	N(4)–P(1)–N(1)	115.6(3)
N(2)–S(1)–Zr	116.4(2)	N(3)–P(2)–N(2)	120.2(3)
S(1)–N(1)–Zr	83.8(2)	N(2)–S(1)–N(1)	109.5(3)
P(1)–N(1)–Zr	148.6(3)	N(4)–S(2)–N(3)	108.3(3)
S(1)–Zr–Cl	124.1(1)	P(1)–N(1)–S(1)	119.1(3)
N(1)Zr–Cl	84.4(1)	P(2)–N(2)–S(1)	116.1(3)
N(1)–Zr–S(1)	39.8(1)	P(2)–N(3)–S(2)	119.6(4)
		P(1)–N(4)–S(2)	116.3(3)

a one-electron donor.[32] Consistent with previous observations,[9,33] coordination of a metal to a $P_2N_4S_2$ ring induces a significant lengthening of the bonds involving the coordinated nitrogen atom. Thus the distances of 1.697(6) Å for N(1)–S(1) and of 1.648(5) Å for N(1)–P(1) are longer than the mean values of 1.636(7) and 1.606(7) Å, respectively, for the other S–N and P–N bonds in **2a**. The effect on the S–N bond lengths is not as dramatic, however, as that observed for $[Li(Ph_4P_2N_4S_2Ph)THF]_2$ for which distances of 1.72(1) and 1.755(9) Å are observed for the S–N bonds involving nitrogen atoms coordinated to lithium.[9]

Reactions of $ZrCp_2Cl(Ph_4P_2N_4S_2{}^tBu)$ with Electrophiles. The application of zirconocene derivatives to the synthesis of organic compounds via electrophilic cleavage of C–Zr[34] or N–Zr[35] bonds is well established. In a similar vein we have investigated reactions of **2a** with electrophilic reagents as a source of functionalized derivatives of the $P_2N_4S_2$ ring.

The reaction of **2a** with 2 molar equiv of HCl gas affords the diprotonated heterocycle $[Ph_4P_2N_4S_2{}^tBuH_2]Cl$ (**4**).[36] The ^{31}P NMR spectrum of **4** showed a singlet at 39.7 ppm, and the ^1H NMR spectrum exhibited a doublet at 10.3 ppm [$^2J(^{31}P-^1H)$ = 21 Hz], attributable to the NH groups, in addition to the expected resonances for the S^tBu and PPh_2 groups. An HMQC $^{15}N-^1H$ 2D NMR experiment provided additional NMR parameters for the NH groups of **4** [$\delta(^{15}N) = -309$ ppm, $^1J(^{15}N-^1H) = 86$ Hz]. The only structure for **4** consistent with these NMR data is one in which a hydrogen atom is attached to each of the geminal nitrogen atoms separated by the two-coordinate sulfur of the $P_2N_4S_2$ ring. This conclusion has been confirmed by the X-ray structural determination of **4** described below.

By contrast, the reaction of **2a** or **2c** with bromine produces the *S*-bromo derivatives $Ph_4P_2N_4(SR)(SBr)$ (**5a**, R = ^{t}Bu; **5b**, R = Ph) as extremely moisture-sensitive yellow-orange solids, which were characterized by ^1H and ^{31}P NMR spectra. The compound **5b** may also be obtained in excellent yields by the bromination of the lithium derivative $[Li(Ph_4P_2N_4S_2Ph)THF]_2$ and the X-ray structure of **5b** is described below. These *S*-bromo derivatives provide a good opportunity to investigate reactions of the $P_2N_4S_2$ ring that occur at the sulfur center, e.g. formation of the radicals $Ph_4P_2N_4S_2R^\bullet$ (cf. $Ph_6P_3N_4S^\bullet$).[37]

