Zirconium Complexes with Phosphinomethanide Ligands: Syntheses, Reactivity, and X-ray Structure Determinations[†]

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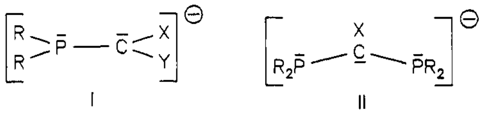
The reactions of $ZrCl_4$ with lithium phosphinomethanides were investigated. With $LiCH_2PMe_2$, **1**, and $Li[CH(PMe_2)_2]$, **2**, the products could not be characterized satisfactorily. With $\{(TMEDA)Li[CH(PMe_2)(SiMe_3)]\}_2$, **3**, a mixture of compounds $Cl_{(4-n)}Zr[CH(PMe_2)(SiMe_3)]_n$ ($n = 1$–4), **4a–d**, was obtained and characterized spectroscopically. Various coordination modes of the phosphinomethanide ligands are observed for $n = 3$ (**4c**) and $n = 4$ (**4d**) by means of NMR spectroscopy. With $(TMEDA)\{Li[C(PMe_2)(SiMe_3)_2]\}_2$, **5**, only disubstitution is observed, and $Cl_2Zr[C(PMe_2)(SiMe_3)_2]_2$, **6**, containing hexacoordinated Zr, was isolated in high yield as red crystals (monoclinic, $C2/c$, with $a = 9.273(1)$ Å, $b = 15.078(2)$ Å, $c = 22.062(2)$ Å, $\beta = 95.09(1)°$, $Z = 4$, $wR = 0.025$). Complex **6** in toluene solution inserts CO into a Zr–C bond, and after a subsequent 1,2-silyl shift a phosphino enolate complex is formed, which dimerizes to give $\{Cl_2Zr[C(PMe_2)(SiMe_3)_2][OC(SiMe_3){=}C(SiMe_3)PMe_2]\}_2$, **7** (yellow crystals: monoclinic, $P2_1/n$, with $a = 10.149(1)$ Å, $b = 16.503$ (2) Å, $c = 19.307(3)$ Å, $\beta = 97.13(1)°$, $Z = 2$, $wR = 0.031$). In THF solution **6** also inserts CO, and spectroscopic evidence indicates a mixture of two compounds: the phosphorus ylide $(Me_3Si)(Me_3SiO)C{=}C(PMe_2)PMe_2{=}C(SiMe_3)_2$ (=L), **8**, and $LZrCl_2$, **9**. With the lithium diphosphinomethanides $(D)Li[C(PR_2)_2(SiMe_3)]$ (D = —, R = Me, **5a**; D = TMEDA, R = Ph, **5b**; D = TMEDA, R = Me, **5c**), the hexacoordinate complex $Cl_2Zr[C(PMe_2)_2(SiMe_3)]_2$, **10**, and the ionic species $[(TMEDA)_2Li]\{Cl_3Zr[C(PR_2)_2(SiMe_3)]_2\}$, **11** (R = Ph) and **12** (R = Me), with heptacoordinated zirconium are obtained, and the latter both were characterized by X-ray structure determinations: **11**, red crystals, orthorhombic, $Pbca$ with $a = 19.016(2)$ Å, $b = 32.385(4)$ Å, $c = 23.906(3)$ Å, $Z = 8$, $wR = 0.070$; **12**·2MePh, red crystals, monoclinic, $P2_1c$ with $a = 16.138(2)$ Å, $b = 13.837(1)$ Å, $c = 25.779(3)$ Å, $\beta = 102.19(1)°$, $Z = 4$, $wR = 0.051$.

Introduction

Zirconocene derivatives have been investigated thoroughly in recent years,[1] mainly because of their potential catalytic and synthetic uses, and various ligands have been introduced to modify the properties and manifold reactions, including also some phosphine ligands. In contrast, zirconium complexes without π-ligands of the cyclopentadienyl type play a much less dominant role, and specifically those with phosphine type ligands are much less abundant. For obvious reasons the zirconium–phosphorus bond in structurally characterized examples is generally weak and ranges from 2.700(2) to 2.874(4) Å.[2] A systematic study of Cp_2Zr^{IV} and Zr^{IV} phosphine complexes has not been described in the literature. Such a study might address the similarities and differences in reactivity. This seems particularly useful, because it not only would allow further insight into the interactions between zirconium and phosphorus but also could provide eventually a new series of zirconium complexes with new properties for catalytic and/or synthetic applications.

Within a new approach to promote the formation of (otherwise) notoriously weak or uncommon metal–phosphorus bonds, we and others have introduced anionic phosphinomethanide and diphosphinomethanide ligands of type **I** or **II**, respectively, into the coordination chemistry of main group and transition metals. With the aid of these ligands, high phosphine coordination numbers could be achieved with main group[3] and lanthanide metal centers,[4] and also transition metal complexes are now numerous.[5]



X,Y = H, SiMe₃, PR₂; R = Me, Ph

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(1) For a recent review, see: Erker, G. *Angew. Chem.* **1989**, *101*, 411; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 397.

(2) (a) Girolami, G. S.; Wilkinson, G.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1984**, 2789. (b) Planalp, R. P.; Andersen, R. A. *Organometallics* **1983**, *2*, 1675. (c) Fryzuk, M. D.; Williams, H. D.; Mettig, S. J. *Inorg. Chem.* **1983**, *22*, 863. (d) Wengrovius, J. H.; Schrock, R. R.; Day, C. S. *Inorg. Chem.* **1981**, *20*, 1844.

(3) Following are some selected examples, giving a guide for some comprehensive references. Li: Karsch, H. H.; Deubelly, B.; Müller, G. *J. Organomet. Chem.* **1988**, *352*, 47. Karsch, H. H.; Zellner, K.; Gamper, S.; Müller, G. *J. Organomet. Chem.* **1991**, *414*, C39. Al: Karsch, H. H.; Appelt, A.; Riede, J.; Müller, G. *Organometallics* **1987**, *6*, 316. Si, Ge, Sn, Pb: Karsch, H. H.; Deubelly, B.; Hanika, G.; Riede, J.; Müller, G. *J. Organomet. Chem.* **1988**, *344*, 153. Karsch, H. H.; Appelt, A.; Hanika, G. *J. Organomet. Chem.* **1986**, *312*, C1. Karsch, H. H.; Keller, U.; Gamper, S.; Müller, G. *Angew. Chem.* **1990**, *102*, 297; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 295.

(4) Karsch, H. H.; Appelt, A.; Müller, G. *Angew. Chem.* **1986**, *98*, 832; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 823. Karsch, H. H.; Ferazin, G.; Kooijmans, H.; Hiller, W. *Angew. Chem.*, in press.

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Particularly with zirconocene metal centers, these ligands show a fascinating variety of coordination modes, including Zr–P bonding.[6] The coordination mode for ligands of type **I** mainly depends on the substituents X and Y: heteroelement substitution at the carbanion reduces its nucleophilicity and promotes metal–phosphorus bonding. Ligands of type **II** mainly, but not exclusively, bind to the metal via the P atoms, which is also the case for zirconocene metal centers.[7]

The interaction of two phosphinomethanide ligands may lead to many unusual reactions: methyl transfer,[8] incorporation of CO under formation of a heterodiene ligand,[9] oxidative coupling,[6,10,11] and in the case of zirconocene metal centers, various kinds of internal metalation reactions.[11] The possibilities to bind more than one phosphinomethanide ligand to one zirconocene metal center are restricted by the steric and electronic requirements. An extension should be possible, however, by more unsaturated zirconium metal centers. The present paper describes the reaction of $ZrCl_4$ with 1–4 equiv of phosphinomethanides of type **I** or **II**.

Experimental Section

A. Preparation and Characterization of Compounds. General procedures and instrumentation were as previously described.[6] $ZrCl_4$ was obtained from commercial sources. The lithium phosphinomethanides were prepared according to the literature: $LiCH_2PMe_2$, **1**;[12] $Li[CH(PMe_2)_2]$, **2**;[12] $\{(TMEDA)Li[CH(PMe_2)(SiMe_3)]\}_2$, **3**;[13] $(TMEDA)\{Li[C(PMe_2)(SiMe_3)_2]\}_2$, **5**;[3] $Li[C(PMe_2)_2(SiMe_3)]$, **5a**;[13] $(TMEDA)Li[C(PPh_2)_2(SiMe_3)]$, **5b**;[14] and $(TMEDA)Li[C(PMe_2)_2(SiMe_3)]$, **5c**.[3]

