

Synthesis and structure of the edge-bridged open zirconocene, $Zr(6,6\text{-dmch})_2(PMe_3)_2$ (dmch = dimethylcyclohexadienyl), and its imine coupling product

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Abstract

The reaction of $ZrCl_4$ with four equivalents of the 6,6-dimethylcyclohexadienyl anion ($6,6\text{-dmch}^-$) in the presence of PMe_3 leads to the 18 electron $Zr(6,6\text{-dmch})_2(PMe_3)_2$. This complex was found to undergo a coupling reaction with two equivalents of $PhCH=NPh$, such that the couplings involved the two termini of the same dienyl ligand, yielding a formal $Zr(\eta^5\text{-dienyl})(\eta^3\text{-allyl})(\pi\text{-amide})_2$ complex. Both metal complexes have been structurally characterized.

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Keywords: Zirconium; Cyclohexadienyl; Trimethylphosphine; π -Amide; Imine coupling

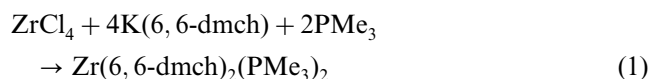
1. Introduction

Zirconium pentadienyl chemistry has recently appeared to offer substantial promise. In related titanium chemistry, it has already been established that pentadienyl ligands may be both more strongly bound and more reactive than cyclopentadienyl [1]. These favorable features should be enhanced for zirconium, whose larger size should lead to improved overlap and bonding with the wide, open-edge dienyl ligands, while its more electropositive nature should also lead to higher reactivity. Perhaps even more important, although η^5 coordination by non-edge-bridged dienyl ligands has appeared quite limited if not unknown for tetravalent metal centers [2], it has recently been demonstrated that $Zr(IV)$ does indeed form η^5 -pentadienyl complexes, thereby allowing for the first general studies of higher valent metal pentadienyl chemistry [3]. We have therefore investigated the synthesis and reaction chemistry of an edge-bridged open zirconocene incorporating the 6,6-dmch (dmch = dimethylcyclohexadienyl) ligand.

2. Results and discussion

2.1. Synthetic and spectroscopic data

The reaction of $ZrCl_4$ with four equivalents of the 6,6-dimethylcyclohexadienyl anion in the presence of PMe_3 was found to lead to the open zirconocene complex, $Zr(6,6\text{-dmch})_2(PMe_3)_2$ (Eq. (1)).

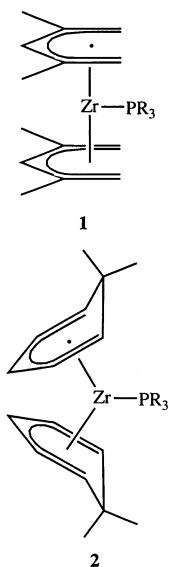


In this reaction, as in the preparations of other open and half-open zirconocenes [3,4], two equivalents of the dienyl anion serve as reducing agents, thereby leading to the formation of the appropriate $Zr(II)$ complexes. However, the formation of an 18 electron bis(phosphine) complex contrasts with the situation for the 2,4- C_7H_{11} (C_7H_{11} = dimethylpentadienyl) ligand, for which 16 electron $Zr(2,4\text{-}C_7H_{11})_2(PR_3)_2$ complexes result, e.g. **1** [4a]. Such a difference is counter-intuitive, given that other data clearly demonstrate that 6,6-dmch and other edge-bridged dienyl ligands are substantially more sterically demanding than 2,4- C_7H_{11} [5]. What appears to be happening here is that the addition of a single ligand to a $M(6,6\text{-dmch})_2$ unit results in a particularly large steric deformation, cf. **2**. This may then open the

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complex up enough that relatively little additional distortion is required to accommodate a second phosphine. For a complex such as **1**, however, one observes a more compact arrangement of the ligands, reflecting a lesser degree of steric problems in the incorporation of the first ligand. As a result, it is the second incorporation of a ligand in a $M(2,4-C_7H_{11})_2$ complex which is generally sterically prohibitive.



The structure of $Zr(6,6-dmch)_2(PMe_3)_2$ is depicted in Fig. 1, and pertinent bonding parameters are provided

Table 1

Crystallographic parameters for $Zr(6,6-dmch)_2(PMe_3)_2$ and $Zr(\eta^5-dmch)\{\eta^5-dmch-[PhC(H)NPh]_2\}$

Empirical formula	$C_{22}H_{40}P_2Zr$	$C_{42}H_{44}N_2Zr$
Formula weight	457.70	668.01
Temperature (K)	200(1)	200(1)
λ (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
Unit cell dimensions		
a (Å)	9.9470(2)	11.8340(3)
b (Å)	11.3701(2)	18.7415(5)
c (Å)	21.1692(4)	15.3913(3)
α (°)	94.3089(12)	97.8557(14)
β (°)		
γ (°)		
Volume (Å ³); Z	2387.44(8); 4	3381.55(14); 4
Density (Calc.)	1.273	1.312
Absolute coefficient (cm ⁻¹)	5.98	3.57
θ Range (°)	2.8–27.5	3.5–27.5
Limiting indices	$-12 \leq h \leq 12$	$-15 \leq h \leq 15$
	$-14 \leq k \leq 13$	$-24 \leq k \leq 22$
	$-27 \leq l \leq 27$	$-19 \leq l \leq 19$
Reflection collected	9078	13 188
Independent reflections; $n: I > n\sigma(I)$	5422; 2	7713; 2
$R(F)$	0.0264	0.0376
$R_w(F^2)$	0.0595	0.0735
Max/min diff. Fourier Peak (e Å ⁻³)	0.38/–0.30	0.50/–0.38

in Table 1. The complex may be seen to possess noncrystallographic C_2 symmetry (**3**), quite unlike other

