Dialkyl Bis[bis(trimethylsilyl)amide] Group 4A Compounds. Phosphine-Induced Transformation of a Bridging Carbene into a Metallacycle. Crystal Structure of Zr[CH₂Si(Me)₂NSiMe₃]₂(Me₂PCH₂CH₂PMe₂)

Zr[CH2Si(Me)2NSiMe3]2(Me2PCH2CH2PMe2)

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1,2-Bis(dimethylphosphino)ethane (dmpe) reacts at room temperature with the bridging carbenes {MCHSi(Me)₂NSiMe₃[N(SiMe₃)₂]}₂, where M is Zr or Hf, or with R₂M[N(SiMe₃)₂]₂ (R = CH₃, C₂H₅, CH₂SiMe₃; M = Zr or Hf) at 60 °C to give the bis(metallacycle) M[CH₂Si(Me)₂NSiMe₃]₂- (Me₂PCH₂CH₂PMe₂) in essentially quantitative yield. The metallacycles are formally derived by addition of a γ-CH bond of a N(SiMe₃)₂ group to a metal–carbon (carbene) bond. Crystal data for the zirconium metallacycle: space group *Pbca*, *a* = 39.1084 (20) Å, *b* = 15.3675 (8) Å, *c* = 10.5524 (21) Å; *V* = 6342 (2) Å³; *Z* = 8; *R* = 2.54%; *R*ʷ = 3.22%; GOF = 1.53. The averaged Zr–C, Zr–N, and Zr–P bond distances are 2.136 ± 0.009, 2.088 ± 0.004, and 2.852 ± 0.003 Å, respectively. The complex has idealized *C₂* symmetry with the two phosphorus atoms occupying cis sites, trans to the two nitrogen atoms, and the remaining two trans sites occupied by the carbon atoms of the metallacyclic rings in a distorted octahedral arrangement. The bis(metallacycle) reacts with carbon monoxide (19 atm room temperature in pentane) to give Zr- [OC(=CH₂)Si(Me)₂NSiMe₃]₂(Me₂PCH₂CH₂PMe₂).

Transition-metal group 4A "carbene" complexes of the type Cp₂Ti(μ-CH₂)ClAlMe₂ (I)[1] undergo many interesting
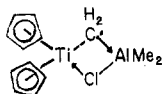

I

reactions with organic molecules.[2] We have prepared recently the metallacyclic, bridging "carbenes" II (where
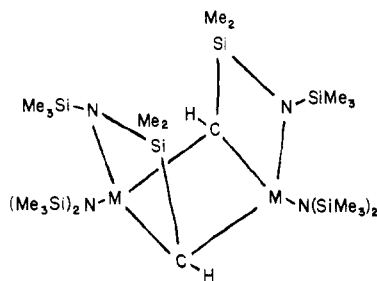
II

M is Ti, Zr, or Hf) in which the three, planar, four-membered rings are in the "tub" conformation.[3] Cleavage of II by Lewis bases along the metal–carbon bonds that

connect the MCSiN planar fragments could generate the monomeric fragement III, where L is a Lewis base. These
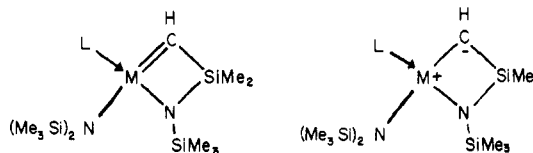
IIIa   IIIb

adducts have a formal relation to I in that the metal–carbon bonds are either double bonds (IIIa) or dipolar ylide-like single bonds (IIIb). Accordingly, we have investigated the reactions of II with Lewis bases.

The dimeric unit in II, M = Zr or Hf, is not cleaved by pyridine, as this Lewis base gives simple 1:2 coordination complexes.[3] The diphosphine Me₂PCH₂CH₂PMe₂ (dmpe), however, reacts with II, M = Zr or Hf, at room temperature to give complexes of stoichiometry III where M is Zr or Hf and L is dmpe in essentially quantitative yield. The NMR spectral properties, however, are not consistent with simple adduct formation. In particular, the bridging carbene group in II (M = Zr) gives a singlet in the ¹H and a doublet in the ¹³C NMR spectrum at δ 7.08 and 201 (*J*ᴄʜ = 122 Hz), respectively.[3] However, the Me₂PCH₂CH₂PMe₂ complex of zirconium has no low-field resonances in the ¹H and ¹³C NMR spectrum; all of the resonances are in the region δ +1.5 to −0.5 and δ 30–5, respectively. The dmpe complex of the hafnium compound has similar NMR spectral properties. The spectral parameters are most consistent with metal–carbon σ bonds that are part of a MCH₂Si(Me)₂NSiMe₃ ring system that we have described previously.[4] If this inference is true, a hydrogen migration must have occurred. In order to unambiguously characterize

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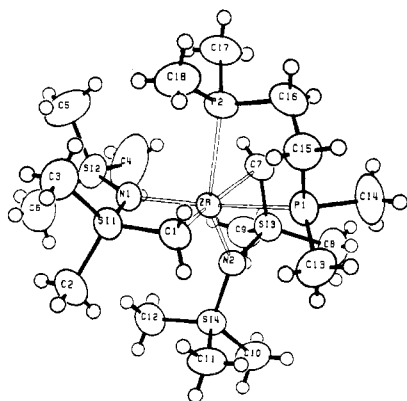
Figure 1. An ORTEP view showing the atom numbering scheme. The non-hydrogen ellisoids represent 50% probability surfaces.
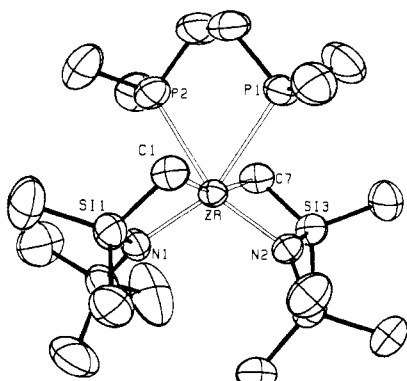

