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Inorganic Heterocyclic Bis(phosphines): Syntheses and Structures of a 1,2-Bis(diazasilaphosphetidino)ethane and Its Nickel, Molybdenum, and Rhodium Complexes

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Synthesis and characterization of a new, highly electron-rich, chelating bis(phosphine), based on the ethanediyl-linked inorganic heterocycle [$Me_2Si(\mu\text{-N}^tBu)_2P$], are reported. Treatment of nickel chloride with this bis(phosphine) afforded square-planar *cis*-{[$Me_2Si(\mu\text{-N}^tBu)_2PCH_2]_2NiCl_2$}, which features isometric nickel–chloride (2.2220(8) Å) and nickel–phosphorus (2.1572(8) Å) bonds. The ligand reacted with *cis*-[$(\text{piperidine})_2Mo(CO)_4$] to form colorless *cis*-{[$Me_2Si(\mu\text{-N}^tBu)_2PCH_2]_2Mo(CO)_4$}, which has distorted octahedral geometry and long Mo–P bonds (2.5461(18) Å). Because of its potential applications in hydrogenation catalysis *cis*-{[$Me_2Si(\mu\text{-N}^tBu)_2PCH_2]_2Rh(COD)$}$BF_4$ was synthesized. This square-planar, cationic rhodium(I) complex, having symmetrical Rh–P (2.250(2) Å) and Rh–C (2.305(6) Å) bonds, is structurally related to bis(phospholano)- and bis(phosphetano)rhodium species.

Introduction

Bis(phosphines) are important ancillary ligands in catalytic and stoichiometric reactions[1−4] because they combine the electronic and steric tunability of phosphines with the stability-imparting properties of chelating ligands. This utility has created a sustained academic and industrial interest in the design and synthesis of these molecules, which is currently centered on their role as chiral auxiliaries.[5−15] Particularly effective for this purpose are cyclic, C_2-symmetric bis(phosphines),[16−18] such as the bis(phosphetanes) (A)[19−26] and the bis(phospholanes) (B), which are shown in Chart 1.[27−32] Although the main reason for the adoption of cyclic structures was to create chirality, an added advantage of heterocycles is their greater compactness and electron-richness over conventional C_2-symmetric bis(phosphines), most of which bear aryl groups. The desirable ligand properties of heterocyclic phosphorus−nitrogen molecules

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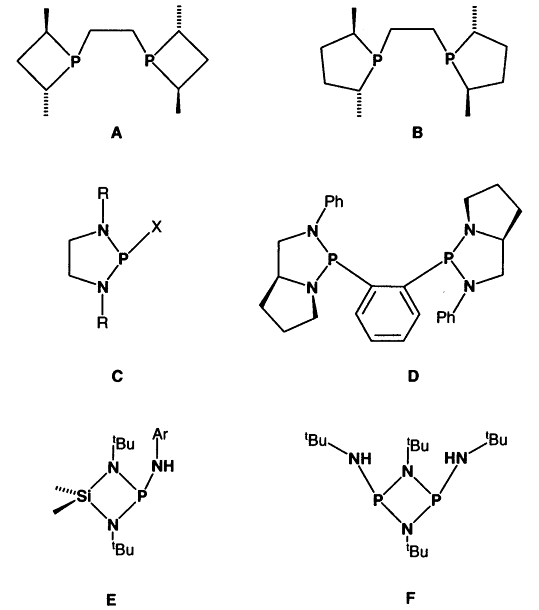
Chart 1



were first demonstrated by the groups of Parry and Paine, who developed the coordination chemistry of diazaphospholidines (C) as cationic and neutral P-donor molecules.[33−39] Modified versions of these organic P−N heterocycles have been reported recently, and complexes bearing C_2-symmetric ligands (D) have shown outstanding enantioselectivities.[40−44]

Cyclic phosphines are not limited to organic ring compounds, of course, and we wondered if inorganic analogues might also be useful electron-rich spectator ligands. There are numerous inorganic heterocyclic phosphines with structures similar to those of their organic counterparts. In diazasilaphosphetidines (E)[45−48] and cyclodiphosphazanes (F),[49−59] for example, one or two phosphorus(III) centers, respectively, are incorporated in four-membered heterocycles. Because of their ease of synthesis, the latter have been previously investigated as P-donor ligands both as cyclodiphosphazanes and as amido-tethered bis(cyclodiphosphazanes) but with limited success.[60−65] In our ongoing work on diazasilaphosphetidines as N-donor ligands, we discovered that the silicon−phosphorus heterocycles (E) are much better phosphorus-donors than the diphosphorus heterocycles (F). By tethering two diazasilaphosphetidines with an alkyl bridge we hoped to mimic the structures of the organic heterocyclic bis(phosphines) A, B, and D. Below we describe the synthesis of a 1,2-bis(diazasilaphosphetidino)ethane (hereafter bdpe or **2**), its solid-state structure, and the syntheses and solid-state structures of three transition metal complexes of this ligand.

Results

Most chelating bis(phosphines) are linked by ethanediyl or *o*-phenylene bridges[1−4] because such linkers yield stable five-membered chelates. To synthesize an analogous inorganic heterocyclic bis(phosphine), we treated 1,2-bis(dichlorophosphino)ethane with 2 equiv of the transfer reagent diazasilaplumbetidine (Scheme 1).[66] This unoptimized one-step reaction produced **2** in only a 28% yield, but synthesis and workup were easier than those for bis(phosphetanes) and bis(phospholanes).[18−32] Both the electronic and the steric properties of **2** can be further modified by using smaller alkyl or aryl N-substituents. Such substituent changes, which are entirely modular, allow the synthesis of bis(phosphines) that are as compact as the popular bis(phosphetanes) (A) and bis(phospholanes) (B). If two different N-substituents are used, the resulting bis(diazasilaphosphetidines) are chiral at phosphorus, and careful choice of reaction conditions may even allow the synthesis of C_2-symmetric versions of **2**.

