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# Zirconocene Derivatives with Phosphinomethanide Ligands: Synthesis, Reactions, and Molecular Structures of $Cp_2\overline{Zr(Cl)[C(P}Me_2)(X)(Y)]$ (X = H, Y = $PMe_2$, $SiMe_3$; X = Y = $SiMe_3$)†

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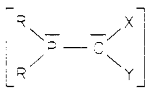
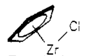
From $Cp_2ZrCl_2$ and the appropriate lithium phosphinomethanides, the novel complexes $Cp_2Zr(Cl)[C(PMe_2)(X)(Y)]$ (X = H, Y = $PMe_2$ (**4**); X = H, Y = $SiMe_3$ (**5**); X = Y = $SiMe_3$ (**6**)) are obtained as crystalline solids and characterized by spectroscopy and by X-ray structure determinations. **4**: monoclinic, $P2_1/n$, $a$ = 16.080 (2) Å, $b$ = 14.047 (1) Å, $c$ = 17.003 (2) Å, $\beta$ = 116.64 (1)°, $V$ = 3432.9 Å$^3$, $Z$ = 8, $T$ = −35 °C, $R_w$ = 0.030, $w = 1/\sigma^2(F_o)$. **5**: monoclinic, $P2_1/c$, $a$ = 15.687 (2) Å, $b$ = 15.898 (2) Å, $c$ = 16.165 (2) Å, $\beta$ = 111.16 (1)°, $V$ = 3759.6 Å$^3$, $Z$ = 8, $T$ = −35 °C, $R_w$ = 0.061. **6**·0.5(toluene): monoclinic, $P2_1/c$, $a$ = 18.585 (2) Å, $b$ = 8.809 (1) Å, $c$ = 16.102 (2) Å, $\beta$ = 103.93 (1)°, $V$ = 2558.6 Å$^3$, $Z$ = 4, $T$ = −40 °C, $R_w$ = 0.053. In all three complexes **4**–**6**, the zirconium atom as part of a metallaphosphacyclopropane ring is the most prominent structural feature. Whereas the Zr–P (**4**, 2.621 (1)/2.632 (1) Å; **5**, 2.634 (1)/2.616 (1) Å; **6**, 2.606 (1) Å) as well as the Zr–Cl (**4**, 2.569 (1)/2.576 (1) Å; **5**, 2.558 (1)/2.572 (1) Å; **6**, 2.554 (1) Å) and the Zr–D distances (where D denotes the centroid of the cyclopentadienyl rings; **4**, 2.42/2.22 and 2.22/2.24 Å; **5**, 2.24/2.24 and 2.23/2.24 Å; **6**, 2.23/2.26 Å) are nearly equal, the Zr–C(1) distances differ considerably in going from **4** (2.413 (2)/2.408 (2) Å) to **5** (2.401 (5)/2.423 (5) Å) and to **6** (2.607 (1) Å), due to steric congestion. Consequently, **6** exists in solution as an $\eta^1$(P)-coordinated 16e complex, as may be deduced from NMR data. Complex **4** exists in solution as an equilibrium mixture of isomers **4** and **4a**, the latter exhibiting a chelating P,P-coordination of the diphosphinomethanide ligand, thus forming the four-membered heterocycle $\overline{Zr{-}P{-}C{-}P}$. At elevated temperatures, all phosphorus nuclei equilibrate, obviously via a common intermediate of **4** and **4a**. Complexes **4** and **5** do not react with CO at ambient temperature and pressure, whereas **6** decomposes above 0 °C in solution.

## Introduction

The important role of zirconocene derivates in homogeneous catalysis, in hydrozirconation, and in other organic reactions has led to enormous activities in this field of chemistry. The ambidentate nature of phosphinomethanide ligands I[1] makes them ideal candidates for modifying the properties of the zirconium center to further enrich the wide range of useful properties of this class of compounds.



I



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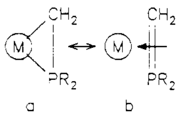

III

A decade ago, Schore et al. reported the first zirconocene phosphinomethanide complex, II.[2] Surprisingly, in this 16e complex the phosphinomethanide ligand is bound to the d$^0$ zirconium center only via carbon ($\eta^1$(C)), which is in marked contrast to many other phosphinomethanide complexes of d$^1$–d$^8$ transition-metal centers (III), where three-membered-ring formation is observed ($\eta^2$(C,P)).[3]

A detailed MO calculation[4] came to the conclusion that increasing electron density at the metal center should promote coordination of type III. Consequently, in zirconium(III) phosphinomethanide complexes (d$^1$), which are catalysts for alkene hydrogenation, $\eta^2$(C,P) coordination is observed.[5] Likewise, when chlorine is replaced by methyl groups and/or the P-bound phenyl groups are replaced by methyl in complex II, three-membered metallacycles should be favored. We and others therefore synthesized IVa–c, but in neither case was the expected three-membered-ring formation observed.[6,7]

Even replacement of $C_5H_5$ by $C_5Me_5$ in complexes II and IV did not alter the $\eta^1$(C) coordination mode.[7a] Thus, it seemed reasonable to conclude that "observation of the predicted Zr–P bonding in structures such as these will be an elusive goal".[7a]

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

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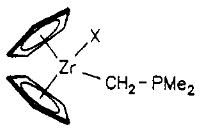
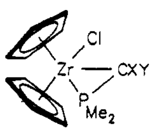
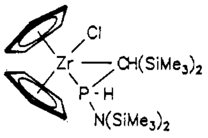


IV

a: X = Cl
b: X = Me
c: X = $CH_2PMe_2$



V



VI

In the course of our investigations on the nucleophilic behavior of phosphinomethanides I, it became evident that this property largely depends on the P and C substituents R, X, and Y. Particularly when X and Y are changed from H to $SiMe_3$ and/or $PMe_2$, the carbon nucleophilicity is reduced, whereas the phosphorus nucleophilicity is increased ("$\alpha$ and $\beta$ effect"). In this paper we describe the utilization of this fact for the synthesis of 18e zirconium complexes of the desired $\eta^2$(C,P) type V. Part of this work has been described in a preliminary note.[8] Meanwhile, the similar complex VI has been prepared by a novel route,[9] which underlines the generality of the concept.

## Experimental Section

**A. Preparation and Characterization of Compounds.** All compounds were prepared and handled under a dry nitrogen atmosphere by using conventional vacuum line techniques. Sodium/potassium alloy was employed for drying and storage of the solvents, which were redistilled immediately prior to their use. $Cp_2ZrCl_2$ and CO were obtained from commercial sources and used without further purification. $Li[CH(PMe_2)_2]$, (1),[10] $\{Li[CH(PMe_2)(SiMe_3)]TMEDA\}_2$ (2),[11] and $[LiC(PMe_2)(SiMe_3)_2]_2TMEDA$ (3)[11] were prepared according to the literature. NMR spectra were recorded on JEOL JNM GX400 ($^{31}P$, 161.7 MHz) and Bruker WP100SY ($^1H$, 100 MHz; $^{13}C$, 25.12 MHz) spectrometers at +20 °C in benzene-$d_6$ unless otherwise stated. Chemical shifts are reported in parts per million and refer to $Me_4Si$ ($^1H$, $^{13}C$) or 85% $H_3PO_4$ ($^{31}P$). Melting points were measured in sealed capillaries and are uncorrected. Elemental analyses were performed by Mikroanalytisches Labor des Anorganisch-chemischen Instituts, Technische Universität München.

