Crystal Structure of $[Zr(dmpe)\{CH_2Si(CH_3)_3\}_4]$ (dmpe = $PMe_2CH_2CH_2PMe_2$).[†] Evidence in Support of the Postulation for the Presence of an Agostic Hydrogen

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$[Zr\{CH_2Si(CH_3)_3\}_4]$ reacts with $PMe_2CH_2CH_2PMe_2$ (dmpe) to form the title compound, $[Zr(dmpe)\{CH_2Si(CH_3)_3\}_4]$. The complex belongs to the triclinic space group $P\bar{1}$, with cell constants a = 9.999(6), b = 10.638(7), c = 19.927(6) Å, α = 76.54(4), β = 83.05(4), γ = 62.29(4)°, and Z = 2. Least-squares refinement based on 3 421 observed reflections led to a final R of 0.063. There is direct evidence for a significant interaction of an α-hydrogen with the zirconium atom. The four Zr–C lengths fall in the pattern: very short [2.215(9) Å], short [2.27(1) Å], and normal [2.312(8), 2.322(8) Å]. The Zr–C–Si angles also reflect the trend in bond lengths with values of 141.5(6), 137.8(6), 130.0(4), and 128.6(4)°, respectively. The hydrogen atoms were located, and the closest Zr $\cdots$ H approach, 2.48 Å, is for a hydrogen atom bonded to the carbon nearest the zirconium.

Recently, Wilkinson and co-workers[1] reported a series of alkylphosphine zirconium compounds. One compound, [1,2-bis(dimethylphosphino)ethane]tetrakis(trimethylsilylmethyl)-zirconium(IV), $[Zr(dmpe)\{CH_2Si(CH_3)_3\}_4]$, prepared *via* the alkylation of $[Zr(dmpe)_2Cl_4]$, showed weak features in the i.r. spectrum which were attributed to distorted alkyl groups. As a result, the authors postulated an interaction between the zirconium atom and the α-protons of an alkyl group. Unfortunately, their synthetic method failed to provide crystals suitable for an *X*-ray diffraction structure analysis.

Working independently we have found that $[Zr(dmpe)\{CH_2Si(CH_3)_3\}_4]$ can also be prepared by the addition of dmpe to a heptane solution of $[Zr\{CH_2Si(CH_3)_3\}_4]$. Slow cooling of the heptane solution affords well formed needle crystals. We have undertaken a single-crystal *X*-ray structure determination and wish to report corroborating evidence for the postulation of the presence of an agostic hydrogen in the molecule.

Results and Discussion

The structure of the molecule is shown in the Figure. We find that there is structural evidence for a substantial interaction of zirconium with one of the α-hydrogen atoms. This is reflected by inference in the pattern of Zr–C bond lengths: 2.215(9), 2.27(1), 2.312(8), and 2.322(8) Å [and angles at the corresponding carbon atoms: 141.5(6), 137.8(6), 130.0(4), and 128.6(4)°]. The expected value for Zr–C is 2.278(4) Å and for Zr–C–Si, 134.5(4)° based on the structure of $[Zr(\eta^5\text{-}C_5H_5)_2\{CH_2Si(CH_3)_3\}_2]$.[2] Thus, the parameters associated with C(1) are indicative of an attraction between the zirconium atom and a hydrogen atom on C(1).[3] The angles P(2)–Zr–C(1) 101.3(3) and P(1)–Zr–C(4) 83.6(3)° also suggest an agostic hydrogen interaction. However, more direct evidence is provided by the locations of the hydrogen atoms in question. The Zr $\cdots$ H[C(1)] separations are 2.48 and 2.70 Å. Those found for the hydrogens related to the second shortest Zr–C bond are 2.55 annd 2.66 Å, while the remaining ones are found at 2.60, 2.80, 2.80, and 2.97 Å. The shortest Zr $\cdots$ H compares favourably with the Ti $\cdots$ H of 2.29 Å found in $[Ti(dmpe)(Et)Cl_3]$[4] after a correction of 0.13 Å for the difference in metallic radii.[5] The pattern of bond lengths and angles is therefore consistent with a significant Zr $\cdots$ H interaction.

