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Zirconocene Derivatives with Phosphinomethanide Ligands: Metal-Promoted Ligand Metalations: Tuning of Regioselectivity and Formation of Novel Zirconaphosphaheterocycles†

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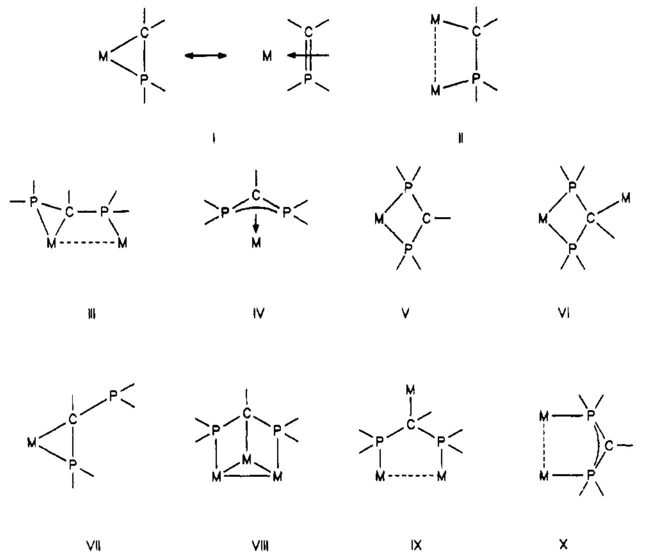
From Cp_2ZrCl_2 and 2 equiv of the appropriate lithium phosphinomethanides $(D)Li[HC(PMe_2)X]$ (D = –, X = PMe_2, **6**; D = TMEDA, X = $SiMe_3$, **7**), the 1,3-zirconaphosphacyclobutane derivatives $Cp_2Zr[CH_2P(Me)CHX]$ (**10** and **11**), containing the first examples of doubly metalated alkylphosphines as chelating ligands, are formed via the known zirconaphosphacyclopropane derivatives $Cp_2(Cl)Zr[C(H)(PMe_2)X]$ (**2** and **3**). An intramolecular pathway is deduced from a cross-coupling experiment with $Cp_2(Cl)Zr[C(H)(PMe_2)(SiMe_3)]$, **3** and **6**. In contrast, **3** (X = $SiMe_3$) reacts with $LiCH_2PMe_2$ (**5**) to give the substitution product $Cp_2Zr[C(H)(PMe_2)(SiMe_3)][CH_2PMe_2]$ (**13**). In the case of **2** (X = PMe_2), again metalation occurs with LiR (R = CH_3, CH_2PMe_2, ${}^tBu$), thereby generating $\{Cp_2Zr[C(PMe_2)_2]\}_2$ (**14**). An X-ray diffraction study of the yellow crystals of **14**·toluene (monoclinic, space group $P2_1/c$, $a = 22.558(1)$ Å, $b = 8.891(1)$ Å, $c = 20.283(1)$ Å, $\beta = 112.33(1)°$, $V = 3763.0$ Å^3, $Z = 4$, $T = 23$ °C, $R_w = 0.042$, $w = 4F_o^2/\sigma^2(F_o^2)$) shows the diphosphinocarbene ligands to function as η^2(C,P)-μ-(C,P′) six-electron ligands to 18e zirconium centers. Only traces of metalation product are observed, however, in the sterically most crowded system $Cp_2(Cl)Zr[C(PMe_2)(SiMe_3)_2]$ (**4**)/$(TMEDA)\{Li[C(PMe_2)(SiMe_3)_2\}_2$ (**8**). Instead, an oxidative phosphinomethanide coupling (P–C) leads to the phosphorus ylide $(Me_2P)(Me_3Si)_2CPMe_2{=}C(SiMe_3)_2$ (**15**), probably via an external reaction in the ligand sphere. However, a metalation product, $Cp_2ZrCH_2SiMe_2C(SiMe_3)PMe_2$ (**17**), can be obtained via a more indirect route from $Cl_2Zr[C(PMe_2)(SiMe_3)_2]_2$ (**9**) and KCp. Insertion of ${}^tBuNC$ into the Zr–C bonds of **11** gives the six-membered heterocycle $Cp_2ZrC({=}N^tBu)CH_2P(Me)C[{=}CH(SiMe_3)]N({}^tBu)$ (**19**). All compounds were characterized by means of NMR spectroscopy.

Introduction

Transition-metal-promoted metalation, i.e. proton abstraction from metal-bonded ligands, is quite common with coordinated phosphines. Frequently it occurs spontaneously at a low-valent metal center[1] or it is induced by the action of a strong base,[2] which is particularly useful in the case of coordinated diphosphinomethanides. Coordinated monophosphinomethanides belong to types I and II, whereas diphosphinomethanide ligands form complexes of types III–X.[3-5]

Chart I



By various routes, but usually not from phosphinomethanide complexes, also doubly metalated species XI–XV could be generated, which alternatively can be

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† Part of the thesis of G. Grauvogl, Technical University of Munich, 1990.

(1) For this now quite trivial class of reactions, we select the following articles as pioneering: The first intramolecular reversible C,H activation of aliphatic carbonhydrogen bonds was reported independently by two groups: (a) Karsch, H. H.; Klein, H.-F.; Schmidbaur, H. *Angew. Chem.* **1975**, *87*, 630; *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 637. Karsch, H. H.; Klein, H.-F.; Schmidbaur, H. *Chem. Ber.* **1977**, *110*, 2200. (b) Rathke, J. W.; Muetterties, E. L. *J. Am. Chem. Soc.* **1975**, *97*, 3272. Harris, T. V.; Rathke, J. W.; Muetterties, E. L. *J. Am. Chem. Soc.* **1978**, *100*, 6966.

(2) Deprotonation of coordinated alkylphosphines by strong bases: Karsch, H. H.; Klein, H.-F.; Kreiter, C. G.; Schmidbaur, H. *Chem. Ber.* **1974**, *107*, 3692. Al-Jibori, S.; Crocker, C.; McDonald, W. S.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1981**, 1572. Mainz, V. V.; Andersen, R. A. *Organometallics* **1984**, *3*, 675.

(3) For a review see: Abicht, H. P. *Z. Chem.* **1985**, *25*, 318.

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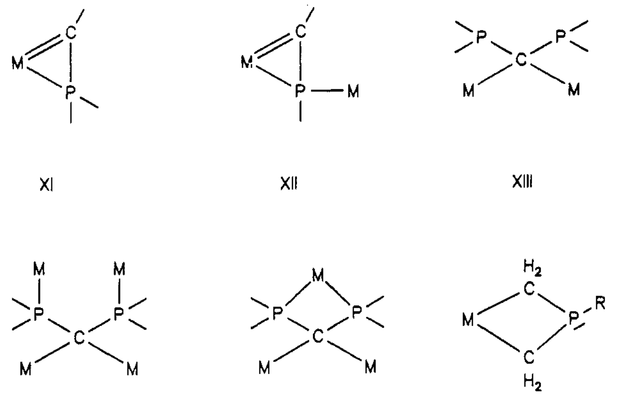
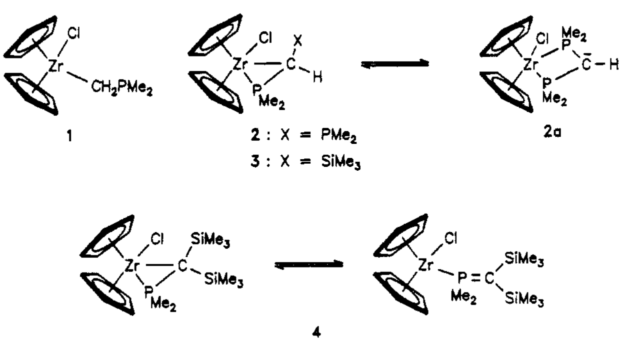
Chart II



described as phosphinocarbene complexes.[5,6] There is no example, however, of a controlled metalation reaction leading specifically to different products by, for example, changing the added base, nor is there an example of a double metalation, where two different alkyl substituents of the coordinated phosphine are metalated. This in turn would lead to complexes of type XVI.

A different approach to complexes with metalated phosphine ligands, i.e. phosphinomethanide complexes, was found in the reaction of transition-metal halides with lithium phosphinomethanides.[3,7] By controlled variation of the carbanion substituents, zirconocene complexes 1–4 could be obtained, which display quite different binding modes, namely η^1(C), η^2(C,P), η^2(P,P), and η^1(P) coordination.[8] Obviously, the zirconocene derivatives are quite sensitive to small changes in the substitution pattern of the phosphinomethanide ligands used. In principle, the residual Zr–Cl functionality in 1–4 also should be exchangeable by phosphinomethanide ligands and it seems reasonable to assume that double phosphinomethanide substitution should even be more sensitive to substituent effects. In case double metalation would occur in these reactions, tuning by the appropriate choice of substituents should be feasible. This paper describes the reaction of Cp_2ZrCl_2 with 2 equiv of appropriately substituted lithium phosphinomethanides and some properties of the products.



