From Dinuclear Zirconium(+3)-Phosphido Complexes {[$Cp_2ZrP(H)R]_2$} to the First Neutral Zirconocene–Phosphinidene Dimers [$(Cp_2ZrPR)_2$] by P–H Dehydrogenation

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Dedicated to Professor Michael Veith on the occasion of his 60th birthday

Keywords: Antiferromagnetic coupling / Phosphido complexes / Silylphosphanes / Zirconium / Phosphorus / P–H bonding activation

The syntheses and structures of the new zirconium(+3) silylphosphanido complexes {[$Cp_2ZrP(H)R]_2$} **1a** {Cp = η^5-C_5H_5; R = $SiMe_2C(i\text{Pr})Me_2$}, **1b** (R = $Si\,i\text{Pr}_3$), and **1c** (R = SiF(*t*Bu)(2,4,6-$i\text{Pr}_3C_6H_2$) are reported. The latter are easily accessible by the reaction of the lithium salts of the corresponding primary silylphosphanes with the Schwartz reagent [$Cp_2Zr(H)Cl$] in THF at –70 °C. They can be isolated in the form of diamagnetic red-black crystals in 68–85 % yield. The central structural motif of the complexes consists of planar (**1a**, **1b**) and slightly puckered Zr_2P_2 rings (**1c**), and contains two d^1-Zr(+3) centers, which are antiferromagnetically coupled (super exchange, through-bond interaction) although the transannular Zr–Zr separation is around 360 pm. Thus, the compounds have a biradicaloid electronic structure. Heating of solutions of **1a–c** in toluene in the presence of Pd/C or [$(Ph_3P)_2Pt(C_2H_4)$] results in catalytic dehydrogenation of the P–H bonds, affording the first neutral zirconocene–phosphinidene dimers [$Cp_2ZrPR]_2$**3a–c** in the form of deep red crystals in 72–88 % yield. The composition of the products is proven by multinuclear NMR spectroscopy, mass spectrometry and correct C,H-combustion analyses. The molecular structures of **3a** and **3c** were additionally confirmed by X-ray crystal structure analyses, showing that they consist of Zr_2P_2 rings with significantly shorter Zr–P distances than those observed in **1a** and **1c**. Interestingly, the dehydrogenation of the mostly sterically crowded derivative **1c** occurs also in boiling toluene solutions without using a catalyst, but the process is prevented in a H_2 atmosphere. This suggests that the Zr(+3) centers in **1c** can serve as active sites for the P–H bonding activation, which, however, are deactivated in the presence of H_2.

Introduction

Metallocene dihalides of the group 4 transition metals (Ti, Zr, Hf) tend to undergo halogen-reductive substitution by reaction with lithium phosphanides. This has been impressively shown by the reaction of zirconocene dihalides with lithium salts of primary and secondary phosphanes which leads solely to the corresponding dinuclear μ_2-phosphanido-bridged zirconium complexes **A** having two Zr(+3) centers (Scheme 1).[1–4] Although the complexes **A** bear two Zr(+3) atoms with a d^1 electronic configuration and possess relatively large Zr–Zr distances ranging between 381 and 355 pm, they are diamagnetic because of strong "through-space" interactions (d_{z^2}–d_{z^2} bond) and "super exchange" (through ligand coupling) as confirmed by ab initio calculations.[5–7] Alternatively, derivatives of **A** with small organic groups at phosphorus are also formed by oxidative addition of tetraorgano-substituted diphosphanes onto the Zr(+2) centers of two zirconocene molecules, generated in situ by reduction of [Cp_2ZrCl_2] with elemental Mg (Scheme 1).[8]

The preference of other zirconocene derivatives to undergo redox processes [Zr(+4) → Zr(+3)] toward primary and secondary phosphanes is also distinctive for related zirconocene hydrido complexes. Thus, reaction of [$Cp_2Zr(H)Cl$] (Schwartz reagent) with primary phosphanes RPH_2 affords in several ligand-exchange and redox processes **A′**, zirconocene dichloride and the respective diphosphane $R_2P_2H_2$ (Scheme 1).[9] To our surprise, and in contrast to the well-established class of dinuclear Zr(+3) phosphido complexes **A**, related complexes of type **B**, bearing two Cp_2Zr moieties and two μ_2-PR (phosphinidene) bridging ligands, are elusive. They represent dimers of zirconocene–phosphinidene complexes [$Cp_2Zr = PR$] which are also difficult to detect. Stephan et al. reported in 1991 the first

