Supplementary Material (ESI) for Chemical Communications

A New Synthetic Entry to Phosphinophosphinidene Complexes. Synthesis and Structural Characterisation of the First Side-on Bonded and the First Terminally Bonded Phosphinophosphinidene Zirconium Complexes [μ-(1,2:2-η-^{t}Bu$_2$P=P){Zr(Cl)Cp$_2$}$_2$] and [{Zr(PPhMe$_2$)Cp$_2$}(η^1-P–P^{t}Bu$_2$)]

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Electronic Supplementary Information

Experimental

All manipulations were performed in flame-dried Schlenk type glassware on a vacuum line. THF and toluene were dried over Na/benzophenone and distilled under nitrogen. Pentane was dried over Na/benzophenone/diglyme and distilled under nitrogen. ^{31}P NMR spectra were recorded on Bruker AC250 and AMX300 spectrometers (external standard 85% H_3PO_4).

^{t}Bu$_2$P–P(SiMe$_3$)Li·2THF was prepared according to literature procedures [G. Fritz, T. Vaahs, J. Härer, *Z. Anorg. Allg. Chem*., 1987, **552**, 11].

Synthesis of [μ-(1,2:2-η-^{t}Bu$_2$P–P){Zr(Cl)cp$_2$}$_2$] (1).

2 [Cp$_2$ZrCl$_2$] + 2 ^{t}Bu$_2$P–P(SiMe$_3$)Li → ^{t}Bu$_2$P–P(SiMe$_3$)$_2$ + 2 LiCl + [μ-(1,2:2-η-^{t}Bu$_2$P=P){Zr(Cl)Cp$_2$}$_2$] (**1**)

A solution of 0.090 g (0.225 mmol) ^{t}Bu$_2$P–P(SiMe$_3$)Li·2THF in 3 ml THF was slowly added at room temperature to a solution of 0.055 g (0.19 mmol) Cp$_2$ZrCl$_2$ in 2 ml THF. The mixture immediately turned brown, was stirred for 1 h and then evacuated at $2\cdot10^{-3}$ Torr for 3 h. The residue was dissolved in about 5 ml THF, filtered and investigated by ^{31}P{^{1}H} NMR. Then the volume was reduced to about 1 ml and the concentrate stored for 3 days at 4^o C. About 0.021 g of dark red crystals of **1** precipitated (32%).

^{31}P NMR of **1** (THF, C$_6$D$_6$, 20^o C) δ = P1 93.9 ppm, d, no P-H coupling; P2 -1.2 ppm, d of m, small ^{3}J(P-H) coupling, ^{1}J(P-P) = -520.6 Hz.

^{1}H NMR of **1** δ = 1.543 d, ^{3}J(P-H) = 13.8 Hz, (C**H**$_3$)$_3$C, (from ^{1}H-^{31}P-COSY experiment).

EI MS (EI = 70 eV, QT = 180°C, DI = 200° C, Mass Spectrometer MAT8200) : m/z 626.9 ($C_{23}H_{36}Cl_2P_2Zr_2$, 0.5%), 592.9(0.5%), 515(1%), 488.9 ($C_{18}H_{31}P_2Zr_2$, 2%), 462.8(8%), 341.9 ($C_{14}H_{22}P_2Zr$, 12%), 293.9 (100%).
Elemental analysis: C 46.8 %, H 5.68 %, $C_{28}H_{38}Cl_2P_2Zr_2$ calc. C 48.74%, H 5.55 %.

The $^{31}P\{^1H\}$ NMR study upon the reaction mixture from the synthesis of **1**.