Reactions of $ZrCl_4$ with 3. $ZrCl_4$ (0.55 g; 2.36 mmol) was dissolved in 40 mL of diethyl ether. At −78 °C, 1.28/1.96/2.05 g (4.72/7.25/7.58 mmol) of **3** were added slowly during 1 h with stirring. Continued stirring for 18 h caused a reddening of the solutions, which were allowed to warm to room temperature. After continued stirring for 1 h, the volatiles were removed in vacuo. The residue was extracted twice with 45 mL of toluene, and subsequently the solvent again was removed in vacuo: red solids (1.06/1.04/0.72 g) remained in all cases and were identified as mixtures of **4a,b,c/4a,b,c,d/4b,c,d** (95%), respectively, by means of NMR spectroscopy. Anal. Calcd for **4d** $C_{24}H_{64}P_4Si_4Zr$ (680.23): C, 42.23; H, 9.48; Cl, O. Found: C, 40.90; H, 9.10; Cl, 3.61. $\{^{1}H\}^{31}P$ NMR (C_6D_6, 20 °C): **4a**, δ(P) −32.25 (s); **4b**, δ(P) −29.06 (s); **4c**, ABC spin system; $\delta(P_A)$ −15.15, $\delta(P_B)$ −28.92, $\delta(P_C)$ −32.72; $^2J(AB)$ = 40.1 Hz; $^2J(AC)$ = 36.5 Hz; $^2J(BC)$ = 4.3 Hz; **4d**, ABCD spin system; $\delta(P_A)$ 9.27, $\delta(P_B)$ −18.97, $\delta(P_C)$ −24.90, $\delta(P_D)$ −45.20; $^2J(AB)$ = 12.9 Hz; $^2J(AC)$ = 21.5 Hz; $^3J(AD)$ = 81.7 Hz; $^2J(BC)$ = 25.8 Hz; $^3J(BD)$ = 23.6 Hz; ^1H NMR (C_6D_6, 20 °C): **4a**, δ 2.53 (d, $^2J_{HCP}$ = 11. 0 Hz, 6H, PCH_3), 2.45 (d, $^2J_{HCP}$ = 18.6 Hz, 6H, PCH_3), 0.45 (s, 18H, $SiCH_3$); **4b**, δ 1.34 (d, $^2J_{HCP}$ = 9.8 Hz, 6H, PCH_3), 1.22 (d, $^2J_{HCP}$ = 9.2 Hz, 6H, PCH_3), 0.44 (s, 9H, $SiCH_3$), 0.36 (s, 9H, $SiCH_3$); **4c**, δ 2.01 (d, $^2J_{HCP}$ = 8.9 Hz, 3H, PCH_3), 1.87 (d, $^2J_{HCP}$ = 7.6 Hz, 3H, PCH_3), 1.86 (d, $^2J_{HCP}$ = 7.3 Hz, 3H, PCH_3), 1.67 (d, $^2J_{HCP}$ = 8.9 Hz, 3H, PCH_3), 1.64 (d, $^2J_{HCP}$ = 8.2 Hz, 3H, PCH_3), 1.16 (d, $^2J_{HCP}$ = 8.2 Hz, 3H, PCH_3), 0.61 (s, 9H, $SiCH_3$), 0.48 (s, 9H, $SiCH_3$), 0.32 (s, 9H, $SiCH_3$); **4d**, δ 1.90 (d, $^2J_{HCP}$ = 8.4 Hz, 3H, PCH_3), 1.80 (d, $^2J_{HCP}$ = 6.2 Hz, 3H, PCH_3), 1.79 (d, $^2J_{HCP}$ = 5.5 Hz, 3H, PCH_3), 1.72 (d, $^2J_{HCP}$ = 6.2 Hz, 3H, PCH_3), 1.58 (d, $^2J_{HCP}$ = 6.6 Hz, 3H, PCH_3), 1.36 (d, $^2J_{HCP}$ = 5.1 Hz, 3H, PCH_3), 1.11 (d, $^2J_{HCP}$ = 5.9 Hz, 3H, PCH_3), 0.90 (d, $^2J_{HCP}$ = 8.8 Hz, 3H, PCH_3), 0.50 (s, 9H, $SiCH_3$), 0.39 (s, 9H, $SiCH_3$), 0.18 (s, 9H, $SiCH_3$), one signal for $SiCH_3$ could not be assigned unambiguously due to superposition with signals of impurities.

Synthesis of Complexes 6, 10, 11, and 12. $ZrCl_4$ and the appropriate lithium phosphinomethanide were combined in a stoichiometric amount of 1:2. At −78 °C, 35 mL of diethyl ether was added, and the mixture was allowed to warm to room temperature with stirring, while the color changed to red. After 18 h, the solvent was removed by evaporation and the residue extracted five to nine times with 50 mL of toluene. From the combined solutions, the solvent was condensed slowly into a trap, and colored solids remained. **6**: 1.10 g (4.72 mmol) of $ZrCl_4$, 2.94 g (5.16 mmol) of **5**; yield 2.24 g (89%); mp 152 °C. Anal. Calcd for $C_{18}H_{48}Cl_2P_2Si_4Zr$ (601.00): C, 35.97; H, 8.05; Cl, 11.08. Found: C, 36.53; H, 8.35; Cl, 12.29. **10**: 0.42 g (1.80 mmol) of $ZrCl_4$, 0.77 g (3.60 mmol) of **5a**; yield 0.95 g (92%). Anal. Calcd for $C_{16}H_{42}Cl_2P_4Si_2Zr$ (576.70): C, 33.32; H, 7.34; Cl, 12.30. Found: C, 35.68; H, 7.58; Cl, 11.40. **11**: 0.44 g (1.91 mmol) of $ZrCl_4$, 2.21 g (3.82 mmol) of **5b**; yield 1.04 g (40%); mp 114 °C dec. Anal. Calcd for $C_{68}H_{90}Cl_3LiN_4P_4Si_2Zr$ (1348.08): C, 60.59; H, 6.73; Cl, 7.89; N, 4.16. Found: C, 59.70; H, 6.61; Cl, 7.50; N, 3.72. **12**: 0.59 g (2.53 mmol) of $ZrCl_4$, 1.67 g (5.06 mmol) of **5c**; yield 1.13 g (52%).

A satisfactory elemental analysis of **12** could not be obtained, due to the presence of some impurities. One of these impurities tentatively can be assigned to *cis*-$Cl_2Zr[C(PMe_2)_2(SiMe_3)]_2$, **10a**. $\{^{1}H\}^{31}P$ NMR (C_6D_6, 20 °C): **6**, δ(P) −7.28 (s); **10**, δ(P) −19.61 (s); **10a** ($C_6D_5CD_3$; −80 °C), AA′BB′ spin system $\delta(P_A)$, −17.90; $\delta(P_B)$, −18.19; $J(AA')$ = 52.2 Hz; $J(AB)$ = 70.4 Hz; $J(AB')$ = −5.9 Hz; $J(BB')$ = 51.0 Hz; **11** ($C_6D_5CD_3$, 20 °C), δ(P) −1.14 (br); $\{^{1}H\}^{31}P$ NMR ($C_6D_5CD_3$, −100 °C); AA′BB′ spin system unresolved, $\delta(P_A)$, −1.38; $\delta(P_B)$, −2.38; **12**, ABCD spin system (partially resolved); $\delta(P_A)$, −23.70; $\delta(P_B)$, −28.18; $\delta(P_C)$, −37.25; $\delta(P_D)$, −40.29; $^2J(AB)$ = 14.0 Hz; $^2J(AC)$ = 36.5 Hz; $^2J(AD)$ = 53.7 Hz; $^2J(BC)$ = 98.6 Hz; $^2J(BD)$ = 35.5 Hz; $^2J(CD)$ unresolved. ^1H NMR (C_6D_6, 20 °C): **6**, δ 1.17 (d, $^2J_{HCP}$ = 8.4 Hz, 12H, PCH_3), 0.40 (s, 36H, $SiCH_3$); **10**, δ 1.23 (br, 24H, PCH_3), 0.28 (s, 18H, $SiCH_3$); **11**, δ 8.31 (br, 2H, H2, H6), 7.99 (br, 2H, H3, H5), 7.06 (br, 1H, H4), −0.20 (s, 18H, $SiCH_3$); **12**, δ 1.76 (br, 24H, PCH_3), −0.16 (s, 18H, $SiCH_3$). $\{^{1}H\}^{13}C$ NMR (C_6D_6, 20 °C): **6**, δ 15.20 (br, PCH_3), 7.13 (s, $SiCH_3$); **10**, δ 20.28 ($(AA'X)_2$ spin system, N = distance of the outermost lines = 28.1 Hz, PCH_3), 4.98 (s, $SiCH_3$); **11**, δ 134.31 (m, C2, C6), 4.20 (s, $SiCH_3$), 0.87 (t, $^1J_{CP}$ = 5.1 Hz, $CSiMe_3$), C1, C3, C5 could not be assigned unambiguously; **12**, δ 22.3 (br, PCH_3), 5.69 (s, $SiCH_3$), 1.94 (t, $^1J_{CP}$ = 5.4 Hz, $CSiMe_3$).

