to bring about this reaction. **6a**, on the other hand, is such a 16e species, and insertions of CO into, e.g., Hf–P[24] bonds are known. Complex **6** indeed reacts readily with CO. The yellow solution turns colorless at 1 atm of CO/0 °C within a few minutes, but this is by no means a clear-cut reaction. A competition with the decomposition of **6** occurs, and again several products are formed, which are discussed in a separate paper.[25]

In conclusion, carbanion shielding by Me_3Si and Me_2P groups in phosphinomethanides reduces the nucleophilicity of the carbon and enhances that of phosphorus to such an extent that the coordination of these ligands to various metal centers can be tuned precisely. In particular η^1(C), η^2(C,P), and η^1(P) coordination to a zirconocene metal center may be realized. The η^2(C,P) coordination results in the formation of metalla–phospha three-membered heterocycles with reduced reactivity of the 18e metal centers due to coordinative saturation. The chlorine atom in these compounds of type $Cp_2(Cl)Zr[C(PMe_2)XY]$ is mobile, however, and cationic zirconocene complexes may be obtained.[25]

Acknowledgment. This work was supported by the Fonds der Chemischen Industrie, Frankfurt/Main, Germany. We also thank Prof. Dr. H. Schmidbaur for financial support and Mr. J. Riede for the collection of the crystallographic data sets.

Supplementary Material Available: Tables of displacement parameters and H atom coordinates (13 pages). Ordering information is given on any current masthead page.

OM920260S

---

[24] Roddick, D. M.; Santarsiero, B. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1985**, *107*, 4670.

[25] Karsch, H. H.; Grauvogl, G. To be submitted for publication.

Zirconocene Derivatives with Diphosphinomethanide Ligands: Syntheses of the Chelate Complexes $Cp_2(Cl)Zr[(R_2P)_2CX]$ and X-ray Structure Determinations for R = Me, Ph and X = $SiMe_3$[†]

Hans H. Karsch,* Brigitte Deubelly, Gregor Grauvogl, Joachim Lachmann,[‡] and Gerhard Müller[‡]

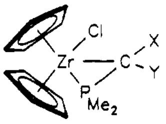
Anorganisch-chemisches Institut, Technische Universität München, D-8046 Garching, Germany

Received May 13, 1992

The novel four-membered chelate complexes $Cp_2(Cl)Zr[(R_2P)_2C(X)]$ (R = Me, X = $SiMe_3$ (**4**); R = Ph, X = $SiMe_3$ (**5**), R = Ph, X = H (**6**)) have been prepared from Cp_2ZrCl_2 and the appropriate lithium diphosphinomethanides in Et_2O. The compounds have been characterized by their NMR spectra and by X-ray structure determinations of **4** and **5**. **4**: monoclinic, $P2_1/c$, $a = 16.284$ (3) Å, $b = 14.463$ (2) Å, $c = 19.252$ (2) Å, $\beta = 97.42$ (1)°, $V = 4496.2$ Å^3, $Z = 8$, $T = 22$ °C, $R_w = 0.073$, $w = 1/\sigma^2(F_o)$. **5**·2(toluene): monoclinic, $P2_1/n$, $a = 19.184$ (3) Å, $b = 11.668$ (2) Å, $c = 22.695$ (3) Å, $\beta = 114.63$ (1)°, $V = 4617.8$ Å^3, $Z = 4$, $T = -50$ °C, $R_w = 0.050$. In both **4** and **5**, the $Cp_2(Cl)Zr$ moiety is coordinated by the $[(R_2P)_2C(SiMe_3)]^-$ ligands via both P atoms (η^2(P,P)), thus forming a four-membered ring. The Zr–P distances are rather long and inequivalent (**4**, 2.844 (5)/2.721 (5) and 2.823 (4)/2.719 (5) Å for two independent molecules; **5**, 2.852 (1)/2.817 (1) Å). The inequivalence of the phosphorus nuclei and the weak Zr–P interaction in **4**–**6** can also be deduced from the ^{31}P NMR spectra. These also reveal that **6** is not in equilibrium with the η^2(C,P)-coordinated complex, which is at variance with the respective findings for $Cp_2(Cl)Zr[(PMe_2)_2CH]$.

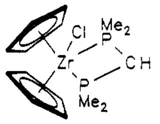
Introduction

In the preceding paper, we reported about a series of phosphinomethanide complexes of the chlorozirconocene fragment.[1] With these complexes (I) we were able to show for the first time that η^1(C) bonding of the ligand, which is observed for I (X = Y = H), can be effectively switched to η^2(C,P) coordination if phosphino or silyl groups are placed at the coordinated carbanionic center. Among complexes I, which in the solid state all adopt a three-membered heterocyclic structure (η^2(C,P) coordination), the *di*phosphinomethanide complex Ia is unique in being in equilibrium with the four-membered chelate complex II (η^2(P,P) coordination) in solution. In a sense II may be regarded as the first neutral diphosphine zirconocene(IV) derivative; unfortunately, it could not be isolated from the mixture of isomers.[1]



I

a: X = H, Y = PMe_2
b: X = H, Y = $SiMe_3$
c: X = Y = $SiMe_3$



II

The η^2(C,P) coordination mode of the phosphinomethanide ligands is a result of a new concept, which allows the tuning of the carbon/phosphorus nucleophilicity in phosphinomethanides III by heteroelement substituents X and Y such as PMe_2 or $SiMe_3$.[1]

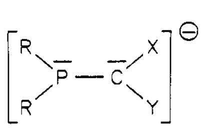
The respective influence of the substituents R at P is less obvious, however. To probe this influence and to obtain a stable complex of type II, we replaced the C–H

[†] This work describes parts of two theses: Deubelly, B. Thesis, Technical University of Munich, 1988. Grauvogl, G. Thesis, Technical University of Munich, 1990.