Experimental Section

A. Preparation of Compounds. All compounds were prepared and handled under a dry nitrogen atmosphere by using conventional vacuum-line techniques. Details for handling of compounds and solvents, equipment, spectroscopic methods, and analytical work were as previously described.[8] However, satisfactory elemental analyses could not be obtained in all cases. Further attempts for purification failed, since column chromatography caused decomposition and/or recrystallization from several solvents did not result in appreciable separation (some of the compounds are oils). NMR data are collected in Tables I–III or, in individual cases, together with the description of preparation of the respective compounds. Chemical shifts are in δ and coupling constants J in Hz (in unambiguous cases, J is not specified). Multiplets in quotation marks, e.g. "dd", denote deceptively simple signals originating from complex spin systems, where N gives the distance between the two outermost lines. Lithium phosphinomethanides, i.e. $LiCH_2PMe_2$ (5),[9] Li[HC(PMe$_2$)$_2$] (6),[9] (TMEDA)Li[HC(PMe$_2$)(SiMe$_3$)] (7),[10] (TMEDA)Li[C(PMe$_2$)(SiMe$_3$)$_2$] (8),[10] Cp$_2$(Cl)Zr[η^2(*C,P*)-CH(PMe$_2$)$_2$] (2),[8] Cp$_2$(Cl)Zr[η^2(*C,P*)-CH(SiMe$_3$)(PMe$_2$)] (3),[8] Cp$_2$(Cl)Zr[η^2(*C,P*)-C(PMe$_2$)(SiMe$_3$)$_2$] (4),[8] and Cl$_2$Zr[η^2(*C,P*)-C(PMe$_2$)(SiMe$_3$)$_2$]$_2$ (9),[11] were prepared according to the literature; Cp_2ZrCl_2 and ^{t}BuNC were from commercial sources.

$\overline{\text{Cp}_2\text{Zr[CH}_2\text{PMe}_2\text{C}}$HX] (10, X = PMe$_2$; 11, X = SiMe$_3$). A 1.9-g (13.4-mmol) amount of Li[HC(PMe$_2$)$_2$] (6) or 5.25-g (9.7-mmol) amount of (TMEDA)Li[HC(PMe$_2$)(SiMe$_3$)] (7) was dissolved in 50 mL of diethyl ether. At −78 °C, 1.95 g (6.7 mmol) or 2.83 g (9.7 mmol) of Cp_2ZrCl_2 was added. With stirring, the mixture was warmed to room temperature and allowed to react 18 h at this temperature, during which time the color changes to brown or dark red, respectively. The solvent was evaporated and the residue dried in vacuo (30 °C/10^{-2} Torr/5 h); the volatiles were collected in a cooled trap (^{31}P NMR (C_6D_6, 20 °C): H$_2$C(PMe$_2$)$_2$ in the case of 6, H$_2$C(SiMe$_3$)(PMe$_2$) in the case of 7). Subsequently, the solid obtained was extracted twice with 40 mL of toluene (for 10) or 40 mL of pentane (for 11). The solvent was again evaporated, and 10 was obtained as a brown solid (2.16 g, 91%) and 11 as a highly viscous, dark red oil (3.60 g, 100%). 10: mp 93 °C. Anal. Calcd for $C_{15}H_{22}P_2Zr$ (355.51): C, 50.68; H, 6.24; Cl, 0. Found: C, 51.07; H, 6.22; Cl, 0. 11: Anal. Calcd

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for $C_{16}H_{25}PSiZr$ (367.66): C, 52.27; H, 6.85; Cl, 0. Found: C, 52.83; H, 7.15; Cl, 0.

Mixture of $Cp_2(Cl)ZrCH_2PMe_2$ (1) and $Cp_2Zr(-CH_2PMeCH_2)$ (12). A 0.78-g (9.51-mmol) amount of $LiCH_2PMe_2$ (5) and 1.41 mL (9.51 mmol) of $Me_2NCH_2CH_2NMe_2$ (TMEDA) were dissolved in 40 mL of toluene. At −78 °C, 6.38 mL (9.51 mmol) of a Li^{t}Bu/pentane solution was added over 10 min with stirring. The mixture was warmed to room temperature (orange-red color). After 2.5 h at this temperature, the solution was cooled to −78 °C and 2.78 g (9.51 mmol) of Cp_2ZrCl_2 was added. After the mixture was stirred for 18 h at room temperature, the volatiles were removed by evaporation. The solid residue was extracted twice with 45 mL of pentane and the solvent again removed in vacuo: 2.31 g of a brown solid was obtained, which was characterized spectroscopically as a mixture of 1 (96%) and 12 (4%).

Reaction of 11 with S, Se, Me_3PSe, LiMe/Et_2O, and MeI. A 0.9-g amount of 11 was dissolved in 35 mL of toluene, and a stoichiometric amount of the substrates was added at −78 °C with stirring. After the mixture was warmed to room temperature and stirred for 18 h, the solutions were filtered and all volatiles removed in vacuo. The solid residue was investigated by means of ^{31}P NMR (C_6D_6).

Attempted Insertion of CO into 10 or 11. A 1–3-mmol amount of 10 or 11 was dissolved in toluene under N_2 pressure. The N_2 was replaced by 1 atm of CO and the solution stirred for 18 h at 20 or 90 °C (in one case with **10**, a stoichiometric amount of $AlCl_3$ was added). The solvent was evaporated and the residue analyzed by means of ^{31}P NMR spectroscopy (C_6D_6). Only in the case of $AlCl_3$ addition was a signal other than that for **10** or **11** observed: **10a**,**b**, 70%; δ(P) −16.00 (s), 30%.

$Cp_2Zr[\eta^1(C)\text{-}CH_2PMe_2][(\eta^2(C,P)\text{-}HC(PMe_2)(SiMe_3)]$ (13). A 0.69-g (1.70-mmol) amount of **3** and 0.14-g (1.70-mmol) amount of **5** were dissolved in 40 mL of diethyl ether at −78 °C. The mixture was stirred at room temperature for 18 h, and subsequently, the solvent was removed in vacuo. The residue was extracted twice with 40 mL of cold toluene, and again, the solvent was evaporated: a brown solid (0.66 g, 88%) was obtained, which decomposed slowly at room temperature. It was characterized by NMR (C_6D_6, 20 °C): **11** was identified as a trace (1%) by ^{31}P NMR; the residual signals are attributable to **13**. ^{1}H NMR: $\delta(C_5H_5)$ 5.33 (br, 10H), $\delta(CH_2)$ 1.56 (dd, $^2J_{HCH}$ = 6.41, $^2J_{HCP}$ = 4.27, 1H)/1.55 (dd, $^2J_{HCH}$ = 6.41, $^2J_{HCP}$ = 13.12, 1H), $\delta(CH_2PCH_3)$ 1.33 (d, 2.74, 6H), $\delta(ZrPCH_3)$ 0.89 (d, 2.75, 3H)/0.86 (d, 4.84, 3H), δ(CH) 0.72 (d, 6.72, 1H), $\delta(SiCH_3)$ 0.18 (s, 9H). $^{13}C\{^1H\}$ NMR: $\delta(C_5H_5)$ 111.30 (s)/111.28 (s), $\delta(CH_2PCH_3)$ 21.57 (br), $\delta(ZrPCH_3)$ 20.88 (d, 16.54)/18.10 (d, 14.70), $\delta(SiCH_3)$ 5.07 (s), δ(CH) −5.35 (d, 45.96). $^{31}P\{^1H\}$ NMR: δ(ZrP) −31.69 (br), $\delta(ZrCH_2P)$ −41.69 (d, 6.4).

$\{Cp_2Zr[\mu(C,P')\text{-}\eta^2(C,P)\text{-}C(PMe_2)_2]\}_2$ (14). (a) To 1.31 g (3.34 mmol) of **2** in 30 mL of diethyl ether was added 0.27 g (3.24 mmol) of **5** at −78 °C. The mixture was stirred 18 h at room temperature. Subsequently, the solvent with all volatiles was condensed into a trap cooled with liquid nitrogen and analyzed by ^{31}P NMR spectroscopy (C_6D_6): only PMe_3 (δ(P) −61.3) was detected. The residue was extracted twice with 40-mL portions of toluene. The combined extracts were evaporated, and a brown solid remained (0.50 g, 42%).

The solid was analyzed by NMR spectroscopy (C_6D_6, 20 °C): **10** was identified as a trace (ca. 1%) by ^{31}P NMR; the residual signals are attributable to **14**. ^{1}H NMR: $\delta(C_5H_5)$ 5.52 (s, 20H), $\delta(PCH_3)$ 1.29 ("dd", N = 10.07, 12H)/1.40 (br, 12H). $^{13}C\{^1H\}$ NMR: $\delta(C_5H_5)$ 105.62 (br), $\delta(PCH_3)$ 20.49 (d, 15.63)/18.00 (br). $^{31}P\{^1H\}$ AA′XX′ spin system, $\delta(P_A)$ 0.97, $\delta(P_X)$ −100.22, $J_{AA'}$ = 70.9, $J_{XX'}$ = 4.3, J_{AX} = ±66.9, $J_{AX'}$ = ±23.4.

(b) To 0.85 g (2.17 mmol) of **2** in 30 mL of toluene was added 1.39 mL (2.17 mmol) of a Li^{t}Bu/pentane solution at −78 °C. With stirring the mixture was warmed to room temperature and the stirring was continued for another 17 h. After filtration, the residue was extracted three times with each 30 mL of toluene. The combined extracts were evaporated and a brown solid remained (0.67 g, 87%). The product was redissolved to give a concentrated toluene solution, and **14** was obtained as yellow needles in the course of several months at +5 °C. Anal. Calcd for $C_{30}H_{44}P_4Zr_2$ (711.02): C, 50.68; H, 6.24; Cl, 0. Found: C, 50.29; H, 6.42; Cl, 0.

(c) In a similar reaction of **2** with a $LiCH_3/Et_2O$ solution, **14** could only be detected spectroscopically as a minor portion of a complex, unidentified mixture of products.

Reaction of 3 with Li^{t}Bu. A 0.92-g (2.28-mmol) amount of **3** was dissolved in 40 mL of toluene and cooled to −78 °C, when 1.46 mL of a 1.56 N solution of Li^{t}Bu in pentane (2.28 mmol) was added. The mixture was stirred at room temperature for 18 h and filtered. The filtrate was evaporated; a yellow solid (0.84 g) was obtained. The $^{31}P\{^1H\}$ NMR spectrum showed the signals of **11** (ca. 5%) besides numerous other signals, which could not be assigned.