Reaction of 6 with CO (Solvent: Toluene). Synthesis of 7. **6** (0.31 g; 0.52 mmol) in 3 mL of toluene was kept under a CO atmosphere (1 atm) at room temperature for 8 weeks. The red violet crystals slowly dissolved, and yellow crystals of **7** deposited at the glass walls. Yield: 0.32 g (100%); mp 179 °C; Anal. Calcd for $C_{38}H_{96}Cl_4O_2P_4Si_8Zr_2$ (1258.02): C, 36.28; H, 7.69; Cl, 11.27. Found: C, 35.54; H, 7.36; Cl, 11.41. $\{^{1}H\}^{31}P$ NMR ($C_6D_5CD_3$, 50 °C): $\delta(P_A)$ 17.51 (d, 45.1 Hz), $\delta(P_B)$ −7.18 (br); (C_6D_6/THF, 20 °C) $\delta(P_A)$ 14.81 (d, 43.0), $\delta(P_B)$ −12.39 (d, 43.0). ^1H NMR ($C_6D_5CD_3$, 50 °C): δ 1.2–1.6 (br, 12H, PCH_3); δ 0.23 (s, 9H, $SiCH_3$), 0.34 (s, 9H, $SiCH_3$), −0.38 to −0.43 (br, 18H, $SiCH_3$). IR (Nujol, cm^{-1}): 1605 (s, ν(CO)). MS (EI, 70 eV): 628 (4.2, $M/2^+ - H$), 470 (2.9, $M/2^+ - H$, $-C(SiMe_3)_2$), 409 (8.2, $M/2^+ - H$; $-C(PMe_2)(SiMe_3)_2$); 231 (54.4, $Me_3SiC{=}C(SiMe_3)(PMe_2)^+$); 219 (26.0, $C(PMe_2)(SiMe_3)_2^+$), 73 (100, $SiMe_3^+$).

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[5] Karsch, H. H. *Chem. Ber.* **1984**, *117*, 783. Karsch, H. H.; Baumgartner, G.; Gamper, S. To be submitted.

[6] Karsch, H. H.; Deubelly, B.; Hofmann, J.; Müller, G. *J. Am. Chem. Soc.* **1988**, *110*, 3654. Karsch, H. H.; Grauvogl, G.; Deubelly, B.; Müller, G. *Organometallics* **1992**, *11*, 4238.

[7] Karsch. H. H.; Deubelly, B.; Grauvogl, G.; Lachmann, J.; Müller, G. *Organometallics* **1992**, *11*, 4245.

[8] Karsch, H. H.; Zellner, K.; Müller, G. *J. Chem. Soc., Chem. Commun.* **1990**, 1621. Karsch, H. H.; Zellner, K.; Müller, G. *Organometallics* **1991**, *10*, 2884.

[9] Karsch, H. H.; Müller, G.; Krüger, C. *J. Organomet. Chem.* **1984**, *273*, 195.

[10] Karsch. H. H.; Deubelly, B.; Müller, G. *J. Chem. Soc., Chem. Commun.* **1988**, 517. Karsch, H. H.; Deubelly, B.; Grauvogl, G.; Müller, G. *J. Organomet. Chem.*, in press.

[11] Karsch, H. H.; Grauvogl, G.; Kawecki, M.; Bissinger, P. *Organometallics* **1993**, *12*, 2757.

[12] Karsch, H. H.; Schmidbaur, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1977**, *32b*, 762.

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

[14] Karsch, H. H.; Grauvogl, G.; Bissinger, P.; Müller, G. *J. Organomet. Chem.*, in press.

Table 1. Crystal Structure Data for 6, 7, 11, and 12

	6	7	11	12·2toluene
formula	$C_{18}H_{48}Cl_2P_2Si_4Zr$	$C_{38}H_{96}Cl_4O_2P_4Si_8Zr_2$	$C_{68}H_{90}Cl_3LiN_4P_4Si_2Zr$	$C_{52}H_{90}Cl_3LiN_4P_4Si_2Zr$
M_r	601.001	1258.023	1348.088	1155.909
cryst syst	monoclinic	monoclinic	orthorhombic	monoclinic
space group	*C*2/*c* (No. 15)	$P2_1/n$ (No. 14)	*Pbca* (No. 61)	$P2_1/c$ (No. 14)
a, Å	9.273(1)	10.149(1)	19.016(2)	16.138(2)
b, Å	15.078(2)	16.503(2)	32.385(4)	13.837(1)
c, Å	22.062(2)	19.307(3)	23.906(3)	25.779(3)
β, deg	95.09(1)	97.13(1)	90.	102.19(1)
V, Å^3	3072.5	3208.7	14722.1	5626.7
Z	4	2 (dimers)	8	4
d_{calcd}, g/cm^3	1.299	1.302	1.216	1.364
μ(Mo Kα), cm^{-1}	7.9	7.6	4.1	5.3
F(000), e	1264	1320	5664	2448
T, °C	23	−50	23	−71
diffractometer	Enraf-Nonius CAD4	Syntex-P2$_1$	Enraf-Nonius CAD4	Enraf-Nonius CAD4
scan	$\vartheta/2\vartheta$	ω	ω	ω
scan width (in ω)	0.8 + 0.35 tan ϑ	0.8	1.0 + 0.35 tan ϑ	0.9
$((\sin\vartheta)/\lambda)_{max}$, Å^{-1}	0.638	0.595	0.571	0.62
hkl range	±11,+19,±28	±12,+19,+22	+21,+37,+27	±19,+17,+31
no. of reflns (measd/unique)	6658/3345	6121/5590	12448/11489	11864/9847
R_{int}	0.020	0.021		0.018
no. of reflns obsd [$F_o \geq 4.0\sigma(F_o)$]	2654	4722	6023	8045
abs corr				
rel transm				
struct soln	autom Patterson	direct methods	direct methods	direct methods
H atoms (found/calcd)	17/7	35/13	–/58	66/24
no. of params refined	147	262	497	432
R^a	0.031	0.034	0.088	0.048
wR^b	0.025	0.039	0.070	0.051
$(\text{shift/error})_{max}$	0.05	0.001	0.003	0.001
$\Delta\rho_{fin}$(max/min), e/Å^3	+0.25/−0.32	+0.64/−0.68	+0.71/−0.77	+0.92/−0.49

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

Reaction of 6 with CO (Solvent: THF). 6 (1.30 g; 2.16 mmol) was dissolved in 40 mL of THF under 1 atm of CO and kept for 18 h at 20 °C. The color of the solution remained unchanged. The solvent was evaporated, and the solid residue was extracted with 50 mL of toluene. After removal of the solvent in vacuo, a red solid (1.12 g) was obtained. Anal. Calcd for **8** $C_{19}H_{48}OP_2Si_4$ (426.88): C, 48.88; H, 10.36; Cl, 0. Anal. Calcd for **9** $C_{19}H_{48}Cl_2OP_2Si_4Zr$ (629.00): C, 36.28; H, 7.69; Cl, 11.27. Found for **8**/**9**: C, 36.50; H, 7.96; Cl, 7.92. $\{^1H\}^{31}P$ NMR (C_6D_6, 20 °C): **8**, δ(P) 6.91 (d, 218.2), −63.75 (d, 218.2); **9**, δ(P) 0.64 (d, br, 206.3), −45.69 (d, br, 206.3).

B. X-ray Structure Determinations of 6, 7, 11, and 12. Yellow (**7**) or red (**6**, **11**, **12**) single crystals of all four compounds were grown from toluene and sealed under argon at dry ice temperature into capillaries. Subsequent examination on the single-crystal diffractometer (Mo Kα radiation, λ = 0.710 69 Å, graphite monochromator) revealed the respective crystal classes, the metrical symmetries of which were confirmed by reduced cell calculations (LePage,[15] DELOS[16]). Exact cell constants were determined by least-squares refinement on the Bragg angles of 25 reflections (**7**: 15 reflections) carefully centered on the diffractometer. Crystal data and values pertinent to data collection, structure solution, and refinement are collected in Table 1.

The measured integrated intensities were corrected for Lp effects and crystal decay (**6**, −2.9%; **11**, −4.7%; **12**, −3.5%) and those of **7** also empirically for absorption (Table 1). After anisotropic refinement of the non-H atoms, hydrogen atoms not located in difference maps were calculated in idealized geometrical positions. For **11** only the H atoms of the anion were considered. The methyl groups of **6** were treated as rigid groups, while in all other structures the H atoms were included as fixed-atom contributions into structure factor calculations. In **11** a disorder of the C atoms of one of the TMEDA molecules was treated with a split-atom model. Four of the phenyl rings of **11** were also slightly disordered. Because this disorder could not be resolved satisfactorily, the phenyl rings were refined as rigid groups with individual isotropic displacement parameters. Likewise, the methyl C atoms at Si(2) could only be refined with isotropic displacement parameters. Because of the large number of parameters, the parameters of **11** were refined in two large blocks. One of the toluene molecules in **12** was disordered with regard to the orientation of the methyl group and was treated with a split model. The H atoms of this group were neglected. Programs used included SHELXS-86[17] for structure solution and SHELX-76[18] for refinement (**6**, **7**, **11**) or SHELXTL-PLUS[19] (**12**), respectively. The final atomic coordinates of the non-H atoms are contained in Tables 2–5. See note at the end of the paper for further crystal structure material available as supplementary material.