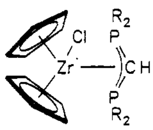
[‡] Present address: Fakultät für Chemie, Universität Konstanz, Universitätsstrasse 10, D-7750 Konstanz 1, Germany.

[1] Karsch, H. H.; Deubelly, B.; Grauvogl, G.; Müller, G. *Organometallics*, preceding paper in this issue.

0276-7333/92/2311-4245$03.00/0

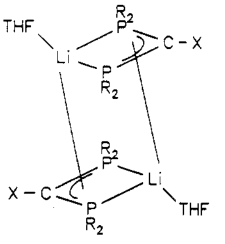


III

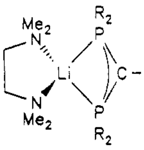


IV

functionality in Ia by a C–$SiMe_3$ functionality, thus disfavoring η^2(C,P) coordination by simultaneously reducing the C and enhancing the P nucleophilicity,[2] which should strongly promote η^2(P,P) coordination. In addition, we replaced the methyl substituents at phosphorus by phenyl groups in order to allow a comparison of the effect of different methyl/phenyl substitution at P. This should in principle reduce the P nucleophilicity, as can be seen in the structures of the lithium phosphinomethanides V and VI.



V



VI

a: R = Me, X = H[2]
b: R = Ph, X = H[3]
c: R = Me, X = $SiMe_3$[3]

a: R = Me[3]
b: R = Ph[2]

Since Li^+ and the $[Cp_2(Cl)Zr]^+$ fragment are closely related,[4] a trend similar to that in V and VI is also to be expected for the zirconocene complexes. Furthermore, it was an open question as to whether a chelating P,P coordination of type IV would be feasible. This kind of diphosphinomethanide ligation was observed in $La[HC(PPh_2)_2]_3$[5] and is involved in the dynamic behavior of Ia/II.[1] The synthesis and spectroscopic characterization of chlorozirconocene diphosphinomethanide complexes of type II, $Cp_2(Cl)Zr[(R_2P)_2CX]$, and X-ray structure determinations for R = Me, Ph and X = $SiMe_3$ are described in this paper.

Experimental Section

A. Preparation and Characterization of Compounds. General procedures, instrumentation, and solvents were as previously described.[1] $Li[(Me_2P)_2C(SiMe_3)]$,[6] $(TMEDA)Li[(Ph_2P)_2CH]$,[7] and $(TMEDA)Li[C(PPh_2)_2(SiMe_3)]$[2] were prepared according to the literature; Cp_2ZrCl_2 was obtained from a commercial source. The NMR spectra refer to TMS (^1H, ^{13}C) and 85% H_3PO_4 (^{31}P) with chemical shifts in δ and coupling constants in Hz. The symbol "t" is used for the deceptively simple appearance of the $X_nAA'X_n'$ and AA'X spin system with N = distance between the outer lines (in Hz).

Synthesis of $Cp_2(Cl)Zr[(Me_2P)_2C(SiMe_3)]$ (4). To 1.0 g (3.42 mmol) of Cp_2ZrCl_2 and 0.73 g (3.42 mmol) of $Li[(Me_2P)_2C(SiMe_3)]$[6] was added 30 mL of Et_2O at −78 °C. With stirring, the mixture was warmed to room temperature within 2 h. The solution was evaporated, and the residue was extracted twice with 30 mL of toluene. The solvent slowly was condensed off, and a yellow crystalline solid was obtained, which was washed with 20 mL of pentane and dried in vacuo: 1.17 g (73.5%); mp 182 °C dec. Anal. Calcd for $C_{18}H_{31}ClP_2SiZr$ (464.15): C, 46.58; H, 6.73; Cl, 7.64. Found: C, 46.32; H, 6.33; Cl, 7.91. MS: *m/e* 398 (16%, $M^+ - C_5H_4$), 383 (17%, $M^+ - C_5H_4 - CH_3$), 333 (31%, $M^+ + 1 - 2C_5H_5$), 317 (38%, $M^+ - 2C_5H_5 - CH_3$), 208 (38%, $HC(PMe_2)_2(SiMe_3)$), 193 (76%, $HC(PMe_2)_2(SiMe_3) - CH_3$), 147 (42%, $HC(PMe_2)(SiMe_3)$), 75 (63%, CH_2PMe_2), 73 (100%, $SiMe_3$). ^1H NMR (C_6D_6): $\delta(C_5H_5)$ 5.72 (d, 1.5, 10 H), $\delta(PCH_3)$ 1.34 (dd, 8.8 Hz, 2.2 Hz, 6 H), $\delta(PCH_3)$ 1.14 (dd, 8.1 Hz, 1.5 Hz, 6 H), $\delta(SiCH_3)$ 0.22 (s, 9 H). $^{13}C\{^1H\}$ NMR (C_6D_6) $\delta(C_5H_5)$ 110.70 (s), $\delta(P_2CSi)$ 10.38 (t, 31.1 Hz), $\delta(PCH_3)$ 23.2 (dd, 13.4 Hz, 8.5 Hz), $\delta(PCH_3)$ 21.66 (dd, 15.9 Hz, 12.2 Hz), $\delta(SiCH_3)$ 5.33 (s, $^1J(SiC) = 50.0$ Hz). ^{31}P NMR $\{^1H\}$ (C_6D_6): $\delta(P_A)$ −36.01, $\delta(P_B)$ −38.74, AB spin system ($^2J(P_AP_B) = 82.4$ Hz).