The bis(phosphine) **2** is a colorless, crystalline compound that is highly soluble in all conventional organic solvents. In the solid state it is stable to moisture and oxygen for short periods of time, but it is readily oxidized and hydrolyzed in solution, thus ruling out the use of protic solvents. It is,

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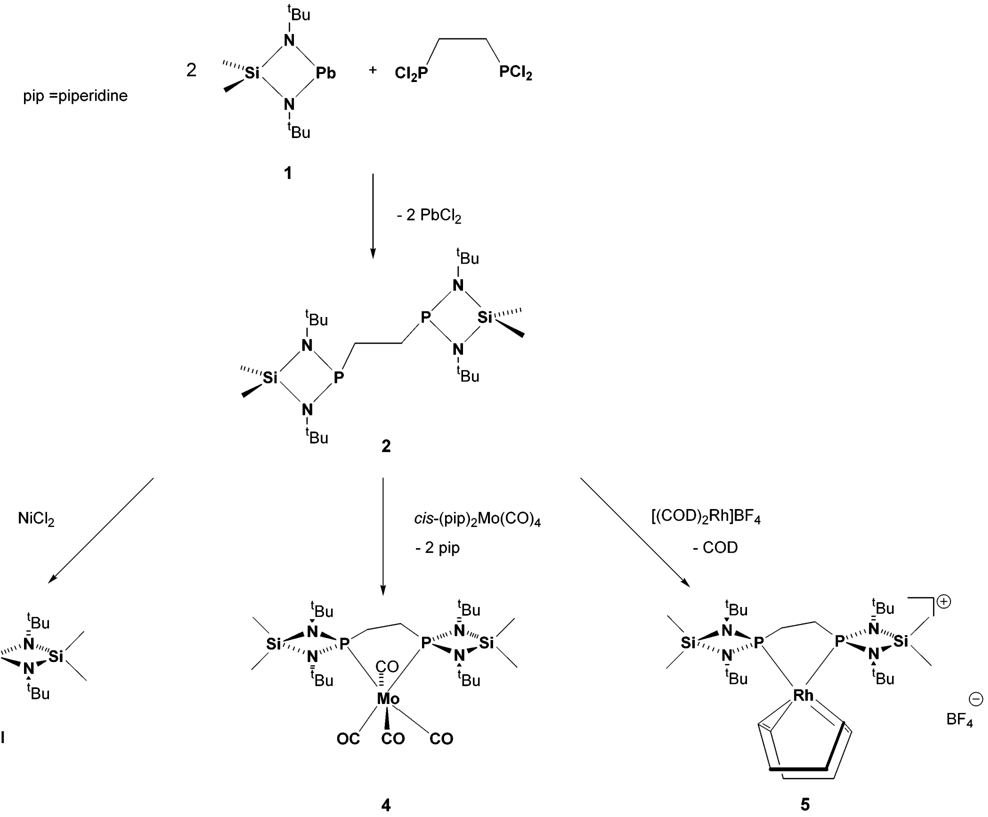
Scheme 1



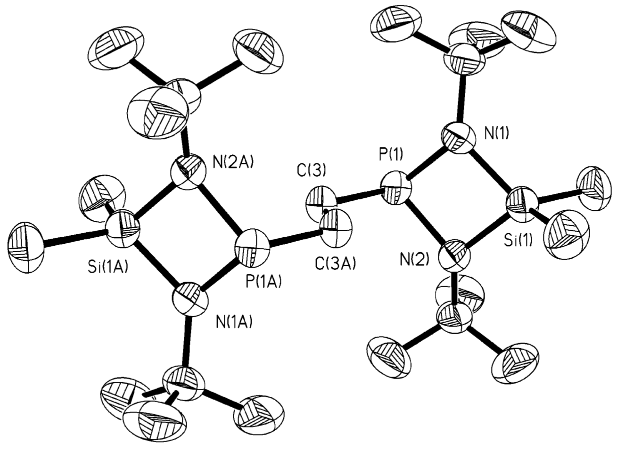


Figure 1. Solid-state structure (35% probability thermal ellipsoids) and partial labeling scheme of **2**. The hydrogen atoms are not shown.

however, thermally stable for 2 days in refluxing THF as the synthesis of **3** proves (vide infra). The structure of the 1,2-bis(diazasilaphosphetidino)ethane was initially characterized by multinuclear NMR techniques. Thus, for example, the ^1H NMR spectrum displayed a three-signal pattern consisting of singlets for the *tert*-butyl and methyl groups and a pseudo-triplet for the ethanediyl-hydrogen atoms. One singlet each was observed in the ^{29}Si and ^{31}P NMR spectra, with chemical shifts indicative of four-coordinate silicon and three-coordinate phosphorus(III).

A single-crystal X-ray analysis confirmed the simple NMR spectra because it showed **2** to be the centrosymmetric molecule depicted in Figure 1. Crystal data and selected bond parameters of this compound are collected in Tables 1 and 2, respectively. The molecule is composed of two planar heterocycles, whose pyramidalized phosphorus atoms are connected by an ethanediyl bridge. Both N−P−N angles are comparatively narrow (84.71(8)°) but less so than the acute C−P−C angles in structurally characterized phosphetanes,[21] which tend to be less than 80°. The exocyclic N−P−C bond angles (104.74(9)°) are almost identical to those of bis(phosphetanes) and bis(phospholanes). The highly pyramidalized phosphorus atom ($\sum_{angles} = 294°$) reveals considerable p character in the endocyclic bonds and consequently high s character in its lone pair of electrons. Both the slightly asymmetrical P−N bonds (1.7278(16) Å) and the symmetrical Si−N bonds (1.7139(17) Å) have similar lengths as those in related diazasilaphosphetidines.[45−48]

To assess the structural and electronic properties of bdpe, we synthesized nickel(II) and molybdenum(0) derivatives for which bis(diphenylphosphino)ethane (hereafter dppe) complexes are known. While **2** bears much closer resemblance to the cyclic organic phosphines A and B, very limited structural information on metal complexes of these ligands, other than rhodium, is available. By contrast, numerous structural and spectroscopic studies of dppe complexes have appeared, and this, together with the intermediacy of dppe in Tolman's steric and electronic parameters,[67,68] made it a good candidate for comparative studies.