Figure 2. An ORTEP view showing the atoms in the inner coordination sphere in $Zr[CH_2Si(Me)_2NSiMe_3]_2$-$(Me_2PCH_2CH_2PMe_2)$. The pseudo C_2 axis passes through the carbon–carbon bond of the ethylene group connecting P(1) and P(2).

Table I. Positional Parameters for

$Zr[CH_2Si(Me)_2NSiMe_3]_2(Me_2PCH_2CH_2PMe_2)$

atom	x	y	z
Zr	0.12125 (1)	0.00159 (2)	0.21589 (3)
P(1)	0.07420 (3)	0.10363 (6)	0.3586 (1)
P(2)	0.15161 (3)	0.04095 (7)	0.4552 (1)
Si(1)	0.17451 (3)	0.09459 (7)	0.0827 (1)
Si(2)	0.19621 (3)	−0.10002 (8)	0.1081 (1)
Si(3)	0.07028 (3)	−0.13359 (6)	0.2026 (1)
Si(4)	0.07360 (3)	−0.03920 (7)	−0.0575 (1)
N(1)	0.16871 (6)	−0.0140 (2)	0.1276 (3)
N(2)	0.08310 (6)	−0.0506 (2)	0.1009 (2)
C(1)	0.13665 (9)	0.1425 (2)	0.1598 (3)
C(2)	0.17352 (11)	0.1076 (3)	−0.0943 (4)
C(3)	0.21667 (10)	0.1408 (3)	0.1343 (5)
C(4)	0.17439 (13)	−0.2049 (3)	0.1401 (7)
C(5)	0.23328 (12)	−0.0929 (3)	0.2192 (5)
C(6)	0.21385 (12)	−0.1056 (4)	−0.0573 (5)
C(7)	0.09970 (9)	−0.1122 (2)	0.3344 (3)
C(8)	0.02413 (10)	−0.1266 (3)	0.2470 (5)
C(9)	0.07524 (10)	−0.2422 (2)	0.1246 (4)
C(10)	0.03177 (10)	−0.0910 (3)	−0.1025 (4)
C(11)	0.06999 (10)	0.0779 (2)	−0.1007 (4)
C(12)	0.10791 (10)	−0.0893 (3)	−0.1543 (4)
C(13)	0.05409 (11)	0.1946 (3)	0.2778 (4)
C(14)	0.03800 (11)	0.0607 (3)	0.4477 (5)
C(15)	0.09828 (11)	0.1569 (3)	0.4850 (4)
C(16)	0.11923 (11)	0.0897 (3)	0.5586 (4)
C(17)	0.16751 (12)	−0.0494 (3)	0.5506 (4)
C(18)	0.18610 (11)	0.1190 (3)	0.4706 (4)

this complex, we carried out a single-crystal X-ray analysis of the zirconium complex.

An ORTEP diagram is shown in Figure 1; Figure 2 shows a view of the inner coordination sphere about the zirco-

Table II. Bond Lengths (Å) in

$Zr[CH_2Si(Me)_2NSiMe_3]_2(Me_2PCH_2CH_2PMe_2)$

Zr	P(1)	2.848 (1)
Zr	P(2)	2.855 (1)
Zr	N(1)	2.091 (2)
Zr	N(2)	2.084 (2)
Zr	C(1)	2.324 (3)
Zr	C(7)	2.309 (3)
Si(1)	N(1)	1.749 (2)
Si(1)	C(1)	1.843 (3)
Si(1)	C(2)	1.879 (3)
Si(1)	C(3)	1.876 (3)
Si(2)	N(1)	1.717 (2)
Si(2)	C(4)	1.855 (4)
Si(2)	C(5)	1.867 (4)
Si(2)	C(6)	1.878 (4)
Si(3)	N(2)	1.741 (2)
Si(3)	C(7)	1.835 (3)
Si(3)	C(8)	1.868 (3)
Si(3)	C(9)	1.870 (3)
Si(4)	N(2)	1.720 (2)
Si(4)	C(10)	1.880 (3)
Si(4)	C(11)	1.862 (3)
Si(4)	C(12)	1.854 (4)
P(1)	C(13)	1.817 (4)
P(1)	C(14)	1.824 (4)
P(1)	C(15)	1.827 (3)
P(2)	C(16)	1.832 (4)
P(2)	C(17)	1.824 (4)
P(2)	C(18)	1.812 (4)
C(15)	C(16)	1.530 (5)