The reaction of **2a** with iodomethane results in the regiospecific methylation of the $P_2N_4S_2$ ring at sulfur to give $Ph_4P_2N_4(SMe)(S^tBu)$ (**6**) as an air stable, white crystalline solid, which was characterized by elemental analyses, ^1H, ^{13}C, and ^{31}P NMR spectroscopy, and mass spectroscopy. *S,S'*-Diorgano derivatives of the type $Ph_4P_2N_4S_2R_2$ in which the organic groups attached to the two sulfur atoms are the same can be prepared by (a) the reaction of $Li_2[Ph_4P_2N_4S_2]$ with 2 molar equiv of MeI[38] or (b) treatment of $Ph_2PN_2(SiMe_3)_3$ with 3 molar equiv of PhSCl.[39] The reaction of **2a** with MeI represents the first synthesis of an *S,S'*-diorgano derivative in which different organic groups are attached to the two sulfur atoms. However, inorganic heterocycles of this type are more conveniently obtained by the reaction of $[Li(Ph_4P_2N_4S_2R)THF]_2$ with alkyl iodides.[40]

Finally, we note in this section that the Ti and Hf derivatives react in a manner similar to **2a** with electrophiles, so that the reactions described above for **2a** can be viewed as applicable to all group 4 derivatives of the $Ph_4P_2N_4S_2R^-$ anion.

X-ray Structure of $[Ph_4P_2N_4S_2{}^tBuH_2]Cl$ (4). The molecular structure and atomic numbering scheme for **4** are shown in Figure 3. Selected bond lengths and bond angles are summarized in Table 7. The mean values of the S–N and P–N bond lengths involving the protonated nitrogen atoms, 1.685(6) and 1.656(6) Å, respectively, are significantly longer than the mean values of the other S–N and P–N bond lengths, which are 1.625(6) and 1.608(6) Å, respectively. The mean value of the endocyclic bond angles at the protonated nitrogens is 122.6(4)° compared to 115.6(4)° for the unprotonated nitrogens. As indicated in Figure 4, compound **4** exists as a dimer in the solid state as a result of hydrogen-bonding between NH protons and the Cl^- counterions. The H–Cl contacts are 2.23 and 2.44 Å, and the corresponding N–Cl distances are 3.096(6) and 3.141(6) Å. The $P_2N_4S_2$ ring in **4** has a long chair conformation with S(1) and S(2) lying out of the best plane formed by the two NPN units by *ca.* 0.88 and 1.12 Å, respectively.

X-ray Structure of $Ph_4P_2N_4(SPh)(SBr)$ (5b). The molecular

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(35) For example, see: Buchwald, S. L.; Wannamaker, M. W.; Watson, B T. *J. Am. Chem. Soc.* **1989**, *111*, 776.

(36) The reaction of **2a** with 1 molar equiv of HCl or the removal of HCl from **4** with DBU yields a product, believed to be $Ph_4P_2N_4S_2{}^tBuH$, which exhibits a broad ^{31}P NMR resonance at *ca.* 33 ppm. We have been unable to isolate a pure sample of this product. The treatment of the lithium derivatives $[Li(Ph_4P_2N_4S_2R)THF]_2$ with HCl also produces compounds of the type $Ph_4P_2N_4S_2RH$ (R = Me, ^{t}Bu, Ph). The full characterization of these products will be the subject of a future publication.

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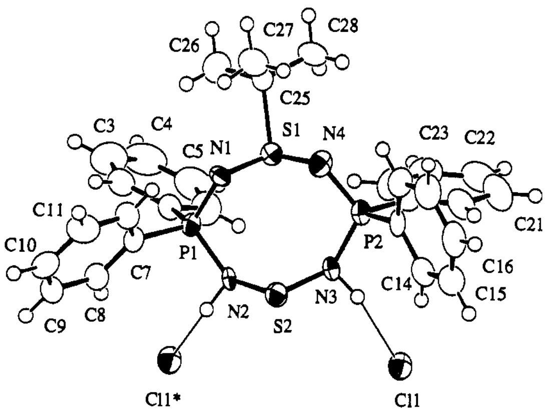

Figure 3. ORTEP drawing of $[Ph_4P_2N_4S_2{}^tBuH_2]Cl$ (**4**) (50% probability ellipsoids). The asterisk indicates a symmetry-related atom.