Synthesis of $Cp_2(Cl)Zr[(Ph_2P)_2C(SiMe_3)]$ (5). Cp_2ZrCl_2 (490 mg, 1.66 mmol) was dissolved in 30 mL of Et_2O and the solution cooled to −78 °C. $(TMEDA)Li[(Ph_2P)_2C(SiMe_3)]$[2] (960 mg, 1.66 mmol) was added and the solution slowly warmed to room temperature with stirring. After 18 h, the solvent was evaporated and the solid residue extracted twice with 40 mL of toluene. Slow evaporation of the toluene yielded an orange, crystalline material: 700 mg (59%); mp 257 °C. Anal. Calcd for $C_{38}H_{39}ClP_2SiZr$ (712.44): C, 64.06; H, 5.52; Cl, 4.98. Found: C, 64.75; H, 5.76; Cl, 4.88. ^1H NMR (C_6D_6): δ(phenyl H2, H6) 8.16 (m, N = 16.8 Hz, 4 H), δ(phenyl H2, H6) 7.93 (m, N = 16.2 Hz, 4 H), δ(phenyl H3, H5) 7.28 ("t", N = 15.0 Hz, 4 H), δ(phenyl H3, H5) 7.22 ("t", N = 15.0 Hz, 4 H), δ(phenyl H4) 7.01 (m, N = 8.5, 4 H), $\delta(C_5H_5)$ 5.61 (s, 10 H), $\delta(SiCH_3)$ −0.14 (s, 9 H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ(phenyl C1) 141.50 ("t", N = 32.6 Hz), δ(phenyl C1) 141.08 ("t", N = 41.4 Hz), δ(phenyl C2, C6) 134.1 ("t", N = 10.1 Hz), δ(phenyl C2, C6) 132.4 ("t", N = 8.7 Hz), δ(phenyl C3, C4, C5) superposition with solvent, $\delta(C_5H_5)$ 112.2 (s), $\delta(P_2CSi)$ 24.93 (t, 30.8 Hz), $\delta(SiCH_3)$ 3.82 (s). $^{31}P\{^1H\}$ NMR ($C_6D_5CD_3$): 20 °C, δ(P) 3.03 (s); −60 °C, $\delta(P_A)$ 2.04, $\delta(P_B)$ 3.04, AB spin system ($J(P_AP_B) = 159.1$ Hz).

Synthesis of $Cp_2(Cl)Zr[(Ph_2P)_2CH]$ (6). To 0.65 g (2.23 mmol) of Cp_2ZrCl_2 in 40 mL of Et_2O was added 1.13 g (2.23 mmol) of $(TMEDA)Li[(Ph_2P)_2CH]$[7] at −78 °C. The mixture was allowed to react with stirring at 0 °C for 18 h, and subsequently, the solvent was evaporated. The residue was extracted three times with 35 mL of toluene. Slow removal of the solvent in vacuo gave 430 mg (30%) of a yellow, crystalline solid: mp 155 °C. Anal. Calcd for $C_{35}H_{31}ClP_2Zr$ (640.25): C, 65.66; H, 4.88; Cl, 5.54. Found: C, 65.40; H, 5.07; Cl, 6.05. ^1H NMR (C_6D_6): δ(phenyl H2, H6) 8.23 ("t", N = 16.8 Hz, 4 H), δ(phenyl H2, H6) 7.75 ("t", N = 16.2 Hz, 4 H), δ(phenyl H3, H5), 7.23 (m, N = 16.2 Hz, 4 H), δ(phenyl H3, H5) 7.15 (m, N = 16.2 Hz, 4 H), δ(phenyl H4) 7.03 (m, N = 6.2 Hz, 4 H), $\delta(C_5H_5)$ 5.71 (d, 1.5 Hz, 10 H), $\delta(P_2CH)$ 2.21 (t, 4.2 Hz, 1 H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ(phenyl C1) 143.4 (m, N = 31.7 Hz), δ(phenyl C2, C6) 133.26 ("t", N = 21.1 Hz), δ(phenyl C3, C5) 131.23 (m, N = 21.1 Hz), δ(phenyl C4) superposition with solvent, $\delta(C_5H_5)$ 112.23 (s), δ(CH) 14.32 (t, 52.6 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta(P_A)$ −8.94, $\delta(P_B)$ −17.83, AB spin system ($J(P_AP_B) = 189.1$ Hz).

B. Crystal Structure Determinations. Suitable single crystals of **4** (yellow) and **5** (orange) were obtained by low-temperature crystallization from toluene. Complex **5** cocrystallizes under these conditions with two molecules of toluene. Crystals of **4** contain two independent molecules per asymmetric unit. They were found to be of limited quality and diffracted poorly at higher Bragg angles. Consequently, the number of "observed" structure factors is rather low and the structure refinement resulted in relatively large standard deviations of the parameters. Reduced cell calculations did not reveal symmetry higher than monoclinic. Exact cell parameters were obtained by a least-squares fit to the Bragg angles of 25 high-angle reflections centered on the diffractometer (Mo Kα radiation, λ = 0.710 69 Å, graphite monochromator). Table I contains the crystal data and important numbers pertinent to data collection and structure refinement.