Table III. Bond Angles (deg) in

$Zr[CH_2Si(Me_2NSiMe_3]_2(Me_2PCH_2CH_2PMe_2)$

P(1)	Zr	P(2)	71.60 (3)
N(1)	Zr	C(1)	76.30 (10)
N(2)	Zr	C(7)	76.27 (9)
P(1)	Zr	N(1)	150.72 (6)
P(2)	Zr	N(2)	153.43 (6)
C(1)	Zr	C(7)	159.72 (10)
P(1)	Zr	C(1)	77.83 (7)
P(1)	Zr	N(2)	93.28 (6)
P(1)	Zr	C(7)	83.95 (8)
P(2)	Zr	N(1)	92.82 (7)
P(2)	Zr	C(1)	85.43 (7)
P(2)	Zr	C(7)	80.40 (8)
N(1)	Zr	N(2)	109.40 (9)
N(1)	Zr	C(7)	118.62 (10)
C(1)	Zr	N(2)	113.30 (9)

Phosphine Ligand

Zr	P(1)	C(13)	117.08 (13)
Zr	P(1)	C(14)	125.10 (13)
Zr	P(1)	C(15)	107.46 (11)
Zr	P(2)	C(16)	109.03 (12)
Zr	P(2)	C(17)	117.95 (13)
Zr	P(2)	C(18)	121.94 (13)
C(13)	P(1)	C(14)	100.63 (19)
C(13)	P(1)	C(15)	102.76 (17)
C(14)	P(1)	C(15)	100.72 (19)
P(1)	C(15)	C(16)	110.13 (24)
C(15)	C(16)	P(2)	110.12 (23)
C(16)	P(2)	C(17)	102.60 (18)
C(16)	P(2)	C(18)	100.97 (19)
C(17)	P(2)	C(18)	101.57 (18)

nium atom. Table I gives the positional parameters, and Tables II and III lists some bond lengths and bond angles, respectively. Table V gives the crystal data.

The complex consists of two $ZrCH_2Si(Me)_2NSiMe_3$ metallacyclic rings and a bidentate $Me_2PCH_2CH_2PMe_2$ group. The geometry of the complex may be viewed as an octahedral tris(chelate) with idealized C_2-symmetry. The idealized C_2 symmetry is destroyed by the "dangling" $SiMe_3$ groups. This is illustrated by the torsion angles

Table IV. Dihedral Angles between Planes

plane no.[a]	plane no.[a]	dihedral angle, deg
1	2	86.3
1	3	95.3
1	4	91.6
1	5	94.9
1	6	94.7
1	7	29.7
2	3	82.6
2	4	6.1
2	5	82.8
2	6	40.3
2	7	69.8
3	4	85.1
3	5	0.5
3	6	120.9
3	7	115.9
4	5	85.4
4	6	36.5
4	7	73.3
5	6	121.2
5	7	115.6
6	7	66.0

[a] Plane 1 contains the ZrP(1)P(2) atoms, plane 2 contains the ZrC(1)N(1) atoms, plane 3 contains the ZrC(7)N(2) atoms, plane 4 contains the N(1)Si(1)C(1) atoms, plane 5 contains the N(2)Si(3)C(7) atoms, plane 6 contains the C(1)ZrC(7) atoms, and plane 7 contains the ZrN(1)N(2) atoms.

around the N(1)-Si(2) and N(2)-Si(4) bonds, the Zr-N-(1)-Si(2)-C(4) and Zr-N(2)-Si(4)-C(10) torsion angles being 16.6° and -171.8°, respectively. The distortion from idealized octahedral symmetry can be described by examining the dihedral angles between the planes that contain the atoms in the coordination sphere of zirconium. A listing of some of the least-squares planes and their dihedral angles is given in Table IV. In particular, the dihedral angles between planes 1 and 2, 1 and 3, 1 and 6, and 2 and 3 are 86.3°, 95.3°, 94.9°, and 82.6°, respectively. In addition the N(1)-Zr-C(1), N(2)-Zr-C(7), and P(1)-Zr-P(2) angles are 76.3 (1)°, 76.3 (1)°, and 71.6 (3)°, respectively. In a regular octahedral these angles are 90°.

The four-membered ZrCSiN rings are essentially planar. The planes defined by ZrC(1)N(1) and C(1)Si(1)N(1) intersect at an angle of 6.1°; the ZrC(7)N(2) and C(7)Si-(3)N(2) planes intersect at an angle of 0.5°. The geometry at N(1) and N(2) is not rigorously trigonal planar, though the deviation from planarity is relatively small. For example, the Si(1) and Si(2) atoms are displaced from the Zr-C(1)-N(1) plane by +0.124 and -0.160 Å, respectively. The near-planar coordination about N(1) and N(2) suggests that the lone pair of electrons associated with each nitrogen atom is not stereochemically active, perhaps due to N-Si p_π-d_π bonding. In support of this contention is the observation that the N(1)Si(2) and N(2)Si(4) bond lengths are 1.717 (2) Å in the related metallacycle ZrN-(CMe₃)Si(Me)₂NCMe₃.[5] Since the tetrahedral covalent radius of silicon is 0.40 Å larger than that of carbon,[6] a N-Si bond length in absence of π bonding would be expected to be 1.87 Å, ca. 0.15 Å longer than found in the dmpe complex.