$(Me_2P)(Me_3Si)_2CPMe_2{=}C(SiMe_3)_2$ (15). A 1.30-g (2.73-mmol) amount of **4** and 0.78-g (1.36-mmol) amount of **8** were combined and dissolved in 40 mL of diethyl ether at −78 °C. After the solution was stirred for 18 h at 0 °C, the solvent was evaporated. The residue was extracted three times with 50 mL of pentane, and the combined extracts were evaporated. The brown oil obtained (1.34 g, 74%) was characterized by $^{31}P\{^1H\}$ NMR (C_6D_6, 20 °C): signals at δ(P) −154.72 (ca. 3%, **16**), −20.46 (ca. 1%, **17**); an AB spin system (ca. 80%), $\delta(P_A)$ 6.42 (d, 21.5) and $\delta(P_B)$ −48.18 (d, 21.5), for **15** was found and assigned. Additional signals are mainly due to the thermolysis of **4**[8] during the reaction time. The manifold of species present rendered the recording of ^{1}H and ^{13}C NMR spectra obsolete.

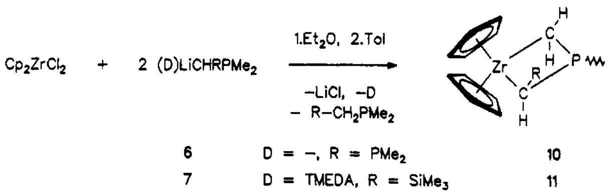
$Cp_2Zr(-CH_2SiMe_2C(SiMe_3)PMe_2)$ (17). To 690 mg (1.15 mmol) of **9**[11] in 30 mL of diethyl ether was added 0.24 g (2.30 mmol) of KC_5H_5 at −78 °C. This mixture was stirred at room temperature for 18 h, and a color change from red to green was observed. The volatiles were removed in vacuo, and the residue was extracted twice with 40 mL of pentane. The extract was evaporated, and a green, viscous oil was obtained (0.51 g, 100%), which was analyzed by $^{31}P\{^1H\}$ NMR (C_6D_6, 20 °C): **17** and traces of **15** (ca. 1%). Anal. Calcd for $C_{19}H_{33}PSi_2Zr$ (439.84): C, 51.89; H, 7.56; Cl, 0. Found: C, 50.26; H, 7.92; Cl, 0. NMR (C_6D_6, 20 °C): ^{1}H NMR, $\delta(C_5H_5)$ 5.81 (d, 1.22, 10H), $\delta(CH_2)$, 1.81 (s, 2H), $\delta(PCH_3)$ 1.17 (d, 7.93, 6H), $\delta(SiCH_3)$ 0.57 (s, 6H)/0.47 (s, 9H); $^{13}C\{^1H\}$ NMR/^{13}C NMR (only additional splittings and J_{HC} coupling constants are listed): $\delta(C_5H_5)$ 111.89 (s)/(d quin, $^1J_{CH}$ = 172.81, "J_{quin}" = 6.44), $\delta(CH_2)$ 71.34 (s)/(t, $^1J_{CH}$ = 114.90), $\delta(PCH_3)$ 24.59 (d, 17.46)/(q, $^1J_{CH}$ = 126.85), $\delta(ZrCH_2SiCH_3)$ 11.04 (d, 5.51)/(q, $^1J_{CH}$ = 114.91), $\delta(SiCH_3)$ 6.95 (d, 1.84)/(q, $^1J_{CH}$ = 116.74); $^{31}P\{^1H\}$ NMR δ(P) −20.46 (s).

Insertion of ^{t}BuNC into 11: Preparation of $Cp_2ZrC(=N\text{-}{}^tBu)CH_2P(Me)C(=CHSiMe_3)N({}^tBu)$ (19). The reaction was carried out as an NMR-tube experiment: 50 mg of **11** in an NMR tube (10 mm of diameter) was dissolved in 3 mL of C_6D_6 and the mixture cooled to 0 °C. Three drops of ^{t}BuNC was added (which according to the resulting spectrum was a slight excess) and the solution warmed to +20 °C, where the spectra (^{1}H, ^{1}H,^{1}H COSY, $^{31}P\{^1H\}$, ^{31}P, $^{13}C\{^1H\}$, ^{13}C) were recorded. ^{1}H NMR: $\delta(C_5H_5)$ 5.80 (s, 5H)/5.75 (s, 5H), δ(=CH) 5.05 (s, 1H), $\delta(CH_2)$ 1.49 (d, 3.57, 1H)/1.33 (br, 1H), $\delta(PCH_3)$ 1.27 (br, 3H), $\delta(CCH_3)$ 0.95 (s, 9H)/0.94 (s, 9H), $\delta(SiCH_3)$ 0.84 (s, 9H). $^{13}C\{^1H\}$ NMR/^{13}C NMR (only additional splittings and J_{HC} coupling constants are listed): δ(P—C=) 175.30 (d, 68.02)/(d, 4.96), $\delta(C_5H_5)$ 105.49 (s)/(d quin, 171.66, "J_{quin}" = 6.11), $\delta(C_5H_5)$ 104.40 (s)/(d quin, 171.66, "J_{quin}" = 6.11), δ(=CH) 81.89 (d, 17.46)/(d, 149.54), $\delta(C\text{–}CH_3)$ 57.88 (s)/(–), $\delta(C\text{–}CH_3)$ 56.14 (s)/(–), $\delta(C\text{–}CH_3)$ 30.44 (s)/(q, 128.17), $\delta(C\text{–}CH_3)$ 30.30 (s)/(q, 128.94), $\delta(SiCH_3)$ 29.87 (s)/(q, 132.75), $\delta(P\text{–}CH_3)$ 29.13 (d, 22.10)/(q, 128.64), $\delta(CH_2)$ 23.48(d, 38.60)/(t, 127.27). $^{31}P\{^1H\}$/^{31}P NMR: δ(P) −47.49 (s)/−47.49 (s).

B. X-ray Structure Determination of 14. A suitable crystal of **14** was sealed at dry-ice temperature under argon in a glass capillary and mounted on a TURBO-CAD4 diffractometer. After a check for higher symmetry 9784 data were collected within a range of 2° ≤ θ ≤ 28°. **14** was found to crystallize in the monoclinic space group $P2_1/c$ (No. 14). Cell constants are as follows: a = 22.558(1) Å, b = 8.891(1) Å, c = 20.283(1) Å, β = 112.33(1)°, V = 3763.0 Å^3, Z = 4, ρ = 1.418 g cm^{-3}, μ(Mo Kα) = 7.4 cm^{-1}. No significant decay was detected during measurement. Out of 9002 unique reflection, 7527 with $F_o \geq 4\sigma$ (F_o) were treated as "observed" and used for structure solution and refinement. The structure was solved by direct methods (SHELXS 86) and completed by Fourier and difference Fourier maps. After anisotropic refinement (SHELX 76) of all heavy atoms (but not the solvent molecule) 28 H atom positions were found, while the rest were calculated in idealized positions. All H atoms were fixed and considered in refinement with an isotropic thermal parameter of $U_{iso(fix)}$ = 0.05 Å^2. The structure converged well for 353 parameters to an R (R_w) value of 0.040 (0.041) (w = 1.5316/$\sigma^2(F_o)$) and a residual electron density of +1.07/−0.55 e Å^{-3}.

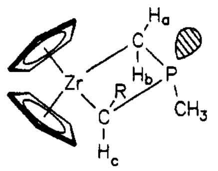
Results and Discussion

1,3-Zirconaphosphacyclobutanes: Synthesis. Two equivalents of the lithium phosphinomethanide Li[HC(PMe$_2$)$_2$] (**6**)[9] or (TMEDA)Li[HC(PMe$_2$)(SiMe$_3$)] (**7**)[10] reacts with Cp$_2$ZrCl$_2$ to give the heterocyclobutanes **10** and **11** in nearly quantitative yield, which were isolated as a brown solid (**10**) or a red oil (**11**). Both complexes are highly air sensitive (eq 1).

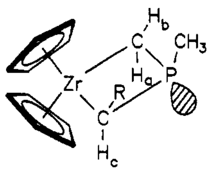


(1)

Pairs of diastereomers are to be expected for **10** and **11**, i.e. **10a,b** and **11a,b**. Indeed, the NMR spectra of **10** and **11** each indicate the presence of two isomers, for both complexes in the ratio **a**:**b** = 3:1.[12] The spectra of **10a,b** and **11a,b** are essentially temperature independent. This rules out a dynamic process, which might be anticipated as a result of a rapid interconversion of bent four-membered rings. A rigid bent structure for the heterocycles is ruled out by the number of isomers and by the fact that only one isomer is detected by NMR for **12** and **16**. This is also in accord with the planar geometry of the heterocycles in structures such as XVII and XIX.



10a, 11a



10b, 11b

Particularly diagnostic are the ^{31}P{^{1}H} NMR spectra, which show signals at surprisingly high field for the phosphorus nuclei incorporated into the four-membered heterocycles (Table I). In the case of **10**, the exocyclic P nuclei (P$_B$) are found in the normal shift range, and in both diastereomers **10a,b**, coupling is observed between the two different P atoms. Quite remarkably the J_{PP} values are very different, however. This parallels the different orientations of the exocyclic "substituent" lone pair/PMe$_2$ in **10a,b**. Likewise the coupling constants J_{PH} and J_{PH}/J_{PH} are quite different in **10a,b** and **11a,b** (Table II, Figure 1). A Karplus type correlation[13] can be used to assign H$_a$ and H$_b$: an approximately parallel orientation of lone pair/H results in a large coupling constant and an antiparallel orientation in a small value. On the basis of this argument, H$_a$, H$_b$, and H$_c$ can be assigned, and likewise, the isomers **a** and **b** of compounds **10** and **11** may be identified: the prevailing isomer **a** in both cases is the sterically less hindered isomer with the groups R and CH$_3$ in anti positions at the ring.