**1. Preparation of $Cp_2Zr(Cl)[C(PMe_2)XY]$ (4–6): General Procedure.** $m$ g/mmol of $Cp_2ZrCl_2$ was dissolved in 40 mL of diethyl ether and the solution cooled to −78 °C. Subsequently $n$ g/mmol of 1, 2, or 3 was added. The mixture was allowed to react 18 h at the reaction temperature $T_R$ with stirring; then the solvent was removed in vacuo. The residue was extracted with 35 mL of toluene three times. Slow evaporation of the solvent from the combined solutions gave a yield of $o$ g/% of compound **4**, **5**, or **6** as a yellow crystalline solid.

**4**: $m$ = 5.16/17.65; $n$ = 2.51/17.65; $T_R$ = 0 °C; $o$ = 4.05/58; mp 132 °C. Anal. Calcd for $C_{15}H_{23}ClP_2Zr$ ($M_r$ 391.97): C, 45.97; H, 5.91; Cl, 9.04. Found: C, 46.27; H, 6.05; Cl, 9.02.

**5**: $m$ = 6.00/20.53; $n$ = 5.55/10.27; $T_R$ = 25 °C; $o$ = 7.50/88; mp 167 °C. Anal. Calcd for $C_{16}H_{23}ClPSiZr$ ($M_r$ 401.11): C, 47.55; H, 6.48; Cl, 8.77. Found: C, 47.76; H, 6.23; Cl, 9.14.

**6**: $m$ = 1.06/3.62; $n$ = 1.03/1.81; $T_R$ = −78 °C; $o$ = 7.50/74; dec pt 0 °C. Anal. Calcd for $C_{19}H_{34}ClPSi_2Zr$ ($M_r$ 476.30): C, 47.91; H, 7.19; Cl, 7.44. Found: C, 47.45; H, 6.85; Cl, 8.24.

Table I. $^1H$ and $^{13}C$ NMR Data for Compounds 4, 4a, 5, and 6

| no. | $T$, °C | assignt | $^1H$ NMR, $\delta$ ($J$, Hz) | $^{13}C\{^1H\}$ NMR, $\delta$ ($J$, Hz) |
|---|---|---|---|---|
| **4**[a] | −60 | $C_5H_5$ | 5.68 (d, 1.5, 5 H) | 108.14 (s) |
| | | | 5.40 (d, 1.8, 5 H) | 107.79 (s) |
| | | $PCH_3$ | 0.56 (d, 8.6, 3 H) | 8.56 (s, br) |
| | | (endo) | 0.91 (d, 9.2, 3 H) | 11.17 (s, br) |
| | | $PCH_3$ | 1.11 (d, 3.7, 3 H) | 13.82 (s, br) |
| | | (exo) | 1.71 (s, br, 3 H) | 18.93 (s, br) |
| | | CH | 0.22 (s, br, 1 H) | 11.80 (s, br) |
| **4a**[a] | −60 | $C_5H_5$ | 5.63 (d, 1.5, 10 H) | 110.38 (s) |
| | | $PCH_3$ | 0.97 (d, 8.2, 6 H) | 22.76 ("t", $N$ = 22.0)[b] |
| | | | 1.37 (d, 8.9, 6 H) | 24.51 (s, br) |
| | | CH | 1.44 (t, 2.0, 1 H) | 30.62 (s, br) |
| **5**[c] | +20 | $C_5H_5$ | 5.68 (s, 5 H) | 108.80 (s)[d] |
| | | | 5.65 (s, 5 H) | 107.95 (s)[e] |
| | | $PCH_3$ | 0.93 (d, 9.5, 3 H) | 15.25 (d, 6.4)[f] |
| | | | 0.85 (d, 8.4, 3 H) | 11.58 (d, 12.4)[g] |
| | | $SiCH_3$ | 0.36 (s, 9 H) | 4.72 (d, 1.5)[h] |
| | | CH | −0.41 (d, 4.0, 1 H) | 0.62 (d, 45.0)[i] |
| **6**[a] | −10 | $C_5H_5$ | 5.62 (d, 1.5, 10 H) | 108.50 (s) |
| | | $PCH_3$ | 1.08 (d, 8.8, 6 H) | 9.17 (d, 65.3) |
| | | $SiCH_3$ | 0.42 (s, 18 H) | 1.35 (d, 1.5) |

[a] Toluene-$d_8$. [b] AA′X spin system. [c] Benzene-$d_6$. [d] $^{13}C$: d·quin (172.8/6.0). [e] $^{13}C$: d·quin (173.3/6.4). [f] $^{13}C$: d·q (6.4/130.1). [g] $^{13}C$: d·q (12.4/130.1). [h] $^{13}C$: d·q·sept (1.5/118.1/1.8). [i] $^{13}C$: d·d (45.0/140.2).

Table II. $^{31}P$ NMR Data for Compounds 4, 4a, 5, and 6

| no. | solvent | $T$, °C | $^{31}P\{^1H\}$ NMR, $\delta$ ($J$, Hz) | $\Delta\delta(P)$[a] |
|---|---|---|---|---|
| **4** | toluene-$d_8$ | +20 | $P_{endo}$ −28.83 (s),<br>$P_{exo}$ −36.75 (s) | +26.77 |
| **4** | toluene-$d_8$ | −60 | $P_{endo}$ −26.95 (s),<br>$P_{exo}$ −34.04 (s) | +28.65 |
| **4a** | toluene-$d_8$ | −60 | $P_A$ −40.37 (d, 126.8) | +15.23 |
| | | | $P_B$ −42.88 (d, 126.8) | +12.72 |
| **5** | benzene-$d_6$ | +20 | −32.18 (s) | +23.72 |
| **6** | toluene-$d_8$ | −10 | 2.63 (s) | +44.85 |
| **6** | toluene-$d_8$ | −80 | 2.20 (s) | +44.42 |

[a] $\Delta\delta(P)$ denotes the coordination shift relative to the parent phosphinomethanes $H_2C(PMe_2)_2$, $H_2C(PMe_2)(SiMe_3)$, and $HC(PMe_2)(SiMe_3)_2$, respectively.

**2. NMR Spectra of 4–6.** The NMR data for complexes **4**–**6** are collected in Tables I and II.

**3. Reaction of 6 with CO.** Complex **6** was dissolved in toluene under $N_2$ and the solution cooled to −78 °C. The dinitrogen atmosphere was replaced by 1 atm of CO, and the solution was warmed to 0 °C until the mixture was colorless (20 min). After evaporation of the solvent, the residue was investigated spectroscopically.

**B. X-ray Structure Determinations.** Suitable single crystals of all three compounds were obtained by low-temperature crystallization in toluene. They were sealed at dry-ice temperature under argon in glass capillaries and directly examined on the diffractometer (Mo K$\alpha$ radiation, $\lambda$ = 0.710 69 Å, graphite monochromator). Complex **6** was found to crystallize with $^1/_2$ equiv of toluene. Complexes **4** and **5** contain two crystallographically independent molecules in the asymmetric unit. After refinement they were found to be enantiomers with respect to the asymmetric coordinated carbon atom; i.e., in the entire centrosymmetric unit cell there are also the respective equivalents related by a center of inversion. Table III contains the crystal data and important numbers pertinent to data collection and structure refinement. Reduced cell calculations did not reveal symmetry higher than monoclinic. Exact cell parameters were obtained by a least-squares fit to the Bragg angles fo 25 high-angle reflections centered on the diffractometer.