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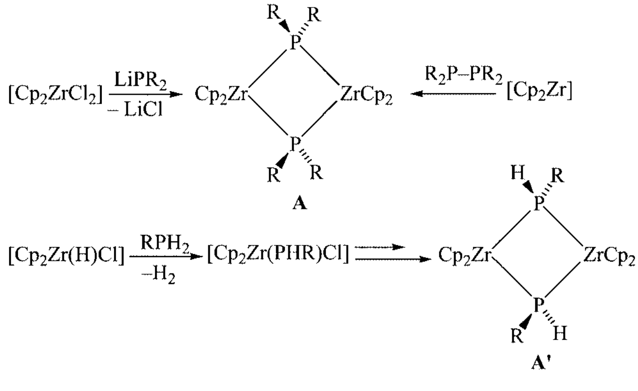
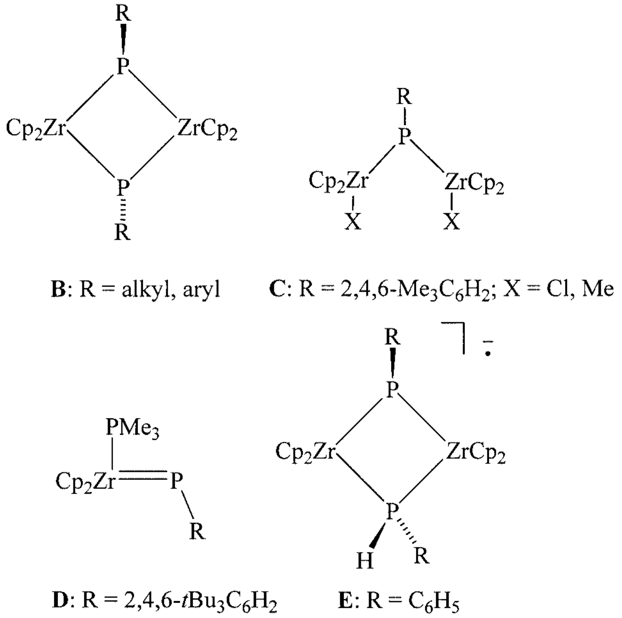


Scheme 1. Synthetic access to dinuclear zirconium(+3) phosphanido complexes **A** and **A′**.

phosphinidene-bridged zirconocene complex **C**[4] and in 1993 the first isolation of the donor-stabilized zirconocene–phosphinidene complex $Cp_2Zr(PMe_3)=PR$ (R = 2,4,6-$C_6H_2tBu_3$) **D**[10] and of the dinuclear complex anion **E** with mixed-valent Zr(+3) atoms (Figure 1).[9,11,12]


B: R = alkyl, aryl

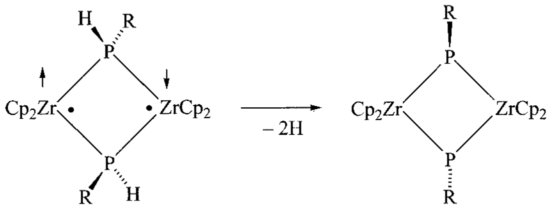
C: R = 2,4,6-$Me_3C_6H_2$; X = Cl, Me

D: R = 2,4,6-$tBu_3C_6H_2$

E: R = C_6H_5

Figure 1. Structural types of zirconocene–phosphinidene complexes.

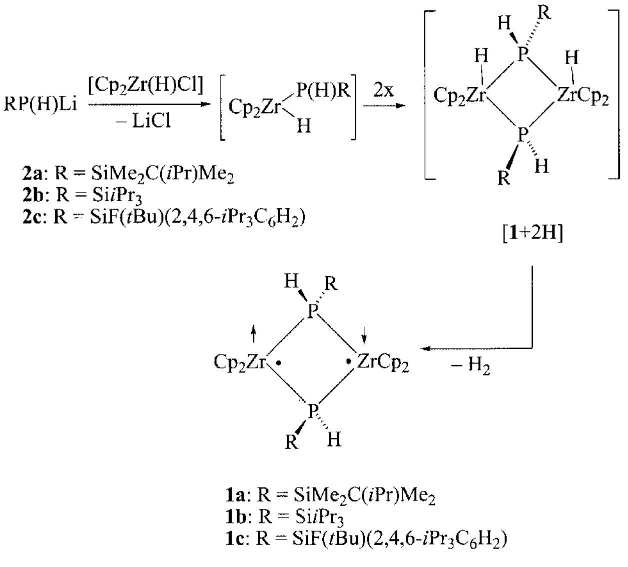
One possibility to synthesize dimeric zirconocene–phosphinidene complexes **B** can be envisioned as the catalytic dehydrogenation of complexes **A** [Equation (1)]. Since the P–H bonds in silylphosphanes are more reactive than those in organophosphanes, we set out to prepare a series of new dinuclear P–H functionalized silylphosphido Zr(+3) complexes **A**, which appeared to be suitable for P–H dehydrogenation experiments according to Equation (1). We report here the synthesis and structural characterization of the latter and their successful conversion into the corresponding dimeric zirconocene–phosphinidene complexes **B**.