Table I. ^{31}P NMR Data for Complexes 10a and 11a,b

		^{31}P{^{1}H}, δ (J, Hz)	^{31}P (J and τ, Hz)
10a[a]		−173.50 (s)	(d, $^2J_{HCP}$ = 30.1)
10b[a]		−182.41 (s)	(m,[c] $\tau_{1/2}$ = 70)
11a[b]	P$_A$	−166.86 (d, $^2J_{PCP}$ = 195.6)	(dd, $^2J_{PCH(a)}$ = 30.1, $^2J_{PCH(b)}$ = 7.0)
	P$_B$	−22.78 (d, $^2J_{PCP}$ = 195.6)	
11b[b]	P$_A$	−178.65 (d, $^2J_{PCP}$ = 18.3)	(m,[c] $\tau_{1/2}$ = 84)
	P$_B$	−28.53 (d, $^2J_{PCP}$ = 18.3)	

[a] C$_6$D$_6$, 20 °C. [b] C$_6$D$_5$CD$_3$, 20 °C. [c] Not fully resolved.

Table II. ^{1}H NMR Data for Complexes 10a,b and 11b (C$_6$D$_6$, 20 °C)

		^{1}H, δ (J, Hz)
10a	C$_5H_5$	5.51 (s), 5.53 (s)
	H_a	2.91 (dd, $^2J_{HCP}$ = 30.82, $^2J_{HCH}$ = 10.86)
	H_b	2.34 (dd, $^2J_{HCP}$ = 6.71, $^2J_{HCH}$ = 10.86)
	H_c	1.96 (d, $^2J_{HCP}$ = 4.75)
	PCH_3	0.80 (d, $^2J_{HCP}$ = 7.02)
	SiCH_3	0.33 (s)
10b	C$_5H_5$	5.56 (s), 5.29 (s)
	$H_{a/b}$	2.79 (d, $^2J_{HCH}$ = 11.59)
	$H_{b/a}$	2.57 (dd, $^2J_{HCH}$ = 11.59, $^2J_{HCP}$ = 6.41)
	H_c	1.83 (s)
	PCH_3	0.90 (d, $^2J_{HCP}$ = 3.06)
	SiCH_3	0.34 (s)
11a	C$_5H_5$	5.49 (s), 5.65 (s)
	H_a	3.09 (dddd, $^2J_{HCP(A)}$ = 30.21, $^2J_{HCH}$ = 10.37, $^4J_{HCPCP}$ = 1.53, $^4J_{HCPCH}$ = 0.61)
	H_b	2.30 (ddd, $^2J_{HCH}$ = 10.37, $^2J_{HCP(A)}$ = 7.02, $^4J_{HCPCH}$ = 0.61)
	H_c	2.54 (ddt, $^2J_{HCP(A)}$ = 7.78, $^2J_{HCP(B)}$ = 4.88, $^4J_{HCPCH_2}$ = 0.61)
	P$_B$CH_3	1.10 (d, $^2J_{HCP(B)}$ = 3.96)
		1.39 (d, $^2J_{HCP(B)}$ = 3.36)
	P$_A$CH_3	0.76 (d, $^2J_{HCP(A)}$ = 7.02)
11b	C$_5H_5$	5.69 (d, $^4J_{HCZrCP}$ = 0.61), 5.28 (s)
	H_a	2.97 (dd, $^2J_{HCP(A)}$ = 33.72, $^2J_{HCH}$ = 11.44)
	H_b	2.64 (dd, $^2J_{HCP(A)}$ = 6.56, $^2J_{HCH}$ = 11.44)
	H_c	2.66 (dd, $^2J_{HCP(A)}$ = 30.82, $^2J_{HCP(B)}$ = 5.49)
	P$_B$CH_3	1.41 (d, $^2J_{HCP(B)}$ = 3.97)
		1.21 (d, $^2J_{HCP(B)}$ = 4.27)
	P$_A$CH_3	0.98 (dd, $^2J_{HCP(A)}$ = 7.78, $^4J_{HCPCP}$ = 2.60)

The ^{1}H–^{1}H coupling constants are ascertained by a ^{1}H,^{1}H-COSY experiment. In line with expectation, two different Cp rings are identified from both the ^{1}H and ^{13}C{^{1}H} NMR spectra (Table III) in all isomers **10a,b** and **11a,b**, and ^{13}C NMR spectra (Table III) confirm the assignment of the CH$_2$ and CH signals.

The drastic high-field shift of the endocyclic P nuclei deserves comment. It is completely in agreement with the findings in complexes XVII[14] (XVIIa, δ(P$_A$) −174.17; XVIIb, δ(P$_A$) −189.78), which exhibit comparable four-membered heterocycles. For XVIII,[15] no ^{29}Si NMR data

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[12] All attempts to grow crystals of **10** or **11** were unsuccessful, obviously due to the mixture of isomers.

[13] Albrand, J. P.; Gagnaire, D.; Robert, J. B. *J. Chem. Soc., Chem. Commun.* **1986**, 1469.

[14] (a) Köpf, H.; Voigtländer, R. *Chem. Ber.* **1981**, *114*, 2731. (b) Hey, E. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1988**, *43B*, 1271.

[15] Berg, F. J.; Petersen, J. L. *Organometallics* **1989**, *8*, 2461; **1991**, *10*, 1599.

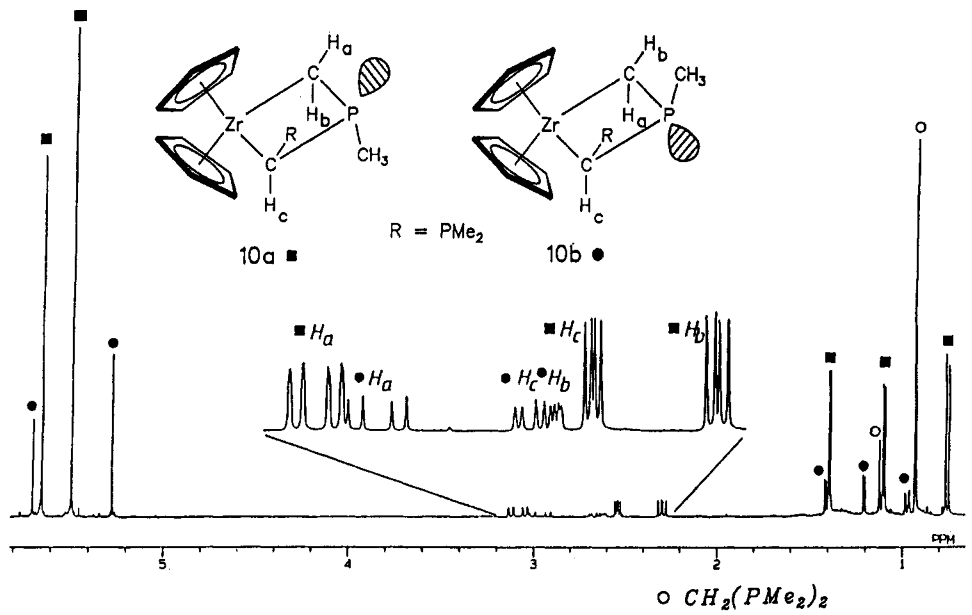


Figure 1. ^{1}H NMR spectrum of **10a,b**.

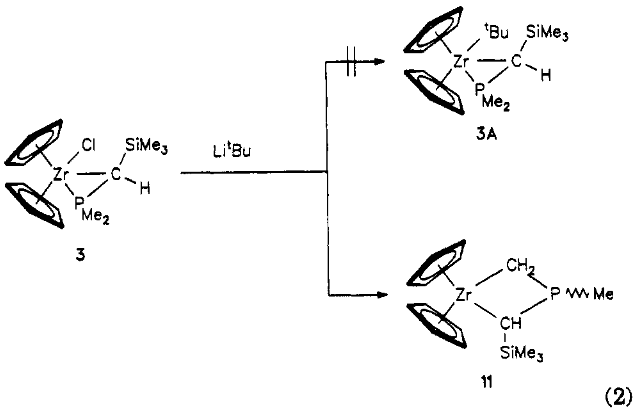
Table III. ^{13}C NMR Data for Complexes **10a,b** and **11a,b** (C_6D_6, 20 °C)