Results and Discussion

1. Monophosphinomethanide Derivatives of $ZrCl_4$.

1.1. Preparation. Thermally unstable alkylzirconium complexes are stabilized considerably by the addition of donor ligands.[20] Due to the lack of β-hydrogens and the possibility of η^2-C,P coordination, phosphinomethanide ligands likewise might lead to stable alkylzirconium complexes. In a first attempt to synthesize phosphinomethanide zirconium complexes, $ZrCl_4$ and $LiCH_2PMe_2$, **1**, were reacted in a 1:4 molar ratio. The red solid obtained could not be characterized spectroscopically, however, due

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(15) Le Page, Y. *J. Appl. Crystallogr.* **1982**, *15*, 255.

(16) Zimmermann, H.; Burzlaff, H. *Z. Kristallogr.* **1985**, *170*, 241.

(17) Sheldrick, G. M. In *Crystallographic Computing 3*; Sheldrick, G. M., Krüger, C., Goddard, R., Eds.; Oxford University Press: Oxford, 1985; p 175.

(18) Sheldrick, G. M. SHELX-76. Program for Crystal Structure Determination. University of Cambridge, Cambridge, England, 1976.

(19) Sheldrick, G. M. SHELXTL-PLUS, Release 4.0 for Siemens R3 Crystallographic Research System. Siemens Analytical Instruments, Inc., Madison, WI, 1989.

(20) Thiele, K. H.; Krüger, J. *Z. Anorg. Allg. Chem.* **1971**, *383*, 272. Clarke, J. F.; Fowles, G. W. A.; Rice, D. A. *J. Organomet. Chem.* **1974**, *76*, 349. Wengrovius, J. H.; Schrock, R. R. *J. Organomet. Chem.* **1981**, *205*, 319.

Table 2. Fractional Atomic Coordinates of the Non-Hydrogen Atoms in 6 with Equivalent Isotropic Displacement Parameters[a]

atom	x/a	y/b	z/c	U_{eq}, Å^2
Zr	0.000 00	0.362 95(2)	0.250 00	0.032
P(1)	−0.068 47(7)	0.491 97(4)	0.320 72(3)	0.035
Si(1)	0.008 73(8)	0.327 05(5)	0.409 46(3)	0.040
Si(2)	0.253 06(7)	0.450 47(5)	0.370 66(3)	0.041
Cl	0.211 72(9)	0.275 05(5)	0.241 57(3)	0.068
C(1)	0.0604(2)	0.4124(1)	0.3518(1)	0.031
C(11)	0.0803(3)	0.3567(2)	0.4890(1)	0.062
C(12)	0.0797(3)	0.2157(2)	0.3905(1)	0.056
C(13)	−0.1879(3)	0.3083(2)	0.4180(1)	0.059
C(21)	0.3772(3)	0.3564(2)	0.3934(1)	0.063
C(23)	0.2703(3)	0.5331(2)	0.4345(1)	0.064
C(22)	0.3404(3)	0.5034(2)	0.3064(1)	0.056
C(31)	−0.2331(3)	0.5011(2)	0.3584(1)	0.056
C(32)	−0.0061(3)	0.6056(2)	0.3273(1)	0.051

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*a_ia_j$.

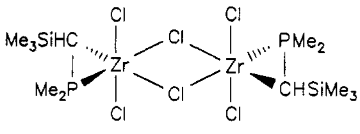
Table 3. Fractional Atomic Coordinates of the Non-Hydrogen Atoms in 7 with Equivalent Isotropic Displacement Parameters

atom	x/a	y/b	z/c	U_{eq}, Å^2
Zr	0.870 65(2)	0.457 61(1)	0.068 38(1)	0.019
Cl(1)	0.687 17(7)	0.528 41(4)	−0.001 07(4)	0.031
Cl(2)	1.033 74(7)	0.574 86(4)	0.051 45(3)	0.029
P(1)	0.723 20(7)	0.457 34(4)	0.169 95(4)	0.028
P(2)	0.723 92(7)	0.328 29(4)	0.019 64(4)	0.025
Si(1)	0.850 73(8)	0.630 12(4)	0.193 36(4)	0.030
Si(2)	1.015 32(8)	0.478 49(5)	0.245 01(4)	0.033
Si(3)	0.806 24(9)	0.140 74(5)	0.006 53(4)	0.034
Si(4)	1.122 54(7)	0.221 96(5)	0.108 00(4)	0.029
O	0.9645(2)	0.354 95(9)	0.098 37(8)	0.024
C(01)	0.8700(3)	0.5170(2)	0.1920(1)	0.025
C(02)	0.8424(3)	0.2464(2)	0.0415(1)	0.026
C(03)	0.9560(3)	0.2747(1)	0.0783(1)	0.024
C(201)	0.6716(3)	0.3226(2)	−0.0740(2)	0.036
C(202)	0.5695(3)	0.3074(2)	0.0548(2)	0.037
C(101)	0.5690(3)	0.5144(2)	0.1625(2)	0.041
C(102)	0.6944(4)	0.3880(2)	0.2398(2)	0.052
C(11)	0.7555(4)	0.6851(2)	0.1184(2)	0.045
C(12)	0.7630(4)	0.6515(2)	0.2712(2)	0.044
C(13)	1.0125(3)	0.6864(2)	0.2069(2)	0.041
C(21)	1.0230(4)	0.5263(2)	0.3336(2)	0.052
C(22)	1.1764(3)	0.4978(2)	0.2108(2)	0.042
C(23)	1.0144(4)	0.3675(2)	0.2662(2)	0.045
C(31)	0.8807(4)	0.0576(2)	0.0646(2)	0.046
C(32)	0.6251(4)	0.1181(2)	−0.0024(2)	0.048
C(33)	0.8613(4)	0.1301(2)	−0.0816(2)	0.051
C(41)	1.2502(3)	0.3007(2)	0.1314(2)	0.040
C(42)	1.1098(3)	0.1591(2)	0.1871(2)	0.041
C(43)	1.1813(3)	0.1609(2)	0.0362(2)	0.047

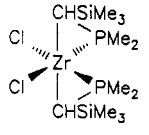
to the manifold of signals. Likewise, the products of the reaction of $ZrCl_4$ with $Li[CH(PMe_2)_2]$ could not be identified. In marked contrast to this result, the reaction of $ZrCl_4$ with $\{(TMEDA)Li[CH(PMe_2)(SiMe_3)]\}_2$, **3**, gave mixtures of compounds **4a–d** (eq 1). **4a–d** are obtained as

$$\underset{(n\,=\,1\text{–}4)}{ZrCl_4 + n/2\ \mathbf{3}} \longrightarrow \underset{\mathbf{4a\text{–}d}}{Cl_{4-n}Zr[CH(PMe_2)(SiMe_3)]_n} \quad (1)$$

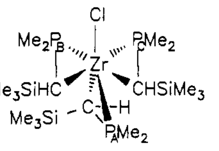
a red solid, which contains mono-, di-, tri-, and tetrasubstituted compounds in increasing amounts on going from $n = 1$ to $n = 4$. Only with $n = 4$ could an approximately pure compound **4d** be obtained. Nevertheless, tentative assignments for the structures of **4a–d** can be made mainly on the basis of $\{^1H\}^{31}P$ NMR data and of steric arguments. Only one isomer is observed for all four compounds, and from steric considerations only one stereoisomer has a minimum of steric strain in either case. The $\{^1H\}^{31}P$ NMR spectra in all cases are in accord with the thus selected structure.



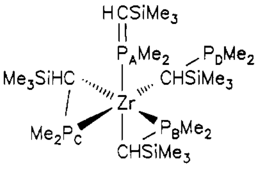
4a



4b



4c

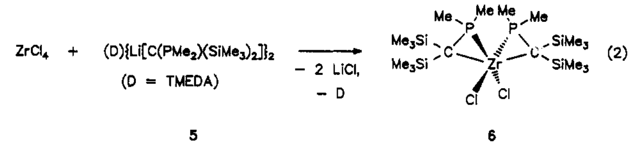


4d

Only one ^{31}P NMR signal in the expected range for η^2-C,P coordination of the ligand (cf **IV**[6]) is observed for the monosubstitution product and attributed to one diastereomer of dimeric **4a**. Alternative structures cannot be ruled out, however. An analogous η^2-C,P coordination might also be expected for **4b**, and consistently, only one ^{31}P NMR signal is found at somewhat lower field than that for **4a**. This indicates the increased steric requirements in **4b** and thus also is consistent with the formulation of two η^2-C,P phosphinomethanide ligands in an octahedral arrangement with two equivalent P atoms. There may be some ambiguity about the conformation of **4b**, which cannot be overcome by the spectroscopic data alone. We prefer the actual assignment on the basis of the similarity to **6**, the structure of which has been determined by an X-ray analysis (see below).

The ^{31}P NMR spectrum of **4c** exhibits an ABC type spin system. From the $\delta(P)$ values, which fall in a narrow range between −15 and −33 ppm, a η^2-C,P coordination mode is likely to operate for all three ligands, in accord with the proposed structure.