The intensity data were corrected for Lorentz–polarization effects and those of **4** also linearly for crystal decay (−8.8%). Absorption corrections were not necessary because of the uniform crystal shape (crystal dimensions: **4**, 0.35 × 0.35 × 0.4 mm^3; **5**·2(toluene), 0.25 × 0.35 × 0.35 mm^3). Both structures were solved by direct methods (SHELXS-86) and completed by Fourier

---

[2] Karsch, H. H.; Grauvogl, G.; Mikulcik, P.; Bissinger, P.; Müller, G. *J. Organomet. Chem.*, submitted for publication.

[3] Karsch, H. H.; Deubelly, B.; Müller, G. *J. Organomet. Chem.* 1988, *352*, 47.

[4] Kos, A. J.; Jemmis, E. D.; Schleyer, P. v. R.; Gleiter, R.; Fischbach, U.; Pople, J. A. *J. Am. Chem. Soc.* 1981, *103*, 4996.

[5] Karsch, H. H.; Appelt, A.; Müller, G. *Angew. Chem.* 1986, *98*, 832; *Angew. Chem., Int. Ed. Engl.* 1986, *25*, 823.

[6] Karsch, H. H.; Appelt, A.; Deubelly, G.; Zellner, K.; Riede, J.; Müller, G. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* 1988, *43B*, 1416.

[7] Brauer, D. J.; Hietkamp, S.; Stelzer, O. *J. Organomet. Chem.* 1986, *299*, 137.

Table I. Crystal Structure Data for 4 and 5•2(toluene)

	4	5·2(toluene)
formula	$C_{18}H_{31}ClP_2SiZr$	$C_{38}H_{39}ClP_2SiZr\cdot 2C_7H_8$
M_r	464.15	896.725
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)
a, Å	16.284 (3)	19.184 (3)
b, Å	14.463 (2)	11.668 (2)
c, Å	19.252 (2)	22.695 (3)
β, deg	97.42 (1)	114.63 (1)
V, Å^3	4496.2	4617.8
Z	8	4
d_{calcd}, g/cm^3	1.371	1.290
μ(Mo Kα), cm^{-1}	7.9	4.2
F(000), e	1920	1872
T, °C	room temp	−50
diffractometer	Enraf-Nonius CAD4	Syntex P2$_1$
scan	$\vartheta/2\vartheta$	ω
scan width (in ω)	1.2 + 0.35 tan ϑ	0.8
$[(\sin\vartheta)/\lambda]_{max}$, Å^{-1}	0.592	0.561
hkl range	±19,+17,+22	+21,+13,±25
no. of rflns (measd/unique)	8418/7829	7439/6771
R_{int}	0.028	0.028
no. of rflns obsd [$F_o \geq 4.0\sigma(F_o)$]	3930	5501
no. of H atoms (found/calcd)	neglected	35/20
no. of params ref	415 (2 blocks)	514 (2 blocks)
R^a	0.088	0.049
$R_w{}^b$	0.073	0.050
$\Delta\rho_{fin}$(max/min), e/Å^3	+1.28/−0.96	+0.75/−0.49

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

Table II. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters for Both Crystallographically Independent Molecules of 4

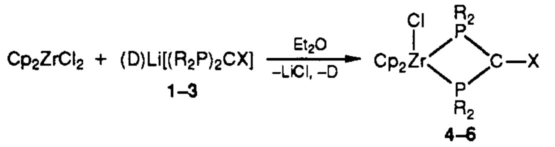
atom	x/a	y/b	z/c	U_{eq},[a] Å^2
		Molecule 1		
Zr(1)	0.4789 (1)	0.6449 (1)	0.2313 (1)	0.031
Cl(1)	0.4801 (3)	0.4710 (3)	0.2617 (3)	0.052
P(1)	0.3906 (3)	0.7500 (3)	0.1212 (3)	0.034
P(2)	0.3687 (3)	0.5656 (3)	0.1304 (2)	0.034
Si(1)	0.2591 (3)	0.6582 (3)	−0.0001 (3)	0.049
C(1)	0.3281 (10)	0.6599 (9)	0.0814 (8)	0.026
C(11)	0.3239 (9)	0.8491 (10)	0.1402 (10)	0.039
C(12)	0.4436 (11)	0.8106 (13)	0.0559 (9)	0.051
C(21)	0.4145 (12)	0.4791 (11)	0.0753 (10)	0.027
C(22)	0.2838 (11)	0.4963 (13)	0.1632 (10)	0.048
C(51)	0.2136 (13)	0.7758 (13)	−0.0259 (11)	0.053
C(52)	0.3096 (12)	0.6120 (15)	−0.0756 (9)	0.065
C(53)	0.1662 (10)	0.5806 (13)	0.0079 (10)	0.046
Cp(1)	0.3519 (11)	0.7017 (17)	0.2820 (9)	0.049
Cp(2)	0.4163 (12)	0.7725 (13)	0.2942 (10)	0.049
Cp(3)	0.4807 (11)	0.7371 (13)	0.3432 (10)	0.046
Cp(4)	0.4673 (15)	0.6436 (12)	0.3581 (11)	0.049
Cp(5)	0.3845 (16)	0.6281 (13)	0.3249 (12)	0.060
Cp(6)	0.5803 (11)	0.6521 (15)	0.1425 (10)	0.057
Cp(7)	0.5901 (9)	0.7369 (13)	0.1796 (11)	0.034
Cp(8)	0.6218 (10)	0.7163 (15)	0.2508 (11)	0.054
Cp(9)	0.6328 (11)	0.6208 (17)	0.2571 (13)	0.064
Cp(10)	0.6079 (11)	0.5838 (13)	0.1883 (15)	0.049
		Molecule 2		
Zr(2)	0.9812 (1)	0.7098 (1)	0.7244 (1)	0.035
Cl(2)	0.9959 (3)	0.8879 (3)	0.7224 (3)	0.060
P(3)	0.8914 (3)	0.5834 (3)	0.6320 (2)	0.033
P(4)	0.8831 (3)	0.7666 (3)	0.6071 (2)	0.033
Si(2)	0.7626 (3)	0.6401 (4)	0.4991 (3)	0.050
C(2)	0.8395 (9)	0.6630 (10)	0.5750 (8)	0.030
C(31)	0.8143 (11)	0.5036 (11)	0.6641 (9)	0.050
C(32)	0.9474 (12)	0.4977 (11)	0.5828 (9)	0.041
C(41)	0.8023 (10)	0.8538 (11)	0.6248 (11)	0.042
C(42)	0.9385 (12)	0.8270 (12)	0.5409 (9)	0.050
C(61)	0.6673 (11)	0.5823 (16)	0.5236 (13)	0.064
C(62)	0.7324 (15)	0.7530 (13)	0.4498 (11)	0.057
C(63)	0.8046 (12)	0.5638 (13)	0.4331 (9)	0.047
Cp(11)	1.1356 (11)	0.7235 (18)	0.7549 (13)	0.064
Cp(12)	1.1189 (12)	0.7391 (15)	0.6801 (13)	0.059
Cp(13)	1.0902 (11)	0.6597 (17)	0.6469 (11)	0.059
Cp(14)	1.0897 (12)	0.5933 (13)	0.7023 (13)	0.067
Cp(15)	1.1162 (12)	0.6289 (16)	0.7674 (13)	0.066
Cp(16)	0.9577 (15)	0.7485 (17)	0.8457 (11)	0.058
Cp(17)	0.8800 (13)	0.7663 (13)	0.8027 (10)	0.056
Cp(18)	0.8454 (13)	0.6873 (13)	0.7745 (10)	0.060
Cp(19)	0.8992 (12)	0.6149 (13)	0.8021 (10)	0.046
Cp(20)	0.9688 (15)	0.6548 (18)	0.8477 (11)	0.076