		$^{13}C\{^1H\}$, δ (J, Hz)	^{13}C (J, Hz)
10a	C_5H_5	108.83 (s)	(dquin, $^1J_{CH}$ = 171.51, "J_{quin}" = 6.71)
		108.43 (d, $^3J_{CZrCP}$ = 0.92)	(dquin, $^1J_{CH}$ = 171.12, "J_{quin}" = 6.71)
	$ZrCSiMe_3$	61.56 (d, $^1J_{CP}$ = 65.26)	(d, $^1J_{CH}$ = 107.73)
	$ZrCH_2$	57.76 (d, $^1J_{CP}$ = 45.96)	(t, $^1J_{CH}$ = 135.00)
	PCH_3	20.14 (d, $^1J_{CP}$ = 30.79)	(q, $^1J_{CH}$ = 127.56)
	$SiCH_3$	2.66 (d, $^3J_{CSiCP}$ = 6.43)	(q, $^1J_{CH}$ = 117.19)
10b	C_5H_5	108.67 (s)	(dquin, $^1J_{CH}$ = 172.11, "J_{quin}" = 6.72)
		107.28 (s)	(dquin, $^1J_{CH}$ = 171.50, "J_{quin}" = 6.72)
	$ZrCSiMe_3$	61.41 (d, $^1J_{CP}$ = 45.50)	(d, $^1J_{CH}$ = 108.33)
	$ZrCH_2$	58.31 (d, $^1J_{CP}$ = 44.12)	(t, $^1J_{CH}$ = 138.08)
	PCH_3	4.66 (d, $^1J_{CP}$ = 1.84)	(q, $^1J_{CH}$ = 114.13)
	$SiCH_3$	1.82 (s)	(q, $^1J_{CH}$ = 114.13)
11a	C_5H_5	109.35 (dd, $^3J_{CZrCP(A/B)}$ = 5.98, $^3J_{CZrCP(B/A)}$ = 0.92)	(dquin, $^1J_{CH}$ = 172.42, "J_{quin}" = 6.87) (dquin, $^1J_{CH}$ = 171.66, "J_{quin}" = 6.87)
	$ZrCPMe_2$	77.98 (dd, $^1J_{CP(A/B)}$ = 49.63, $^1J_{CP(B/A)}$ = 35.39)	(d, $^1J_{CH}$ = 122.41)
	$ZrCH_2$	59.05 (dd, $^1J_{CP(A)}$ = 45.05, $^3J_{CPCP}$ = 10.11)	(t, $^1J_{CH}$ = 134.82)
	PCH_3	22.60 (dd, $^1J_{CP}$ = 21.60, $^3J_{CPCP}$ = 4.60)	(q, $^1J_{CH}$ = 126.29)
		19.80 (dd, $^1J_{CP}$ = 17.92, $^3J_{CPCP}$ = 12.87)	(q, $^1J_{CH}$ = 122.83)
		19.05 (dd, $^1J_{CP}$ = 29.18, $^3J_{CPCP}$ = 4.37)	(q, $^1J_{CH}$ = 126.29)
11b	C_5H_5	108.63 (s)	(dquin, $^1J_{CH}$ = 171.66, "J_{quin}" = 6.87)
		108.11 (d, $^3J_{CZrCP}$ = 5.51)	(dquin, $^1J_{CH}$ = 172.43, "J_{quin}" = 6.30)
	$ZrCPMe_2$	71.42 (dd, $^1J_{CP(A/B)}$ = 51.48, $^1J_{CP(B/A)}$ = 44.48)	(d, $^1J_{CH}$ = 129.87)
	$ZrCH_2$	60.78 (dd, $^1J_{CP(A)}$ = 44.58, $^3J_{CPCP}$ = 4.14)	(t, $^1J_{CH}$ = 134.04)
	PCH_3	22.86 (d, $^1J_{CP}$ = 20.22)	(q, $^1J_{CH}$ = 124.56)
		21.30 (dd, $^1J_{CP}$ = 12.18, $^3J_{CPCP}$ = 3.45)	(q, $^1J_{CH}$ = 122.83)
		10.67 (dd, $^1J_{CP}$ = 25.97, $^3J_{CPCP}$ = 19.99)	(q, $^1J_{CH}$ = 125.27)

are available, and for XIX,[16] no unusual ^{31}P NMR shifts are reported. In complexes of type XX,[17] $\delta(^{13}C_A)$ indeed is at higher field than the other ^{13}C resonances. The NMR spectra thus allow for an unambiguous structural assignment for **10** and **11**, which represent the first complexes with doubly metalated alkylphosphine ligands of type XVI. The presence of the respective phosphinomethanes in the reaction mixtures according to eq 1 (cf. Figure 1) suggests that their formation is due to the metalation of a coordinated phosphinomethanide by a second one.

Intra- versus Intermolecular Metalation. In principle, the metalation of the ligand in **2** and **3** by an added lithium phosphinomethanide could proceed via an intramolecular or an intermolecular pathway (Scheme I).

To test the possibility of an intermolecular route, Li^{t}Bu was used as a base to metalate **3**. The bulkiness of this very effective base should prevent a simple substitution reaction. In fact, the substitution product **3A** could not be observed. Instead, **11** was identified spectroscopically as a reaction product, but only in very low yield (ca. 5%; eq 2).



(2)

Quite obviously, an intermolecular metalation reaction occurs, but it is rather unfavorable. Regarding the high yield in the metalation reaction of **2** and **3** with lithium phosphinomethanides, an alternative pathway has to be considered. To confirm this pathway as being intramo-

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[16] (a) Gell, K. I.; Schwartz, J. *Inorg. Chem.* **1980**, *19*, 3207. (b) Schmidbaur, H.; Pichl, R.; Müller, G. *Chem. Ber.* **1987**, *120*, 39.

[17] Seetz, J. W. F. L. Thesis, Vrije Universiteit Amsterdam, 1983. Seetz, J. W. F. L.; Van de Heisfeeg, B. J. J.; Alkerman, O. S.; Bickelhaupt, F. I. *Abstracts of Papers*, XIth International Conference of Organometallic Chemistry, Callaway Gardens Pine Mountain, GA, Oct 10–14, 1983; p 96.

Scheme I. Reaction of 3 with 6: Intra- versus Intermolecular Metalation

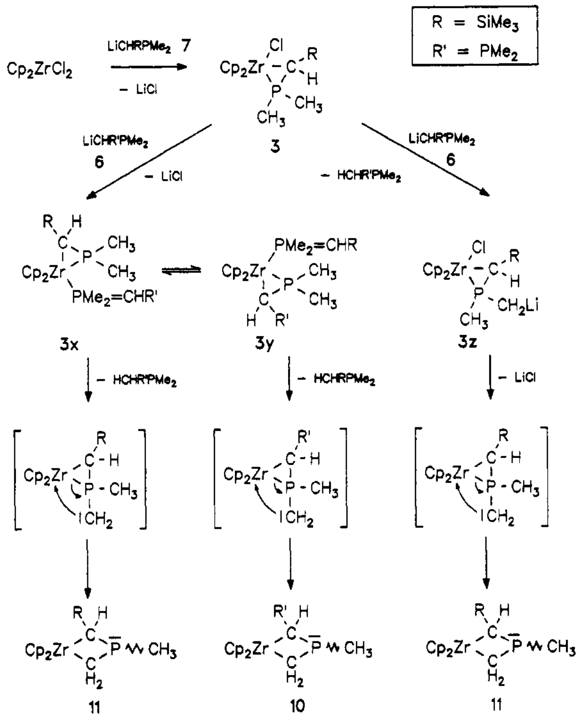
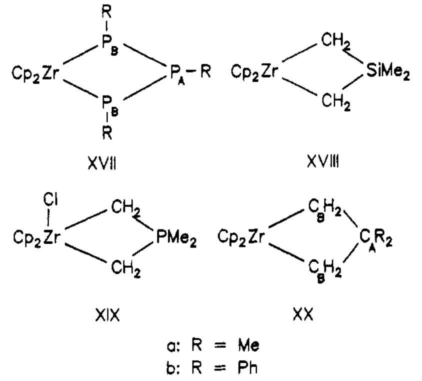


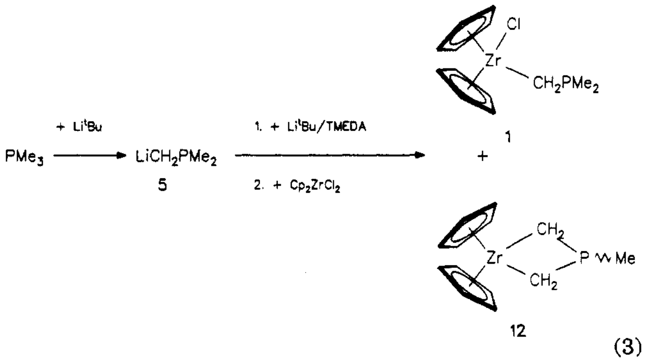
Chart III



lecular, a cross reaction of 3 with 6 was undertaken (Scheme I). An intermolecular reaction should yield 11 exclusively. Instead, a mixture of 10 and 11 in a 2:1 ratio was obtained and consequently both $H_2C(PMe_2)_2$ and $H_2C(PMe_2)(SiMe_3)$ were detected spectroscopically in a 1:2 molar ratio. This result may be rationalized by a sequence as given in Scheme I.

After the initial Cl^- substitution by the phosphinomethanide, the intermediate may interconvert and establish an equilibrium between **3x** and **3y**. The final product ratio of 10 to 11 should then depend on the relative basicity of the generated carbanionic (ylidic) functions in the intermediate **3x** and **3y**. It seems reasonable to assume that this is related to the basicities of the phosphinomethanides $[HC(PMe_2)_2]^-$ and $[HC(PMe_2)(SiMe_3)]^-$. Although this is not known precisely, the time needed to metalate with Li^nBu their conjugated acids $H_2C(PMe_2)_2$ (1 week) and $H_2C(PMe_2)(SiMe_3)$ (3 weeks) roughly parallels the product ratio in the above reaction. In principle, the attack of the phosphinomethanide $[HC(PMe_2)_2]^-$ at 3 could proceed via the carbon or via the phosphorus atom, but a C attack would cause severe steric crowding. Furthermore, the free phosphine functionality thus generated is not likely to effect the metalation, nor is this feasible for the carbon of the (polar) Zr–C bond, since the metalation of a $P-CH_3$ functionality is determined by the ability of approach of the metalating moiety.[18] This clearly favors the P attack pathway as exemplified by **3x** and **3y**. Therefore, we conclude that the formation of the novel zirconaphosphaheterocycles **10** and **11** is an intramolecular process, initiated by substitution of the chloride in **2** or **3** by the entering phosphinomethanides, which binds to the metal via the lone pair of the phosphorus atom, thus leading to **3x**/**3y** as intermediates.

Dependence of Metalation on the C Substituents. We first examine the zirconocene-centered interaction of two phosphinomethanides, which bear no other carbanion substituents than hydrogen: no metalation occurs. We reexamined the previously reported synthesis of $Cp_2Zr(CH_2PMe_2)_2$,[19] but no trace of $Cp_2\overline{Zr[CH_2PMeC}H_2]$ (**12**) could be detected. Thermolysis of $Cp_2Zr(CH_2PMe_2)_2$ at +20 and +90 °C in toluene solution does yield some PMe_3, but **12** could also not be detected. A small amount of **12** seems to be present, however, in the reaction mixtures obtained according to eq 3.