Results and Discussion

Synthesis and Structures of 1a–1c

The new bulkily substituted dinuclear Zr(+3) silylphosphanido complexes **1a**–**1c** are easily accessible in 78 (**1a**), 68 (**1b**), and 85% yield (**1c**), by conversion of [$Cp_2Zr(H)Cl$] with the corresponding lithium silylphosphanides **2a**–**2c** in THF at –70 °C. The complexes were isolated in the form of black-red crystals, which are well soluble in aprotic aromatic solvents. Although the mechanism of the reaction is unknown and no intermediate could be detected by means of NMR spectroscopy, we assume that the initial product is the respective zirconocene-hydrido-phosphanide, which subsequently undergoes dehydrogenative dimerization to the final products **1a**–**1c** [Equation (2)]. The diamagnetic complexes have been characterized by multinuclear NMR spectroscopy and correct elemental analyses. The ^{31}P NMR spectra exhibit doublets relatively upfield with respect to *P*-alkyl-substituted derivatives **A**,[4,9,13] because of the σ-donor effect of the silyl group. However, the magnitudes of $^1J(^{31}P\text{-}^1H)$ coupling constants [236 Hz (**1a**), 228 Hz (**1b**), and 255 Hz (**1c**)] reflect identical electronic features for the P–Zr donor-acceptor bonds. The ^1H NMR spectra of **1a**–**1c** show only one type of C_5H_5 "Cp" protons, which suggests *trans* configuration or fast configurational inversion of the coordinated P atoms. The presence of dynamic



2a: R = $SiMe_2C(iPr)Me_2$
2b: R = $SiiPr_3$
2c: R = $SiF(tBu)(2,4,6\text{-}iPr_3C_6H_2)$

1a: R = $SiMe_2C(iPr)Me_2$
1b: R = $SiiPr_3$
1c: R = $SiF(tBu)(2,4,6\text{-}iPr_3C_6H_2)$

exchange processes seems unlikely because the VT ^{1}H and ^{31}P NMR spectra are invariant from –75 to +80 °C. In fact, the preference for the *trans* configuration of the silyl groups at phosphorus is confirmed by single-crystal X-ray diffraction analyses (Figure 2, Table 1). The P atoms in **1a**–**1c** have distorted tetrahedral coordinates, and the position of the P–H hydrogen atoms could be localized from the difference Fourier map and refined. The four-membered Zr_2P_2 ring is planar in **1a** and **1b**, but slightly puckered in the case of **1c** (Zr_2P/Zr_2P' angle 3.8°) because of the larger steric demand of the silyl group.

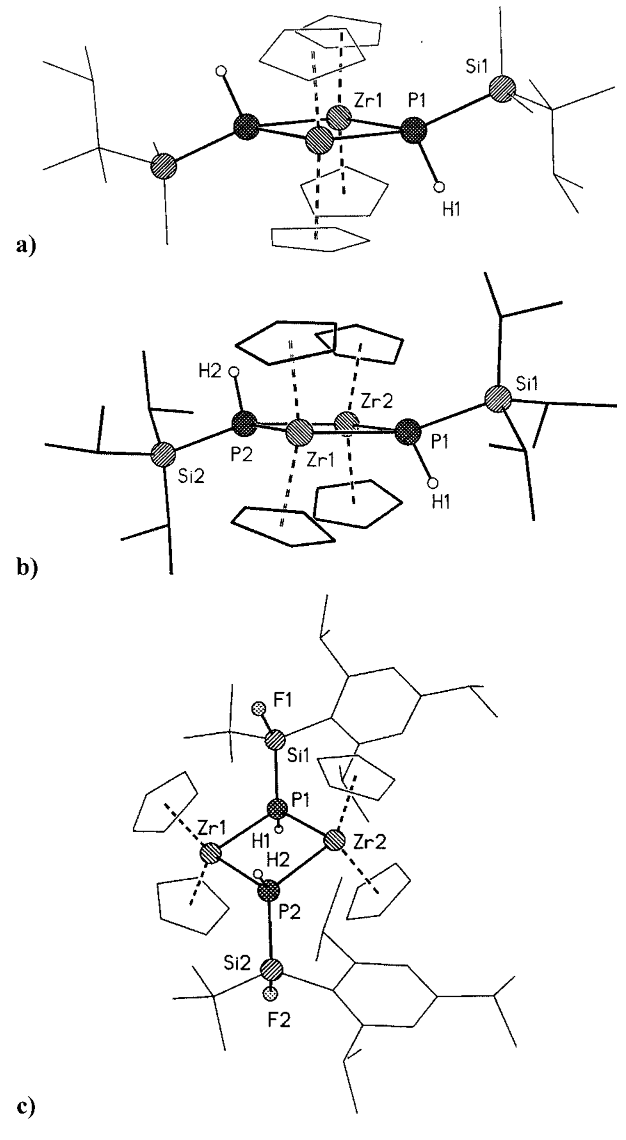
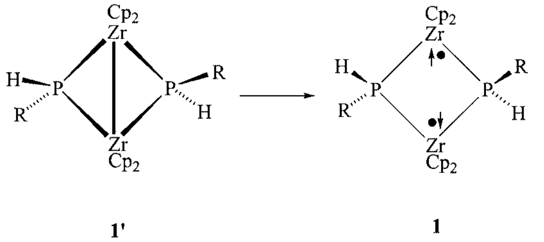


Figure 2. Molecular structures of **1a** (a), **1b** (b), and **1c** (c); the H atoms of the organic groups are omitted for clarity.

Table 1. Selected distances [pm] and angles [°] for **1a**, **1b**, and **1c**.