The two zirconium-nitrogen bond lengths in the dmpe complex are 2.091 (2) and 2.084 (2) Å. These distances are close to those found in II, M = Zr, of 2.057 ± 0.014[3] and

Table V. Crystal Data (25 °C) for
$\overline{Zr[CH_2Si(Me_2)NSiMe_3]_2(Me_2PCH_2CH_2PMe_2)}$

space group	*Pbca*
a, Å	39.1084 (20)
b, Å	15.3675 (8)
c, Å	10.5524 (21)
V, Å³	6342 (2)
Z	8
mol wt, amu	560.12
d_{calcd}, g cm⁻³	1.18
μ_{calcd}, cm⁻¹	5.96
reflctns collected	4688
reflctns unique	4137
reflctns, $I > 3\sigma(I)$	2750
R_F, %	2.54
R_{wF}, %	3.22
variables	244
GOF	1.53
diffractometer	Enraf-Nonius CAD-4
monochromator	highly oriented graphite
radiation	Mo Kα, 0.710 73 Å
scan range, type	$3° \leqslant \theta \leqslant 45°$, ω
scan speed	0.63-6.7° min⁻¹
scan width	$\Delta\theta = (0.50 + 0.347 \tan \theta)°$

2.070 (3) Å in Zr[N(SiMe₃)₂]₃Cl.[9]

The two zirconium-carbon bond lengths of 2.324 (3) and 2.307 (3) Å are within the range observed for Zr-C(sp³) bond lengths which range from 2.25 to 2.37 Å.[7] The averaged zirconium-carbon bond length of 2.188 ± 0.025 Å in the metallacyclic "carbene" complex II, M = Zr, is 0.13 Å shorter than that found in the dmpe complex. This difference is readily explained by noting that the ionic or covalent radius of Zr(IV) in four-coordination is 0.13 Å shorter than that in six-coordination.[8] This bond length relation further supports our earlier contention that the bridging carbon atom in II, M = Zr, is best viewed as being sp³ hybridized rather than sp² hybridized.[3]

The zirconium-phosphorus bond lengths are 2.848 (1) and 2.855 (1) Å, slightly longer than those found in the six-coordinate complex $\overline{ZrCl_2[N(SiMe_2CH_2PMe_2)_2]}$ of 2.794 (1) and 2.803 (1) Å.[10a] The zirconium-phosphorus lengths may be compared with the averaged zirconium-(II)-phosphorus bond length of 2.770 ± 0.026 Å in (η^5-C₈H₁₁)Zr(dmpe)₂H[10b] and the averaged zirconium(III)-phosphorus bond length of 2.835 ± 0.004 Å in Zr₂Cl₄(μ-Cl)₂(P-n-Bu₃)₄.[10c] Further, the averaged hafnium-phosphorus bond length in Hf(η-buta-1,3-diene)₂(dmpe) is 2.691 ± 0.006 Å.[10d]

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The P(1)ZrP(2) bond angle is the dmpe complex is 71.60 (3)°. This is very close to the value found for the two independent angles in $(\eta^5\text{-}C_3H_{11})Zr(dmpe)_2H^{10a}$ of 74.3 (1)° and 73.0 (1)° and to 72.0 (3)° in $Hf(\eta\text{-buta-1,3-diene})_2$-$(dmpe)$.[10c] The normalized bite of $Me_2PCH_2CH_2PMe_2$ in III, defined by Kepert as the phosphorus–phosphorus distance divided by the metal–phosphorus distance,[11] is 1.17.

Having determined the solid-state structure of III, M = Zr, the NMR spectra can be rationalized. The molecule has C_2 symmetry and the methyls of the Me_2Si and Me_2P groups and the hydrogens of the $ZrCH_2Si$ groups are diastereotopic. The ^1H NMR spectrum of the methylene groups connnecting the zirconium and silicon atoms is an ABX_2 spin system, where A and B are the protons and X is the phosphorus nuclei, with $\delta(A)$ 0.15, $\delta(B)$ −0.49, and $\delta(X)$ $(^{31}P\{^1H\})$ −28.5 $(^2J_{AB} = 14$ Hz, $^3J_{AX} = {}^3J_{BX} = 3.2$ Hz). The $^1H\{^{31}P\}$ NMR spectrum simplifies to a AB spectrum, confirming the coupling constant assignment. The ^{13}C NMR spectrum contains a pair of doublets centered at δ 28.4 with $^1J_{CH} = 121$ and 125 Hz, due to the metallacyclic methylene groups. The $^{13}C\{^1H\}$ NMR spectrum in the above region simplifies to a slightly broadened resonance, indicating that $^2J_{CP}$ is on the order of the natural line width. The remaining resonances for the zirconium complex, which are similar to those of the hafnium complex, are given in the Experimental Section.

It is interesting to speculate on the role of $Me_2PCH_2CH_2PMe_2$ relative to pyridine, since the latter forms a simple coordination complex with II, whereas the former causes the rearrangement of II to the bis(metallacycle). It is tempting to suggest that the phosphine cleaves the dimeric unit in II giving III, L = dmpe. The γ-CH bond in the coordinated $N(SiMe_3)_2$ group then becomes activated by interaction with the metal atom, perhaps similar to the interaction found in the solid state for Yb-$[N(SiMe_3)_2]_2(dmpe)$,[12] followed by intramolecular addition of the γ-CH bond across the Zr–C bond giving the bis-(metallacycle). Alternatively, the Lewis base could induce the γ-hydrogen migration in the intact dimer II followed by zirconium–carbon bond cleavage. Some alkyl migrations to metal carbenes giving new metal alkyls, $M(=CH_2)(R) \rightarrow M\text{—}CH_2R$, which are somewhat analogous to the transformation reported in this paper, have been described previously.[13]