Treatment of $NiCl_2$ with **2** in boiling THF proceeded slowly (Scheme 1), but it furnished, upon cooling, orange plates in good yields. The color of the compound suggested

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Table 1. Crystallographic Data for **2**, **3**·THF, **4**, and **5**

	2	**3**·THF	**4**	**5**
chemical formula	$C_{22}H_{52}N_4P_2Si_2$	$C_{52}H_{120}Cl_4N_8Ni_2O_2P_4Si_4$	$C_{26}H_{52}MoN_4O_4P_2Si_2$	$C_{30}H_{64}BF_4N_4P_2RhSi_2$
fw	490.80	1385.02	698.78	788.60
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$Pna2_1$ (No. 33)
T, °C	19	20	20	20
a, Å	12.5368(16)	13.3924(15)	8.880(2)	21.064(2)
b, Å	10.4604(17)	15.5672(18)	23.187(4)	18.3790(10)
c, Å	12.6864(14)	19.414(2)	18.009(3)	10.068(3)
α, deg		72.680(2)		
β, deg	114.147(7)	93.964(18)	92.724(14)	
γ, deg		82.222(2)		
V, Å^3	1518.1(4)	3727.8(7)	3703.9(13)	3897.7(12)
Z	2	2	4	4
ρ_{calcd}, g cm^{-3}	1.074	1.234	1.253	1.344
λ, Å	0.710 73	0.710 73	0.710 73	0.710 73
μ, cm^{-1}	2.38	8.38	5.38	6.27
$R(F)$,^{a} $I > 2\sigma(I)$	0.0406	0.0543	0.0517	0.0395
$R_w(F^2)$,^{b} all data	0.1264	0.1449	0.1545	0.1062

^{a} $R = \sum|F_o - F_c|/\sum|F_o|$. ^{b} $R_w = \{[\sum w(F_o^2 - F_c)^2]/[\sum w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o)^2 + (xP)^2 + yP]$ where $P = (F_o^2 + 2F_c^2)/3$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **2**

P−C	1.866(2)	N−P−N(av)	84.71(8)
P−N(av)	1.7278(16)	P−N−Si(av)	94.28(8)
Si−N(av)	1.7139(17)	N−Si−N(av)	85.56(8)
Si−C(av)	1.872(2)	C−Si−C(av)	108.75(12)
		N−P−C(av)	104.74(9)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **3**·THF and (dppe)$NiCl_2$

	3·THF	(dppe)$NiCl_2$
Bond Lengths		
Ni−P(av)	2.1572(8)	2.151(2)
Ni−Cl(av)	2.2220(8)	2.200(2)
P−N(av)	1.688(3)	
P−C(bridg, av)	1.843(3)	1.835(5)
P−Ph(av)		1.809(5)
Si−N(av)	1.742(3)	
Si−Me(av)	1.857(4)	
Bond Angles		
Cl−Ni−Cl(av)	93.21(3)	95.47(6)
P−Ni−P(av)	89.82(3)	86.93(6)
P−Ni−Cl(cis, av)	88.52(3)	88.84(6)
P−Ni−Cl(trans, av)	177.53(4)	175.12(6)
Ph−P−Ph(av)		106.4(2)
N−P−N(av)	86.33(12)	
N(or Ph)−P−C(av)	108.55(13)	104.9(2)
P−N−Si(av)	95.24(12)	
N−Si−N(av)	83.07(12)	
Me−Si−Me(av)	110.03(19)	

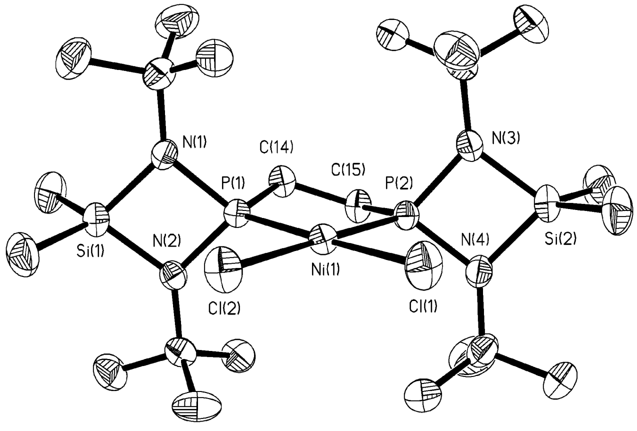

Figure 2. Solid-state structure of one of the crystallographically independent molecules of **3**. The 35% probability thermal ellipsoids are drawn. The solvent molecule (THF) and the hydrogen atoms are not shown.

a square-planar complex, and this was confirmed by the appearance of a sharp singlet in the ^{31}P NMR spectrum at 157.6 δ and downfield of free ligand. The ^1H NMR spectrum showed a four-peak pattern consisting of two singlets for the diastereotopic $SiMe_2$ groups, one singlet for the equivalent N^tBu groups, and one doublet for the ethanediyl bridge.

A single-crystal X-ray diffraction analysis, selected data of which are listed in Tables 1 and 3, was undertaken on a THF solvate of this compound, namely, *cis*-[(bdpe)$NiCl_2$]·THF = **3**·THF. This nickel complex crystallizes with two independent but isostructural molecules, one of which is shown in Figure 2. The perfectly planar ($\sum_{angles} = 360°$) cis-substituted nickel atom has symmetrical Ni−Cl (2.2220(8) Å) and Ni−P (2.1535(3) Å) bonds, which enclose angles ranging from 88.52 to 93.21°. While the latter bonds are almost identical in length to those in *cis*-[(dppe)$NiCl_2$],[69,70] the Ni−Cl bonds are 0.028(2) Å longer than in the dppe analogue. The P−N and Si−N bonds of the planar diazasilaphosphetidine rings are shorter (0.040(3) Å) and longer (0.028(3) Å), respectively, than those in free **2**, suggesting a polarization of the N lone-pair electrons toward the phosphorus atom and thus enhanced P−N bonding.

Although the successful synthesis and structure of **3**·THF showed that **2** might be a useful ligand, it was difficult to obtain much information on the electronic properties of the bis(phosphine) from this complex. We therefore synthesized an $Mo(CO)_4$ derivative because this metal fragment has served as a benchmark for exploring the donor/acceptor properties of phosphines.[71−78] Addition of **2** to a solution of

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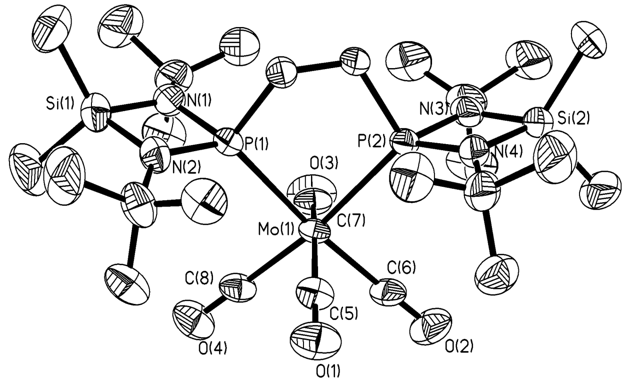


Figure 3. Solid-state structure and partial labeling scheme of **4** (35% probability thermal ellipsoids).