1a	**1b**	**1c**
Zr1–P1 265.7(1)	Zr1–P1 268.0(1)	Zr1–P1 270.0(1) Zr1–P2 268.9(1)
P1–Si1 225.4(2)	P1–Si1 228.5(1)	P1–Si1 225.3(2)
Zr1–Zr1A 364.2(3)	Zr1–Zr1A 357.3(3)	Zr1–Zr2 360.8(2) Si1–F1 161.9(2)
P1–Zr1–P1A 93.53(3)	P1–Zr1–P1A 96.73(4)	P1–Zr1–P2 95.55(4)
Zr1–P1–Zr1A 86.47(3)	Zr1–P1–Zr1A 83.27(3)	P1–Zr2–P2 96.06(4) Zr1–P1–Zr2 84.10(4) Zr1–P2–Zr2 84.15(3)

This is in contrast to other derivatives with *cis* configuration of the substituents at phosphorus, with folding-angles up to 30.6°.[13] The Zr–P distances as well as the endocyclic Zr–P–Zr and P–Zr–P angles are inconspicuous and practically identical with those in *P*-alkyl-substituted derivatives and related phosphanido-bridged Zr(+3) complexes.[4,5,9,13] The most remarkable geometrical feature is the relatively large Zr–Zr′ separation of 3.64 (**1a**), 3.57 (**1b**), and 3.61 (**1c**), which shows that there is no common transannular bonding between the d^1-Zr centers although the compounds are diamagnetic (singlet ground-state) due to antiferromagnetic coupling by ligand-mediated superexchange. Similar distances were observed in related *P*-alkyl-substituted derivatives.[9,13] According to results of ab initio calculations,[6] the extension of the transannular Zr–Zr distance results from two opposite effects: attractive Zr–Zr through-bond versus repulsive ligand-ligand interactions at the Zr and P atoms. In other words, the hypothetical form **1′** with a "short" Zr–Zr distance and a butterfly-like structure possesses much higher ring strain than the "bond-stretch" isomer **1** (Scheme 2).

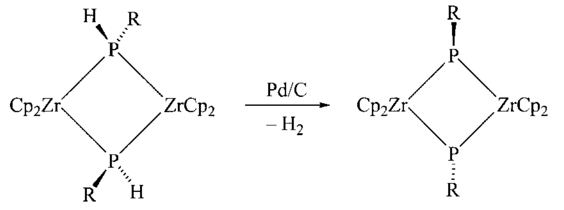


Scheme 2. Bond-stretch isomerization of **1′** to the biradicaloid **1**.

While this situation is widespread in multinuclear transition-metal complexes with unpaired electrons, similar structural and electronic features are scarce in main-group chemistry. The first iso(valence)electronic main-group metal analog, the Sn_2N_2-heterocyclobutane $[ClSn–N(SiMe_3)]_2$, which also has a biradicaloid structure and a singlet ground state, has been discovered only recently.[14]

Formation of the Dimeric Zirconocene–Phosphinidene 3a–3c by P–H Dehydrogenation of 1a–1c

Since the P–H bond in silylphosphanes is more reactive with regard to homolytic and heterolytic fission than that in organophosphanes, we expect that the P–H bonds in **1a**–**1c** can be dehydrogenated by typical dehydrogenation catalysts, leading to the first zirconocene–phosphinidene dimers. In fact, heating of solutions of **1a**–**1c** in toluene at 70 °C in the presence of Pd/C as a dehydrogenation catalystfurnishes the first neutral zirconocene–phosphinidene dimers **3a**–**3c** in good yields [Equation (3)]. Instead of Pd/C, the Pt complex $[(Ph_3P)_2Pt(C_2H_4)]$ can also be used as a catalyst (10^{-2} mol-%).

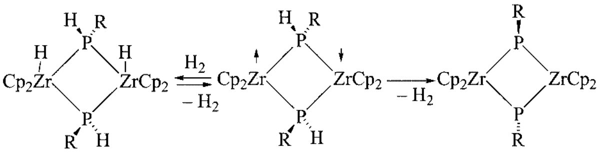


(3)

1a–c

3a: R = $SiMe_2C(i\text{Pr})Me_2$
3b: R = $Si\,i\text{Pr}_3$
3c: R = $SiF(t\text{Bu})(2,4,6\text{-}i\text{Pr}_3C_6H_2)$

The dehydrogenation is completed after about 8 h and its progress can be monitored by ^{31}P NMR spectroscopy. Surprisingly, the dehydrogenation of the mostly sterically crowded derivative **1c** occurs also in boiling toluene solutions without using a catalyst. This irreversible process is complete after 24 h. In line with that, **3c** is inert toward H_2 in boiling toluene in a sealed tube. However, the conversion of **1c** into **3c** is hampered in a sealed tube or in H_2/D_2 gas at 1 atm without P–H/P–D exchange. Although the mechanism is still unknown we assume the dehydrogenation process involves the Zr(+3) centers as active sites. Apparently, the latter are deactivated in the presence of H_2, affording [**1c** + 2 H] as transient species in a reversible reaction [Equation (4)]. It should be mentioned here that compounds of the type [**1** + 2 H] are also possible transient species for the synthesis of **1a**–**c** [see Equation (2)] but they could not yet be detected.