The AMNX type pattern of the ^{31}P NMR spectrum of the homoleptic complex **4d** (Figure 1) indicates the presence of a rigid complex with four different bonded ligands, two of which coordinate again in a η^2-C,P fashion. A low-field signal (P_A) is assigned to a η^1-P-coordinated phosphinomethanide ligand, thus forming a P–metal substituted phosphorus ylide (cf. ref 6), and the remaining signal (P_D) is observed at high field corresponding to a η^1-C-coordinated ligand. Thus **4d** is the first example in which all possible coordination modes of monophosphinomethanide ligands in mononuclear complexes, i.e., η^1-C, η^1-P, and η^2-C,P, are coexisting simultaneously. It has to be emphasized, however, that the assignment of $\delta(P)$ signals of **4d** is somewhat arbitrary: P_B and P_C may mutually be exchanged. The ^1H NMR data are also in accord with the proposed structures of **4a–d**, although the signal of the methanide proton could not be assigned in either case, due to superposition of signals of the mixtures (in the spectrum of **4d**, some impurities (about 5%) due to **4b** and **4c** are present). In contrast to the aforementioned reactions, only two of the fully substituted phosphinomethanide ligands can be bound to zirconium according to eq 2, even with an excess of **5**.



5 **6**

Table 4. Fractional Atomic Coordinates of the Non-Hydrogen Atoms in the Anion of 11 with Equivalent Isotropic Displacement Parameters[a]

atom	x/a	y/b	z/c	U_{eq}, Å^2
Zr	0.71653(5)	0.36797(3)	0.033538(4)	0.044
P(1)	0.6418(1)	0.36158(9)	0.1332(1)	0.047
P(2)	0.7800(2)	0.38265(8)	0.1409(1)	0.046
P(3)	0.7378(2)	0.35503(9)	−0.0806(1)	0.054
P(4)	0.8468(2)	0.38869(9)	−0.0217(1)	0.054
Cl(1)	0.7014(2)	0.44207(8)	0.0287(1)	0.072
Cl(2)	0.7589(2)	0.29865(8)	0.0452(1)	0.063
Cl(3)	0.5960(1)	0.3536(1)	0.0000(1)	0.072
Si(1)	0.1818(2)	0.4092(1)	0.2530(1)	0.058
Si(2)	0.8769(2)	0.3756(1)	−0.1530(2)	0.084
C(1)	0.7008(5)	0.3840(3)	0.1795(4)	0.040
C(2)	0.8240(5)	0.3715(3)	−0.0886(4)	0.054
C(11)	0.5589(5)	0.3885(4)	0.1414(4)	0.044
C(12)	0.5066(6)	0.3755(4)	0.1780(5)	0.064
C(13)	0.4490(7)	0.3999(5)	0.1901(6)	0.076
C(14)	0.4414(6)	0.4367(5)	0.1643(6)	0.071
C(15)	0.4898(7)	0.4498(4)	0.1255(6)	0.073
C(16)	0.5488(6)	0.4263(4)	0.1146(5)	0.054
C(21)	0.6173(6)	0.3098(3)	0.1547(5)	0.049
C(22)	0.6462(6)	0.2899(4)	0.1993(6)	0.064
C(23)	0.6273(8)	0.2503(5)	0.2135(6)	0.084
C(24)	0.5767(9)	0.2301(4)	0.1855(8)	0.085
C(25)	0.5470(7)	0.2483(5)	0.1396(7)	0.087
C(26)	0.5680(8)	0.2876(4)	0.1249(5)	0.077
C(31)	0.8422(5)	0.3441(3)	0.1690(5)	0.047
C(32)	0.8328(6)	0.3264(4)	0.2215(5)	0.062
C(33)	0.8818(8)	0.2998(4)	0.2432(5)	0.073
C(34)	0.9423(7)	0.2911(4)	0.2147(7)	0.080
C(35)	0.9515(7)	0.3073(5)	0.1635(6)	0.077
C(36)	0.9021(7)	0.3326(4)	0.1402(5)	0.061
C(41)	0.8301(7)	0.4295(4)	0.1543(5)	0.059
C(42)	0.7936(7)	0.4663(4)	0.1511(6)	0.078
C(43)	0.831(1)	0.5029(5)	0.1605(7)	0.117
C(44)	0.904(1)	0.5032(6)	0.1704(8)	0.107
C(45)	0.9357(9)	0.4679(6)	0.1743(8)	0.111
C(46)	0.9000(8)	0.4313(4)	0.1661(6)	0.074
C(51)	0.6813(4)	0.3813(4)	−0.1311(4)	0.090*[b]
C(52)	0.6534(4)	0.3635(4)	−0.1794(4)	0.132*
C(53)	0.6141(4)	0.3874(4)	−0.2165(4)	0.151*
C(54)	0.6026(4)	0.4291(4)	−0.2053(4)	0.148*
C(55)	0.6305(4)	0.4469(4)	−0.1570(4)	0.185*
C(56)	0.6698(4)	0.4230(4)	−0.1199(4)	0.129*
C(61)	0.7250(6)	0.3011(2)	−0.0996(3)	0.066*
C(62)	0.6579(6)	0.2845(2)	−0.1063(3)	0.111*
C(63)	0.6498(6)	0.2428(2)	−0.1192(3)	0.130*
C(64)	0.7089(6)	0.2177(2)	−0.1256(3)	0.121*
C(65)	0.7761(6)	0.2343(2)	−0.1189(3)	0.159*
C(66)	0.7841(6)	0.2760(2)	−0.1059(3)	0.097*
C(71)	0.8647(5)	0.4439(2)	−0.0235(5)	0.079*
C(72)	0.8923(5)	0.4652(2)	0.0221(5)	0.138*
C(73)	0.9018(5)	0.5079(2)	0.0191(5)	0.153*
C(74)	0.8836(5)	0.5292(2)	−0.0295(5)	0.164*
C(75)	0.8559(5)	0.5978(2)	−0.0751(5)	0.188*
C(76)	0.8465(5)	0.4651(2)	−0.0722(5)	0.134*
C(81)	0.9214(4)	0.3638(3)	−0.0049(3)	0.067*
C(82)	0.9359(4)	0.3213(3)	−0.0138(3)	0.090*
C(83)	0.9981(4)	0.3003(3)	−0.0015(3)	0.112*
C(84)	1.0557(4)	0.3218(3)	0.0198(3)	0.136*
C(85)	1.0512(4)	0.3643(3)	0.0287(3)	0.191*
C(86)	0.9891(4)	0.3853(3)	0.0164(3)	0.184*
C(101)	0.6263(7)	0.3765(4)	0.2938(4)	0.094
C(102)	0.6347(6)	0.4583(3)	0.2412(5)	0.080
C(103)	0.7608(7)	0.4200(4)	0.2880(5)	0.093
C(111)	0.8401(8)	0.4105(5)	−0.2042(6)	0.148*
C(112)	0.8839(8)	0.3279(4)	−0.1927(6)	0.138*
C(113)	0.9675(8)	0.3913(4)	−0.1383(6)	0.138*

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*a_ia_j$. [b] (*) Refined isotropically.

Table 5. Fractional Atomic Coordinates of the Non-Hydrogen Atoms in the Anion of 12 with Equivalent Isotropic Displacement Parameters[a]

atom	x/a	y/b	z/c	U_{eq}, Å^2
Zr	0.742 36(2)	0.367 63(3)	0.153 25(1)	0.025
P(1)	0.698 17(7)	0.371 18(9)	0.249 34(4)	0.035
P(2)	0.586 50(7)	0.439 35(8)	0.163 85(5)	0.032
P(3)	0.832 05(7)	0.320 02(9)	0.078 25(5)	0.037
P(4)	0.685 45(7)	0.419 42(9)	0.047 57(4)	0.034
Cl(1)	0.668 27(7)	0.214 43(8)	0.133 72(5)	0.044
Cl(2)	0.794 91(7)	0.533 82(7)	0.164 37(4)	0.039
Cl(3)	0.875 39(6)	0.301 21(8)	0.211 45(4)	0.039
Si(1)	0.531 60(9)	0.4692(1)	0.275 72(6)	0.048
Si(2)	0.790 83(9)	0.3821(1)	−0.044 13(5)	0.052
C(1)	0.6004(3)	0.4279(3)	0.2324(2)	0.036
C(2)	0.7674(3)	0.3692(4)	0.0218(2)	0.038
C(01)	0.4908(3)	0.3753(4)	0.1298(2)	0.050
C(02)	0.5570(3)	0.5643(3)	0.1441(2)	0.044
C(03)	0.7701(3)	0.4357(5)	0.3025(2)	0.058
C(04)	0.6932(4)	0.2527(4)	0.2808(2)	0.063
C(05)	0.6750(4)	0.5491(4)	0.0310(2)	0.055
C(06)	0.5829(3)	0.3780(5)	0.0113(2)	0.062
C(07)	0.8506(4)	0.1903(4)	0.0710(2)	0.062
C(08)	0.9402(3)	0.3653(5)	0.0881(2)	0.062
C(09)	0.5570(4)	0.5938(5)	0.3013(3)	0.078
C(10)	0.5408(4)	0.3882(6)	0.3352(3)	0.084
C(11)	0.4167(3)	0.4714(5)	0.2422(3)	0.068
C(12)	0.8365(5)	0.2703(7)	−0.0659(3)	0.099
C(13)	0.8692(6)	0.4793(8)	−0.0472(3)	0.127
C(14)	0.6973(4)	0.4131(5)	−0.0965(2)	0.075

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*a_ia_j$.