1) δ = P1 93.9 ppm (d), P2 -1.2 ppm (d), ^1J(P-P) = -520.6 Hz, [μ-(1,2:2-η-^{t}Bu$_2$P2=P1){Zr(Cl)Cp$_2$}$_2$] (**1**).
a) δ = P1 44.6 ppm (d), P2 -200.7 ppm (d), ^1J(P-P) = -399.6 Hz, ^{t}Bu$_2$P1–P2(SiMe$_3$)$_2$.
b) δ(P) 21.0 (s), ^{t}Bu$_2$PH formed *via* splitting of the P-P bond in the ^{t}Bu$_2$P–P group.
c) δ = P1 470.5 ppm (d), P2 72.2 ppm (d), ^1J(P-P) = -331.9 Hz.
d) δ = P1 67.3 ppm (d), P2 -9.1 ppm (d), ^1J(P-P) = -521.6 Hz, probably [(1,2-η-^{t}Bu$_2$P1=P2–SiMe$_3$){Zr(Cl)Cp$_2$}]. A ^{31}P NMR experiment established no direct ^1J(P-H) coupling, a small ^3J(P-H) coupling of P1 and a very small ^3J(P-H) coupling at P2, very good soluble in pentane (dark red solution).
e) δ = P1 19.1 ppm (d), P2 -197.6 ppm (d), ^1J(P-P) = -189.5 Hz, ^1J(P-H) = 189.2 Hz ^{t}Bu$_2$P1–P2(SiMe$_3$)H.
f) δ = P1 54.1 ppm (d), P2 -98.6 ppm (d,d), P3 -178.9 ppm (d,d), ^1J(P1-P2) = -316.6 Hz, ^1J(P2-P3) = -270.1 Hz, ^1J(P1-P3) = 42.0 Hz.

The stability of solutions of **1** in THF is limited. **1** precipitates from the THF reaction mixture, however an attempt to crystallise **1** from a solution in THF resulted in the formation of a significant amount of decomposition products.

Synthesis of [{Zr(PPhMe$_2$)Cp$_2$}(η-P–P^{t}Bu$_2$)] (2).

$[Cp_2ZrCl_2] + 2\ ^tBu_2P–P(SiMe_3)Li + PPhMe_2 \rightarrow\ ^tBu_2P–P(SiMe_3)_2 + [\{Zr(PPhMe_2)Cp_2\}(\eta\text{-}P–P^tBu_2)]$ (**2**) + 2 LiCl

A solution of 0.411 g (1.03 mmol) ^{t}Bu$_2$–P(SiMe$_3$)Li·2THF in 2 ml DME was added to 0.7 ml (5.07 mmol) PhPMe$_2$ and 0.156 g (0.53 mmol) [Cp$_2$ZrCl$_2$] in 2 ml DME at about -35 °C. A dark red solution formed immediately. After stirring for 1 h, the reaction mixture was studied with $^{31}P\{1H\}$ NMR, than the solvent was evaporated, the residue dissolved in 8 ml pentane, filtered, and the brown solution concentrated to about 4 ml. While standing for 5 days, the color of the solution turned to dark green and

finally to dark blue, and dark blue crystals of **2** (shaped like blocks) precipitated (0.12 g, 44% yield). An attempt to dissolve **2** in THF-d_8 led to a partial decomposition of this compound.

$^{31}P\{^1H\}$ NMR of [{Zr(P3PhMe$_2$)Cp$_2$}(η-P1–P2^{t}Bu$_2$)] (**2**); δ(P1) 728.2 (d,d), δ(P2) 64.6 (d), δ(P3) 6.5 (d), ^{1}J(P1-P2) = -283.7 Hz, ^{2}J(P1-P3) = 15.3 Hz.

Anal. Calc. C 58.29%; H 7.35%. Found C 58.9%; H 7.7%.

The $^{31}P\{^1H\}$ NMR study upon the reaction mixture from the synthesis of **2**.

2) δ(P1) 728.2 (d,d), δ(P2) 64.6 (d), δ(P3) 6.5 (d), ^{1}J(P1-P2) -283.7 Hz, ^{2}J(P1-P3) 15.3 Hz; [{Zr(P3PhMe$_2$)Cp$_2$}(η-P1–P2^{t}Bu$_2$)] (**2**)

a) δ = P1 44.3 ppm (d), P2 -200.6 ppm (d), ^{1}J(P-P) = -400.5 Hz, ^{t}Bu$_2$P1–P2(SiMe$_3$)$_2$.

b) δ(P) 21.0 (s), ^{t}Bu$_2$PH.