(4)

[1c+2H] **1c** **3c**

The ^{31}P nucleus in **3a** (δ = 238.9 ppm) **3b** (δ = 229.8 ppm) and **3c** (δ = 260.3 ppm) undergoes a drastic downfield shift of $\Delta\delta$ = 337.5 (**3a**), 362.3 (**3b**) and 346.6 ppm (**3c**), respectively. The strong deshielding of the ^{31}P nucleus is characteristic for μ_2-bridging phosphinidene ligands and reflects a higher contribution of the paramagnetic term to the chemical shift.[15] The ^{31}P chemical shifts of **3a**–**3c** are similar to the values of the hitherto only known neutral zirconium phosphinidene complexes **C** (δ = 325.5, 303.0 ppm; see Figure 1).[4,16] The ^{1}H, ^{31}P, and ^{13}C NMR spectra of the products clearly indicate that there is only one configurational isomer present in solution even at low (–75 °C) and high temperatures (+85 °C). The composition of the novel complexes were confirmed by mass spectrometry and correct elemental analyses. In the cases of **3a** and **3c**, the molecular structures were established by X-ray diffraction analyses (Figure 3, Table 2). Compounds **3a** and **3c** crystallize in the monoclinic space group $P2_1/c$ and in the orthorhombic space group *Pbca*, respectively.

Table 2. Selected bond lengths [pm] and angles [°] for **3a** and **3c**.

3a	**3c**
Zr1–P1 259.8 (3)	Zr1–P1 265.2 (4)
Zr1–P1A 261.7 (4)	Zr1–P2 263.0 (4)
P1–Si1 223.4 (5)	P1–Si1 220.8 (4)
Zr1–Zr1A 372.5 (1)	Zr1–Zr2 372.8 (2)
	Si1–F1 162.3 (8)
P1–Zr1–P1A 88.8 (1)	P1–Zr1–P2 89.7 (1)
Zr1–P1–Zr1A 91.2 (1)	P1–Zr2–P2 89.7 (1)
Zr1–P1–Si1 130.6 (2)	Zr1–P1–Zr2 89.6 (1)
Zr1A–P1–Si1 124.4 (2)	Zr1–P2–Zr2 90.0 (1)
	Zr1–P1–Si1 123.0 (2)
	Zr2–P2–Si2 124.3 (2)

Similar to the geometrical features of **1a** and **1c**, the Zr_2P_2 ring is planar in **3a** but is slightly puckered in **3c** because of steric repulsion (folding angle Zr_2P/Zr_2P' 10.6°). The P atoms have distorted pyramidal coordinates, with the sum of bonding angles amounting to 346.3 (**3a**), and 335.1 and 337.4° (**3c**). As expected, the Zr–P separations in **3a** [259.8(3), 261.7(4) pm] and **3c** [263.0(4), 265.2(4) pm] are significantly shorter than those for the Zr–P single bonds in **1a** [265.7(1) pm] and **1c** [268.9(1), 270.0(1) pm]. The values are between those of the Zr–P single bonds in **C** [264.8(3), 264.3(2) pm] and the Zr=P double bond in D [250.5(4) pm] but similar to the values observed for the re-

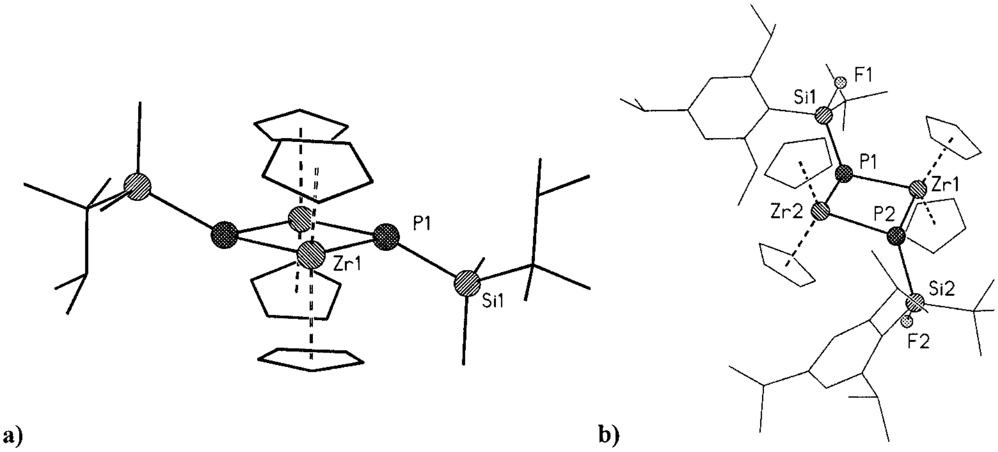


Figure 3. Solid-state structure of **3a** (a) and **3c** (b); H atoms are omitted for clarity.

lated anionic zirconocene–phosphinidene dimer **E** [259.1(5), 256.8(5) pm] (see Figure 1). The transannular Zr–Zr separations in **3a**, and **3c** are approximately 10 pm longer than in the precursors **1a**, and **1c**, but practically identical with the values in **E**.