The intensity data were corrected for Lorentz–polarization effects. Corrections for crystal decay were not considered necessary, as the repeated measurement of three standard reflections showed only random intensity fluctuations. An absorption correction was only done for **6**·0.5(toluene) because of the unfavorable

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**Table III. Crystal Structure Data for 4, 5, and 6•0.5(toluene)**

| | 4 | 5 | 6·0.5(toluene) |
|---|---|---|---|
| formula | $C_{15}H_{23}ClP_2Zr$ | $C_{16}H_{26}ClPSiZr$ | $C_{19}H_{34}ClPSi_2Zr\cdot 0.5C_7H_8$ |
| $M_r$ | 391.97 | 404.12 | 522.37 |
| cryst syst | monoclinic | monoclinic | monoclinic |
| space group | $P2_1/n$ (No. 14) | $P2_1/c$ (No. 14) | $P2_1/c$ (No. 14) |
| $a$, Å | 16.080 (2) | 15.687 (2) | 18.585 (2) |
| $b$, Å | 14.047 (1) | 15.898 (2) | 8.809 (1) |
| $c$, Å | 17.003 (2) | 16.165 (2) | 16.102 (2) |
| $\beta$, deg | 116.64 (1) | 111.16 (1) | 103.93 (1) |
| $V$, Å$^3$ | 3432.9 | 3759.6 | 2558.6 |
| $Z$ | 8 | 8 | 4 |
| $d_{calcd}$, g/cm$^3$ | 1.517 | 1.428 | 1.356 |
| $\mu$(Mo K$\alpha$), cm$^{-1}$ | 9.6 | 8.6 | 6.9 |
| $F$(000), e | 1600 | 1664 | 1092 |
| $T$, °C | −35 | −35 | −40 |
| diffractometer | Syntex $P2_1$ | Syntex $P2_1$ | Syntex $P2_1$ |
| scan | $\omega$ | $\omega$ | $\omega$ |
| scan width (in $\omega$), deg | 0.9 | 0.9 | 0.8 |
| $[(\sin \vartheta)/\lambda]_{max}$, Å$^{-1}$ | 0.595 | 0.606 | 0.595 |
| *hkl* range | +19,+16,±20 | +18,+19,±19 | +22,+10,±19 |
| no. of rflns (measd/unique) | 6548/6053 | 7844/6931 | 4987/4509 |
| $R_{int}$ | 0.021 | 0.043 | 0.020 |
| no. of rflns obsd [$F_o \geq 4.0\sigma(F_o)$] | 5227 | 5708 | 3890 |
| abs cor | no | no | yes |
| rel tranmissn | | | 0.82–1.00 |
| no. of H atoms (found/calcd) | 35/11 | 19/33 | 19/15 |
| no. of params ref | 375 (on all rflns) | 391 (on all rflns) | 229 (on all rflns) |
| $R^a$ | 0.035 | 0.058 | 0.051 |
| $R_w{}^b$ | 0.030 | 0.061 | 0.053 |
| $\Delta\rho_{fin.}$(max/min), e/Å$^3$ | +0.37/−0.43 | +0.70/−0.90 | +1.9/−0.61 |

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

crystal shape (maximum crystal dimensions 0.3 × 0.35 × 0.45 mm$^3$). Absorption corrections for 4 and 5 were not considered necessary because of the much more uniform crystal shapes. All three structures were solved by Patterson methods (SHELX-76, SHELXS-86) and completed by Fourier techniques. Hydrogen atoms not found in difference maps were calculated at idealized geometrical positions (XANADU). The structures of 4 und 5 were refined with anisotropic displacement parameters; the methyl groups were treated as rigid groups. In 4 H(1) and H(2) at the coordinated carbon were refined isotropically; all other hydrogen atoms in 4 and 5 were held constant with $U_{iso}$ = 0.065 Å$^2$. The heavily disordered molecule of toluene was refined isotropically with half-occupancy near a center of inversion. The toluene methyl group could not be located; neither were the toluene hydrogen atoms. The residual electron density had pronounced maxima around this disordered toluene molecule. The final refinement of all three structures was done with SHELX-76 using all unique reflections. Tables IV–VI contain the fractional coordinates of the non-hydrogen atoms, Table VII summarizes the most important bond distances and angles for all structures. See the note at the end of the paper for supplementary material available.

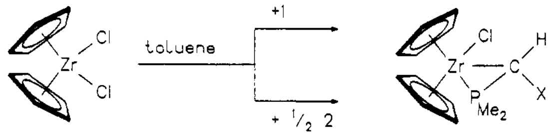
## Results and Discussion

**Preparation and Characterization of 4 and 5.** The stabilization of carbanions by elements of the third period is a well-known phenomenon.[12] As discussed in the Introduction, further substitution of the carbanionoid carbon in phosphinomethanides I by silyl or phosphino groups (ligands VIIa,b) should render them ideal candidates for

$[Me_2P-CH(X)]^-$ $Li[CH(PMe_2)_2]$ $[Li[CH(PMe_2)(SiMe_3)]\cdot TMEDA]_2$

VII a: X = $PMe_2$ b: X = $SiMe_3$ 1[10] 2[11]

the attempted synthesis of 18e $\eta^2$(*C*,*P*)-phosphinomethanide complexes of the chlorozirconocene fragments. This can be achieved by reaction of $Cp_2ZrCl_2$ with the lithiated phosphinomethanides 1 and 2, respectively, in toluene or ether (eq 1). Both 4 and 5 are obtained as



4: X = $PMe_2$
5: X = $SiMe_3$

(1)

yellow crystalline solids. Their NMR spectra in toluene-$d_8$ or $C_6D_6$ (+20 °C) are in full accord with the proposed structure of an 18e zirconaphosphacyclopropane derivative. In particular, the $^{31}P$ signals (4: $P_{endo}$) at −28.83 and −32.18 ppm for 4 and 5, respectively, are at lower field than in the 16e $\eta^1$(C)-coordinated complex IVa[13]– a good indication of the metal coordination. More convincing, however, is the splitting of signals in the $^1H$ and $^{13}C\{^1H\}$ NMR spectra due to the chiral C atom in the three-membered ring (Table I), which clearly demonstrates the $\eta^2$(C,P) coordination that is also observed in the solid state (vide infra).

From the $^{31}P$ NMR spectrum of 4, the presence of the additional species 4a is evident: an AB spin system ($\delta(P_A)$ −40.37, $\delta(P_B)$ −42.88, $J$(AB) = 126.8 Hz) accompanies the signals of 4. The appearance of the spectrum is temperature-dependent (Figure 1), revealing the equilibrium shown by eq 2. If the spectrum is recorded immediately after solid 4 is dissolved in toluene-$d_8$ at −78 °C, only the signals of 4 are detected, suggesting that formula 4 in fact represents the solid-state structure. After a short period of time, the signals of 4a (AB spin system) appear and increase on warming the solution ($\Delta G°$ = 1.6 kJ/mol). The constitution of 4a as a four-membered heterocycle with a chelating, P,P-coordinated diphosphinomethanide ligand with inequivalent P atoms is confirmed by the appropriate

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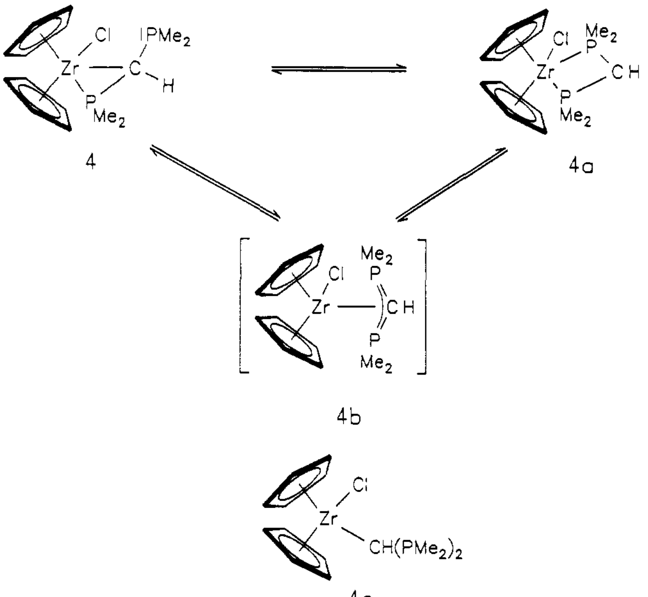
(12) Schleyer, P. v. R.; Clark, T.; Kos, A. J.; Spitznagel, G. W.; Rhode, C.; Arad, D.; Houk, K. N.; Rondan, N. G. *J. Am. Chem. Soc.* **1984**, *106*, 6467.