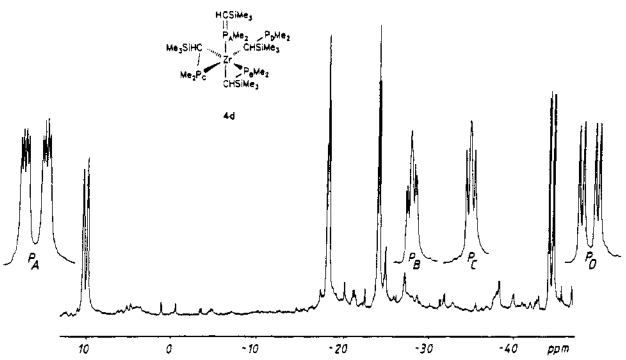


Figure 1. $\{^1H\}^{31}P$ NMR spectrum of **4d** (C_6D_6; 20 °C; H_3PO_4 external standard).

Red crystals of **6** are obtained from toluene solution, which in the ^{31}P NMR spectrum give rise to only one singlet resonance at $\delta(P) = -7.28$ ppm. The ^1H and ^{13}C NMR data indicate magnetically equivalent PCH_3 and $SiCH_3$ groups. Thus a 12e complex with η^2-P,C-coordinated ligands has to be envisaged, which is confirmed by an X-ray structure analysis.

1.2. Molecular Structure of 6. Important bond distances and angles of **6** are summarized in Table 6. Two phosphinomethanide ligands $[C(PMe_2)(SiMe_3)_2]^-$ are η^2-connected via phosphorus and carbon to the zirconium center. Together with the two chlorine substituents they complete a distorted octahedral coordination. The mutual trans arrangement of the carbon atoms minimizes the steric interaction of the silyl groups. Alternatively, the η^2-bonded phosphinomethanide ligands may be considered to occupy one coordination site (Figure 2), thus generating a distorted tetrahedral environment at the metal center. The entire complex has crystallographic C_2 symmetry, and the 2-fold axis passes through the zirconium center and bisects the angle Cl–Zr–Cl′. Distortions from an idealized geometry obviously arise from the presence of two three-membered rings Zr–C–P and from the steric bulk of the ligands. In **6** the phosphinomethanide ligands may be regarded as heteroolefinic ligands to the metal. In compounds of this type, the P–C bond length can be taken as a measure of the residual "ylidic character" of the ligand. Hence it should increase with short metal–P bonds and long

Table 6. Important Interatomic Distances (Å) and Angles (deg) in the Molecular Structure of 6 with Esd's in Units of the Last Significant Figure in Parentheses[a]

Zr–P(1)	2.607(1)	Zr–Cl	2.390(1)
Zr–C(1)	2.385(2)	P(1)–C(1)	1.786(2)
P(1)–C(31)	1.807(2)	P(1)–C(32)	1.810(2)
C(1)–Si(1)	1.901(2)	C(1)–Si(2)	1.888(2)
Si(1)–C(11)	1.875(3)	Si(2)–C(21)	1.866(3)
Si(1)–C(12)	1.864(3)	Si(2)–C(22)	1.872(3)
Si(1)–C(13)	1.871(3)	Si(2)–C(23)	1.877(3)
Cl–Zr–Cl′	112.6(1)	P(1)–Zr–C(1)	41.6(1)
Cl–Zr–P(1)	134.9(1)	Cl′–Zr–P(1)	97.0(1)
Cl–Zr–C(1)	96.9(1)	Cl′–Zr–C(1)	103.1(1)
P(1)–Zr–P(1)′	83.5(1)	C(1)–Zr–C(1)′	143.6(1)
P(1)–Zr–C(1)′	106.3(1)	Zr–P(1)–C(1)	62.5(1)
C(1)–P(1)–C(31)	116.0(1)	C(1)–P(1)–C(32)	114.0(1)
C(31)–P(1)–C(32)	99.7(1)	Zr–C(1)–P(1)	75.9(1)
P(1)–C(1)–Si(1)	120.8(1)	P(1)–C(1)–Si(2)	117.9(2)
Si(1)–C(1)–Si(2)	110.4(1)		

[a] See Figure 2 for atom numbering.

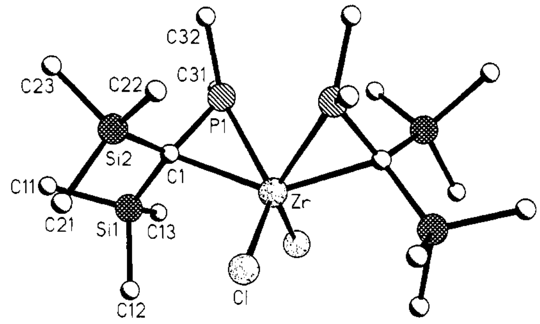


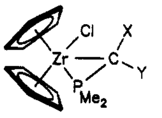
Figure 2. Molecular structure of 6 and crystallographic numbering scheme adopted. H atoms are omitted.

Table 7. Selected Bond Distances (Å) and Angles (deg) of III–V and 6

	III[a]	IV[a]	V	6
Zr–Cl	2.569(1)	2.558(1)	2.554(1)	2.390(1)
Zr–P(1)	2.621(1)	2.634(1)	2.606(1)	2.607(1)
Zr–C(1)	2.413(2)	2.401(5)	2.607(3)	2.385(2)
P_{endo}–C(1)	1.764(3)	1.744(5)	1.761(1)	1.786(2)
C(1)–Zr–P	40.8(1)	40.3(1)	39.5(1)	41.6(1)
Si(1)–C(1)–Si(2)			106.8(2)	110.4(1)
Zr–C(1)–Si(1)/(2)			118.7(2) 118.3(2)	116.2(1) 111.5(1)

[a] Mean of two independent molecules in the cell (enantiomers).

metal–C bonds, but steric congestion may obscure this trend. In this context a comparison with **III–V** is informative.[6]



III: X = H, Y = PMe_2
IV: X = H, Y = $SiMe_3$
V: X = $SiMe_3$, Y = $SiMe_3$

Nevertheless, it appears that a heteroolefinic description of the bonding is a better mirror of the observed trends than is the heterocycle/P-ylide view, at least in zirconium complexes such as **6**, thus suggesting a close structural relationship between **6** and Cp_2ZrCl_2. Likewise, some other important structural features of **6** can be understood by comparison with those of **V**. The Zr–P distances are equally short, suggesting that 2.60 Å is the lower limit for this type of bonding, whereas the distances Zr–Cl and Zr–C(1) are considerably shorter in **6** (Table 7). This obviously reflects the lower coordination number and electronic unsaturation in **6** and/or the high steric congestion in **V**.

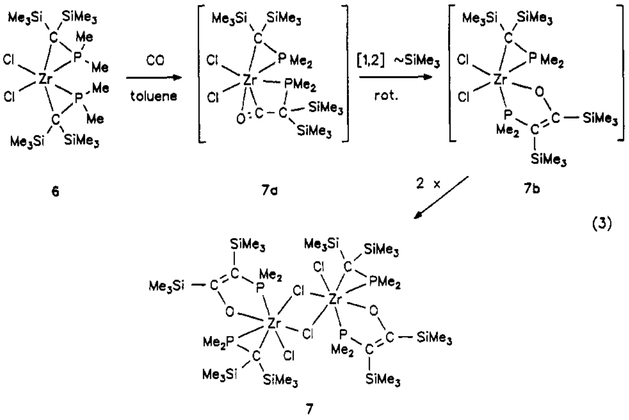
Table 8. Important Interatomic Distances (Å) and Angles (deg) in the Molecular Structure of 7 with Esd's in Units of the Last Significant Figure in Parentheses[a]

Zr–P(1)	2.610(1)	Zr–P(2)	2.704(1)
Zr–Cl(1)	2.452(1)	Zr–Cl(2)	2.593(1)
Zr–C(01)	2.404(2)	Zr–O	1.994(2)
P(1)–C(01)	1.777(3)	P(2)–C(02)	1.823(3)
Cl(1)–Zr–Cl(2)	91.7(1)	P(1)–Zr–P(2)	85.3(1)
Cl(2)–Zr–P(1)	122.0(1)	Cl(1)–Zr–P(1)	86.8(1)
Cl(1)–Zr–P(2)	80.7(1)	Cl(2)–Zr–P(2)	151.4(1)
Cl(1)–Zr–O	150.1(1)	Cl(2)–Zr–O	112.4(1)
P(1)–Zr–O	94.5(1)	P(2)–Zr–O	69.7(1)
Cl(1)–Zr–C(01)	102.5(1)	Cl(2)–Zr–C(01)	83.4(1)
P(1)–Zr–C(01)	41.3(1)	P(2)–Zr–C(01)	125.1(1)
O–Zr–C(01)	97.8(1)	O–Zr–Cl(2)′	112.4(1)
Cl(1)–Zr–Cl(2)′	91.7(1)	Cl(2)–Zr–Cl(2)′	74.6(1)
P(1)–Zr–Cl(2)′	122.6(1)	P(2)–Zr–Cl(2)′	151.4(1)
C(01)–Zr–Cl(2)′	83.4(1)	Zr–Cl(2)–Zr′	105.4(1)
Zr–P(1)–C(01)	63.1(1)	Zr–C(01)–P(1)	75.6(1)
Zr–P(2)–C(02)	100.7(1)	Zr–O–C(03)	136.3(1)
O–C(03)–C(02)	119.7(2)	P(2)–C(02)–C(03)	111.1(2)

[a] See Figure 3 for atom numbering.