Conclusions

The dinuclear zirconium(+3) silylphosphanido complexes **1a**–**c** are suitable precursors for the synthesis of the first neutral zirconocene–phosphinidene dimers **3a**–**c**. The latter do not tend to dissociate in hot toluene solutions because of strong Zr–P σ bonds and partial P–Zr π-donor interactions. The desired dehydrogenation of the P–H bonds in **1a**–**c** is an irreversible process which succeeds in the presence of the well-known dehydrogenation catalysts Pd/C and $[(Ph_3P)_2Pt(C_2H_4)]$, and is certainly relieved by the sterically crowded organosilyl groups. Particularly noteworthy is the fact that **1c** undergoes voluntary dehydrogenation even without a catalyst; but the conversion is prevented in the presence of relatively high concentrations of H_2. The results suggest that the Zr(+3) centers in **1c** serve as active sites in the P–H bonding activation process. However, further (kinetic) studies are necessary in order to establish the mechanism. The results led also to the challenging questionywhether or not other Zr(+3) compounds could also be employed as efficient dehydrogenation reagents or catalysts for primary and secondary phosphanes. Respective investigations are currently in progress.

Experimental Section

General Remarks: All manipulations were carried out at anaerobic conditions under dry argon using standard Schlenk techniques. Solvents were refluxed over an appropriate drying agent, distilled and degassed prior to use. NMR spectra were recorded in C_6D_6 at ambient temperature with a Bruker Avance250 spectrometer operating at 250.1 MHz (^{1}H), 101.3 MHz (^{31}P), and 235.4 MHz (^{19}F). Chemical shifts were reported relative to TMS (^{1}H), 85% aqueous H_3PO_4 (^{31}P), and $CFCl_3$ (^{19}F) at δ = 0 ppm. EI-MS measurements were recorded with a Varian MAT CH7 spectrometer at 70eV. Combustion analyses were performed at the Analytical Service Laboratory of the Faculty of Chemistry in Bochum with a CHNO Rapid instrument (Heraeus).

Preparation of $\{(\eta^5\text{-}C_5H_5)_2ZrP(H)SiMe_2C(i\text{Pr})Me_2\}_2$ (1a): A solution of $LiP(H)SiMe_2C(i\text{Pr})Me_2$ (8.79 mmol, freshly prepared from the corresponding silylphosphane with BuLi in THF at –78 °C) in THF (30 mL) was slowly added to a suspension of $[(\eta^5\text{-}C_5H_5)_2Zr(H)Cl]$ (2.26 g, 8.79 mmol) in THF (50 mL) at –70 °C. The reaction mixture was allowed to warm up to room temperature within 8 h and subsequently all volatile components were evaporated off in vacuo (10^{-3} Torr). The solid residue was redissolved in toluene (70 mL), filtered, and the clear red solution was concentrated to about 30 mL to give, after 1d at –20 °C, deep red crystals of **1a**. Yield: 2.7 g (3.43 mmol, 78%). ^{1}H NMR: δ = 4.92 (s, 20 H, C_5H_5), 2.18 [sept, 2 H, $^3J_{H,H}$ = 6.9 Hz, $CH(CH_3)_2$], 1.26 [s, 12 H, $C(CH_3)_2$], 1.09 [d, 12 H, $^3J_{H,H}$ = 7.0 Hz, $CH(CH_3)_2$], 0.51 [s, 12 H, $Si(CH_3)_2$] ppm. ^{31}P NMR: δ = –106.6 (d, $^1J_{P\text{-}H}$ = 236.8 Hz) ppm. MS: *m/z* (%) = 791 $[M\text{-}H_2]^+$ (1), 708 $[M\text{-}C(i\text{Pr})Me_2]^+$ (1), 621 $[791 - 2\{C(i\text{Pr})Me_2\}]^+$ (0.8), 563 $[621 - SiMe_2]^+$ (0.8), 85 $[C(i\text{Pr})Me_2]^+$ (58), 73 $[SiMe_3]^+$ (85), 43 $[i\text{Pr}]^+$ (100). $C_{36}H_{60}P_2Si_2Zr_2$ (793.4): calcd. C 54.50, H 7.60; found C 54.40, H 7.70.

Preparation of $\{(\eta^5\text{-}C_5H_5)_2ZrP(H)Si\textit{i}Pr_3\}_2$ (1b): The compound was prepared by a procedure similar to that for **1a**, using the corresponding silylphosphane (2.15 mmol) as starting material. Crystallization in toluene afforded red crystals of **1b**. Yield: 0.6 g (0.73 mmol, 68%). ^{1}H NMR: δ = 4.92 (s, 20 H, C_5H_5), 1.28 [d, 36 H, $^3J_{H,H}$ = 6.8 Hz, $CH(CH_3)_2$], 1.06 [sept, 6 H, $^3J_{P\text{-}H}$ = 6.9 Hz, $CH(CH_3)_2$] ppm. ^{31}P NMR: δ = –132.6 (d, $^1J_{P\text{-}H}$ = 228 Hz) ppm. MS: *m/z* (%) = 819 $[(M\text{-}H_2)^+$, 1], 157 $[(Si(i\text{Pr})_3)^+$, 100], 115 $[Si(i\text{Pr})_2)^+$, 78], 43 $[(i\text{Pr})^+$, 40]. $C_{38}H_{64}P_2Si_2Zr_2$ (821.5): calcd. C 55.55, H 7.85; found C 55.43, H 7.80.