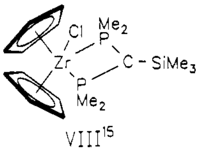
(13) This result should not be overemphasized, however, since several factors should be operative: the coordination shift, the "ring size effect",[14] and the increased steric bulk in going from IVa to 4 and 5.

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

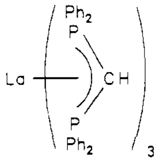


(2)

$^1$H NMR signals (Table I) and by comparison with the related complex VIII, the structure of which has been determined by X-ray analysis.[15] If the sample is warmed further, all signals coalesce and a new singlet resonance ($\Delta P$ −35.46) appears at +100 °C ($\Delta G$ = 52.1 kJ/mol; see Figure 1). By analogy to IV,[16] it seems tempting to assign this signal to the 16e $\eta^1$(C)-coordinated species **4c**. Alternatively, a transition state is plausible, which involves a $\pi$-allylic type of coordination (**4b**), similar to that in the lanthanum complex IX, reported by us a number of years ago.[16]



VIII[15]



IX[16]

We strongly favor this latter route because of the observation that the high-temperature $^{31}$P shift is just the weighted average of the respective signals for **4**/**4a** and because of the lack of reactivity with CO (vide supra). Though unique for the early transition metals, this dynamic behavior is not unprecedented and resembles observations in late-transition-metal[17] as well as main-group-metal[18] metal complexes with diphosphinomethanide ligands.

**Molecular Structures of 4 and 5.** In the solid state, crystals of **4** and **5** contain both enantiomers as crystallographically independent molecules in the asymmetric unit. In either case, the enantiomers differ slightly in their structural parameters, but the overall appearance is identical. Figures 2 and 3 each show the molecular structure of one of the two enantiomers. Table VII contains important distances and angles together with those of **6** and IVa[7a] for comparison.

In **4** and **5**, the zirconium atoms attain their closed 18e shell by, first, two cyclopentadienyl rings, whose centroids (D) are in the normal Zr–D distance range of 2.24/2.22, 2.22/2.24 Å (**4**) and 2.24/2.24, 2.23/2.24 Å (**5**) and enclose

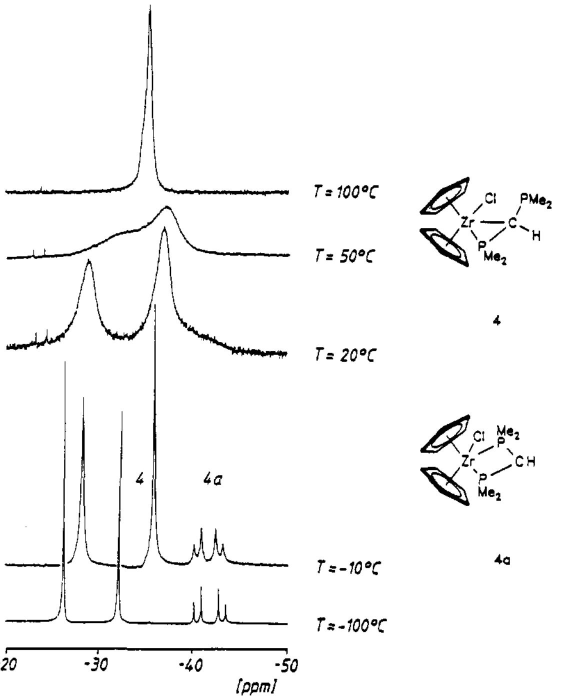


**Figure 1.** $^{31}$P{$^1$H} NMR spectra of **4** at various temperatures.

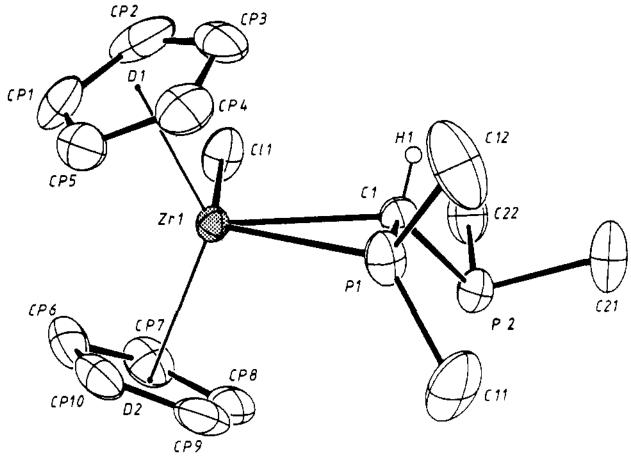


**Figure 2.** Molecular structure of one of the crystallographically independent molecules of **4** in the crystal form and the atomic numbering scheme adopted (ORTEP; ellipsoids at the 50% probability level; hydrogen atoms omitted for clarity except for that at C(1), which was drawn with an arbitrary radius).

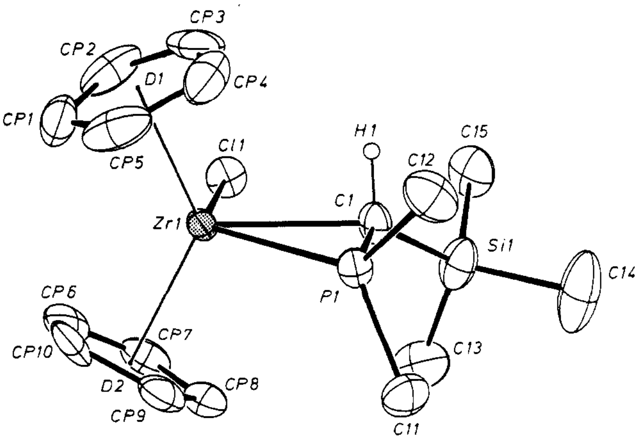


**Figure 3.** Molecular structure of one of the crystallographically independent molecules of **5** in the crystal form.

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[15] (a) Karsch, H. H.; Deubelly, B.; Grauvogl, G.; Müller, G. To be submitted for publication. (b) Deubelly, B. Thesis, Technical University of Munich, 1988.

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

[17] Karsch, H. H. *Chem. Ber.* **1984**, *117*, 783.

[18] Karsch, H. H.; Appelt, A.; Hanika, G. *J. Organomet. Chem.* **1986**, *312*, C1.