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a^*_i a^*_j \mathbf{a}_i\mathbf{a}_j$.

syntheses. The hydrogen atoms in the structure of 4 were entirely neglected because their inclusion at idealized geometrical positions in the structure factor calculations was not found to give a significantly better fit to the observed data. Those of 5·2(toluene) were largely found, including some at the cocrystallized toluene molecules. The remainder were calculated at idealized geometrical positions (XANADU). All hydrogen atoms were held constant in the final refinement cycles (U_{iso} = 0.05 Å^2). For both structures the parameters were divided into two blocks and refined with an enlarged version of SHELX-76. Tables II and III contain the fractional coordinations of the nonhydrogen atoms, Table IV summarizes the most important bond distances and angles for both structures. See the note at the end of the paper for supplementary material available.

Results and Discussion

All three complexes 4–6 were obtained by essentially the same method as depicted in eq 1. They are obtained as



(1)

1, 4: D = –, R = Me, X = SiMe$_3$
2, 5: D = TMEDA, R = Ph, X = SiMe$_3$
3, 6: D = TMEDA, R = Ph, X = H

yellow or orange crystals from toluene. All compounds are modestly air-sensitive but are thermally stable with high melting points.

The NMR spectra show 4–6 to be essentially rigid on the NMR time scale. This follows from the $^{13}C\{^1H\}$ and/or ^1H NMR spectra, which each show two sets of signals for the substituents at P(1) and P(2), as expected for a structure of type II. In contrast to the case for molecules of type I,[1] the lone Cp signal for 4–6 indicates molecular mirror symmetry. Complex 5 seems to be an exception from the postulated rigidity, however, as the $^{31}P\{^1H\}$ NMR spectra show. Only for 4 and 6 is the expected AB type of spectrum observed, whereas the spectrum of 5 consists of a single line at 20 °C. When the temperature is lowered to −60 °C, an AB splitting emerges also in this case. This might in principle indicate that P(1) and P(2) are equilibrated by a dynamic process which is observed for Ia/II and which involves a type IV coordination of the phosphinomethanide ligand. Considering the fact that both δ values for the phosphorus nuclei P(1) and P(2) are very close together and that the P substituents remain inequivalent, it seems much more likely that this observation is due to a random equivalence (equal chemical shift) for P(1) and P(2) in the temperature range from −40 to +20 °C. This idea is firmly backed by the observation that the dynamic exchange process in Ia/II (where it should be much more favorable) occurs only at high temperatures. The same holds for 6, where the exchange process is not observed at all. A small temperature dependence of the ^{31}P NMR chemical shifts is a common phenomenon and is also observed in the spectra of 4 and 6. The small shift

Table III. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters for 5•2(toluene)