It is possible to test these two alternative mechanisms by performing a crossover experiment. We can examine the existence of an equilibrium, II $\rightleftharpoons$ III, L = pyridine, PMe_3, or dmpe, as well as an equilibrium in absence of a Lewis base, II $\rightleftharpoons$ (III-L), by performing a crossover experiment between II, M = Zr, and II, M = Hf, in presence or absence of a Lewis base. Heating an equimolar mixture of II, M = Zr, and II, M = Hf, to 80 °C for 6 h alone or in presence of a small amount (ca. 10 mol %) of pyridine, PMe_3, or dmpe followed by examination of the resulting product by ^1H NMR spectroscopy showed no crossover. That is, in the case of no added Lewis base, the only resonances that were observed in the ^1H NMR experiment were due to II, M = Zr, and II, M = Hf. In the case of added Lewis base, resonances in the ^1H NMR spectrum due to pure II, M = Zr, and II, M = Hf, and small amounts of pyridine or PMe_3 adducts of II or of the bis(metalla-cycle) dmpe complex were observed. Hence, the equilib-

rium constant for II $\rightleftharpoons$ III or II $\rightleftharpoons$ (III-L) is very small.

As a control experiment, to check our ability to detect the crossover product, an equimolar mixture of $Me_2Zr[N-(SiMe_3)_2]_3$ and $Et_2Hf[N(SiMe_3)_2]_2$ (chosen because these two alkyls decompose at similar rates) was pyrolyzed at 80 °C for 1.5 h.[3] The yellow material that was isolated by crystallization showed resonance in the ^1H NMR spectrum characteristic of II, M = Zr, and II, M = Hf, and resonances due to another species in area ratio 1:1:2. That is, the ^1H NMR spectrum showed the methine resonances for II, M = Zr, at δ 6.96 and for II, M = Hf, at δ 4.75 and an AB pattern, $\delta(A)$ 6.21, $\delta(B)$ 5.48 $(J_{AB} = 1.6$ Hz) in addition to the ther methyl–silicon resonances between δ 1 and 0. Addition of $Me_2PCH_2CH_2PMe_2$ to the NMR tube and examination of the mixture by $^{31}P\{^1H\}$ NMR spectroscopy showed resonances due to the dmpe complexes of the bismetallacycles of zirconium and hafnium in equal amounts. This experiment strongly suggests that the AB pattern observed in the ^1H NMR spectrum is due to the crossover product II, where one M is Zr and the other is Hf.

The lack of crossover between the bridging carbenes suggests that monomeric units such as III, L = py or PMe_3, or III-L do not form, and that the γ-elimination occurs in the dimeric complex. If III, L = dmpe, is formed during the conversion, it is converted to the bis(metallacycle) complex irreversibly and the backward rate constant in II $\rightleftharpoons$ III, L = dmpe, is small relative to the rate of conversion of III, L = dmpe, to the bis(metallacycle).[14a]

The zirconium metallacycle $\overline{Zr[CH_2Si(Me)_2NSiMe_3]_2}$-$(dmpe)$ reacts with carbon monoxide at 20 atm, 20 °C in pentane, to give IV. The structure IV is suggested due to
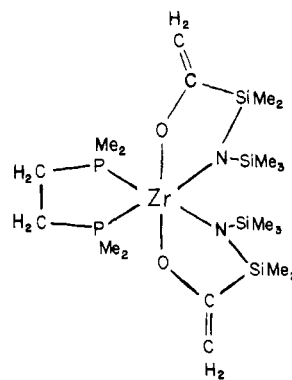
IV

the similarity of the ^1H and ^{13}C NMR spectra with those of the similar thorium complex described earlier;[14b] see Experimental Section for details.

Experimental Section

Elemental analyses were by the microanalytical laboratory of this department. All operations were performed under nitrogen. The NMR spectra were recorded on a Fourier transform machine operating at 250.0 MHz for ^1H, 63.1 MHz for ^{13}C, and 72.9 MHz for ^{31}P and are reported relative to Me_4Si and 85% H_3PO_4, respectively. The ^1H NMR spectra were measured in benzene-d_6 at 22 °C, and the chemical shifts are reported relative to Me_4Si using $\delta(PhH)$ 7.15.

$\overline{Zr[CH_2Si(Me)_2NSiMe_3]_2}(Me_2PHC_2CH_2PMe_2)$. (a) From

(11) Kepert, D. L. *Prog. Inorg. Chem.* 1977, *23*, 1–65.

(12) Tilley, T. D.; Andersen, R. A.; Zalkin, A. *J. Am. Chem. Soc.* 1982, *104*, 3725–3727.

(13) (a) Sharp, P. R.; Schrock, R. R. *J. Organomet. Chem.* 1979, *171*, 43–51. (b) Hayes, J. C.; Pearson, G. D. N.; Cooper, N. J. *J. Am. Chem. Soc.* 1981, *103*, 4648–4650 and references therein.

(14) (a) The observation of crossover in the pyrolysis of the zirconium and hafnium alkyls, however, does not help us understand the molecularity of the reaction to give II. It simply says that an intermolecular step occurs at some time in the course of the reaction, not when it occurs. (b) Simpson, S. J.; Andersen, R. A. *Ibid.* 1981, *103*, 4063–4066.