Table 1. Selected bond lengths (Å) and angles (°) for $[Zr(dmpe)\{CH_2\text{-}Si(CH_3)_3\}_4]$

Zr–P(1)	2.876(2)	Zr–P(2)	2.972(2)
Zr–C(1)	2.215(9)	Zr–C(2)	2.322(8)
Zr–C(3)	2.312(8)	Zr–C(4)	2.27(1)
P(1)–C(17)	1.80(1)	P(1)–C(19)	1.808(9)
P(1)–C(20)	1.83(1)	P(2)–C(18)	1.88(1)
P(2)–C(21)	1.80(1)	P(2)–C(22)	1.79(1)
Si(1)–C(1)	1.84(1)	Si(1)–C(5)	1.84(1)
Si(2)–C(2)	1.831(8)	Si(1)–C(8)	1.86(1)
Si(3)–C(3)	1.848(8)	Si(3)–C(11)	1.86(1)
Si(4)–C(4)	1.83(1)	Si(4)–C(14)	1.82(2)
P(1)–Zr–P(2)	70.46(8)	P(1)–Zr–C(1)	171.5(3)
P(2)–Zr–C(1)	101.3(3)	P(1)–Zr–C(2)	80.1(2)
P(2)–Zr–C(2)	76.8(2)	C(1)–Zr–C(2)	99.7(4)
P(1)–Zr–C(3)	79.1(2)	P(2)–Zr–C(3)	75.2(2)
C(1)–Zr–C(3)	97.1(4)	C(2)–Zr–C(3)	147.0(3)
P(1)–Zr–C(4)	83.6(3)	P(2)–Zr–C(4)	154.0(3)
C(1)–Zr–C(4)	104.7(4)	C(2)–Zr–C(4)	101.6(3)
C(3)–Zr–C(4)	101.2(4)	Zr–P(1)–C(17)	110.9(4)
Zr–P(1)–C(19)	118.6(3)	Zr–P(2)–C(18)	106.1(4)
Zr–P(1)–C(20)	119.2(4)	Zr–C(1)–Si(1)	141.5(6)
Zr–P(2)–C(21)	121.8(4)	Zr–C(2)–Si(2)	128.6(4)
Zr–C(3)–Si(3)	130.0(4)	Zr–C(4)–Si(4)	137.8(6)

Experimental

Crystals of $[Zr(dmpe)\{CH_2Si(CH_3)_3\}_4]$ were sealed under Ar in glass capillaries. Crystal data: $C_{22}H_{60}P_2Si_4Zr$, M = 589.2, triclinic, a = 9.999(6), b = 10.638(7), c = 19.927(6) Å, α = 76.54(4), β = 83.05(4), γ = 62.29(4)°, U = 1 825 Å^3 space

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[*] [1,2-Bis(dimethylphosphino)ethane](trimethylsilylmethyl-*C*,H^α)tris-(trimethylsilylmethyl)zirconium(IV).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx.

Table 2. Fractional atomic co-ordinates for [Zr(dmpe){$CH_2Si(CH_3)_3$}$_4$]