atom	x/a	y/b	z/c	U_{eq}, Å^2
Zr	0.28411 (2)	0.01243 (3)	0.65646 (2)	0.024
Cl	0.17599 (7)	0.1546 (1)	0.59763 (6)	0.036
P(1)	0.26506 (6)	−0.0014 (1)	0.52670 (5)	0.023
P(2)	0.35168 (6)	−0.16446 (9)	0.61077 (5)	0.023
Si	0.33533 (8)	−0.2007 (1)	0.46588 (6)	0.030
C(1)	0.3229 (2)	−0.1200 (3)	0.5310 (2)	0.024
C(111)	0.2993 (3)	0.1270 (4)	0.5001 (2)	0.027
C(112)	0.2539 (3)	0.2252 (4)	0.4786 (2)	0.035
C(113)	0.2841 (3)	0.3246 (4)	0.4659 (2)	0.039
C(114)	0.3603 (3)	0.3286 (4)	0.4748 (3)	0.048
C(115)	0.4053 (3)	0.2326 (4)	0.4965 (3)	0.041
C(116)	0.3752 (3)	0.1327 (4)	0.5082 (2)	0.033
C(121)	0.1680 (2)	−0.0175 (4)	0.4617 (2)	0.029
C(122)	0.1101 (3)	−0.0623 (4)	0.4757 (2)	0.033
C(123)	0.0373 (3)	−0.0838 (4)	0.4271 (3)	0.040
C(124)	0.0229 (3)	−0.0593 (5)	0.3633 (3)	0.045
C(125)	0.0811 (3)	−0.0122 (5)	0.3485 (2)	0.045
C(126)	0.1521 (3)	0.0092 (4)	0.3973 (2)	0.038
C(211)	0.4563 (2)	−0.1766 (3)	0.6546 (2)	0.026
C(212)	0.5045 (3)	−0.1450 (4)	0.6255 (2)	0.032
C(213)	0.5838 (3)	−0.1498 (4)	0.6594 (2)	0.041
C(214)	0.6152 (3)	−0.1852 (4)	0.7240 (3)	0.043
C(215)	0.5689 (3)	−0.2145 (4)	0.7534 (2)	0.036
C(216)	0.4902 (3)	−0.2093 (4)	0.7199 (2)	0.029
C(221)	0.3209 (3)	−0.3150 (4)	0.6087 (2)	0.027
C(222)	0.2476 (3)	−0.3434 (4)	0.5628 (2)	0.032
C(223)	0.2198 (3)	−0.4539 (4)	0.5574 (2)	0.039
C(224)	0.2638 (3)	−0.5390 (4)	0.5978 (3)	0.041
C(225)	0.3369 (3)	−0.5132 (4)	0.6429 (2)	0.041
C(226)	0.3657 (3)	−0.4036 (4)	0.6490 (2)	0.033
Cp(11)	0.4183 (3)	0.0505 (4)	0.7336 (3)	0.043
Cp(12)	0.4131 (3)	0.0891 (4)	0.6731 (2)	0.034
Cp(13)	0.3635 (3)	0.1842 (4)	0.6553 (2)	0.029
Cp(14)	0.3397 (3)	0.2061 (4)	0.7047 (2)	0.031
Cp(15)	0.3743 (3)	0.1228 (4)	0.7539 (2)	0.038
Cp(21)	0.2045 (3)	−0.1615 (4)	0.6583 (2)	0.032
Cp(22)	0.2764 (3)	−0.1725 (4)	0.7134 (2)	0.036
Cp(24)	0.2143 (3)	−0.0149 (4)	0.7269 (3)	0.045
Cp(23)	0.2807 (3)	−0.0828 (5)	0.7557 (2)	0.043
Cp(25)	0.1671 (3)	−0.0680 (4)	0.6684 (3)	0.040
CS(1)	0.3954 (3)	−0.3322 (4)	0.4979 (2)	0.038
CS(2)	0.3796 (3)	−0.1114 (5)	0.4222 (3)	0.053
CS(3)	0.2433 (3)	−0.2527 (5)	0.4015 (3)	0.062
C(11)[a]	0.5157 (3)	0.1279 (5)	0.9156 (2)	0.054
C(12)[a]	0.4705 (4)	0.0421 (7)	0.9222 (3)	0.071
C(13)[a]	0.4817 (5)	−0.0747 (7)	0.9095 (3)	0.086
C(14)[a]	0.5384 (5)	−0.0987 (6)	0.8911 (3)	0.079
C(15)[a]	0.5829 (4)	−0.0156 (6)	0.8826 (3)	0.067
C(16)[a]	0.5715 (3)	0.0953 (5)	0.8948 (3)	0.055
Ct(1)[a]	0.5084 (4)	0.2501 (6)	0.9300 (3)	0.083
C(21)[a]	0.1276 (7)	0.1905 (9)	0.2326 (4)	0.109
C(22)[a]	0.0579 (5)	0.1712 (8)	0.1832 (5)	0.093
C(23)[a]	0.0482 (6)	0.066 (1)	0.1536 (5)	0.119
C(24)[a]	0.097 (2)	−0.013 (1)	0.1689 (8)	0.209
C(25)[a]	0.167 (1)	0.011 (2)	0.222 (1)	0.203
C(26)[a]	0.1809 (6)	0.106 (1)	0.2515 (7)	0.137
Ct(2)[a]	0.141 (1)	0.292 (2)	0.2650 (7)	0.298

[a] C atoms of cocrystallized toluene molecules; Ct = toluene methyl groups.

Table IV. Selected Bond Distances (Å) and Angles (deg) in the Molecular Structures of 4 and 5•2(toluene)[a]