$\overline{\{ZrCHSi(Me)_2NSiMe_3[N(SiMe_3)_2]\}}_2$ and $Me_2PCH_2CH_2PMe_2$. 1,2-Bis(dimethylphosphine)ethane (0.5 mL, 0.003 mol) was added to a solution of $\overline{\{ZrCHSi(Me)_2NSiMe_3[N(SiMe_3)_2]\}}_2$ (0.63 g, 0.000 77 mol) in toluene (10 mL). The solution was heated to 75 °C for 36 h; the solution changed from yellow to orange. After the solution was cooled to room temperature, the volatile material was removed under reduced pressure and the residue was heated (70 °C) under reduced pressure for 2 h. The orange-yellow paste was dissolved in pentane (30 mL) and filtered, and the filtrate was evaporated to ca. 4 mL. Cooling (–70 °C) afforded yellow prisms in near quantitative yield: mp 114–116 °C; ^{1}H NMR (PhH-d_6, 25 °C) δ 1.27 (PCH₂, 8 H, broadened resonance which is approximately a triplet), 0.96 (PMe₂, 12 H, an apparent three-line pattern with a separation between the outermost lines of 4.9 Hz), 0.82 and 0.53 (diastereotopic SiMe₂, 6 H each, s), 0.48 (SiMe₃, 18 H, s), 0.15 and –0.49 (diastereotopic ZrCH₂, 2 H each, doublet of triplets $^2J_{HH}$ = 14 Hz, $^3J_{HP}$ = 3.2 Hz); ^{13}C NMR δ 28.4 (ZrCH₂, doublet of doublets, $^1J_{CH}$ = 121 and 125 Hz), 26.6 (PCH₂, triplet, $^1J_{CH}$ = 122 Hz, of "triplets" with the separation between the outermost lines being 13.5 Hz), 13.0 (PMe₂, quartet, $^1J_{CH}$ = 135 Hz, of multiplets extending over 58 Hz), 7.50 and 6.20 (diastereotopic SiMe₂, quartet, $^1J_{CH}$ = 117 Hz), 4.90 (NSiMe₃, quartet, $^1J_{CH}$ = 115 Hz); ^{31}P{^{1}H} NMR δ –28.5; the coordination chemical shift is 20.5 ppm. Anal. Calcd for C₁₈H₅₀N₂P₂Si₄Zr: C, 38.6; H, 8.94; N, 5.01; P, 11.1. Found: C, 37.6; H, 8.81; N, 4.72; P, 10.1.

(b) From Thermolysis of ZrR₂[N(SiMe₃)₂]₂, R = Me, Et, or Me₂SiCH₂, in the Presence of Me₂PCH₂CH₂PMe₂. Neat 1,2-bis(dimethylphosphino)ethane (1 mL, 0.006 mol) and dimethylbis[bis(trimethylsilyl)amide]zirconium (0.94 g, 0.0021 mol) were heated to 60 °C for 8 h. During this time a gas was evolved and the solution turned red. The red-yellow solution was exposed to vacuum at 60 °C for 2.5 h. After the solution was cooled to room temperature, the residue was dissolved in pentane (20 mL) and filtered, and the filtrate was concentrated to ca. 5 mL. Cooling (–70 °C) yielded yellow prisms which were recrystallized from pentane (ca. 3 mL) at –20 °C in 72% (0.84 g) yield. The prisms had the same melting point and infrared spectrum as those prepared by method 1a. Similar yields of the same material were obtained by thermolysis of ZrEt₂[N(SiMe₃)₂]₂ and Zr(CH₂SiMe₃)₂[N(SiMe₃)₂]₂ in presence of Me₂PCH₂CH₂PMe₂.

$\overline{Hf[CH_2Si(Me)_2NSiMe_3]}_2(Me_2PCH_2CH_2PMe_2)$. 1,2-Bis-(dimethylphosphino)ethane (0.65 mL, 0.0039 mol) and diethylbis[bis(trimethylsilyl)amide]hafnium (0.90 g, 0.0016 mol) in toluene (15 mL) were heated (75 °C) for 3 h. The volatile material was removed under reduced pressure, and the white residue was heated (70 °C) under reduced pressure for 1 h. After the solution was cooled to room temperature, the solid was dissolved in pentane (20 mL) and filtered, and the filtrate was cooled to –15 °C and then to –70 °C. The colorless prisms were collected by filtration and dried under reduced pressure: yield was 89% (0.92 g); ^{1}H NMR (PhH-d_6, 25 °C) δ 1.29 (PCH₂, 8 H, br, $ν_{1/2}$ = 8 Hz), 1.01 (PMe₂, 12 H, an apparent three-line pattern with a separation between the outermost lines of 7.4 Hz), 0.76 and 0.51 (SiMe₂, 6 H each, s), 0.44 (SiMe₃, 18 H, s), 0.060 and –0.47 (ZrCH₂, 2 H each, each resonance is a doublet of triplets, $^2J_{HH}$ = 14 Hz, $^3J_{PH}$ = 3.6 Hz). ^{13}C NMR δ 29.8 (ZrCH₂, doublets of doublets, $^1J_{CH}$ = 121 Hz), 28.1 (PCH₂, triplet, $^1J_{CH}$ = 122 Hz, of "triplets", the separation between the outermost lines being 13.5 Hz), 12.5 (PMe₂, quartet, $^1J_{CH}$ = 128 Hz of multiplets, $ν_{1/2}$ = 18 Hz), 7.4 and 6.0 (diastereotopic SiMe₂, quartet, $^1J_{CH}$ = 118 Hz), 5.0 (NSiMe₃, quartet, $^1J_{CH}$ = 117 Hz); ^{31}P{^{1}H} NMR δ –34.5; the coordination chemical shift is 14.5 ppm. Anal. Calcd for C₁₈H₅₀HfN₂P₂Si₄: C, 33.4; H, 7.73; N, 4.33. Found: C, 32.5; H, 7.74; N, 3.92.