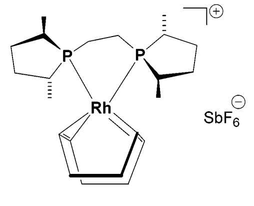
Table 4. Selected Bond Lengths (Å) and Angles (deg) for **4** and (dppe)Mo(CO)$_4$

	4	(dppe)Mo(CO)$_4$
Bond Lengths		
Mo−P(av)	2.5461(18)	2.497(2)
Mo−CO(ax, av)	2.019(3)	2.041(9)
Mo−CO(eq, av)	1.990(3)	1.986(8)
P−Ph(av)		1.838(4)
P−C(av)	1.850(1)	1.845(7)
P−N(av)	1.718(6)	
Si−N(av)	1.723(7)	
Si−Me(av)	1.863(2)	
Bond Angles		
P−Mo−P	83.19(6)	80.2(1)
P−Mo−CO(cis, eq, av)	89.5(7)	94.7(2)
P−Mo−CO(trans, eq, av)	172.1(7)	173.9(2)
P−Mo−CO(ax, av)	96.8(2)	88.9(1)
Ph−P−Ph(av)		101.9(2)
N−P−N(av)	83.7(8)	
N(or Ph)−P−C(av)	105.2(3)	104.6(3)
P−N−Si(av)	96.4(3)	
N−Si−N(av)	83.5(3)	
Me−Si−Me(av)	109.6(5)	

cis-[(piperidine)$_2$Mo(CO)$_4$][79] produced a colorless solid (**4**) in good yield. The ^{13}C NMR spectrum, showing a doublet of doublets for the equatorial carbonyls (219.7 δ, $J_{PC} = 31.6$, 10.2 Hz) and one triplet (217.2 δ, $J_{PC} = 8.9$ Hz) for the axial carbonyl ligands, was characteristic of a cis-chelated complex. The structure assignment was supported by a solution-phase IR spectrum, which displayed three bands at 2008, 1918, and 1894 cm^{-1} for the two A$_1$ and the unresolved B$_1$ and B$_2$ modes, respectively. In comparative studies on the electronic properties of *cis*-[(L)$_2$Mo(CO)$_4$] species, the A$_1$ mode of higher energy has been used, and we will adhere to this convention.[71−78] The value of 2008 cm^{-1} for **4** is 32 and 12 cm^{-1} lower than those of the corresponding bis(diphenylphosphino)ethane and bis(dimethylphosphino)ethane derivatives, respectively, and indicative of a very electron-rich phosphine.[77]

We studied **4** by single-crystal X-ray analysis to ascertain if this apparent electron-richness of **2** was also reflected in the structure of this complex. Relevant data collection and bond parameters are listed in Tables 1 and 4, respectively. As the thermal ellipsoid plot in Figure 3 shows, **4** is an octahedral, *cis*-bis(phosphine) complex. The disposition of the heterocyclic rings—being perpendicular to the equatorial plane of the complex—forces the *tert*-butyl groups to be parallel to the axial carbonyl ligands. Repulsive interactions between these axial carbonyl groups and the bulky *tert*-butyl substituents have closed the CO−Mo−CO angle to 161.8°. All equatorial bond angles, however, are very close to 90°, suggesting little or no steric crowding by the bdpe ligand in this plane. The molybdenum−phosphorus bonds (2.5461(18) Å) are among the longest reported; they are significantly longer than those in *cis*-[(dppe)Mo(CO)$_4$] (2.497(2) Å) and in *cis*-{[P(N(H)Ph)$_2$]$_2$NPh]Mo(CO)$_4$} (2.48(1) Å). By contrast, the molybdenum−carbon bonds, especially those in the equatorial plane, are comparatively short (average 1.990(3) Å), cf. Mo−C = 2.06(1) Å in Mo(CO)$_6$.[80] There are almost no discernible differences between the P−N (1.718(6) Å) and the Si−N (1.723(7) Å) bonds of the diazasilaphosphetidine moieties of **4** and those of free ligand.

Chart 2



G

Bis(phosphino) complexes of rhodium are important hydrogenation and hydroformylation catalysts,[81] and for this reason we synthesized a rhodium(I) analogue of **2** that structurally resembles the highly versatile hydrogenation catalyst {[(*R*,*R*)-Me-bpe]Rh(COD)}SbF$_6$ (G, Chart 2) reported by Burk et al.[27] When solutions of [(COD)$_2$Rh]$^+$ salts were treated with **2** (Scheme 1), they slowly turned orange-red. NMR spectra obtained on the red crystalline products were consistent with a bis(phosphino)cyclooctadiene rhodium complex. Thus, only one signal, with very strong (201 Hz) rhodium−phosphorus spin−spin coupling, appeared in the ^{31}P NMR spectrum. This value is more than 50 Hz larger than that of G and related bis(phospholane) and bis(phosphetane) complexes and one of the largest, if not the largest, Rh(I)−P coupling constant reported for such a complex.[82,83]

To compare the bond parameters of **5** directly with those of *cis*-{[(*R*,*R*)-Me-bpe]Rh(COD)}SbF$_6$, we did an X-ray analysis, whose crystal data and selected bond parameters are collected in Tables 1 and 5, respectively. Figure 4 shows two perspective views of square-planar **5**; one perpendicular and one parallel to the coordination plane. The high symmetry of this molecule is reflected in almost isometric Rh−P (average 2.2493(15) Å) and Rh−C (average 2.305(6) Å) bonds. While the Rh−P bonds are slightly (0.020(2) Å) shorter than those in {[(R,R)-Me-bpe]Rh(COD)]}SbF$_6$,[27] the

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[79] Strohmeier, W.; Gerlach, K.; v. Hobe, D. *Chem. Ber.* **1961**, *94*, 164.

(80) Brockway, L. O.; Ewens, R. V. G.; Lister, M. W. *Trans. Faraday Soc.* **1938**, *34*, 1350.