**Table IV. 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) | 0.20988 (2) | 0.06950 (2) | 0.14431 (1) | 0.021 |
| Cl(1) | 0.07160 (5) | −0.02440 (5) | 0.14169 (4) | 0.041 |
| P(1) | 0.36376 (5) | 0.09507 (5) | 0.28951 (5) | 0.034 |
| P(2) | 0.23248 (5) | 0.08410 (5) | 0.37662 (4) | 0.033 |
| C(1) | 0.2717 (2) | 0.0373 (2) | 0.2998 (2) | 0.026 |
| C(11) | 0.4003 (3) | 0.2010 (3) | 0.3574 (2) | 0.071 |
| C(12) | 0.4678 (2) | 0.0213 (3) | 0.3327 (3) | 0.071 |
| C(21) | 0.3228 (2) | 0.0422 (3) | 0.4835 (2) | 0.059 |
| C(22) | 0.1444 (2) | −0.0034 (2) | 0.3669 (2) | 0.042 |
| Cp(1) | 0.1886 (3) | −0.0145 (2) | 0.0049 (2) | 0.051 |
| Cp(2) | 0.2025 (3) | −0.0860 (2) | 0.0645 (3) | 0.058 |
| Cp(3) | 0.2927 (3) | −0.0792 (2) | 0.1321 (2) | 0.055 |
| Cp(4) | 0.3367 (2) | −0.0020 (2) | 0.1120 (2) | 0.047 |
| Cp(5) | 0.2711 (2) | 0.0372 (2) | 0.0334 (2) | 0.044 |
| Cp(6) | 0.1066 (2) | 0.1896 (2) | 0.0366 (2) | 0.043 |
| Cp(7) | 0.0799 (2) | 0.1903 (2) | 0.1040 (2) | 0.045 |
| Cp(8) | 0.1549 (3) | 0.2249 (2) | 0.1804 (2) | 0.046 |
| Cp(9) | 0.2270 (2) | 0.2482 (2) | 0.1585 (2) | 0.044 |
| Cp(10) | 0.1970 (2) | 0.2265 (2) | 0.0701 (2) | 0.040 |
| H(1)[b] | 0.281 (2) | −0.020 (2) | 0.305 (2) | 0.038 (9) |
| | | Molecule 2 | | |
| Zr(2) | 0.32408 (2) | 0.31564 (2) | 0.77734 (1) | 0.020 |
| Cl(2) | 0.33790 (5) | 0.19002 (4) | 0.89293 (4) | 0.032 |
| P(11) | 0.17314 (5) | 0.34362 (5) | 0.62873 (4) | 0.028 |
| P(12) | 0.07392 (5) | 0.27608 (5) | 0.73639 (5) | 0.031 |
| C(2) | 0.1654 (2) | 0.2612 (2) | 0.7037 (2) | 0.023 |
| C(111) | 0.1386 (2) | 0.2861 (2) | 0.5225 (2) | 0.048 |
| C(112) | 0.0895 (2) | 0.4396 (2) | 0.6030 (2) | 0.051 |
| C(121) | −0.0270 (2) | 0.2265 (2) | 0.6423 (2) | 0.047 |
| C(122) | 0.0969 (2) | 0.1770 (2) | 0.8140 (2) | 0.041 |
| Cp(11) | 0.4065 (2) | 0.4237 (2) | 0.9065 (2) | 0.050 |
| Cp(12) | 0.3207 (3) | 0.4081 (2) | 0.9050 (2) | 0.049 |
| Cp(13) | 0.2518 (2) | 0.4478 (2) | 0.8284 (2) | 0.040 |
| Cp(14) | 0.2957 (2) | 0.4913 (2) | 0.7814 (2) | 0.037 |
| Cp(15) | 0.3914 (2) | 0.4768 (2) | 0.8305 (2) | 0.042 |
| Cp(16) | 0.4859 (2) | 0.2812 (2) | 0.7923 (2) | 0.040 |
| Cp(17) | 0.4433 (2) | 0.1935 (2) | 0.7813 (2) | 0.041 |
| Cp(18) | 0.3683 (2) | 0.1898 (2) | 0.6960 (2) | 0.040 |
| Cp(19) | 0.3674 (2) | 0.2765 (2) | 0.6542 (2) | 0.037 |
| Cp(20) | 0.4382 (2) | 0.3333 (2) | 0.7140 (2) | 0.038 |
| H(2)[b] | 0.166 (2) | 0.203 (2) | 0.686 (2) | 0.025 (7) |

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

**Table V. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters for Both Crystallographically Independent Molecules of 5**

| atom | $x/a$ | $y/b$ | $z/c$ | $U_{eq}$, Å$^2$ |
|---|---|---|---|---|
| | | Molecule 1 | | |
| Zr(1) | 0.38360 (3) | 0.11120 (3) | 0.13225 (3) | 0.021 |
| Cl(1) | 0.39879 (9) | −0.04642 (8) | 0.10903 (9) | 0.035 |
| P(1) | 0.50630 (9) | 0.19396 (8) | 0.26234 (8) | 0.026 |
| Si(1) | 0.5753 (1) | 0.0065 (1) | 0.3343 (1) | 0.042 |
| C(1) | 0.5288 (3) | 0.0885 (3) | 0.2487 (3) | 0.028 |
| C(11) | 0.4970 (4) | 0.2161 (4) | 0.3701 (4) | 0.042 |
| C(12) | 0.6005 (4) | 0.2618 (4) | 0.2660 (4) | 0.044 |
| C(13) | 0.4908 (6) | −0.0380 (4) | 0.3795 (5) | 0.062 |
| C(14) | 0.6696 (5) | 0.0470 (5) | 0.4325 (5) | 0.082 |
| C(15) | 0.6225 (5) | −0.0804 (4) | 0.2846 (4) | 0.052 |
| Cp(1) | 0.3185 (4) | 0.1678 (6) | −0.0237 (4) | 0.062 |
| Cp(2) | 0.3696 (6) | 0.1002 (4) | −0.0288 (4) | 0.057 |
| Cp(3) | 0.4571 (5) | 0.1222 (5) | 0.0164 (5) | 0.059 |
| Cp(4) | 0.4643 (5) | 0.1988 (5) | 0.0524 (4) | 0.050 |
| Cp(5) | 0.3766 (6) | 0.2291 (4) | 0.0283 (4) | 0.057 |
| Cp(6) | 0.2166 (4) | 0.0900 (4) | 0.1014 (4) | 0.048 |
| Cp(7) | 0.2593 (4) | 0.0424 (4) | 0.1770 (4) | 0.045 |
| Cp(8) | 0.3067 (4) | 0.0988 (4) | 0.2475 (4) | 0.039 |
| Cp(9) | 0.2911 (4) | 0.1797 (4) | 0.2148 (4) | 0.039 |
| Cp(10) | 0.2353 (4) | 0.1749 (4) | 0.1232 (4) | 0.043 |
| | | Molecule 2 | | |
| Zr(2) | 0.11798 (3) | −0.16653 (3) | −0.13436 (3) | 0.020 |
| Cl(2) | 0.11942 (9) | −0.00478 (7) | −0.13400 (8) | 0.033 |
| P(2) | −0.01242 (8) | −0.25301 (8) | −0.25095 (8) | 0.022 |
| Si(2) | −0.0525 (1) | −0.07249 (9) | −0.35345 (9) | 0.029 |
| C(2) | −0.0249 (3) | −0.1433 (3) | −0.2567 (3) | 0.025 |
| C(21) | −0.1084 (3) | −0.3081 (3) | −0.2375 (4) | 0.029 |
| C(22) | −0.0077 (4) | −0.2971 (3) | −0.3521 (3) | 0.030 |
| C(23) | −0.1108 (4) | 0.0214 (4) | −0.3279 (4) | 0.042 |
| C(24) | 0.0488 (4) | −0.0354 (4) | −0.3786 (4) | 0.040 |
| C(25) | −0.1329 (4) | −0.1230 (4) | −0.4583 (4) | 0.048 |
| Cp(11) | 0.2855 (4) | −0.1652 (5) | −0.1045 (4) | 0.050 |
| Cp(12) | 0.2468 (4) | −0.1248 (4) | −0.1870 (4) | 0.041 |
| Cp(13) | 0.1953 (4) | −0.1847 (4) | −0.2475 (4) | 0.040 |
| Cp(14) | 0.2031 (4) | −0.2620 (4) | −0.2037 (4) | 0.036 |
| Cp(15) | 0.2599 (4) | −0.2509 (4) | −0.1148 (4) | 0.049 |
| Cp(16) | 0.1650 (4) | −0.1593 (4) | 0.0319 (4) | 0.046 |
| Cp(17) | 0.0795 (4) | −0.1213 (3) | −0.0003 (4) | 0.036 |
| Cp(18) | 0.0152 (4) | −0.1824 (4) | −0.0458 (3) | 0.033 |
| Cp(19) | 0.0618 (4) | −0.2583 (4) | −0.0378 (3) | 0.038 |
| Cp(20) | 0.1531 (4) | −0.2467 (4) | 0.0102 (4) | 0.041 |