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Zr	0.152 88(8)	0.107 42(9)	0.248 35(4)
P(1)	−0.134 9(3)	0.126 0(3)	0.303 0(1)
P(2)	−0.094 6(3)	0.361 6(3)	0.165 7(1)
Si(1)	0.414 8(3)	0.192 5(3)	0.108 8(1)
Si(2)	0.155 5(3)	0.299 2(3)	0.383 5(1)
Si(3)	0.181 8(3)	−0.172 9(3)	0.153 4(1)
Si(4)	0.431 8(4)	−0.225 9(3)	0.369 3(2)
C(1)	0.355(1)	0.117(2)	0.192 8(6)
C(2)	0.076 4(9)	0.296 8(9)	0.305 9(4)
C(3)	0.092 2(9)	0.013 5(9)	0.169 7(4)
C(4)	0.247(1)	−0.088(1)	0.335 8(5)
C(5)	0.315(1)	0.201(1)	0.035 1(5)
C(6)	0.388(2)	0.378(1)	0.109(1)
C(7)	0.620(1)	0.075(1)	0.098 0(7)
C(8)	0.130(1)	0.182(1)	0.463 8(5)
C(9)	0.361(1)	0.246(2)	0.369 0(6)
C(10)	0.066(2)	0.484(1)	0.402 9(6)
C(11)	0.386(1)	−0.232(1)	0.131 7(7)
C(12)	0.100(1)	−0.186(1)	0.078 0(5)
C(13)	0.162(2)	−0.312(1)	0.228 6(6)
C(14)	0.587(2)	−0.757(2)	0.307 3(8)
C(15)	0.493(2)	−0.189(2)	0.440 4(7)
C(16)	0.446(2)	−0.412(2)	0.387(2)
C(17)	−0.284(1)	0.258(1)	0.246 2(6)
C(18)	−0.274(1)	0.388(1)	0.216 0(6)
C(19)	−0.196(1)	0.176(1)	0.386 2(5)
C(20)	−0.168(1)	−0.032(1)	0.314 0(7)
C(21)	−0.142(1)	0.358(1)	0.082 5(5)
C(22)	−0.110(1)	0.541(1)	0.151 9(6)
H(1A)	0.392(1)	0.127(2)	0.242 3(6)
H(1B)	0.392(1)	0.048(2)	0.160 4(6)
H(2A)	0.106 3(9)	0.360 2(9)	0.264 9(4)
H(2B)	−0.032 9(9)	0.348 6(9)	0.300 8(4)
H(3A)	0.104 9(9)	0.079 7(9)	0.123 2(4)
H(3B)	−0.018 4(9)	0.053 2(9)	0.157 9(4)
H(4A)	0.214(1)	−0.039(1)	0.378 0(5)
H(4B)	0.218(1)	−0.149(1)	0.314 6(5)

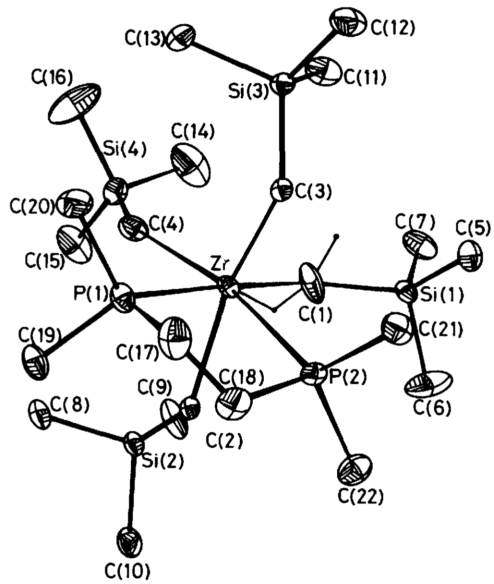

Figure. View of [Zr(dmpe){$CH_2Si(CH_3)_3$}$_4$] including the hydrogen atoms bonded to C(1)

group $P\bar{1}$, D_c = 1.12 g cm^{-3} for $Z = 2$, $F(000) = 636$, Mo-K_α radiation (λ = 0.710 69 Å). Least-squares refinement based on 3 421 observed reflections led to a final $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0.063$. The details of data collection and refinement are as given by Holton *et al.*[6] The hydrogen atoms were clearly visible on the final difference Fourier map. The co-ordinates were refined for one cycle and then allowed to ride on the bonded carbon atom. An empirical absorption correction was done according to Churchill and Hollander.[7] Anisotropic thermal parameters were used for all the non-hydrogen atoms. Selected bond lengths and angles are given in Table 1 and atomic co-ordinates in Table 2.

Acknowledgements

D. C. H. thanks the Chevron Research Company for supporting this work. J. L. A. is grateful to the National Science Foundation for support.

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Received 3rd *February* 1986; *Paper* 6/227