(81) Dickson, R. S. *Homogeneous Catalysis with Compounds of Rhodium and Iridium*; Kluwer Academic: Hingham, MA, 1985.

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(83) Parish, R. V. *NMR, NQR, EPR and Mössbauer Spectroscopy in Inorganic Chemistry*; Ellis-Horwood: Chichester, 1990.

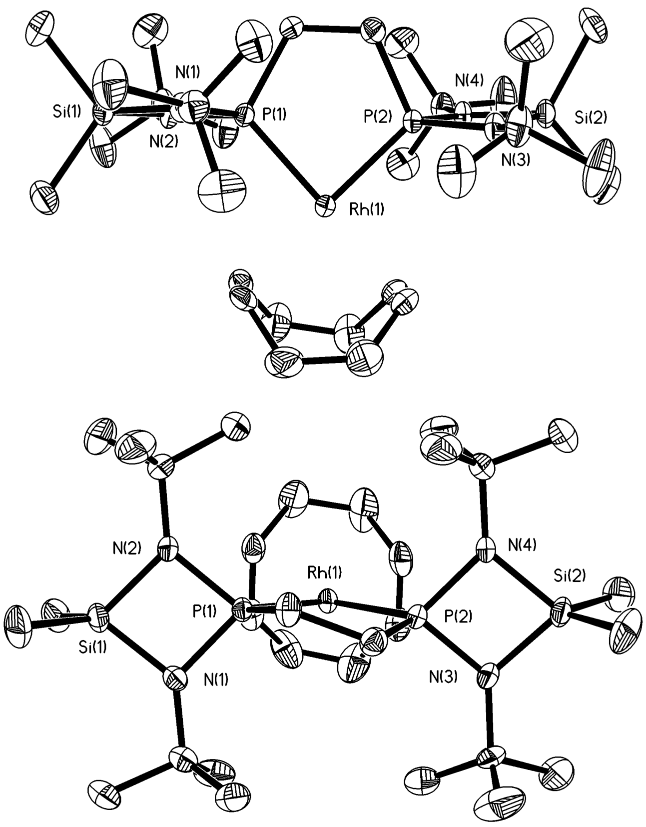

Figure 4. Views of the solid-state structure (35% probability thermal ellipsoids) of **5** from above (top) and within (bottom) the coordination plane. The tetrafluoroborate counterion and the hydrogen atoms are not shown.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for **5** and [(*R*,*R*)-Me-BPE)Rh(COD)]SbF_6

	5	[(*R*,*R*)-Me-BPE)Rh(COD)]SbF_6
	Bond Lengths	
Rh−P(1)	2.2466(15)	2.258(2)
Rh−P(2)	2.2521(14)	2.276(2)
Rh−C(COD)	2.303(6)	2.209(7)
Rh−C(COD)	2.302(6)	2.268(6)
Rh−C(COD)	2.312(7)	2.211(6)
Rh−C(COD)	2.304(7)	2.273(3)
P−N(av)	1.703(5)	
P−C(av)	1.849(6)	
Si−N(av)	1.743(6)	
Si−C(av)	1.859(8)	
	Bond Angles	
P−Rh−P	87.40(5)	83.25(6)
N−P−N	85.4(3)	
P−N−Si	95.7(3)	
N−Si−N	83.0(2)	

Rh−C bonds are 0.065(6) Å longer. The shorter rhodium−phosphorus bonds can be rationalized in terms of the greater electron-richness of **2**, while the long rhodium−carbon bonds may be the result of increased steric repulsion between the bis(phosphine) and the cyclooctadiene moieties. It is revealing that the Rh−C bonds in the chiral complex form two distinct groups, one long and one short, because of the two sets of diastereotopic methyl substituents on the phospholane ring. By contrast, in achiral **5** all Rh−C bonds are equidistant. The P−N and Si−N bonds in the ligand moieties are 1.703(5) Å and 1.743(6) Å long, revealing a similar polarization of the ligand as had been observed for **3**. The P−Rh−P bite angle (87.40(5)°) enclosed by **2** is somewhat larger than that in the bis(phospholano)rhodium complex G (83.25(6)°).

Discussion

Phosphines are outstanding spectator ligands because they can be sterically and electronically modified. This propensity for incremental tuning is crucially important in catalysis, where even minor changes in the electronic and steric properties of these ancillary ligands can significantly alter rates and product distribution of the reactions catalyzed by their complexes. Although, in principle, size and donor/acceptor properties of tertiary phosphines can be altered independently of each other, many electron-rich phosphines are bulky, while electron-poor phosphines tend to be compact.[67,68]

The success of arylphosphines and bis(diarylphosphines) suggests that electron-withdrawing phosphines have inherent advantages in most homogeneously catalyzed reactions. There are a number of catalytic processes, however (the hydrogenation of aldehydes and ketones being particularly noteworthy),[84−86] in which trialkylphosphine-ligated rhodium complexes exhibit superior performance.

It would, therefore, be desirable to have available compact but electron-rich bis(phosphines). Recent studies by Woollins et al. have shown that mixed dialkyl/aminophosphines, specifically piperazine-bridged bis(diisopropylphosphines), are excellent donors.[87−89] On the basis of these findings, we set out to develop an alkyl-tethered bis(diazasilaphosphetidino)ethane and to evaluate its potential as a chelating bis(phosphine) ligand.

Inorganic phosphorus−nitrogen heterocycles have previously been investigated as bis(phosphines) but with mixed success.[90] Some time ago, Norman reported the chelation of $Mo(CO)_4$ by anilido-tethered bis(anilido)phosphines (H) and cyclodiphosphazanes (I) (Chart 3).[60−62] More recently, Krishnamurthy used cyclodiphosphazanes as P-donor ligands to molybdenum tetracarbonyl and isolated species such as J.[63−65] The Mo−P bond lengths in the structurally characterized H and J, being 2.48(1) and 2.480(2) Å, respectively, are similar to those of *cis*-[(dppe)Mo(CO)$_4$] (2.497(2) Å),[68] but the coordination chemistry of these heterocycles as P-donors turned out to be more complex than had been anticipated. This was partly so because cyclodiphosph(III)azanes can undergo cis−trans isomerism−properties that are undesirable in a spectator ligand−but more importantly because these

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[84] Fujitsu, H.; Matsumura, E.; Takeshita, K.; Mochida, I. *J. Chem. Soc., Perkin Trans.* **1981**, *1*, 2650.