1.3. Reactions of 6. Both functionalities in **6**, the chloride and the phosphinomethanide ligands, are susceptible to attack by appropriate reagents. The substitution of Cl^- by cyclopentadienyl ligands with concomitant metalation of a $SiCH_3$ group and ring closure to a zircona heterocycle has already been described.[11]

1.3.1. Reaction with CO in Toluene. In toluene solution, **6** takes up 1 equiv of CO (eq 3). The yellow crystals of **7** obtained show an IR band at 1605 cm^{-1}, which indicates CO insertion into the Zr–C bond.



(3)

The NMR data ($\{^1H\}^{31}P$: AB spin system) are not completely conclusive whether **7a**, **7b**, or **7** is present, although the ^1H NMR data render a structure **7a** unlikely (meaningful ^{13}C NMR data could not be obtained due to low solubility). An X-ray structure determination proves the formation of a dinuclear phosphino enolate complex **7**, presumably formed according to eq 3 via **7a**, including a 1,2-shift of the $SiMe_3$ group.

1.3.2. Molecular Structure of 7. Bond distances and angles are given in Table 8. Complex **7** crystallizes from toluene solution as a centrosymmetric dimer (Figure 3). The zirconium centers are heptacoordinated. The resulting coordination geometry is highly irregular, certainly also a consequence of the two chelating ligands with their reduced bite angles. With regard to distances and angles, the Zr–C(01)–P(1) three-membered ring is virtually identical with the respective Zr–C–P ring in the parent complex

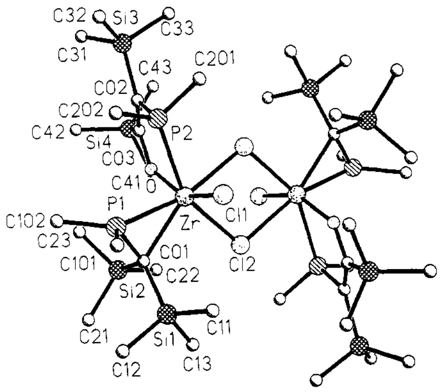
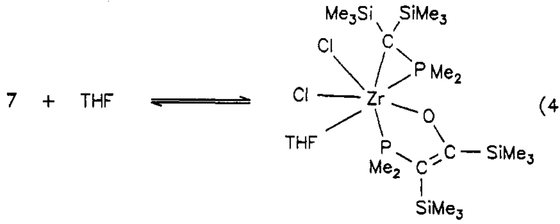


Figure 3. Molecular structure of 7 and crystallographic numbering scheme adopted. The monomeric units can mutually be transferred into each other by the symmetry operation $-x$, $-y$, $-z$. H atoms omitted.

6. The enolate five-membered ring is approximately planar (maximum deviation of the oxygen atom: 0.12 Å). The C(O2)–C(O3) double bond is slightly elongated (1.360(4) Å), and the C(O3)–O bond (1.380(3) Å) as well as the Zr–O bond (1.991(2) Å) are within the expected range. The terminal Zr–Cl(1) bond (2.452(1) Å) is slightly longer than that in 6, obviously due to the higher coordination number. The symmetrically bridging Cl(2) atoms form considerably longer Zr–Cl bonds (2.593(1) Å), as expected, but are only slightly longer than the terminal Zr–Cl bonds in III–V. Obviously, the dimerization is not appreciably hindered by steric congestion. It seems reasonable to assume that the five-membered phosphino enolate ring in 7 causes much less steric strain than the three-membered Zr–C–P ring, since the lower coordinated 6 is monomeric, whereas 7 is dimeric.

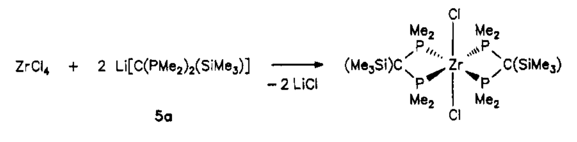
Though relatively short, the Zr–Cl–Zr bridges obviously are cleaved, upon dissolution of 7 in THF: a new AB type $\{^1H\}^{31}P$ NMR spectrum appears which is similar to that of 7, but with slightly modified parameters. It is reasonable to assume that monomeric 7c is formed, which cannot be isolated, however, since on evaporation of the solvent dimeric 7 forms again (eq 4). The exact stereochemistry of 7c could not be established, as yet.



7c (4)

1.3.3. Reaction with CO in THF. The slight changes in the NMR spectra of 6, if recorded in THF, indicate that the interaction is weak, obviously again due to steric congestion. If CO is allowed to react with a solution of 6 in THF, the reaction pathway is changed decisively, however. No 7 or 7a is observed in the $\{^1H\}^{31}P$ NMR spectrum of a C_6D_6 solution of the red solid obtained. Instead, two similar AB type spectra appear. By comparison, the observed data correspond to those of similarly substituted phosphorus ylides.[21] Unfortunately, from ^1H and ^{13}C NMR spectra meaningful data could not be derived due to considerable line broadening. Additional evidence for the nature of one of the two species, namely, 8, came from the fact that the same spectrum was obtained from a minor component observed in the reaction of V with CO.[6] Since in V a Cp_2Zr and in 6 a Cl_2Zr moiety is present, 8 should be a metal-free compound, but a definitive assignment was not possible. Nevertheless, we tentatively derive Scheme 1 for the reaction of 6 with CO in THF. The basic idea in this scheme is that the added THF coordinates more effectively to the zirconium after CO insertion due to release of steric strain and thus prevents a η^2-coordination of the acyl functionality. The free oxygen of the carbonyl group now is available for a 1,3-shift of a silyl group, which is preferred over the 1.2-shift due to Si–O bond formation. A P–C coupling reaction, which is well-known in the chemistry of phosphinomethanides with oxidants (e.g., Cp_2TiCl_2),[10] accompanied by a 1,2 silyl shift, as known from the formation of 7, completes the reaction. Partial loss of "$ZrCl_2$" may be attributed to the inherent instability of undercoordinated zirconium(II) compounds, but the fate of this particle could not be established. At present, it remains open to question whether the content of Zr(II) is responsible for the observed line broadening in the ^1H and ^{13}C spectra. The presence of the $ZrCl_2$ fragment in the mixture of 8 and 9 is evident from the elemental analysis. The formation of stereoisomers of 8 and 9, which seems unlikely in light of the proposed pathway, is not observed. Further evidence for the proposed mechanism is derived from the fact that 7c does not rearrange to 8 or 9.

2. Diphosphinomethanide Derivatives of $ZrCl_4$. 2.1. Preparation. As with the fully substituted phosphinomethanide $[C(PMe_2)(SiMe_3)_2]^-$, described above, $ZrCl_4$ forms only a disubstitution product (red crystals) with $[C(PMe_2)_2(SiMe_3)]$ (eq 5). The trans octahedral

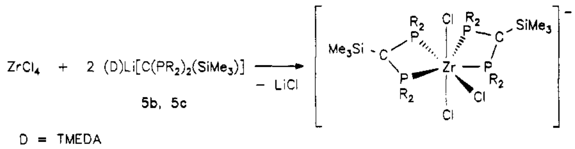


(5)

5a

10

coordination in 10 is confirmed by the single $\{^1H\}^{31}P$ NMR resonance and a single set of resonances in the ^1H and ^{13}C NMR spectra, which are not temperature dependent. This is in contrast to the $\{^1H\}^{31}P$ NMR spectrum of 11 and 12 (red crystals) obtained according to eq 6. Whereas at room



(6)

5b, 5c

D = TMEDA
R = Ph: 5b; 11
R = Me: 5c; 12

$[Li(TMEDA)_2]^+$
11, 12

temperature only a single line is observed for 11 and 12, at −100 °C an AA′BB′ spin system is observed for 11. Due to the low solubility, the signal/noise ratio is small, however, and exact parameters could not be extracted with confidence. In contrast, for 12 at −100 °C an ABCD spin system is obtained, which is in accord with the actually observed small deviations from an ideal C_{2v} symmetry in the solid state, as revealed from the X-ray analysis.