Pyrolysis of Me₂Zr[N(SiMe₃)₂]₂ and Et₂Hf[N(SiMe₃)₂]₂. The zirconium complex (0.94 g, 0.0021 mol) and the hafnium complex (1.2 g, 0.0021 mol) were intimately mixed then heated to 80 °C for 1.5 h. The resulting yellow glass was dissolved in pentane (15 mL), and the solution was filtered. The filtrate was evaporated to ca. 3 mL, and cooling to –70 °C afforded pale yellow crystals, 1.7 g (87% yield). The ^{1}H NMR spectrum is described in the text. 1,2-Bis(dimethylphosphino)ethane (0.5 mL, 0.003 mol) was added to the mixed isomers (0.5 g, 0.001 mol) in toluene (10 mL), and the pale yellow solution was heated at 75 °C for 36 h. After the solution was cooled to room temperature, the volatile material was removed under reduced pressure giving an orange

paste. The orange paste was dissolved in benzene-d_6, and the solution was examined by ^{31}P{^{1}H} NMR spectroscopy. The spectrum showed single resonances at δ –28.3, –32.3, and –49.0 due to the zirconium metallacycle, the hafnium metallacycle, and free phosphine, respectively.

Attempted Crossover of II, M = Zr, and II, M = Hf. A mixture of the zirconium complex (0.46 g, 0.000 56 mol) and the hafnium complex (0.56 g, 0.000 56 mol) was warmed to 80 °C for 6 h. After the mixture was cooled to room temperature, the solid was dissolved in benzene-d_6. Examination of this solution by ^{1}H NMR spectroscopy showed resonances due to II, M = Zr, and II, M = Hf, and no resonances due to the crossover product.

Attempted Crossover of II, M = Zr, and II, M = Hf, in the Presence of Lewis Bases. The experiment above was repeated with similar amounts of II in the presence of pyridine (5 μL, 0.000 06 mol), PMe₃ (6 μL, 0.000 06 mol), and dmpe (10 μL, 0.000 06 mol). In the first two cases only small amounts of an adduct of II (M = Zr and Hf) were observed, and in the third case small amounts of the bis(metallacycle) dmpe complexes were observed, in addition to unreacted II. In no case was the crossover product observed.

$\overline{Zr[OC(\!=\!CH_2)Si(Me_2)N(SiMe_3)]}_2(Me_2PCH_2CH_2PMe_2)$.

The complex $\overline{Zr[CH_2Si(Me)_2NSiMe_3]}_2(Me_2PCH_2CH_2PMe_2)$ (0.60 g, 0.0011 mol) in pentane (30 mL) was introduced into a heavy-walled bottle, and the bottle was pressurized to 19 atm with carbon monoxide. The solution was stirred at this pressure for 20 h. The pressure was released, and the pentane solution was concentrated to ca. 5 mL. Cooling to –70 °C yielded white needles in 86% yield (0.57 g): IR (Nujol) 1568 cm^{-1}; ^{1}H NMR (PhH-d_6, 25 °C) δ 0.52 (Me₃Si, 9 H, s), 0.48 and 0.71 (Me₂Si, 3 H each, s), 4.36 and 4.86 (C=CH₂, an AB with small wing peaks, 1 H each, s), 1.07 and 1.16 (PMe₂, diastereotopic 3 H each, pseudotriplets J = 2.3 Hz), 1.29 (PCH₂, broadened singlet, 4 H); ^{13}C NMR δ 4.85 (Me₃Si, q, $^1J_{CH}$ = 117 Hz), 5.90 and 5.45 (diastereotopic Me₂Si, q, $^1J_{CH}$ = 118 Hz), 11.3 (PMe₂, q, $^1J_{CH}$ = 132 Hz, the $ν_{1/2}$ of each line is ca. 17 Hz), 25.7 (PCH₂, a pseudotriplet of triplets, the separation of the outermost lines being 32 Hz), 96.3 (doublet of doublets due to C=CH₂ with J_{CH} = 154 Hz), 179 (C=CH₂, s); ^{31}P{^{1}H} NMR δ 27.5 (s). Anal. Calcd for C₂₀H₅₀N₂O₂P₂Si₄Zr: C, 39.0; H, 8.13; N, 4.55. Found: C, 39.8; H, 8.53; N, 4.60.

X-ray Study. Crystals of the zirconium complex, grown from pentane at –15 °C, were loaded into quartz capillaries under argon; the capillaries were then flame sealed. Precession photographic work indicated orthorhombic Laue symmetry (*Pmmm*) and preliminary cell parameters.

The crystal used for the data collection was a fragment of ca. 0.30 × 0.32 × 0.35 mm. The crystal was mounted on an Enraf-Nonius automated diffractometer and centered in the beam.[15] Automatic peak search and indexing methods yielded the primitive orthorhombic cell obtained from the photographic data. Inspection of the systematic absences showed that they were consistent only with the space group *Pbca* (No. 61). The final values of the unit cell parameters are given in Table V together with details of the data collection procedure.