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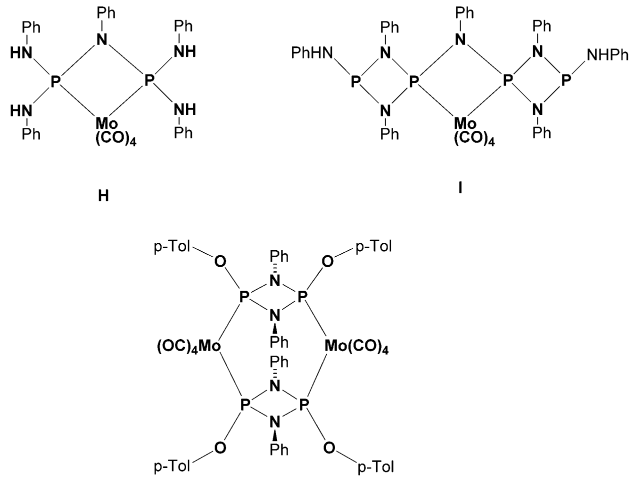
[90] An anilido-tethered bis(diazasilaphosphetidine) was reported to have been synthesized, but it was not fully characterized. See ref 60.

Chart 3

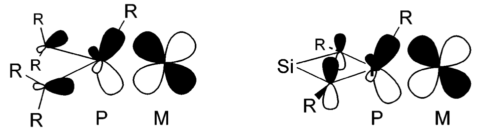


H

I

J

Chart 4



K

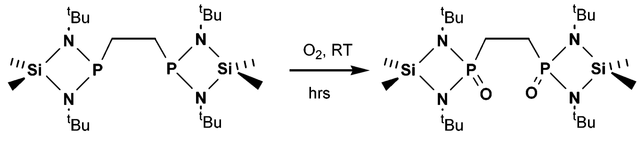
L

ligands had unspectacular donor properties. Thus, the high-energy $\nu_{CO}(A_1)$ bands of H, I, and *cis*-[(dppe)Mo(CO)$_4$] appear at 2036, 2038, and 2040 cm^{-1}, respectively, suggesting that bis(cyclodiphosphazanes) are no better donors than bis(diphenylphosphino)ethane.

These results can be understood in terms of the electronic structure of these heterocyclic phosphines. Aminophosphines are more electron-rich than the electronegativity of nitrogen might lead one to believe because the N-to-σ*(PR) π-donation competes with metal d-to-σ*(PR) π-back-donation for the empty σ*(PR) orbital (Chart 4).[91] Any structural modification that increases the intramolecular N-to-σ*(PR) flow should therefore increase the electron-richness of aminophosphines. In cyclic aminophosphines (L) these orbitals are better aligned than in acyclic ones (K), leading to a particularly strong N-to-P electron donation. The substitution of silicon for phosphorus in these heterocycles makes the ligand more resistant to ring opening, and the lesser electronegativity of silicon increases the donor properties of the remaining phosphorus atom. This explains both why diazasilaphosphetidines do not undergo ring-opening and why they are better donors than acyclic aminophosphines and cyclodiphosphazanes.

The greater electron-richness of diazasilaphosphetidines is impressively demonstrated by the increasing susceptibilities of the bis(phosphines) F, A, and **2** to oxidation. Thus, while the cyclodiphosphazane F is unaffected by dioxygen and the bis(phospholane) A requires weeks for the completion of this reaction, **2** is converted to the corresponding P(V) compound within hours at room temperature (Scheme 2).

Scheme 2



2

Ease of synthesis, structural similarities to bis(phosphetanes) and bis(phospholanes), and electron-richness thus distinguish 1,2-bis(diazasilaphosphetidino)ethanes from related, chelating, inorganic bis(phosphines). Ultimately, however, the utility of a ligand rests on its ease of use and its ability to stabilize a wide variety of transition metal ions. By synthesizing zero-, mono-, and divalent transition metal complexes of **2**, we intended to show that this bis(phosphine) fulfills the general requirements of a good ancillary ligand.

One might expect the electron-donating bdpe to be a better ligand than arylphosphines in the comparatively electron-poor, 16-electron complexes **3** and **5**. While the X-ray structural results did not prove this decisively, it was reassuring that the metal−phosphorus bonds of **3** and **5** are as short, or shorter, than those of analogous bis(diphenylphosphino)ethane and of bis(phospholano)ethane complexes. In both **3** and **5**, the metal−ligand bonds trans to bdpe are longer (in **5** significantly so) than those in the dppe and bis(phospholane) complexes. It is not possible to ascribe the bond lengthening in these square-planar complexes to a strong trans influence, because bdpe, being neither a good σ-donor nor a good π-acceptor, cannot exert a strong trans influence. Steric repulsion between the *tert*-butyl groups of the bdpe ligand and the ligands trans to them are more likely responsible for the elongated bonds.

We expected bdpe to bind comparatively weakly to the electron-rich Mo(CO)$_4$ fragment, and indeed, structural studies on **4** confirmed these assumptions. These data show unusually long Mo−P bonds and comparatively short M−CO bonds, suggesting that bdpe does not compete well with CO for electron density and is thus a very poor acceptor. The most conclusive information on the electronic properties of **2** comes from IR spectroscopy, which reveals the second-lowest $\nu_{CO}(A_1)$ band of any *cis*-[(P$_2$)Mo(CO)$_4$] complex studied to date, being surpassed only by that of the above-mentioned bis(diisopropylphosphino)piperazine.[77] It may be recalled that the $\nu_{CO}(A_1)$ modes in the corresponding IR spectra of bis(dimethylphosphino)ethane and phenylphosphetane appear at 2020 and 2222 cm^{-1}, respectively. Yet, even these values are significantly higher than the corresponding band of **4**, which appears at 2008 cm^{-1}, thereby further supporting the electron-richness of **2**.

Although electron-richness in phosphines is generally attributed to outstanding σ-donor properties, this explanation cannot be invoked for **2** because both the small endocyclic angles and the high Rh−P coupling constants imply lone-pair electrons with very high s character. We therefore assign the electron-richness of **2** to intramolecular N-to-P π-donation, which prevents effective metal-to-ligand back-donation.