2.2. Molecular Structures of 11 and 12. Important bond distances and angles in the molecular structures of 11 and 12 are given in Table 9. An ionic structure

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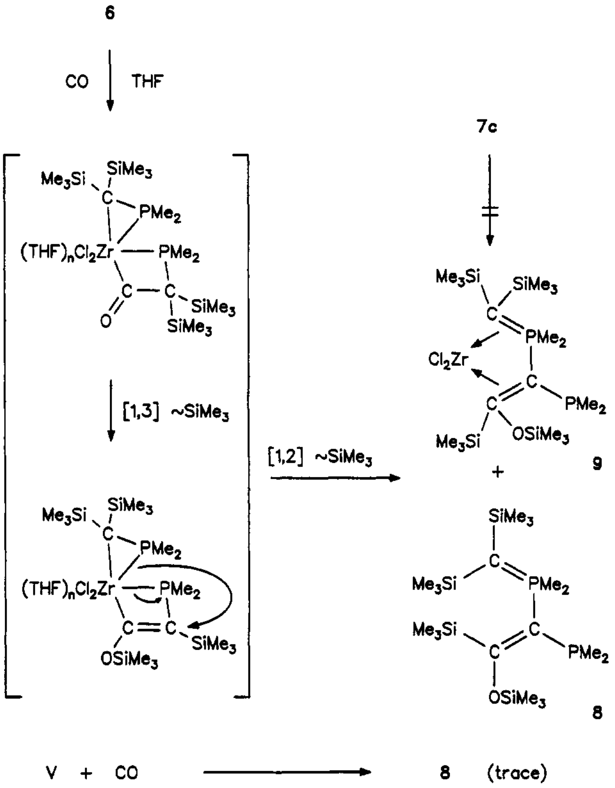
[21] Karsch, H. H. *Chem. Ber.* **1982**, *115*, 1956.

Scheme 1. Proposed Pathway for the Reaction of 6 with CO in THF



consisting of [Li(TMEDA)$_2$]$^+$ cations and well-separated metalate anions makes up the structural identity of 11 and 12. Figures 4 and 5 show views of the anions of 11 and 12. The cations show the expected four-coordinate tetrahedral Li centers, which deserve no further comment here.

In the 14e zirconate anions, the metal centers adopt an approximately pentagonal bipyramidal coordination geometry with four P atoms and one Cl atom (Cl(3)) in the equatorial plane (maximum deviation of P(3) from the best plane through the four atoms P(1), P(2), P(4), and Cl(3): 11, −0.54 Å; 12, 0.36 Å). The remaining Cl atoms, Cl(1) and Cl(2), occupy the apical positions. The Cl(1)–Zr–Cl(2) fragments are not strictly linear, however, and this may explain the inequivalence of the P atoms as observed in the ^{31}P NMR spectra of 12. The Zr–Cl distances for the apical Cl atoms Cl(1)/Cl(2) are shorter than the Zr–Cl distance of the equatorial Cl(3) atom, but these values do not differ too much from those of comparable complexes (e.g., III–V, 6, 7). The Zr–P bonds are much longer (2.72–2.88 Å) than those in monophosphinomethanide complexes with three-membered Zr–C–P rings, but correspond to those of zirconocene complexes with diphosphinomethanide ligands[7] and of comparable complexes.[22] The four membered rings Zr–P–C–P as well as the atoms C(1)/C(2) are essentially planar in 11 and 12. Not quite unexpected, the Zr–P bonds are considerably shorter in 12 than in 11, documenting again the superior donor capabilities of the methyl-substituted phosphino groups. As a consequence, the Zr–Cl bonds are shorter in 11 than in 12. Interestingly, in both complexes the P atoms "trans" to Cl(3) (P(2)/P(4)) form drastically longer bonds to zirconium than the P atoms situated more in a "cis" position. On purely steric grounds one would rather expect the contrary. This phenomenon has also been found in phosphinomethanide complexes of zirconocene[7] with comparable substructures.

The endocyclic P–C distances are considerably shorter than the exocyclic ones. This is in line with common observations in diphosphinomethanide complexes (cf., e.g., ref 7).

Table 9. Important Interatomic Distances (Å) and Angles (deg) in the Molecular Structures of 11 and 12 with Esd's in Units of the Last Significant Figure in Parentheses[a]

	11	12
Zr–P(1)	2.781(3)	2.719(1)
Zr–P(2)	2.877(3)	2.771(1)
Zr–P(3)	2.790(3)	2.729(1)
Zr–P(4)	2.886(3)	2.779(1)
Zr–Cl(1)	2.420(3)	2.434(1)
Zr–Cl(2)	2.401(3)	2.447(1)
Zr–Cl(3)	2.473(3)	2.519(1)
P(1)–C(1)	1.735(9)	1.733(4)
P(2)–C(1)	1.765(9)	1.742(5)
P(3)–C(2)	1.73(1)	1.740(4)
P(4)–C(2)	1.748(9)	1.745(5)
P(1)–Zr–P(2)	57.5(1)	59.0(1)
P(3)–Zr–P(4)	57.5(1)	58.8(1)
P(1)–Zr–P(3)	154.2(1)	158.4(1)
P(2)–Zr–P(4)	90.5(1)	83.4(1)
P(2)–Zr–P(3)	146.8(1)	141.7(1)
P(1)–Zr–P(4)	147.9(1)	142.4(1)
P(1)–Zr–Cl(1)	93.1(1)	89.6(1)
P(2)–Zr–Cl(1)	85.9(1)	85.2(1)
P(3)–Zr–Cl(1)	96.9(1)	87.4(1)
P(4)–Zr–Cl(1)	81.3(1)	88.6(1)
P(1)–Zr–Cl(2)	90.1(1)	91.6(1)
P(2)–Zr–Cl(2)	84.9(1)	87.2(1)
P(3)–Zr–Cl(2)	85.7(1)	95.0(1)
P(4)–Zr–Cl(2)	89.0(1)	84.7(1)
P(1)–Zr–Cl(3)	77.9(1)	79.5(1)
P(2)–Zr–Cl(3)	135.2(1)	138.5(1)
P(3)–Zr–Cl(3)	77.8(1)	79.7(1)
P(4)–Zr–Cl(3)	133.7(1)	137.9(1)
Cl(1)–Zr–Cl(2)	166.6(1)	170.4(1)
Cl(1)–Zr–Cl(3)	93.5(1)	97.2(1)
Cl(2)–Zr–Cl(3)	100.0(1)	92.4(1)
Zr–P(1)–C(1)	100.7(3)	100.3(2)
Zr–P(2)–C(1)	96.4(3)	98.2(1)
Zr–P(3)–C(2)	101.5(3)	100.6(2)
Zr–P(4)–C(2)	97.6(3)	98.6(1)
P(1)–C(1)–P(2)	102.0(5)	102.2(2)
P(3)–C(2)–P(4)	103.4(5)	101.9(2)

[a] See Figures 4 and 5 for atom numbering.

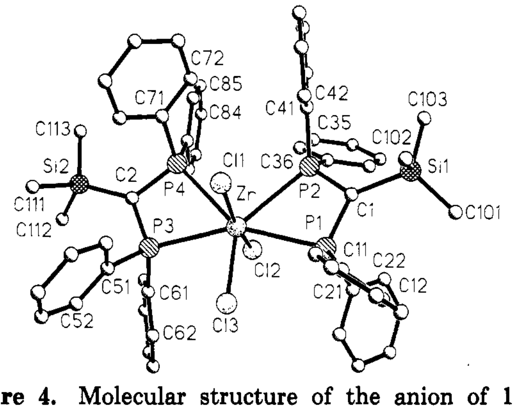


Figure 4. Molecular structure of the anion of 11 and crystallographic numbering scheme adopted. H atoms omitted.

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(22) (a) See, for example: Fryzuk, M. D.; Williams, H. D.; Rettig, S. J. *Inorg. Chem.* 1983, *22*, 863. (b) Planalp, R. P.; Andersen, R. A. *Organometallics* 1983, *2*, 1675 and references cited therein.

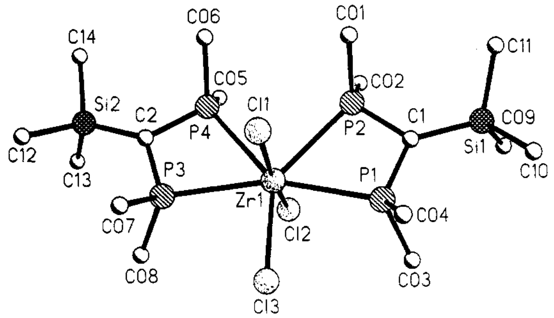

Figure 5. Molecular structure of the anion of 12 and crystallographic numbering scheme adopted. H atoms omitted.

Conclusion

Like Cp_2Zr moieties, also $ZrCl_2$ moieties are suitable for forming stable complexes with fully substituted phosphinomethanide ligands. In contrast to the former, they allow coordination of two of these ligands, the resulting complexes still being coordinatively unsaturated. With sterically less demanding phosphinomethanide ligands, i.e., $[CH(SiMe_3)(PMe_2)]^-$, up to four ligands can be arranged around the metal center. All these complexes promise a rich and unusual chemistry, as exemplified by the CO insertion reaction of **6**. Furthermore, we expect **6** to be a prototype of compounds which may mimic to some extent the chemistry of Cp_2ZrCl_2, but with much more active reactivity sites.

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Supplementary Material Available: Complete tables of atomic coordinates, displacement parameters, and bond distances and angles (67 pages). Ordering information is given on any current masthead page.

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