(3)

Whereas the monometalation of PMe_3 by Li^tBu is well known,[7] double metalation to give $Li_2[(CH_2)_2PMe]$ has not been achieved as yet.[20] Also in the present case, the yield of **12** is very low (ca. 4%) and it could not be isolated in pure form. However, the ^{31}P NMR high-field shift (**12**: $\delta(P)$ −194.69) is diagnostic enough to justify the assumption of the formation of **12**. The main product in the reaction is $Cp_2(Cl)Zr(CH_2PMe_2)$,[19] as deduced from a signal at $\delta(P)$ −36.60. It might well be that the double metalation is an intramolecular metalation at the zirconium center similar to the reaction according to eq 2.

In all cases known to date, C-unsubstituted phosphinomethanide ligands bind to a zirconocene metal center via the carbon atom.[19,21] This might also be expected to be the case in the reaction of the zirconaphosphacyclopropane derivative **3** with the lithium phosphinomethanide **5**, and in fact the thermally unstable compound **13** is obtained (eq 4).

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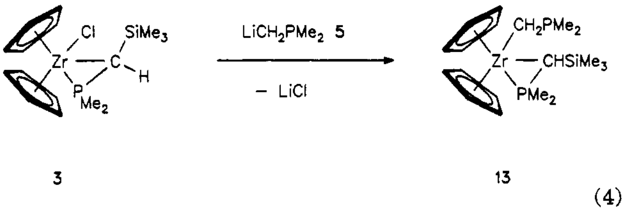
(18) (a) Karsch, H. H. *Chem. Ber.* **1984**, *117*, 3123. (b) Crabtree, R. H.; Holt, E. M.; Lavin, M.; Morehouse, S. M. *Inorg. Chem.* **1985**, *273*, 1986.

(19) Karsch, H. H.; Müller, G.; Krüger, C. *J. Organomet. Chem.* **1984**, *273*, 195.

(20) Double metalation of $RP(CH_2X)_2$ (X = Ph, $SiMe_3$) has been reported recently: Kolodiazhnyi, O. I.; Ustenko, S. N. *Phosphorus, Sulfur Silicon Relat. Elem.* **1993**, *75*, 229.

(21) (a) Engelhardt, L. M.; Jacobsen, G. E.; Raston, C. L.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1984**, 220. (b) Young, S. J.; Olmstead, M. M.; Knudsen, M. J.; Schore, N. E. *Organometallics* **1985**, *4*, 1432.

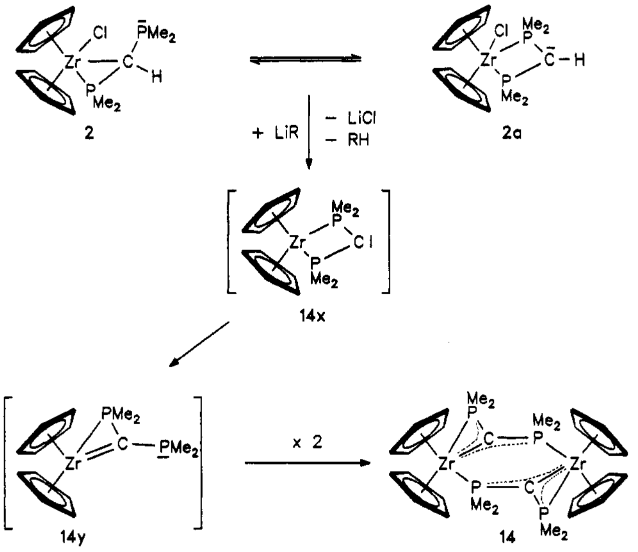


Only a trace of 11 (ca. 1%) is formed along with 13,[22] which again ascertains that the C coupling of a phosphinomethanide to a metal center is not a favorable path for P–CH$_3$ metalation. It might well be that 11 is formed by an intermolecular process (cf. eqs 2 and 3).

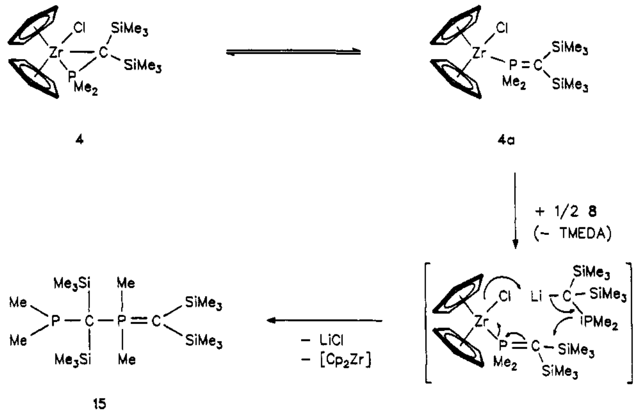
Rather surprisingly, in the analogous reaction of 2 with 5 (Scheme II), a quite different product, 14, is isolated. In accordance with the reaction of eq 4, however, a trace of 10 (ca. 1%) is found spectroscopically. 14 is also obtained from 2 and Li^{t}Bu. The different course in the reaction of 2 and 3 with organolithium reagents can easily be explained by the equilibrium 2 ⇌ 2a (Scheme II).[8] Obviously, an intermolecular metalation of the central carbanionic C atom in 2a occurs, leading to the $\eta^2(P,P)$-diphosphinocarbene complex 14x, which rearranges to the corresponding η^2(C,P) complex 14y and, by dimerization, gives rise to 14 in good yields for R = ^{t}Bu.[24] R–H can be detected in the reaction mixtures spectroscopically. The resulting complex 14 represents a new entry into phosphinocarbene complexes (cf. XI–XV). The AA′XX′ spin system observed in the ^{31}P{^{1}H} NMR of 14 was calculated with a set of parameters suitable for structure 14, and both spectra are in perfect accordance.

Under the assumption that P$_A$, P$_X$, and the carbene C atom of 14 lie in one plane (in analogy with 2 and 3) and that there is a planar centrosymmetric overall arrangement, only one Cp and a pair of PCH$_3$ resonances are expected, and this is indeed the case: the ^{1}H and ^{13}C{^{1}H} NMR spectra are very simple. The molecular structure of 14 in the solid deviates from this assumption, as shown by an X-ray structure determination (see below).

Scheme II. Formation of 14 from 2 (R = Me, CH$_2$PMe$_2$, ^{t}Bu)



Scheme III. Formation of 15 from 4 and (TMEDA){Li[C(PMe$_2$)(SiMe$_3$)$_2$]}$_2$ (8)



We now turn to more heavily substituted phosphinomethanide ligands: if the steric bulk of the phosphinomethanide ligands is increased, again the reaction course changes considerably. In the reaction of 4, which in solution is present as the 16e species 4a,[8] with the bis(silyl)-substituted lithium phosphinomethanide 8,[10] again no simple substitution seems feasible for steric reasons. Instead, according to Scheme III, a redox process with an oxidative P–C coupling of the phosphinomethanide ligands, yielding the sterically highly hindered phosphorus ylide 15, occurs. Similar coupling reactions have been observed for the analogous titanium complexes[25] but are new at zirconium metal centers. New also is the fact that the coupling does not connect the two P atoms of the ligands, which with fully C substituted phosphinomethanides is observed exclusively at titanium centers. This comparison allows for a proposal of a reaction pathway taking place in the external ligand sphere (Scheme III). It involves a simultaneous or consecutive attack of the lithium phosphinomethanide LiC(PMe$_2$)(SiMe$_3$)$_2$ at the Zr–Cl and the ylidic carbon functionalities of 4a. As a prerequisite, LiC(PMe$_2$)(SiMe$_3$)$_2$ should exhibit a Li–C, but not a Li–P, bond, which in ethereal solutions of 8 is likely to be the case.[26]

The reaction of 4 with 8 is by no means a clean reaction; the thermolysis of 4[8] competes effectively. Furthermore, traces of two other species are detected in the reaction mixture by ^{31}P NMR spectroscopy: a signal at δ(P) −154.72 can be assigned to the 1,3-zirconaphosphacyclobutane derivative 16, which is not unexpected in light of the results given above and again may be due to an intermolecular attack of the base lithium phosphinomethanide on a PCH$_3$ functionality.

In addition, a signal at δ(P) −20.46 is assigned to complex 17, where a SiCH$_3$ functionality has been metalated. This novel kind of metalation prevails, if the two bulky phosphinomethanide ligands are held closely together at

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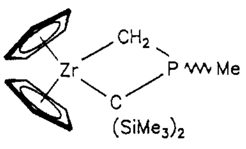
[22] On a HMO basis it has been pointed out that central (as in 13) and lateral positions of a PR$_2$ group are very close in energy.[23] A clear distinction for 13 cannot be made; the assignment is based solely on comparison with 2–4.[8]

[23] Hofmann, P.; Stauffert, P.; Schore, N. E. *Chem. Ber.* **1982**, *115*, 2153.

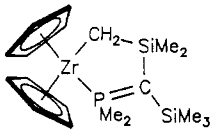
[24] A different pathway for the reaction of 2 with 5 (substitution of Cl$^-$ by [CH$_2$PMe$_2$] and subsequent intramolecular metalation of [CH(PMe$_2$)$_2$]$^-$ by [CH$_2$PMe$_2$]$^-$) cannot be ruled out, however.

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

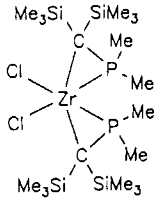
[26] NMR measurements for 8 in hydrocarbon solvents show the presence of several species, not identical with that in the solid state.[10] In donor solvents (D), only one ^{31}P NMR signal is detectable (δ(P) −33.82), presumably (TMEDA)(D)LiC(PMe$_2$)(SiMe$_3$)$_2$ and D$_3$LiC(PMe$_2$)(SiMe$_3$)$_2$, which both rapidly exchange their ligand sphere. Quite remarkably, in (PMDETA)Li[HC(PMe$_2$)(SiMe$_3$)] only a Li–C contact is observed in the solid state: Karsch, H. H.; Zellner, K.; Mikulcik, P.; Lachmann, J.; Müller, G. *Organometallics* **1990**, *9*, 190.