	4[b]		5·2(toluene)	
	molecule 1	molecule 2		
Zr(1)–Cl(1)	2.581 (4)	2.589 (4)	Zr–Cl	2.555 (1)
Zr(1)–P(1)	2.844 (5)	2.823 (4)	Zr–P(2)	2.852 (1)
Zr(1)–P(2)	2.721 (5)	2.719 (5)	Zr–P(1)	2.817 (1)
Zr(1)–D(1)[c]	2.20	2.23	Zr–D(1)	2.21
Zr(1)–D(2)	2.23	2.22	Zr–D(2)	2.24
C(1)–P(1)	1.77 (2)	1.73 (2)	C(1)–P(2)	1.738 (4)
C(1)–P(2)	1.74 (2)	1.74 (2)	C(1)–P(1)	1.752 (4)
C(1)–Si(1)	1.81 (2)	1.83 (2)	C(1)–Si	1.849 (5)
D(1)–Zr(1)–D(2)	131.5	131.5	D(1)–Zr–D(2)	127.2
Cl(1)–Zr(1)–P(1)	132.7 (2)	132.5 (2)	Cl–Zr–P(2)	132.3 (1)
Cl(1)–Zr(1)–P(2)	74.7 (1)	74.4 (1)	Cl–Zr–P(1)	76.6 (1)
P(1)–Zr(1)–P(2)	58.0 (1)	58.1 (1)	P(1)–Zr–P(2)	57.3 (1)
P(1)–C(1)–P(2)	100.7 (8)	101.8 (8)	P(1)–C(1)–P(2)	102.2 (3)
P(1)–C(1)–Si(1)	130.1 (9)	127.8 (9)	P(2)–C(1)–Si	126.1 (2)
P(2)–C(1)–Si(1)	127.6 (8)	130.3 (9)	P(1)–C(1)–Si	130.4 (2)
C(1)–P(1)–Zr(1)	97.8 (5)	98.0 (5)	C(1)–P(2)–Zr	99.7 (2)
C(1)–P(2)–Zr(1)	103.1 (5)	101.7 (5)	C(1)–P(1)–Zr	100.6 (2)

[a] Estimated standard deviations are given in parentheses; geometrically equivalent parameters are each on one line. [b] The atom numbering is given only as for molecule 1 (Figure 1); the atom numbering for molecule 2 may be deduced from Table II. [c] D = centroid of the Cp rings.

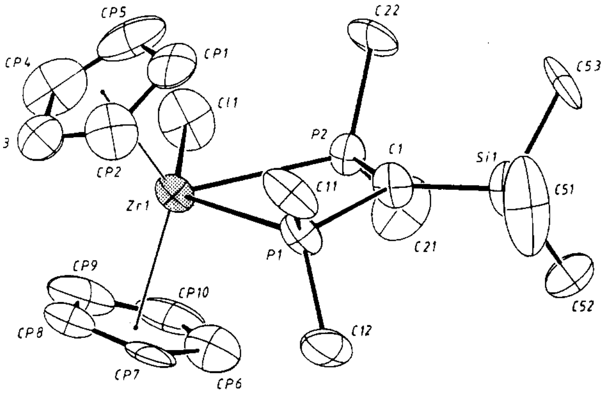


Figure 1. Molecular structure of one of the crystallographically independent molecules of 4 in the crystal form and the atomic numbering scheme adopted (ORTEP; ellipsoids at the 50% probability level; hydrogen atoms omitted for clarity).

difference in 5 for P(1) and P(2) has its equivalence in the small differences in the Zr–P distances of the solid-state structure (vide infra). In fact, it turns out that these distances and the Δδ(P) values are correlated (cf. Table V). It is necessary, however, to keep in mind that ^{31}P shifts are subject to ring[8] and to substitution effects and therefore Δδ values for 4 and 5 should not be compared. In any case, Δδ for 5 and 6 should be comparable—but they are not (Table V). The small coordination shift for P(2) in 6 could be attributed to a type I coordination, but the trends in the coupling constants and the observation that only one Cp signal is found (type I coordination implies a chiral C atom and therefore requires two Cp signals) ascertains the proposed type II structure also for 6. At present, there is no explanation for the observed shift differences for P(1) and P(2) in 6 other than a gross difference in the Zr–P bond lengths, which is in contrast to what is observed for 5. At this point, it might be helpful to recall that the fragments $[Cp_2Zr(Cl)]^+$ and $[(donor)_2Li]^+$ have surprising electronic similarities (frontier orbitals, electronegativity, d^0 electron configuration).[4] In V, the $[HC(PPh_2)_2]^-$ complex (Vb) is indeed distinguished by drastically different Li–P distances (2.607 (6)/3.056 (6) Å), thus confirming our assumptions concerning 6. Unfortunately, single crystals of 6 were not of sufficient quality for an X-ray structure determination, but 4 and 5 were studied by this method.

Both 4 and 5 contain a $Cp_2(Cl)Zr$ fragment complexed by a chelating diphosphinomethanide ligand, which is bound exclusively via the two phosphorus atoms. The plane of the four-membered heterocycle formed bisects the angle opened by the Cp rings. The planarity of the four-membered ring may be judged from the small angle between the planes Zr, P(1), P(2) and P(1), P(2), C(1), which is 6.3/5.9° in 4 and 4.6° in 5. In both independent molecules of 4 the chlorine atoms are coplanar within standard deviations with the ZrP_2C heterocycle, but in 5

---

(8) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

Table V. $^{31}P\{^1H\}$ **NMR Data for Compounds 4–6, Ia, and II ($C_6D_5CD_3$; δ; *J*, Hz) and Zr–P Distances (Å)**

P_2 in $Cp_2(Cl)ZrP_2$	no.	*T* (°C)	δP(1) (Δδ)[a]	δP(2) (Δδ)[a]	*J*(PP)	Zr–P[b]	Zr–P
$(Me_2P)_2C(SiMe_3)$	**4**	+20	−36.26 (8.8)	−38.53 (6.6)	82.4	2.844 (5)	2.721 (5)
$(Ph_2P)_2C(SiMe_3)$	**5**	+20	3.03 (15.31)				
	5	−60	3.04 (15.32)	2.04 (14.32)	159.1	2.852 (2)	2.817 (1)
$(Ph_2P)_2CH$	**6**	+20	−8.94 (12.56)	−17.83 (3.67)	189.1		
$(Me_2P)_2CH$	Ia[c]	−60	−26.95 (28.75)	−34.04 (21.66)[d]	0	2.621 (1)	
$(Me_2P)CH$	II	−60	−40.37 (15.33)	−42.88 (12.82)	126.8		

[a] Coordination shift relative to the parent phosphinomethane: $HC(PMe_2)_2(SiMe_3)$ (δ(P) −45.10), $HC(PPh_2)_2(SiMe_3)$ (δ(P) −12.28), $H_2C(PPh_2)_2$ (δ(P) −21.50), $H_2C(PMe_2)_2$ (δ(P) −55.70). [b] P atom "trans" to Cl. [c] $P(1) = P_{endo}$; $P(2) = P_{exo}$. [d] No Zr–P bond.