Preparation of $\{(\eta^5\text{-}C_5H_5)_2ZrP(H)SiF(t\text{Bu})(2,4,6\text{-}i\text{Pr}_3C_6H_2)\}_2$ (1c): The compound was prepared by a procedure similar to that for **1a**, using the corresponding fluorosilylphosphane (2.3 mmol) as starting material. Crystallization in toluene afforded prismatic-shaped black crystals of **1b**. Yield: 1.1 g (0.98 mmol, 85%). ^{1}H NMR: δ = 7.33 (s, 4 H, *m-H*), 5.08 (s, 20 H, C_5H_5), 3.97 [sept, 4 H, $^3J_{H,H}$ = 6.9 Hz, $o\text{-}CH(CH_3)_2$], 2.94 [sept, 2 H, $^3J_{H,H}$ = 6.9 Hz, $p\text{-}CH(CH_3)_2$], 1.57 [s, 18 H, $C(CH_3)_3$], 1.43 [d, 12 H, $^3J_{H,H}$ = 6.9 Hz, $p\text{-}CH(CH_3)_2$], 1.36 [d, 24 H, $^3J_{H,H}$ = 6.9 Hz, $o\text{-}CH(CH_3)_2$] ppm. ^{31}P NMR: δ = –86.3 (dd, $^1J_{P\text{-}H}$ = 255.2, $^2J_{P\text{-}F}$ = 63.8 Hz) ppm. ^{19}F NMR: δ = –149.8 (d, $^2J_{P\text{-}F}$ = 63.6 Hz) ppm. MS: *m/z* (%) = 1119 $[(M\text{-}H_2)^+$, 1], 307 $\{[FSi(t\text{Bu})(2,4,6\text{-}i\text{Pr}_3C_6H_2)]^+$, 31}, 203 $[(i\text{Pr}_3C_6H_2)^+$, 48], 43 $[(i\text{Pr})^+$, 100]. $C_{58}H_{86}F_2P_2Si_2Zr_2$ (1121.9): calcd. C 62.09, H 7.72; found C 61.89, H 7.61.

Preparation of $\{(\eta^5\text{-}C_5H_5)_2ZrPSiMe_2C(i\text{Pr})Me_2\}_2$ (3a): A solution of **1a** (0.83 g, 1.05 mmol) in toluene (40 mL) was heated in the presence of Pd/C (0.1 g) at 70 °C for 8 h. After filtration and concentration of the solution to about 20 mL in vacuo, the reaction solution was stored at 6 °C to afford red-black crystals. Yield: 0.6 g (0.76 mmol, 72%). ^{1}H NMR: δ = 6.29 (s, 20 H, C_5H_5), 1.61 [sept, 2 H, $^3J_{H,H}$ = 6.9 Hz, $CH(CH_3)_2$], 0.91 [d, 12 H, $^3J_{H,H}$ = 7.0 H, $CH(CH_3)_2$], 0.77 [s, 12 H, $C(CH_3)_2$], 0.64 [s, 12 H, $Si(CH_3)_2$] ppm. ^{31}P NMR: δ = 238.9 ppm (s). MS: *m/z* (%) = 791 $[(M)^+$, 4], 706 $[(M\text{-Thex})^+$, 3.5], 563 $[(M\text{-}2(\text{Thex})\text{-}SiMe_2)^+$, 2.5], 505 $[(M\text{-}2(C(i\text{Pr})Me_2)\text{-}2(SiMe_2))^+$, 3.5], 438 $[(504\text{-}(C_5H_5))^+$, 3], 85 $[(C(i\text{Pr})Me_2)^+$, 25], 73 $[(SiMe_3)^+$, 100], 43 $[(i\text{Pr})^+$, 35]. $C_{36}H_{58}P_2Si_2Zr_2$ (791.4): calcd. C 54.63, H 7.38; found C 54.46, H 7.30.

Preparation of $\{(\eta^5\text{-}C_5H_5)_2ZrPSi\textit{i}Pr_3\}_2$ (3b): The compound was synthesized by a procedure similar to that for **3a**, starting from **1b** (1.50 g, 1.82 mmol). Yield: 1.31 g (1.59 mmol, 87.4%). ^{1}H NMR: δ = 4.98 (s, 20 H, C_5H_5), 1.34 [d, 36 H, $^3J_{H,H}$ = 6.7 Hz, $CH(CH_3)_2$], 1.11 [sept, 6 H, $^3J_{P\text{-}H}$ = 6.9 Hz, $CH(CH_3)_2$] ppm. ^{31}P NMR: δ = 229.8 (s) ppm. MS: *m/z* (%) = 819 $[M]^+$ (1), 157 $[Si(i\text{Pr})_3]^+$ (100), 115 $[Si(i\text{Pr})_2]^+$ (78), 43 $[i\text{Pr}]^+$ (40). $C_{38}H_{62}P_2Si_2Zr_2$ (819.5): calcd. C 55.69, H 7.62; found C 55.45, H 7.60.