D–Zr–D angles of 128.9/130.5° (**4**) and 127.7/123.3° (**5**). Second, the chlorine atom lies in a plane perpendicular to and bisecting the angle D–Zr–D, Zr–Cl distances being 2.569 (1)/2.576 (1) (**4**) and 2.552 (1)/2.572 (1) Å (**5**). Third, the phosphinomethanide ligands adopt an $\eta^2$-coordination mode, the coordinating atoms C and P being coplanar with the Zr and Cl atoms (maximum deviation of an atom from the best plane through these four atoms: P(1), C(1), 0.04 Å; P(11), −0.05 Å (**4**); P(2), 0.03 Å (**5**). (This coordination geometry is well-known from the few other structurally characterized Cp$_2$ZrL$_3$ complexes[19] (L = two-electron donor) and has its origin in the disposition of the most important acceptor orbitals of the Cp$_2$Zr$^{2+}$ fragment.[4,5a,20]) This coordination mode gives rise to a novel three-membered zircona–phospha heterocycle. Most noteworthy, the ring carbon atoms C(1) lie in a central position between the chlorine and the phosphorus atoms, or in other words, the coordinating phosphorus atom is "exo" with respect to C(1) and Cl. The Zr–C(1) distances (**4**, 2.413 (2)/2.408 (2) Å; **5**, 2.401 (5)/2.423 (5) Å) as well as the Zr–P(1) distances (**4**, 2.621 (1)/2.632 (1) Å; **5**, 2.634 (1)/2.161 (1) Å) again are virtually identical in all four molecules. This also holds true for the short P(1)–C(1) distances (**4**, 1.764(3)/1.767(3) Å; **5**, 1.744(5)/1.753 (5) Å) (vide supra). Within the three-membered ring, the angles at zirconium are rather small and amount only to 40.8 (1)/40.7 (1)° (**4**) and 40.2 (1)/40.5 (1)° (**5**). The exocyclic PMe$_2$ (in **4**) and SiMe$_3$ (**5**) groups at C(1) are oriented in such a way that steric interactions with the methyl groups at P(1) are minimized (gauche) but exhibit no other peculiarities. It is noteworthy, however, that the specific orientation of the methyl groups at P(2) in **4** allows for an easy formation of **4a** and **4b** by Zr–C(1) bond cleavage and subsequent slight rotation around the P(1)–C(1) bond. The only significant difference between **4** and **5** concerns the exocyclic angle at C(1) (P(1)–C(1)–P(2)/Si), which is much smaller in **4** than in **5**. Tentatively, this may be ascribed to a higher degree of carbanion stabilization, and hence planarization, by a silyl as compared to a phosphino group. All structural features in the solid state are in perfect accord with the spectroscopic findings (vide supra): Simple silyl or phosphino C-substitution switches the coordination of phosphinomethanides to the Cp$_2$(Cl)Zr fragment from

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(19) See, e.g.: Silver, M. E.; Eisenstein, O.; Fay, R. C. *Inorg. Chem.* **1983**, *22*, 759. Silver, M. E.; Fay, R. C. *Organometallics* **1983**, *2*, 44. Thewalt, U.; Lasser, W. *Z. Naturforsch., B: Anorg. Chem. Org. Chem.* **1983**, *38B*, 1501. Erker, G.; Schlund, R.; Krüger, C. *J. Chem. Soc., Chem. Commun.* **1986**, 1403. Diel, B. N.; Hope, H. *Inorg. Chem.* **1986**, *25*, 4448. Schmidbaur, H.; Pichl, R.; Müller, G. *Chem. Ber.* **1987**, *120*, 39. Hey, E.; Atwood, J. L.; Bott, S. G. *J. Chem. Soc., Chem. Commun.* **1987**, 421. Buchwald, S. L.; Nielsen, R. B.; Dewan, J. C. *Organometallics* **1988**, *7*, 2324. Thewalt, U.; Friedrich, R. *Z. Naturforsch., B: Anorg. Chem. Org. Chem.* **1991**, *46B*, 475.

(20) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

**Table VI. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters for 6•0.5(toluene)**

| atom | $x/a$ | $y/b$ | $z/c$ | $U_{eq}$, Å$^2$ |
|---|---|---|---|---|
| Zr | 0.1841 (1) | 0.1839 (1) | 0.3013 (1) | 0.020 |
| P | 0.2765 (1) | 0.0289 (1) | 0.4180 (1) | 0.023 |
| Cl | 0.2132 (1) | 0.2332 (1) | 0.1566 (1) | 0.031 |
| Si(1) | 0.3456 (1) | −0.0676 (1) | 0.2654 (1) | 0.027 |
| Si(2) | 0.3982 (1) | 0.2258 (1) | 0.3593 (1) | 0.025 |
| C(1) | 0.3199 (2) | 0.0830 (4) | 0.3367 (2) | 0.021 |
| C(2) | 0.2678 93) | −0.1760 (5) | 0.4296 (3) | 0.036 |
| C(3) | 0.3227 (2) | 0.0728 (5) | 0.5285 (3) | 0.034 |
| C(11) | 0.3879 (3) | 0.0142 (5) | 0.1804 (3) | 0.037 |
| C(12) | 0.4132 (3) | −0.2102 (5) | 0.3297 (3) | 0.041 |
| C(13) | 0.2709 (3) | −0.1904 (5) | 0.1982 (3) | 0.042 |
| C(21) | 0.3954 (2) | 0.3571 (5) | 0.2666 (3) | 0.032 |
| C(22) | 0.4115 (2) | 0.3528 (6) | 0.4560 (3) | 0.039 |
| C(23) | 0.4925 (2) | 0.1331 (5) | 0.3841 (3) | 0.037 |
| Cp(1) | 0.1138 (3) | 0.4203 (6) | 0.3237 (3) | 0.043 |
| Cp(2) | 0.1707 (3) | 0.4674 (5) | 0.2868 (3) | 0.038 |
| Cp(3) | 0.2384 (2) | 0.4414 (5) | 0.3475 (3) | 0.032 |
| Cp(4) | 0.2212 (3) | 0.3787 (5) | 0.4207 (3) | 0.035 |
| Cp(5) | 0.1450 (3) | 0.3622 (5) | 0.4050 (3) | 0.039 |
| Cp(6) | 0.0524 (2) | 0.1297 (6) | 0.2185 (3) | 0.040 |
| Cp(7) | 0.0944 (2) | 0.0147 (6) | 0.1935 (3) | 0.038 |
| Cp(8) | 0.1239 (3) | −0.0787 (5) | 0.2637 (3) | 0.041 |
| Cp(9) | 0.0976 (3) | −0.0222 (5) | 0.3330 (3) | 0.039 |
| Cp(10) | 0.0529 (2) | 0.1044 (6) | 0.3050 (3) | 0.040 |
| C001[a] | 1.0170 (3) | −0.0356 (6) | 0.5121 (5) | 0.059 |
| C002[a] | 0.9444 (3) | −0.0616 (6) | 0.4657 (5) | 0.033 |
| C003[a] | 0.8958 (3) | 0.0601 (6) | 0.4418 (5) | 0.055 |
| C004[a] | 0.9198 (3) | 0.2078 (6) | 0.4643 (5) | 0.046 |
| C005[a] | 0.9924 (3) | 0.2338 (6) | 0.5106 (5) | 0.075 |
| C006[a] | 1.0410 (3) | 0.1121 (6) | 0.5345 (5) | 0.064 |