In conclusion, the 1,2-bis(diazasilaphosphetidino)ethane **2** is a versatile and highly electron-rich, ancillary ligand. The

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(91) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 3rd ed.; Wiley-Interscience: New York, 2001.

ligand has a number of attractive features, namely, ease of synthesis, modular design, and compactness at phosphorus, that outweigh its sensitivity to moisture. The most promising application of bis(phosphines) of this type is as spectator ligands in homogeneous hydrogenation catalysis, particularly in enantioselective hydrogenations. This will require chiral, or better yet, C_2-symmetric versions of **2**. Synthetic pathways toward such ligands have been devised, and methods to resolve the enatiomers are currently being investigated.

Experimental Section

General Procedures. All experiments were performed under an atmosphere of purified nitrogen or argon, using standard Schlenk techniques. Solvents were dried and freed of molecular oxygen by distillation under an atmosphere of nitrogen from sodium or potassium benzophenone ketyl immediately before use. NMR spectra were recorded on a Bruker AVANCE-500 NMR spectrometer. The ^{1}H, ^{13}C, ^{29}Si, and ^{31}P NMR spectra are referenced relative to $C_6D_5\textit{H}$ (7.15 ppm) or $C\textit{H}DCl_2$ (5.32 ppm), $\textit{C}_6D_6$ (128.0 ppm) or $\textit{C}HDCl_2$ (54.00 ppm), TMS (0.0 ppm), and P(OEt)$_3$ (137.0 ppm), respectively. In all cases, positive chemical shift values indicate higher frequencies and downfield shifts. Melting points were obtained on a Mel-Temp apparatus and are uncorrected. Elemental analyses were performed by E and R Microanalytical Services, Parsipanny, NJ. The reagents 1,2-bis(dichlorophosphino)ethane, anhydrous NiCl$_2$, and [(COD)$_2$Rh]BF$_4$·nH$_2$O were purchased from Aldrich and used as received, while Me$_2$Si(μ-N^{t}Bu)$_2$Pb[66] and *cis*-[(piperidine)$_2$Mo(CO)$_4$][79] were synthesized by published procedures.

Syntheses. [Me$_2$Si(μ-N^{t}Bu)$_2$PCH$_2$]$_2$ = bdpe (2). A stirred, cold (0 °C) solution of 1,2-bis(dichlorophosphino)ethane (5.215 g, 22.50 mmol) in 35 mL of hexanes was treated dropwise with a solution of [Me$_2$Si(μ-N^{t}Bu)$_2$Pb] (18.34 g, 45.00 mmol) in hexanes (70 mL). After the addition was complete, the milky-white mixture was stirred at room temperature for 20 h and then brought to reflux to ensure completion of the reaction. The reaction mixture was allowed to cool, filtered through a medium-porosity frit, and then concentrated in vacuo. After the solution had been stored at −21 °C for several days, colorless crystals (3.04 g, 27.6%) separated. mp: 94−96 °C. ^{1}H NMR (500.13 MHz, benzene-d_6, 26 °C): δ 1.95 (t, 4 H, J_{PH} = 6.3 Hz, CH$_2$), 1.21 (s, 36 H, N^{t}Bu), 0.43 (s, 6 H, CH$_3$), 0.42 (s, 6 H, CH$_3$). ^{13}C{^{1}H} NMR (125.76 MHz, benzene-d_6, 26 °C): δ 50.5 (d, J_{PC} = 12.6 Hz, N^{t}Bu), 34.1 (dd, J_{PC} = 47.9 Hz, J_{PC} = 3.2 Hz, CH$_2$), 32.5 (t, J_{PC} = 2.9 Hz, N^{t}Bu), 8.2 (s, SiCH$_3$), 6.3 (s, SiCH$_3$). ^{31}P{^{1}H} NMR (202.46 MHz, benzene-d_6, 26 °C): δ 143.9 (s). ^{29}Si NMR (99.36 MHz, benzene-d_6, 26 °C): δ 12.1 (s). Anal. Calcd for $C_{22}H_{52}N_4P_2Si_2$: C, 53.84; H, 10.68; N, 11.42. Found: C, 53.70; H, 10.76; N, 11.33.

***cis*-{[Me$_2$Si(μ-N^{t}Bu)$_2$PCH$_2$]$_2$NiCl$_2$} = *cis*-[(bdpe)NiCl$_2$] (3).** Solid samples of **2** (0.96 g, 2.0 mmol) and NiCl$_2$ (0.25 g, 2.0 mmol) were mixed in 40 mL of THF, and the suspension was refluxed for 48 h. The ensuing orange-colored solution was cooled to room temperature to produce thin, orange plates (0.81 g, 1.3 mmol). Yield: 66%. mp: 354 °C dec. ^{1}H NMR (500.13 MHz, benzene-d_6, 25 °C): δ 1.60 (d, J = 17.1 Hz, 4 H, CH$_2$), 1.42 (s, 36 H, ^{t}Bu), 0.81 (s, 6 H, Me), 0.24 (s, 6 H, Me). ^{13}C{^{1}H} NMR (125.76 MHz, benzene-d_6, 25 °C): δ 52.35 (s), 37.90 (dd, J_{PC} = 16.6 Hz), 33.69 (s), 5.94 (s), 5.49 (s). ^{31}P{^{1}H} NMR (202.46 MHz, benzene-d_6, 25 °C): δ 157.6 (s). Anal. Calcd for $C_{22}H_{52}Cl_2N_4NiP_2Si_2$: C, 42.59; H, 8.45; N, 9.03. Found: C, 42.73; H, 8.53; N, 8.84.