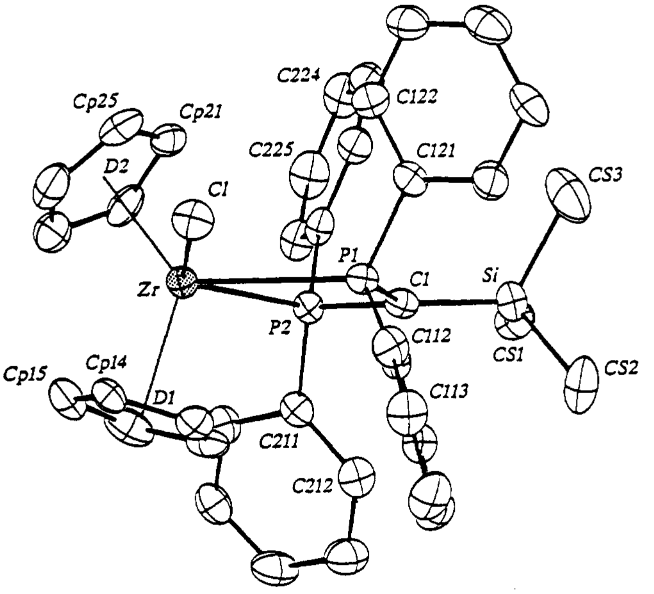


Figure 2. Molecular structure of **6** in the crystal form.

the deviation of a chloride atom of −0.51 Å from the best plane through Z, P(1), P(2), and C(1) is observed. Since intramolecular steric forces can most probably be ruled out to account for the the nonpolarity, it might well be caused by packing forces exerted on the bulky $Cp_2(Cl)Zr$ and $(PPh_2)_2C(SiMe_3)$ fragments. The planar carbanionic C(1) atom is not involved in any bonding to zirconium, which definitely rules out a type I or IV structure. In **5**, the nearly perpendicular conformation of the phenyl rings at each phosphorus with respect to each other obviously reduces steric strain. The Zr–P distances are in the upper range for phosphine–zirconium interactions, which according to a literature survey usually range between 2.66 and 2.87 Å. This is in marked contrast to the Zr–P bonds in complexes of type I, where they are found to be expectionally short.[1] Not unexpectedly, in both complexes **4** and **5** the lateral P atoms (P(1)/P(3) in **4**; P(2) in **5**) "trans" to the chlorine atom have noticeably *longer* bonds to Zr than the central P atoms in the Zr coordination sphere. On purely steric grounds one is tempted to expect the opposite. The bonds in **4** are shorter, however, than in **5**, which is due to the better σ-donor character of the PMe_2 groups as compared to the PPh_2 groups. The observed differences in the Zr–P bond lengths are larger in **4** than in **5**, in line with the NMR data, which indicate a larger Δδ(P) value for **4** than for **5** (vide infra). The Zr–Cl bond distances are comparable to those in other chlorozirconocene four-membered-ring chelates[9] and also to those in compound I.[1] As might be expected, the shorter Zr–P distances in **4** correspond to longer Zr–Cl bonds in **5** and vice versa. A certain influence of the different P substituents is reflected not only in the different Zr–P distances but also in the different P–C(1) bond lengths within the heterocycle. In all cases the P–C(1) bonds are shortened, with respect to normal P–C single bonds, as is also the case in the respective lithium compounds V and VI and in the zirconium heterocycles I. In **4**, the shorter Zr–P bonds correspond to shorter P–C(1) bonds, in line with the suggested ylidic, i.e., zwitterionic, representation of the arrangement.[1,2] Although in **4** the effect is obscured by the rather large standard deviations, it is a well-documented phenomenon in the structural chemistry of metal complexes of phosphinomethanides bearing alkyl groups at phosphorus. In **5**, on the other hand, an alternating short/long correlation is found for the Zr–P/P–C(1) distances, respectively. This again points to the extra stabilization *P*-phenyl substituents exert on phosphorus ylides.[2]

In conclusion, P,P coordination of diphosphinomethanides to zirconocene(IV) fragments is strongly favored over P,C coordination by reducing the nucleophilicity of the carbanion with *C*-silyl substituents. The structures of the resulting four-membered heterocycles Zr–P–C–P show trends with respect to P substitution similar to those in lithium complexes Li–P–C–P.

Acknowledgment. This work was supported by the Fonds der Chemischen Industrie, Frankfurt/Main, Germany. We also thank Prof. Dr. H. Schmidbaur for financial support and Mr. J. Riede for the data collection.

Supplementary Material Available: Tables of displacement parameters for **4** and **5** and a table of H atom coordinates for **5** (9 pages). Ordering information is given on any current masthead page.

OM920261K

---

(9) See ref 1 and literature cited therein (ref 19).