[a] Disordered toluene with $^1/_2$ occupancy.

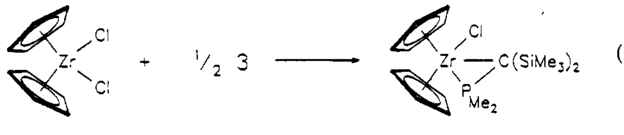
**Table VII. Selected Bond Distances (Å) and Angles (deg) in 4, 5, 6•0.5(toluene), and IVa with Estimated Standard Deviations in Parentheses**

| | 4[a] | 5[a] | 6·0.5(toluene) | IVa[b] |
|---|---|---|---|---|
| Zr–Cl | 2.569 (1)<br>2.576 (1) | 2.558 (1)<br>2.572 (1) | 2.554 (1) | 2.457 (2) |
| Zr–P(1) | 2.621 (1)<br>2.632 (1) | 2.634 (1)<br>2.616 (1) | 2.606 (1) | |
| Zr–C(1) | 2.413 (2)<br>2.408 (2) | 2.401 (5)<br>2.423 (5) | 2.607 (1) | 2.272 (6) |
| Zr–D[c] | 2.24/2.22<br>2.22/2.24 | 2.24/2.24<br>2.23/2.24 | 2.23/2.26 | 2.22/2.20 |
| P(1)–C(1) | 1.764 (3)<br>1.767 (2) | 1.744 (5)<br>1.753 (5) | 1.761 (4) | 1.833 (7) |
| C(1)–P(2),Si | 1.811 (3)<br>1.803 (2) | 1.848 (5)<br>1.847 (5) | 1.889 (4)/1.892 (4) | |
| D–Zr–D | 128.9<br>130.5 | 127.7<br>129.3 | 122.6 | 129.4 |
| Cl–Zr–C(1) | 81.4 (1)<br>83.6 (1) | 81.7 (1)<br>81.6 (1) | 81.4 (1) | 95.4 (2) |
| Cl–Zr–P(1) | 122.1 (1)<br>124.2 (1) | 121.8 (1)<br>122.1 (1) | 120.0 (1) | |
| P(1)–Zr–C(1) | 40.8 (1)<br>40.7 (1) | 40.2 (1)<br>40.5 (1) | 39.5 (1) | |
| Zr–C(1)–P(1) | 76.0 (1)<br>76.5 (1) | 77.1 (2)<br>75.7 (2) | 70.2 (1) | 129.9 (3) |
| P(1)–C(1)–P(2),Si | 118.9 (1)<br>118.5 (1) | 128.8 (3)<br>129.7 (3) | 119.3 (2)/120.3 (2) | |
| Zr–C(1)–P(2),Si | 128.1 (1)<br>128.6 (1) | 134.4 (3)<br>130.5 (2) | 118.7 (2)/118.3 (2) | |
| Si(1)–C(1)–Si(2) | | | 106.8 (2) | |
| Zr–P(1)–C(1) | 63.3 (1)<br>62.8 (1) | 62.7 (2)<br>63.8 (2) | 70.3 (1) | |

[a] The values for both independent molecules are given. [b] From ref 7a. [c] Centroid of the Cp rings.

$\eta^1$(C) as in IVa to $\eta^2$(C,P). This implies that as one goes from IVa to 4 and 5, the zirconium increases its coordination number with increasing size of the ligand. Apparently, the electronic influence dominates, and steric factors play only a minor role. It is well-known, on the other hand, that bulky groups stabilize small rings, and this should also contribute to the stability of 4 and 5.

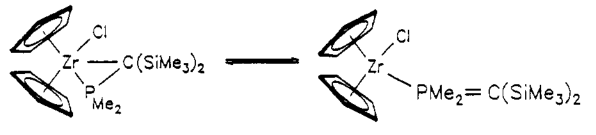
**Preparation and Characterization of 6.** At this point, one is attempted to speculate whether it is possible to further reduce the carbanionic nucleophilicity in phosphinomethanides to such an extent that a novel $\eta^1$(P) coordination mode is feasible. In order to address this problem, a complex analogous to 4 and 5 but with a second silyl group at the carbanionic center was prepared by reacting $Cp_2ZrCl_2$ with $\{Li[C(PMe_2)(SiMe_3)_2]\}_2$TMEDA (**3**)[11] (eq 3). Again, yellow crystals could be obtained from toluene.



(3)

6

The spectroscopic data (Table I) clearly show that in contrast to the case for 4 and 5, in solution, all Cp, $CH_3$, and $SiMe_3$ groups are equivalent. A further decisive difference is seen in the $^{31}$P NMR spectrum (touene-$d_8$, −10 °C): $\delta$(P) is found at +2.63 ppm as a single line and remains essentially unchanged on cooling up to −80 °C. The coordination shift (relative to the parent phosphinomethane $HC(PMe_2)(SiMe_3)_2$: $\Delta\delta$(P) +44.85) exceeds the respective values of 4 ($\Delta\delta$(P) +26.77) and 5 ($\Delta\delta$(P) +23.72) considerably. This and the unusually large coupling $^1J$(PC) = 65.3 Hz in the $PCH_3$ resonance, which is in the range typical of methyl phosphorus ylides, as, e.g. in $Me_3P{=}CH_2$,[21] suggests that, in solution, the P-zirconium-substituted phosphorus ylide **6a** is predominant. In light of the solid-state structure (vide infra), the equilibrium (4) should be operating.



(4)

6 6a

**Molecular Structure of 6.** The X-ray structure determination (Figure 4, Table VII) shows 6 to exist in the solid state again as a zircona–phospha three-membered ring, in line with the findings for 4 and 5. The overall geometry is very similar to that of the latter; in particular, the C(1) atom again adopts a central position between the Cl and P ligating atoms. Also, most bond lengths and angles are quite similar in magnitude in 4–6. There are two noticeable differences, however. The Zr–C(1) bond in 6 amounts to 2.607 (1) Å, exceeding drastically that in 4 and 5 by nearly 0.2 Å. As a matter of fact, this is the largest value observed for a zirconium–alkyl bond to date.