16

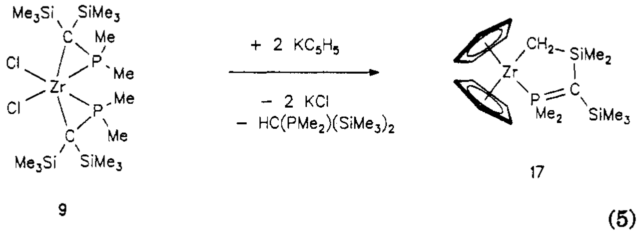


17



9

the metal center. This is not feasible at a zirconocene metal center for steric reasons, but it is the case in the zirconium complex **9**.[11] An exchange of the Cl$^-$ by Cp$^-$ ligands in **9** yields a green oil, which according to the NMR spectra contains **17** as a major product (eq 5).



(5)

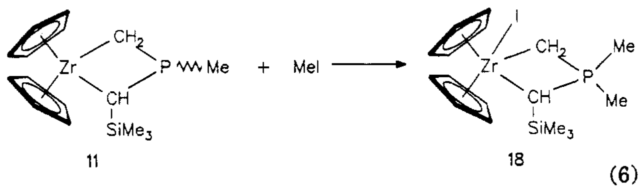
In addition, traces of **15** (1%) are detected spectroscopically. The nature of **17** can be unambiguously derived from the ^{1}H and ^{13}C{^{1}H} NMR spectra.

Reactivity of 1,3-Zirconaphosphacyclobutane Derivatives. The 16e zirconaphosphacyclobutanes **10** and **11** seem to be ideal candidates for a reactivity study. On the one hand, they should exhibit a reactivity similar to that of XVIII[15] and XX,[17] which is dominated by the electrophilic zirconium center and the mobile Zr–C bond.

On the other hand, the additional nucleophilic phosphine functionality in the four-membered ring should allow for an enhanced reactivity pattern. In this paper, preliminary results are included for a first comparison. No reaction at all was observed with THF, PMe$_3$, AlCl$_3$, and LiMe in a solution of **11** in C$_6$D$_6$. With elemental sulfur and selenium, complexes **10** and **11** react readily in toluene solution, but not in a well-defined fashion. The large number of signals observed in the ^{31}P{^{1}H} NMR spectra of the reaction mixtures rendered an assignment obsolete. To provide milder reaction conditions, Me$_3$PSe was used instead of selenium, but again, assignable spectra could not be obtained.

In the reaction of **11** with methyl iodide, the major product, which is soluble in toluene, exhibits a ^{31}P NMR signal at δ(P) +5.00.[27] This is indicative for the formation of an ylide complex of type XIX (eq 6). Because these compounds are reasonably well described and because some other (minor) signals along with that of **18** are also observed, a full characterization of **18** was not undertaken.

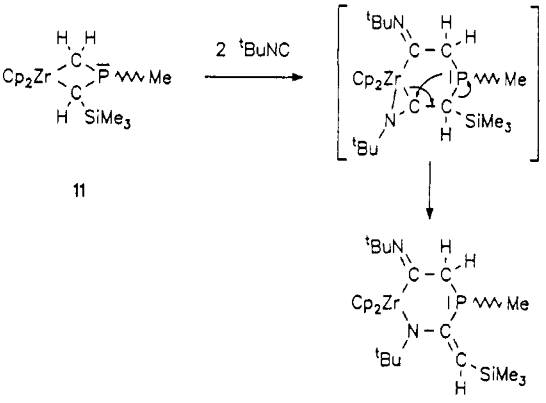
Both the reaction with S/Se and with MeI demonstrate, however, that the phosphorus atom in **11** indeed is



(6)

nucleophilic.[27] This aspect will be exploited further in future work.

A common feature of 16e zirconocene alkyl complexes is the ready insertion of carbon monoxide and isocyanides. However, **10** and **11** do not react with CO under ambient conditions. Even at elevated temperatures (up to +90 °C in toluene), no reaction is observed. The only case where a reaction could be observed was the reaction of **11** with CO in toluene at 90 °C in the presence of a stoichiometric amount of AlCl$_3$. In the IR spectrum, a band at 1518 cm^{-1} can be ascribed to ν(CO), but in the ^{31}P{^{1}H} NMR spectrum several signals indicate a mixture of compounds, which could not be separated and identified. The reluctance of **10** and **11** to react with CO probably may not be ascribed to an inherent nonreactivity but to the lack of stabilization pathways for the initial product. The oxygen atom cannot attain a central position, and therefore a reverse reaction predominates. This argument is augmented by the fact that ^{t}BuNC readily inserts in a similar manner into **11**, as is known for Cp$_2$Zr[CH$_2$SiMe$_2$CH$_2$] (XVIII).[15] A 1,2-silyl shift in the latter case corresponds to a 1,2-phosphino shift and thus explains readily the formation of **19** (eq 7).



(7)

Complex **19** combines several features of the various products observed in the reaction of XVIII with isocyanides and thus is unprecedent and represents a novel type of heterocycle. Similarities may also be found in the insertion reaction of ^{t}BuNC into [(Me$_3$Si)$_2$N]$_2$ZrCH$_2$Si(Me)$_2$NSiMe$_3$.[28] Though **19** was only obtained in solution, it could be fully characterized spectroscopically. The ^{31}P NMR signal at δ(P) –47.49 is in the normal range for alkylphosphines. Two ^{t}Bu groups are detected in the ^{1}H and ^{13}C{^{1}H} NMR spectra. The CH$_2$ and C=CH(SiMe$_3$) resonances are in full accord with respective resonances from the ^{t}BuNC insertion into XVIII. ^{13}C and ^{1}H, ^{1}H COSY NMR spectra confirm the assignment of signals.

Molecular Structure of 14. Yellow crystals of **14**·toluene were obtained from concentrated toluene solutions over a period of 9 months at +5 °C. Two Cp$_2$Zr fragments are bridged by two (Me$_2$P)$_2$C ligands in a η^2(C,P)-μ(C,P′)

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[27] This again confirms that the presence of two stereoisomers of **10** and **11** is attributable to a pyramidal P atom.

[28] Simpson, S. J.; Andersen, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 4063.

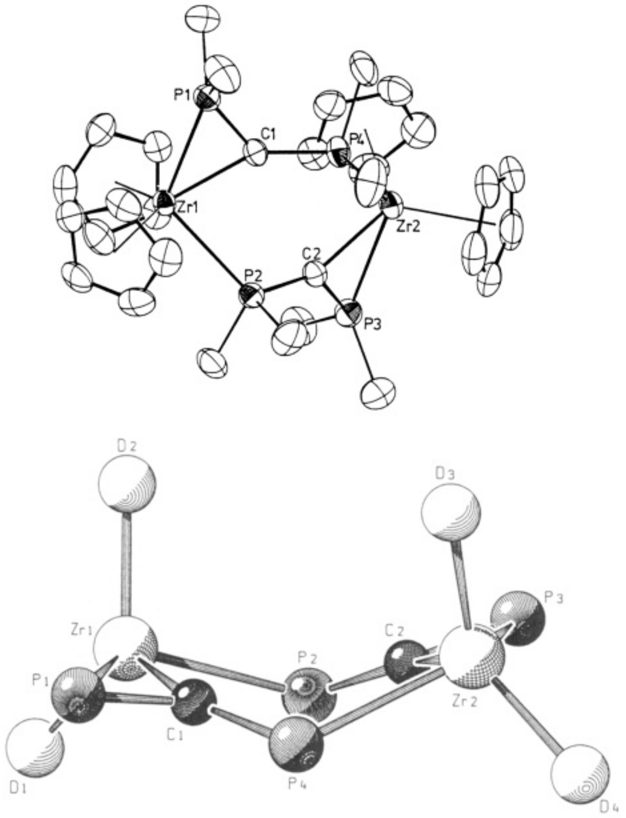

Figure 2. (a, top) Molecular structure of **14** in the crystal form (ORTEP; ellipsoids at the 50% probability level; hydrogen atoms omitted for clarity). (b, bottom) Central molecular framework of **14** in the crystal form (Schakal, arbitrary radii).

Table IV. Crystal Structure Data for 14·toluene

formula	$C_{30}H_{44}P_4Zr_2 \cdot C_7H_8$
M_r	803.162
cryst syst	monoclinic
scape group	$P2_1/c$
a, Å	22.558(1)
b, Å	8.891(1)
c, Å	20.283(1)
β, deg	112.33(1)
V, Å^3	3763.0
Z	4
d_{calcd}, g/cm^3	1.418
μ(Mo Kα), cm^{-1}	7.4
F(000), e	1656
T, °C	23
diffractometer	Syntex $P2_1$
scan	θ–θ
scan width (in ω), deg	$1.1 + 0.35 \tan \theta$
$[(\sin \theta)/\lambda]_{max}$, Å^{-1}	0.661
hkl range	$\mp$28, +11, +25
no. of rflns obsd (measd/unique)	9784/9002
R_{int}	0.029
no. of rflns obsd ($F_o \geq 4.0\sigma(F_o)$)	7527
abs cor	none
no. of H atoms (found/calcd)	28/16
no. of params refined	353
R^a	0.040
$R_w{}^b$	0.042
$\Delta\rho_{fin}$ (max/min), e/Å^3	+1.07/–0.55

^{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 $\sum w(|F_o| - |F_c|)^2$ ($w = 1/\sigma^2(F_o)$).