c) δ(P1) 468.7 (d), δ(P2) 72.8 (d), ^{1}J(P-P) = -331.9 Hz.

g) δ(P1) 47.6 (d), δ(P2) -242.3 ppm (d), ^{1}J(P-P) = -274.7 Hz; ^{t}Bu$_2$P1–P2(SiMe$_3$)Li (substract).

h) δ(P1) 560.4 (d), δ(P2) 53.7 (d), ^{1}J(P-P) = -339.5 Hz.

i) δ(P1) 55.7 (d), δ(P2) -123.9 (d,d), δ(P3) -197.6 (d,d), ^{1}J(P1-P2) = -316.6 Hz, ^{1}J(P2-P3) = -297.5 Hz, ^{1}J(P1-P3) = 28.3 Hz. No ^{1}J(P-H) coupling was observed. This data set is similar to **f** (synthesis of **1**).

Although solutions of **2** in DME are indefinitely stable in the presence of an excess of PPhMe$_2$ at ambient temperature, an attempt to dissolve **2** in THF-d_8 resulted in a decomposition of a part of the compound and formation of a significant amount of free PPhMe$_2$ together with a small amount of ^{t}Bu$_2$PH. It's a noteworthy property of **2** how easily it looses the tertiary phosphane ligand and undergoes further decompositions.

Crystal data of 1: $C_{28}H_{38}Cl_2P_2Zr_2$; T = 170(2) K; wavelength 71.073 pm (Mo Kα); monoclinic, $P2_1/n$ (No. 14), a =1074.89(4) pm, b = 2394.32(10) pm, c = 1155.29(5) pm, β = 102.026(3) °; Z = 4; absorption coefficient 1.026 mm^{-1}; crystal size 0.4x 0.35x0.15 mm^3; θ range for data collection 1.70 - 25.50 °, reflections collected = 15035, unique reflections = 5063; completeness (to θ = 25.50 °) = 93.8%; data = 4713, restraints = 0, parameters = 313; final R indices [I>2σ(I)] R1 = 0.0206, wR2 = 0.0530; R indices (all data) R1 = 0.0228, wR2 = 0.0539 (all data); H atoms refined as riding on the respective heavy atoms; diffractometer Stoe IPDS. **CCDC 225538**

Crystal data of 2: $C_{26}H_{39}P_3Zr$; T = 150(0.2) K; wavelength 71.073 pm (Mo Kα); triclinic, $P\bar{1}$ (No. 2), a = 931.2(2) pm, b = 1157.4(2) pm, c = 2522.0(5) pm, α= 78.91(3)º, β = 87.11(3)º; γ = 85.26(3)º, Z = 4; Two molecules present in the asymmetric unit, absorption coefficient 0.606 mm^{-1}; crystal size 0.5x 0.4x0.3 mm^3; θ range for data collection 1.65 - 25.50º, reflections collected = 10154, unique reflections

= 9876; completeness (to θ = 25.50 °) = 100.00%; data = 9876, restraints = 0, parameters = 526; final R indices [I>2σ(I)] R1 = 0.1011, wR2 = 0.2533; R indices (all data) R1 = 0.1659, wR2 = 0.3115 (all data); all H atoms refined isotropically as riding on heavy atoms; diffractometer KUMA KM4. **CCDC 232586**

Table 1. Selected bond lengths [A] and angles [deg] for both molecules of **2**.