Obviously, due to steric and/or electronic effects, the Zr–C(1) bond is weakened drastically and this clearly is responsible for the equilibrium (4) in solution. At closer sight, one further notes that the Zr–P(1) distance in 6 is slightly but significantly shorter than that in 4 and 5. Thus, the effects dominating in solution are also clearly operating in the solid state, in line with the above-given interpretation. At this point, it should also be mentioned that Zr–P distances in complexes 4–6 are the shortest ever observed for phosphine–zirconium interactions (2.66–2.87 Å) and rather resemble those in phosphido complexes of zirconium (2.54–2.63 Å). Apparently due to steric congestion, the angles Zr–C(1)–Si and P(1)–C(1)–Si drop again

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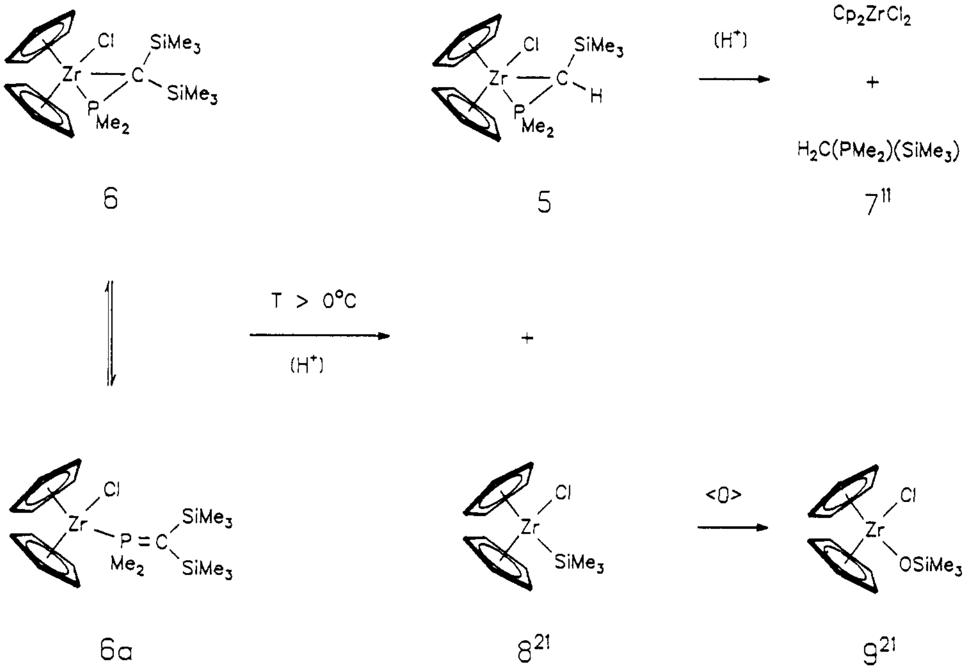
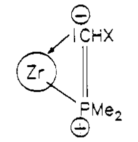
[21] Schmidbaur, H.; Richter, W.; Wolf, W.; Köhler, F. H. *Chem. Ber.* 1975, *108*, 2649.

**Scheme I. Thermolytic Decomposition of 6**

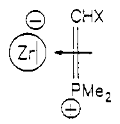


in 6 as compared to those in 5, obviously for the sake of the angle Si(1)–C(1)–Si(2), which is only 106.8 (2)°.

A comparison of the data for the 18e complexes 4–6 with those for the 16e complex IVa (Table VII) reveals that the increasing coordination number and electronic saturation increases the Zr–C(1) and Zr–Cl bond distances. In particular, Zr–C(1) varies from IVa (2.276 (6) Å) to 2.41 Å (mean) in 4 and 5 and to 2.607 (1) Å in 6. The Zr–Cl distance, on the other hand, is much less affected but holds the trend. This demonstrates that variance of the coordination number is less important than steric and electronic influences. The coordination of phosphorus to zirconium in 4–6 causes some ylidic character,[22] as can be seen in the P–C(1) bond lengths and as exemplified by formula X. Alternatively, a heteroolefin type of coordination (XI) may be considered. In IVa no such bond shortening is observed. Another feature is of interest: As expected, the bond angle Cl–Zr–C(1) decreases with increasing coordination number; i.e., it is noticeably larger in the 16e species IVa than in the 18e species 4–6. On the other hand, D–Zr–D decreases significantly on going from 5 to 6 but not so much from IVa to 4. The Zr–D distances are nearly constant in all compounds. Obviously, the cyclopentadienyl rings are much less affected by changes in the coordination sphere, unless steric strain becomes dominant.



X



XI

**Reactivity of 4–6.** The equilibrium (4) also seems responsible for another important difference between 6 and 4/5: The former is thermally unstable, and in solution it decomposes above 0 °C, slowly forming a black precipitate. According to NMR data the remaining liquid phase contains a number of species, which are identified by comparison with either authentic samples or literature values. Scheme I summarizes our observations.

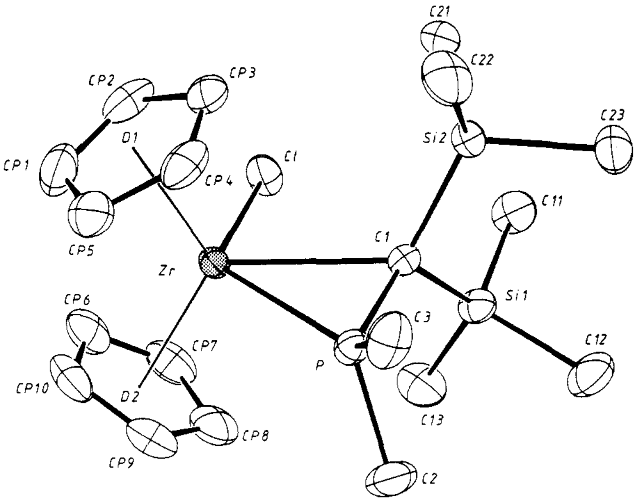


Figure 4. Molecular structure of 6 in the crystal form.

As primary decomposition products, 5 and 8[23] are formed by loss of a silyl group, which migrates to Zr. Further decomposition results from protic and oxygen impurities. The origin of $H^+$ and ⟨O⟩ might be $H_2O$. Since the decomposition according to Scheme I is also observed under very carefully controlled conditions (silylated, dried, and evacuated glassware, rigorously dried solvents, and dinitrogen atmosphere), no obvious source is plausible besides some residual Si–OH functionality of the glass devices. It is important to note that no $Me_3SiCl$ or $(Me_3Si)_2O$ could be detected in the mixture, as might be inferred from the structure of 6, but the predominance of 6a explains this readily.

In contrast to IVa and IVc, which readily insert CO,[6,7b] the lack of a vacant coordination site in 4 and 5 explains the failure of thermally induced insertion of carbon monoxide into the Zr–C bond. It furthermore confirms that no 16e species such as, e.g., 4c, has a long enough lifetime

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

[23] Tilley, T. D. *Organometallics* 1985, *4*, 1452.

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 $\eta^1$(C), $\eta^2$(C,P), and $\eta^1$(P) coordination to a zirconocene metal center may be realized. The $\eta^2$(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

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[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.

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# 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 = $SiMe_3$[†]

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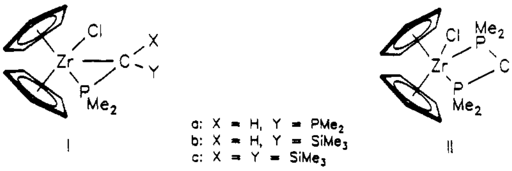
*Received May 13, 1992*

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 ($\eta^2$(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 $\eta^2$(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 $\eta^1$(C) bonding of the ligand, which is observed for I (X = Y = H), can be effectively switched to $\eta^2$(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 ($\eta^2$(C,P) coordination), the *di*phosphinomethanide complex Ia is unique in being in equilibrium with the four-membered chelate complex II ($\eta^2$(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]



The $\eta^2$(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

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[†] 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.

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