***cis*-{[Me$_2$Si(μ-N^{t}Bu)$_2$PCH$_2$]$_2$Mo(CO)$_4$} = *cis*-[(bdpe)Mo(CO)$_4$] (4).** A stirred solution of **2** (0.232 g, 0.473 mmol) in THF (15 mL) was treated dropwise with a solution of (piperidine)$_2$Mo(CO)$_4$ (0.179 g, 0.473 mmol) dissolved in 10 mL of THF. The mixture was stirred at room temperature for 14 h and then refluxed for an additional 14 h. The resulting brown solution was allowed to cool to room temperature, filtered through a medium-porosity frit, and concentrated in vacuo. Several crops of colorless crystals 0.167 g (50.5%) precipitated from a refrigerated (−21 °C) solution. mp: 234−237 °C. ^{1}H NMR (500.13 MHz, benzene-d_6, 26 °C): δ 1.86 (d, 4 H, J_{HH} = 19.1 Hz, CH$_2$), 1.29 (s, 36 H, N^{t}Bu), 0.47 (s, 6 H, CH$_3$), 0.36 (s, 6 H, CH$_3$). ^{13}C{^{1}H} NMR (125.76 MHz, benzene-d_6, 26 °C): δ 219.7 (dd, J_{PC} = 31.6 Hz, J_{PC} = 10.2 Hz, CO(eq)), 217.2 (t, J_{PC} = 8.9 Hz, CO(ax)), 51.7 (s, N^{t}Bu), 45.9 (dd, J_{PC} = 19.6 Hz, J_{PC} = 4.1 Hz, CH$_2$), 33.4 (s, N^{t}Bu), 8.9 (s, CH$_3$), 5.6 (s, CH$_3$). ^{31}P{^{1}H} NMR (202.46 MHz, benzene-d_6, 26 °C): δ 193.7 (s). IR$_{CO}$ (THF): 2008, 1918, 1894 cm^{-1}. Anal. Calcd for $C_{26}H_{52}MoN_4O_4P_2$: C, 44.69; H, 7.50; N, 8.02. Found: C, 44.77; H, 7.87; N, 7.56.

***cis*-{[Me$_2$Si(μ-N^{t}Bu)$_2$PCH$_2$]$_2$Rh(COD)}BF$_4$ = *cis*-[(bdpe)Rh(COD)]BF$_4$ (5).** A 100-mL round-bottomed flask equipped with addition funnel, inlet, and stir bar was charged with [Rh(COD)$_2$]BF$_4$ (0.303 g, 0.746 mmol) and 20 mL of dichloromethane. A sample of **2** (0.366 g, 0.746 mmol), dissolved in 20 mL of dichloromethane, was then added dropwise to the orange suspension at room temperature, along with an additional 5 mL of dichloromethane. The solution was refluxed for 2 days and then filtered cold through a medium porosity frit. The solvent was removed in vacuo and replaced with 8 mL of THF, whereupon several crops of ruby-red plates crystallized at −21 °C. Yield: 0.369 g (62.7%). Dec: 230 °C, mp: 255−257 °C. ^{1}H NMR (500.13 MHz, dichloromethane-d_2, 26 °C): δ 5.64 (br s, 4 H, CH (COD)), 2.54 (d, J_{HH} = 8.9 Hz, 4 H, CH$_2$ (COD)), 2.30 (d, J_{HH} = 11.5 Hz, 4 H, CH$_2$ (COD)), 2.12 (d, J_{HH} = 18.7 Hz, 4 H, CH$_2$), 1.39 (s, 36 H, N^{t}Bu), 0.62 (s, 6 H, CH$_3$), 0.53 (s, 6 H, CH$_3$). ^{13}C{^{1}H} NMR (125.76 MHz, dichloromethane-d_2, 26 °C): δ 108.2 (dd, J_{PC} = 5.3 Hz, J_{PC} = 9.9 Hz, COD), 52.57 (s, N^{t}Bu), 39.54 (dd, J_{PC} = 8.6 Hz, J_{PC} = 38.5 Hz, CH$_2$), 33.80 (s, N^{t}Bu), 29.89 (s, COD), 6.5 (s, CH$_3$), 6.4 (s, CH$_3$). ^{31}P{^{1}H} NMR (202.46 MHz, dichloromethane-d_2, 26 °C): δ 159.9 (d, J_{RhP} = 201.0 Hz). Anal. Calcd for $C_{30}H_{64}BF_4N_4P_2RhSi_2$: C, 45.69; H, 8.18; N, 7.11. Found: C, 45.57; H, 8.07; N, 6.98.

X-ray Crystallography. Compound 3·THF. A suitable, single crystal was coated with oil, affixed to a glass capillary, and centered on the diffractometer in a stream of cold nitrogen. Reflection intensities were collected with a Bruker SMART CCD diffractometer, equipped with an LT-2 low-temperature apparatus, operating at 193 K. Data were measured using ω scans of 0.3° per frame for 30 s until a complete hemisphere had been collected. The first 50 frames were recollected at the end of the data collection to monitor for decay. Cell parameters were retrieved using SMART[92] software and refined with SAINT[93] on all observed reflections. Data were reduced with SAINT, which corrects for Lp and decay. An empirical absorption correction was applied with SADABS.[94] The structures were solved by direct methods with the SHELXS-90[95] program and refined by full-matrix least-squares methods on F^2 with SHELXL-97,[96] incorporated in SHELXTL Version 5.10.[97]

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(92) *SMART* Version 4.043 Software for the CCD Detector System, Bruker Analytical X-ray Systems: Madison, WI, 1995.

(93) *SAINT Software for the CCD Detector System*, Version 4.035; Bruker Analytical X-ray Systems: Madison, WI, 1995.

(94) *SADABS* program for absorption corrections using the Bruker CCD Detector System. Based on: Blessing, R. H. *Acta Crystallogr., Sect. A* **1995**, *51*, 33.

(95) G. M. Sheldrick. *SHELXS-90, Program for the Solution of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1990.

(96) G. M. Sheldrick. *SHELXL-97, Program for the Solution of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.

Compounds 2, 4, and 5. The crystals were sealed inside argon-filled glass capillaries, and the intensity data were collected on a Bruker P4 diffractometer. The structures were solved by direct methods with SHELXL-NT Version 5.10[98] and refined analogously to **3**·THF.

Acknowledgment. We thank North Dakota EPSCoR for an AURA undergraduate fellowship to S.J.M., Chevron-Phillips for a research assistantship to I.S., and the National Science Foundation for a GAANN fellowship to G.R.L. This paper is dedicated to Professor Robert W. Parry—an exemplary human being, a great chemist, and the first editor of this Journal—in honor of his 85th birthday.

Supporting Information Available: Crystallographic data for compounds **2**, **3**·THF, **4**, and **5** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC020524V

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(97) *SHELXTL* 5.10 (PC Version); Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1998.

(98) *SHELXTL NT Program Library for Structure Solution and Molecular Graphics*, Version 5.10; Bruker Analytical X-ray Systems: Madison, WI, 1999.