first molecule:		
	Zr(1)-P(1)	2.488(3)
	Zr(1)-C(10)	2.491(13)
	Zr(1)-C(6)	2.502(13)
	Zr(1)-C(7)	2.503(13)
	Zr(1)-C(8)	2.512(13)
	Zr(1)-C(9)	2.514(14)
	Zr(1)-C(5)	2.524(12)
	Zr(1)-C(1)	2.524(11)
	Zr(1)-C(2)	2.532(12)
	Zr(1)-C(4)	2.536(13)
	Zr(1)-C(3)	2.548(13)
	Zr(1)-P(3)	2.734(3)
	P(1)-P(2)	2.200(5)
	P(2)-C(23)	1.909(12)
	P(2)-C(19)	1.949(13)
	P(3)-C(11)	1.822(12)
	P(3)-C(13)	1.836(12)
	P(3)-C(12)	1.836(12)
second molecule:		
	Zr(2)-C(39)	2.478(14)
	Zr(2)-P(4)	2.482(3)
	Zr(2)-C(38)	2.500(14)
	Zr(2)-C(35)	2.504(14)
	Zr(2)-C(31)	2.509(14)
	Zr(2)-C(37)	2.508(13)
	Zr(2)-C(32)	2.521(14)
	Zr(2)-C(36)	2.528(12)
	Zr(2)-C(34)	2.533(13)
	Zr(2)-C(30)	2.536(14)
	Zr(2)-C(33)	2.541(14)
	Zr(2)-P(6)	2.738(3)
	P(4)-P(5)	2.215(5)
	P(5)-C(52)	1.913(13)
	P(5)-C(48)	1.931(12)
	P(6)-C(47)	1.813(13)
	P(6)-C(40)	1.827(13)
	P(6)-C(46)	1.835(13)
first molecule:		
	P(1)-Zr(1)-C(10)	141.7(4)
	P(1)-Zr(1)-C(6)	115.4(4)
	P(1)-Zr(1)-C(7)	87.7(3)
	P(1)-Zr(1)-C(8)	91.1(3)
	P(1)-Zr(1)-C(9)	122.6(3)
	P(1)-Zr(1)-C(5)	77.9(3)
	P(1)-Zr(1)-C(1)	103.8(3)
	P(1)-Zr(1)-C(2)	131.3(3)
	P(1)-Zr(1)-C(4)	86.3(3)
	P(1)-Zr(1)-C(3)	117.6(4)
	P(1)-Zr(1)-P(3)	88.49(10)
	C(10)-Zr(1)-P(3)	103.7(4)
	C(6)-Zr(1)-P(3)	131.9(3)

C(7)-Zr(1)-P(3)	118.4(3)
C(8)-Zr(1)-P(3)	86.0(3)
C(9)-Zr(1)-P(3)	77.7(3)
C(5)-Zr(1)-P(3)	114.3(3)
C(1)-Zr(1)-P(3)	132.9(3)
C(2)-Zr(1)-P(3)	108.8(3)
C(4)-Zr(1)-P(3)	83.4(3)
C(3)-Zr(1)-P(3)	80.4(3)
P(2)-P(1)-Zr(1)	115.53(16)
C(11)-P(3)-Zr(1)	115.7(4)
C(13)-P(3)-Zr(1)	118.0(4)
C(12)-P(3)-Zr(1)	115.8(4)
second molecule:	
C(39)-Zr(2)-P(4)	140.6(4)
P(4)-Zr(2)-C(38)	122.9(3)
P(4)-Zr(2)-C(35)	114.7(4)
P(4)-Zr(2)-C(31)	101.2(4)
P(4)-Zr(2)-C(37)	91.5(3)
P(4)-Zr(2)-C(32)	77.6(3)
P(4)-Zr(2)-C(36)	87.8(3)
P(4)-Zr(2)-C(34)	120.4(4)
P(4)-Zr(2)-C(30)	130.3(4)
P(4)-Zr(2)-C(33)	88.6(4)
C(39)-Zr(2)-P(6)	105.2(4)
P(4)-Zr(2)-P(6)	88.58(11)
C(38)-Zr(2)-P(6)	79.0(3)
C(35)-Zr(2)-P(6)	132.9(4)
C(31)-Zr(2)-P(6)	132.5(3)
C(37)-Zr(2)-P(6)	87.7(3)
C(32)-Zr(2)-P(6)	110.2(3)
C(36)-Zr(2)-P(6)	119.4(3)
C(34)-Zr(2)-P(6)	81.9(3)
C(30)-Zr(2)-P(6)	111.3(4)
C(33)-Zr(2)-P(6)	81.3(4)
P(5)-P(4)-Zr(2)	116.87(17)
C(47)-P(6)-Zr(2)	116.1(5)
C(40)-P(6)-Zr(2)	118.5(4)
C(46)-P(6)-Zr(2)	115.7(4)