Table 7. Selected Bond Distances (Å) and Bond Angles (deg) for $[Ph_4P_2N_4S_2{}^tBuH_2]$ (**4**)

	Bond Distances		
S(1)–N(1)	1.638(6)	P(1)–N(1)	1.603(6)
S(1)–N(4)	1.613(6)	P(1)–N(2)	1.661(6)
S(2)–N(2)	1.677(6)	P(2)–N(3)	1.651(6)
S(2)–N(3)	1.694(6)	P(2)–N(4)	1.612(6)
	Bond Angles		
N(1)–S(1)–N(4)	106.2(3)	S(1)–N(1)–P(1)	113.9(4)
N(2)–S(2)–N(3)	102.6(3)	S(2)–N(2)–P(2)	122.6(4)
N(1)–P(1)–N(2)	112.1(3)	S(2)–N(3)–P(2)	122.7(4)
N(3)–P(2)–N(4)	114.2(3)	S(1)–N(4)–P(2)	117.3(4)

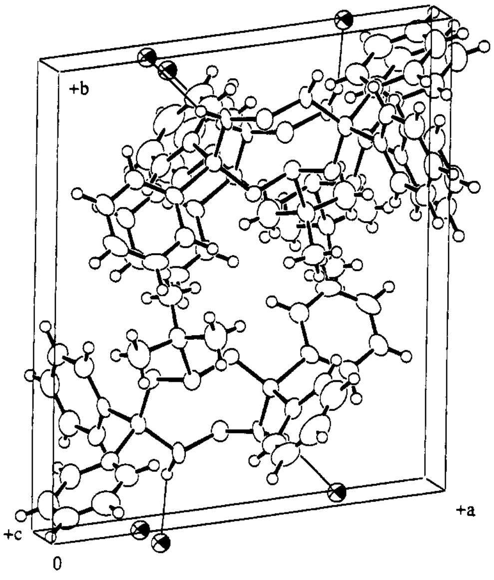

Figure 4. Packing diagram for $[Ph_4P_2N_4S_2{}^tBuH_2]Cl$ (**4**).

structure and atomic numbering scheme for **5b** are shown in Figure 5. Pertinent endocyclic bond distances and bond angles for **5b** are compared with the corresponding values for the related symmetrical derivatives $Ph_4P_2N_4S_2Ph_2$[39] and $Ph_4P_2N_4S_2Br_2$[41] in Table 8. The S–Br distance of 2.573(5) Å is significantly longer than the values of 2.454(7) and 2.440(8) Å reported for *d*(S–Br) in $Ph_4P_2N_4S_2Br_2$.[41] Long sulfur–halogen bonds are also a feature of the structures of the related six-membered rings $Ph_4P_2N_3SX$ (X = Cl, I).[42,43] They are indicative of significant ionic contributions to the S–X bond. In contrast to the long chair conformation observed for the $P_2N_4S_2$ ring in both $Ph_4P_2N_4S_2Ph_2$[39] and $Ph_4P_2N_4S_2Br_2$,[41] the eight-membered ring in **5b** has an "envelope" conformation with an almost planar N(1)S(1)N(4)P(2)N(3) unit and the other three atoms [S(2), N(2) and P(1)] lie well out of and on the same side of this plane. An interesting feature of the solid-state structure of **5b** is the face-to-face arrangement of the phenyl group on S(2) and one of the phenyl groups on P(1) (see Figure 5). The distance between the centroids of these two C_6H_5 rings is 3.53 Å. It is not clear whether this represents a π–π interaction or a packing effect.

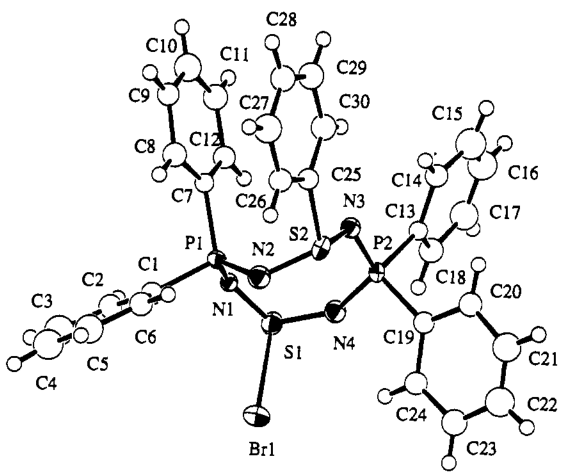

Figure 5. ORTEP drawing of $Ph_4P_2N_4(SPh)(SBr)$ (**5b**) (50% probability ellipsoids).