The 4688 raw intensity data were converted to structure factor amplitudes and their esd's by correction for scan speed, background, and Lorentz and polarization factors.[16] Inspection of

(15) The instruments at the University of California, College of Chemistry X-ray Crystallographic Facility (CHEXRAY), under the direction of Dr. F. J. Hollander, consists of two Enraf-Nonius CAD-4 diffractometers, one controlled by a DEC PDP 8/a with a RK05 disk and the other by a DEC PDP 8/e with a RL01 disk.

(16) All calculations were performed on a PDP 11/60 equipped with 128 kilowords of memory, twin RK07 28 MByte disk drives, versatec printer/plotter, and TU10 tape drive using a locally modified Nonius-SDP (Structure Determination Package Users Guide, April 1980–Molecular Structure Corp., College Station, TX 77840) software operating under RSX-11M. The data reduction formulae are $F_o{}^2 = \omega(Lp)^{-1}(C - 2B)$, $\sigma_o(R_o)^2 = \omega(Lp)^{-1}(C + 4B)^{1/2}$, $F_o = (F_o{}^2)^{1/2}$, and $\sigma_o(F) = \sigma_o(F_o)^2(2F_o)^{-1}$, where C is the total count in the scan, B is the sum of the two background counts, and ω is the scan speed (deg min^{-1}). $(Lp)^{-1} = \sin 2\theta (1 + \cos^2 2\theta_m)(1 + \cos^2 2\theta_m - \sin^2 2\theta)^{-1}$ is the correction for Lorentz and polarization effects for a reflection with scattering angle 2θ and radiation monochromatized with a 50% perfect single-crystal monochromator with scattering angle $2\theta_m$.

the azimuthal scan data showed a maximum variation of ±2% on I and an average variation of only ±1%. No absorption correction was performed and no correction for crystal decomposition was necessary. After removal of the systematically absent reflections the remaining 4137 unique data were used to calculate the Patterson synthesis that was used to calculate the zirconium atom position. Subsequent cycles of least-squares refinement followed by Fourier syntheses located all of the non-hydrogen atoms. Refinement of all atomic positions and anisotropic thermal parameters converged to residuals[17] $R = 4.75\%$ and $wR = 7.41\%$. The idealized positions of the hydrogen atoms were then calculated and included in structure factor calculations with B_{iso} approximately equal to the largest amplitude of vibration for the carbon atom to which they were attached. The least-squares refinement was run to convergence. The R value for all 4137 data was 6.70%.

The quantity minimized by the least-squares program was $\sum w(|F_o| - |F_c|)^2$ where w is the weight of a given observation. The p factor,[17] used to reduce the weight of intense reflections, was set at 0.025 throughout the refinement. The analytical forms for the scattering factor tables for the neutral atoms were used,[18a] and all non-hydrogen scattering factors were corrected for real and imaginary components of anomalous dispersion.[18b] Inspection of the residuals ordered in ranges of $(\sin\theta)/\lambda$, $|F_o|$, and the value of the individual indexes showed no unusual features or trends.

The pseudo A center in the cell, caused by the packing, is shown by a 2:1 increase in $\langle F_o \rangle$ for those reflections with $k + l = 2n$ and a concomitant small reduction in the residuals for those reflections. There was no evidence of secondary extinction in the low-angle, high-intensity data. The largest peak in the final difference Fourier map had an electron density of 0.25 e Å^{-1} near P2. The remaining peaks were not correlated with the structure.

The thermal parameters of the non-hydrogen atoms are given in the supplementary material as are the F_o and F_c values.

Registry No. Zr[CH$_2$Si(Me)$_2$NSiMe$_3$]$_2$-(Me$_2$PCH$_2$CH$_2$PMe$_2$), 87174-17-2; {ZrCHSi(Me)$_2$NSiMe$_3$[N-(SiMe$_3$)$_2$]}$_2$, 83666-35-7; ZrMe$_2$[N(SiMe$_3$)$_2$]$_2$, 70969-30-1; ZrEt$_2$-[N(SiMe$_3$)$_2$]$_2$, 83666-33-5; Zr(CH$_2$SiMe$_3$)$_2$[N(SiMe$_3$)$_2$]$_2$, 83681-35-0; Et$_2$HF[N(SiMe$_3$)$_2$]$_2$, 70969-31-2; Hf[CH$_2$Si(Me)$_2$NSiMe$_3$]$_2$-(Me$_2$PCH$_2$CH$_2$PMe$_2$), 87155-74-6; Zr[OC(=CH$_2$)Si(Me$_2$)N-(SiMe$_3$)]$_2$(Me$_2$PCH$_2$CH$_2$PMe$_2$), 87155-75-7.

Supplementary Material Available: Listing of anisotropic thermal parameters and observed and calculated structure factors (19 pages). Ordering information is given on any current masthead page.

(17) $R = \sum ||F_o| - |F_c|| (\sum |F_o|)^{-1}$, $wR = \{\sum w(|F_o| - |F_c|)^2 (\sum wF_o^2)^{-1}\}^{1/2}$, and GOF $= \{\sum w(|F_o| - |F_c|)^2(n_o - n_v)^{-1}\}^{1/2}$, where n_o is the number of observations, n_v is the number of variable parameters, and the weights w were given by $w = 4F_o^2[\sigma^2(F_o^2)]^{-1}$ $(\sigma^2(F_o^2) = \sigma_o^2(F_o^2) + (pF^2)^2$, where p is the factor used to lower the weight of intense reflection).

(18) (a) Cromer, D. T.; Waber, J. T. "International Tables for X-Ray Crystallography"; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2B, (b) Cromer, D. T. *Ibid.* Table 2.3.1.