Preparation of $\{(\eta^5\text{-}C_5H_5)_2ZrPSiF(t\text{Bu})(2,4,6\text{-}i\text{Pr}_3C_6H_2)\}_2$ (3c): A solution of **1c** (1.23 g, 1.09 mmol) in toluene (50 mL) was refluxed for 12 h. Concentrating the solution to about 20 mL and cooling at 4 °C afforded brown-red crystals. Alternatively, the desired product was also accessible upon heating the solution for 8 h at 50 °C in the presence of Pd/C (0.1 g). Yield: 0.87 g (0.77 mmol, 71%). ^{1}H NMR: δ = 7.31 (s, 4 H, *m-H*), 6.40 (s, 20 H, C_5H_5), 4.59 [sept, 4 H, $^3J_{H,H}$ = 6.9 Hz, $o\text{-}CH(CH_3)_2$], 2.79 [sept, 2 H, $^3J_{H,H}$ = 6.9 Hz, $p\text{-}CH(CH_3)_2$], 1.02 [s, 18 H, $C(CH_3)_3$], 1.23 [d, 12 H, $^3J_{H,H}$ = 6.9 Hz, $p\text{-}CH(CH_3)_2$], 1.15 [d, 24 H, $^3J_{H,H}$ = 6.9 Hz, $o\text{-}CH(CH_3)_2$] ppm. ^{31}P NMR: δ = 260.3 (s) ppm. ^{19}F NMR: δ = –133.6 (s) ppm. MS: *m/z* (%) = 1119 $[M]^+$ (1), 307 $[FSi(t\text{Bu})(2,4,6\text{-}i\text{Pr}_3C_6H_2)]^+$ (38), 203 $[i\text{Pr}_3C_6H_2]^+$ (51), 43 $[i\text{Pr}]^+$ (100). $C_{58}H_{84}F_2P_2Si_2Zr_2$ (1119.9): calcd. C 62.20, H 7.56; found C 62.02, H 7.51.

Table 3.Crystallographic data for **1a**, **1b**, **1c**, **3a,** and **3c**.

	1a	**1b**	**1c**	**3a**	**3c**
Empirical formula	$C_{36}H_{60}P_2Si_2Zr_2$	$C_{38}H_{64}P_2Si_2Zr_2$	$C_{58}H_{86}F_2P_2Si_2Zr_2$	$C_{36}H_{58}P_2Si_2Zr_2$	$C_{58}H_{84}F_2P_2Si_2Zr_2$
Formula mass	793.40	821.45	1121.83	791.38	1119.81
Temperature [K]	203(2)	213(2)	203(2)	203(2)	203(2)
Crystal system	monoclinic	triclinic	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P2_1/c$	*Pcab*
a	11.452(1)	8.474(1)	14.793(5)	11.247(5)	18.96(1)
b	16.495(2)	10.797(1)	20.032(6)	16.522(8)	20.25(1)
c	10.247(1)	11.568(1)	20.064(7)	10.335(6)	30.59(1)
α	90	77.47(1)	90	90	90
β	94.18(1)	87.28(1)	101.36(4)	95.44(2)	90
γ	90	71.24(1)	90	90	90
V [Å^3]	1930.5(3)	978.0(2)	5829(3)	1911(2)	11743(10)
Z	2	1	4	2	8
$D_{\text{calcd.}}$ [g cm^{-3}]	1.365	1.395	1.278	1.375	1.267
$F(000)$	828	430	2360	824	4704
Crystal size [mm]	0.3 × 0.2 × 0.2	0.3 × 0.1 × 0.2	0.4 × 0.35 × 0.35	0.2 × 0.2 × 0.1	0.6 × 0.4 × 0.05
$\Theta_{\text{max.}}$[degr.]	2.34 to 24.99	2.04 to 22.50	1.73 to 25.02	2.20 to 22.50	1.61 to 23.02
Measured reflections	3334	2733	10295	2610	7690
Unique reflections	3331	2526	7531	2443	3649
Abs. coeff. [cm^{-1}]	0.708	0.701	0.494	0.715	0.491
Parameters	194	203	626	191	619
Goodness-of-fit on F^2	0.970	0.960	1.012	0.925	0.963
R_1 [$I > 2\sigma(I)$]	0.0545	0.0305	0.0383	0.0890	0.0765
wR_2 (all data)	0.1487	0.0746	0.0875	0.2669	0.2309

X-ray Crystallographic Study: Crystals of **1a**, **1b,1c**, **3a**, and **3b** were mounted on top of a thin glass fiber. Data were collected with a Siemens-Stoe AED2 (**1c** and **3b**) and a Bruker-AXS SMART 1000 (**1a**, **1b**, and **3a**) diffractometer with graphite monochromated Mo-$K\alpha$ radiation (λ = 0.71073 Å). The crystal data are summarized in Table 3. Structures were solved by direct methods (SHELX-97) and refined (SHELXL-97) by full-matrix least-squares methods. The positions of the P–H hydrogen atoms were localized in the difference Fourier map and refined. All other hydrogen atoms were introduced at calculated positions (riding model), included in structure factor calculations, and not refined.

CCDC-250811 to -250815 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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