Table 8. Endocyclic Bond Distances (Å) and Bond Angles (deg) for $Ph_4P_2N_4(SPh)(SBr)$, $Ph_{P2}N_4(SPh)_2$, and $Ph_{P2}N_4(SBr)_2$

bond	$Ph_4P_2N_4(SPh)(SBr)$[a]	$Ph_4P_2N_4(SPh)_2$[b]	$Ph_4P_2N_4(SBr)_2$[c]
S(1)–N(1)	1.54(1)	1.620(4)	1.521(6)
S(1)–N(4)	1.54(1)	1.624(5)	1.532(6)
S(2)–N(2)	1.63(2)	1.620(4)	1.521(6)
S(2)–N(3)	1.65(1)	1.624(5)	1.531(6)
P(1)–N(1)	1.63(1)	1.622(5)	1.613(6)
P(1)–N(2)	1.61(1)	1.614(4)	1.629(6)
P(2)–N(3)	1.58(1)	1.622(5)	1.613(6)
P(2)–N(4)	1.65(1)	1.614(4)	1.629(6)

angle	$Ph_4P_2N_4(SPh)(SBr)$[a]	$Ph_{P2}N_4(SPh)_2$[b]	$Ph_{P2}N_4(SBr)_2$[c]
N(1)–S(1)–N(4)	118.7(9)	108.8(2)	116(1)
N(2)–S(2)–N(3)	112.7(8)	108.8(2)	112(1)
N(1)–P(1)–N(2)	119.2(8)	119.7(2)	118(1)
N(3)–P(2)–N(4)	119.4(8)	119.7(2)	121(1)
S(1)–N(1)–P(1)	136(1)	117.4(3)	132(1)
S(2)–N(2)–P(1)	124(1)	117.1(3)	137(1)
S(2)–N(3)–P(2)	121.4(9)	117.4(3)	144(1)
S(1)–N(4)–P(2)	139(1)	117.1(1)	145(1)

[a] This work. [b] Taken from ref 39. [c] Bond distances and bond angles taken from parts b and a of ref 41, respectively.

Attempted Reactions of $ZrCp_2Cl(Ph_4P_2N_4S_2{}^tBu)$ with Nucleophiles. In an attempt to replace the chloride ligand in **2a** by hydride or an alkyl group, reactions with the strong nucleophiles $Li[Et_3BH]$ and methyllithium were investigated. Surprisingly, the zirconium complex **2a** was unaffected by either of these reagents. Thus, in distinct contrast to the susceptibility of the Zr–N and Zr–S bonds in **2a** to cleavage by electrophiles, the Zr–Cl linkage appears to be effectively shielded from nucleophilic attack by the combined steric bulk of the heterocyclic PNS ligand and the two Cp groups. Presumably, the nitrogen and sulfur sites are more accessible to attack by external reagents than the metal center.

Conclusions. The first early transition metal complexes of $Ph_4P_2N_4S_2R^-$ anion have been prepared by metathetical reactions of the lithium derivatives of these anions with the metallocene dihalides MCp_2Cl_2 (M = Ti, Zr, Hf). The η^2-N,S bonding mode observed for the heterocyclic ligand in Group 4 metal complexes provides support for the notion that the $Ph_4P_2N_4S_2R^-$ anion is an

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adaptable ligand that can readily adjust its hapticity to accommodate the electronic and/or steric requirements of a specific metal center. Further investigations of the versatility of these cyclic S–N ligands in complexes with early transition metals, lanthanides and actinides are in progress. The group 4 complexes provide a useful, and sometimes preferable, alternative to the lithium derivatives $[Li(Ph_4P_2N_4S_2R)]_2$ for the regiospecific functionalization of the $P_2N_4S_2$ ring.

Acknowledgment. We thank Dr. D. D. McIntyre and Prof. H. J. Vogel for the HMQC spectrum of **4** and the NSERC (Canada) for financial support.

Supplementary Material Available: Text giving experimental details and listings of crystal data, bond lengths, bond angles, and anisotropic temperature factors for **2a**, **4**, and **5b** and listings of torsion angles for **4** and **5b** (43 pages). Ordering information is given on any masthead page.