Table V. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters for 14·toluene

atom	x/a	y/b	z/c	U(eq),^{a} Å
Zr1	0.36433(2)	0.02759(4)	0.36753(2)	0.025
Zr2	0.22489(2)	–0.00200(4)	0.09350(2)	0.029
P1	0.43854(5)	–0.1365(1)	0.32836(5)	0.032
P2	0.23590(5)	0.0223(1)	0.28475(5)	0.030
P3	0.14971(5)	0.1505(1)	0.13589(5)	0.034
P4	0.31710(5)	–0.1798(1)	0.19035(5)	0.031
C1	0.3611(2)	–0.1065(4)	0.2750(2)	0.028
C2	0.2116(2)	0.0504(4)	0.1930(2)	0.029
C11	0.4999(2)	–0.0713(5)	0.2966(2)	0.050
C12	0.4654(2)	–0.3321(5)	0.3531(2)	0.048
C21	0.1918(2)	0.1596(5)	0.3163(2)	0.045
C22	0.1931(2)	–0.1479(5)	0.2927(2)	0.050
C31	0.1517(2)	0.3553(5)	0.1497(2)	0.053
C32	0.0696(2)	0.1064(6)	0.1319(2)	0.053
C41	0.2892(2)	–0.3654(5)	0.2056(2)	0.053
C42	0.3755(2)	–0.2461(5)	0.1536(2)	0.045
C111	0.4164(2)	–0.0298(5)	0.5027(2)	0.039
C112	0.3568(2)	0.0349(5)	0.4939(2)	0.038
C113	0.3088(2)	–0.0620(5)	0.4507(2)	0.041
C114	0.3390(2)	–0.1893(5)	0.4355(2)	0.043
C115	0.4053(2)	–0.1689(5)	0.4686(2)	0.041
C121	0.3374(2)	0.2889(4)	0.3120(2)	0.036
C122	0.3943(2)	0.2474(4)	0.3048(2)	0.034
C123	0.4436(2)	0.2394(4)	0.3726(2)	0.038
C124	0.4165(2)	0.2802(5)	0.4219(2)	0.042
C125	0.3511(2)	0.3103(4)	0.3854(2)	0.044
C211	0.2928(2)	0.2386(5)	0.1142(2)	0.042
C212	0.2439(2)	0.2530(5)	0.0466(2)	0.047
C213	0.2559(2)	0.1447(6)	0.0025(2)	0.049
C214	0.3099(2)	0.0623(5)	0.0417(2)	0.046
C215	0.3330(2)	0.1225(5)	0.1117(2)	0.042
C221	0.2034(2)	–0.2661(5)	0.0370(3)	0.051
C222	0.1564(2)	–0.2417(5)	0.0653(2)	0.050
C223	0.1161(2)	–0.1282(6)	0.0246(3)	0.049
C224	0.1393(2)	–0.0819(6)	–0.0274(2)	0.051
C225	0.1915(2)	–0.1705(6)	–0.0210(2)	0.052
C31	0.0241(4)	0.542(1)	0.2067(5)	0.136
C32	0.0318(4)	0.6453(8)	0.1644(4)	0.115
C33	–0.0161(6)	0.673(1)	0.0868(6)	0.197
C34	–0.0596(6)	0.581(1)	0.0623(6)	0.214
C35	–0.0615(4)	0.4617(9)	0.1114(5)	0.132
C36	–0.0291(4)	0.4225(9)	0.1786(5)	0.135
C37	0.0615(4)	0.503(1)	0.2722(5)	0.164

^{a} U(eq) = $^1/_3$ ($U_1U_2U_3$), where U_1, U_2, and U_3 are the eigenvalues of the **U**(ij) matrix. Esd's are given in parentheses.

ligation mode, thus resulting in a central six-membered ZrCPZrCP ring annealed by two three-membered ZrCP rings. Figure 2a shows an overall view of the molecular structure and Figure 2b the central skeleton. The arrangement of the two Cp_2Zr moieties reflects considerable steric strain: The D–Zr–D angles (D denotes the centroid of the Cp rings) are compressed (123.9/123.0°), approaching the respective value of solid **4** (122.6°).[8] Furthermore, one of the two Cp rings at each side is slipped away from a true η^5 coordination: Zr1–C112 and Zr–C225 are significantly longer (2.634(4)/2.622(4) Å) than the mean of the remaining four Zr–C distances in the respective rings (2.578/2.574 Å). Consequently, the Zr–D distances at each side are not equal (Zr1–D1/D2, 2.297/2.273 Å; Zr2–D3/D4, 2.276/2.295 Å) and longer than in solid **4** (2.23/2.26 Å).[8] In contrast to a planar or centrosymmetric arrangement, as derived from the NMR data in solution, the six-membered ring is folded along the P2···P4 axis by 41.9°. Due to small distortions there is also no other symmetry element, but the deviation from C_{2v} symmetry is only marginal and thus a comprehensive description of the halves of the molecule is justified. Due to the nearly planar C1/C2 atoms, the halves of the six-membered rings are each bridged by a PMe_2 group (P1/P3) in an approximately coplanar fashion along the Zr1–C1/Zr2–C2 linkage. Thus, P1/C1/P2 and P3/C2/P4 roughly lie in a plane perpendicular to the D_2Zr planes. This arrangement mimics the type of coordination geometry in other 18e zirconocene complexes, e.g. in the parent compound **2** (the chlorine in **2** is replaced by the P2/P4 atoms). Therefore,

Table VI. Selected Bond Distances (Å) and Angles (deg) in 14·toluene with Estimated Standard Derivations in Parentheses

Zr1–P1	2.564(1)	Zr2–P3	2.562(1)
Zr1–P2	2.742(1)	Zr2–P4	2.753(1)
Zr1–C1	2.202(3)	Zr2–C2	2.199(3)
Zr1–D1/D2[a]	2.297/2.273	Zr2–D3/D4[a]	2.2759/2.2950
P1–C1	1.690(4)	P3–C2	1.698(4)
P1–C11	1.829(5)	P3–C31	1.841(5)
P1–C12	1.847(5)	P3–C32	1.821(5)
P2–C2	1.748(3)	P4–C1	1.750(4)
P2–C21	1.837(5)	P4–C41	1.833(5)
P2–C22	1.835(5)	P4–C42	1.8040(5)
D1[a]–Zr1–D2[a]	123.93	P1–C1–Zr1	81.31(1)
P1–Zr1–P2	117.6(1)	P1–C1–P4	129.2(2)
P1–Zr1–C1	40.7(1)	Zr1–C1–P4	149.4(2)
P2–Zr1–C1	77.5(1)	C1–P4–Zr2	118.6(1)
C1–P1–Zr1	58.1(1)	C41–P4–C42	97.2(2)
C11–P1–C12	100.4		
D3[a]–Zr2–D4[a]	123.03	P3–C2–Zr2	81.3(1)
P3–Zr2–P4	118.8(1)	P3–C2–P2	130.4(2)
P3–Zr2–C2	40.7(1)	Zr2–C2–P2	148.3(2)
P4–Zr2–C2	78.3(1)	C2–P2–Zr1	118.7(1)
C2–P3–Zr2	58.0(1)	C21–P2–C22	98.3(2)
C31–P3–C32	100.7(2)		

[a] Centroid of the Cp rings.

a structural comparison of 2 and (half of) 14 is meaningful. As in 2, the carbon atoms C1/C2 adopt a central position within the denoted plane. All distances within the three-membered rings Zr1–P1–C1/Zr2–P3–C2 are significantly shortened, compared to the case for 2, but this is especially true for the Zr1Zr2–C1/C2 bond lengths, which are shortened by more than 0.2 Å. Though still in the range of normal Zr–C single bonds, this might well reflect their nature as "long Zr–carbene bonds" within a three-membered ring. However, considering all distances involving the C1/C2 atoms, this simply may also reflect their sp^2 nature in an ylidic type of bonding (P–C and Zr–C ylide). The Zr1/Zr2–P1/P3 distances are the shortest found in (phosphine)zirconium complexes and fall in the range for zirconium phosphide complexes, whereas the (with regard to the tricycles) exocyclic Zr1/Zr2–P2/P4 bonds are in a normal range. The C1/C2–P1/P3 distances are in the typical range for phosphorus ylides, whereas for the C1/C2–P2/P4 bonds, which are shorter than the P–CH_3 bonds, only a weak—if any—residual ylidic character should be ascribed. The angles within the tricycle $\overline{\text{ZrCP}}$ were close to those found in 2, the angles at C1/C2 being slightly opened for about 5° at the expense of that at P1/P3, whereas the angles at Zr1/Zr2 remain unaffected. All other distances and angles are within the expected range. Thus, in obedience to the 18e rule, the nature of the unique C1/C2 atoms in 14 is best regarded as a metalated "free" carbanion (C-metalated ylide) carrying a high electron density and therefore being highly nucleophilic.

Conclusion

A systemic variation of the C substituents in phosphinomethanide ligands allows for a tuning of their metalating properties at a metal center. If two phosphinomethanide ligands interact in the coordination sphere of a zirconium metal center, simple substitution (no metalation), PCH_3 metalation, $SiCH_3$ metalation, and phosphinocarbene formation are feasible simply by varying the substituents from H to $SiMe_3$ or PMe_2. In one case, also an oxidative coupling of two phosphinomethanides is observed. The resulting phosphorus ylide is unique by the bulkiness of the groups bonded together. The subtle balance of substituent influences in these kinetically controlled reactions is best demonstrated by the balance of main products and traces of byproducts in corresponding reactions, which also contributes to the reliability and predictability of the proposed mechanistic aspects. Some tentative reactivity studies with the zirconaphosphacyclobutanes indicate that the scope of new and unexpected results is still growing, and therefore, further studies are needed.

Acknowledgment. This work was supported by the Fonds der Chemischen Industrie. We also thank Prof. Dr. H. Schmidbaur for generous support.

Supplementary Material Available: Tables of displacement parameters and H atom coordinates (8 pages). Ordering information is given on any current masthead page.

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