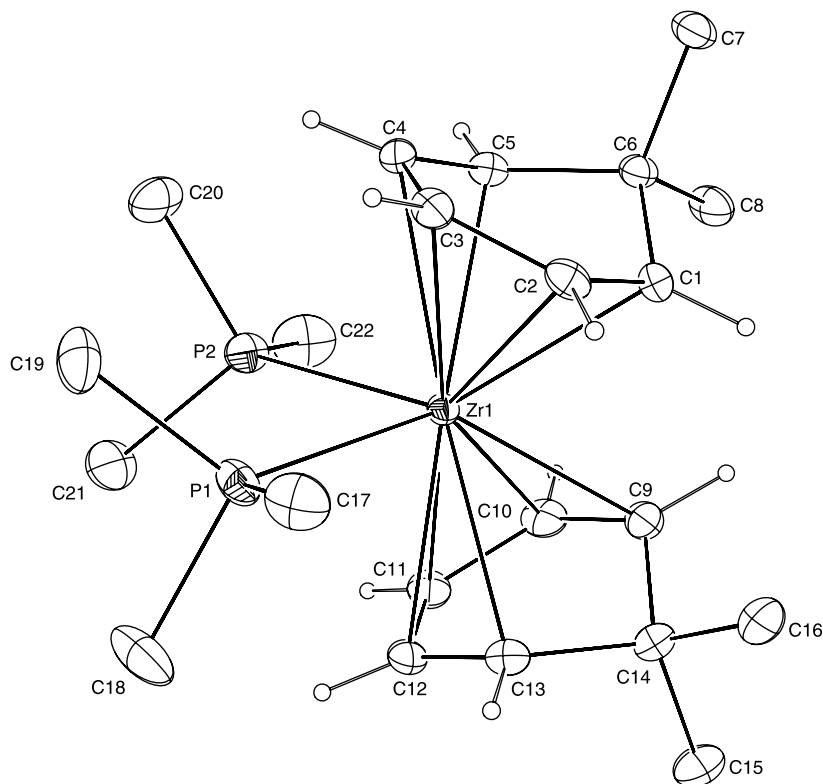
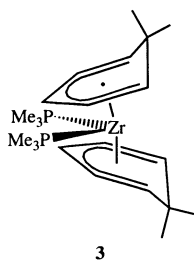


Fig. 1. **1**: Solid state structure of $Zr(6,6-dmch)_2(PMe_3)_2$ (**3**).

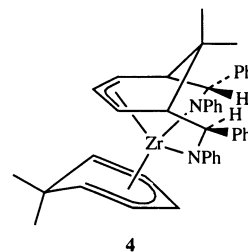
bis(ligand) complexes of open and half-open metallocenes, with the exception of $\text{Zr}(\text{C}_5\text{H}_7)_2(\text{dmpe})$ [6]. In this case (**3**), one phosphine ligand is located opposite to the electronically open edge of the diene ligand, the other to the side, analogous to the related $\text{Zr}(\text{C}_5\text{H}_5)(2,6,6\text{-tmch})(\text{PMe}_3)_2$. The interplanar angle of 48.3° for the diene ligands, and the P–Zr–P angle of $88.68(2)^\circ$ are similar to their counterparts in $\text{Zr}(\text{C}_5\text{H}_5)(2,6,6\text{-tmch})(\text{PMe}_3)_2$, 47.6 and $88.38(10)^\circ$, but differ more from the values of 32.3 and $74.7(1)^\circ$ found for $\text{Zr}(\text{C}_5\text{H}_7)_2(\text{dmpe})$. The average Zr–C distance of 2.502 Å may be compared to Zr–C(Cp) and Zr–C(2,6,6-tmch) distances of 2.529 and 2.466 Å, respectively, in $\text{Zr}(\text{C}_5\text{H}_5)(2,6,6\text{-tmch})(\text{PMe}_3)_2$. The lengthening of the Zr–C bond distances for the open diene ligands in the former complex is as expected, based upon the greater steric demands of these ligands, and possibly also due to their greater competition with each other for bonding to the metal center. The fact that the Zr–C(6,6-dmch) bonds in **3** are still shorter than the Zr–C(Cp) bonds in the 2,6,6-tmch complex reflects the stronger bonding interactions that low valent metal centers typically generate with open diene ligands, as opposed to C_5H_5 [1,2]. Also in accord with the proposed increased steric crowding for **3** is its Zr–P distance of 2.738(2) Å, as compared to values of 2.664(4) and 2.725(3) Å in the 2,6,6-tmch complex.



3

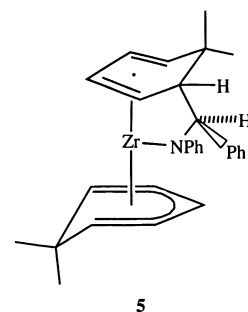
The divalent $\text{Zr}(6,6\text{-dmch})_2(\text{PMe}_3)_2$ complex reacts with $\text{PhCH}=\text{NPh}$, leading to the incorporation of two equivalents of imine and loss of the PMe_3 ligands. Due to the presence of two reactive dmch ligands, two possible general reaction paths could be followed. Either each dmch ligand could undergo a single coupling, or one could undergo both couplings. While in the latter case one would expect the couplings to occur with the diene termini (i.e. 1,5 dicoupling), an alternative 1,4 dicoupling could not be ruled out entirely, as such processes have been observed for dmch/ketone couplings, for both titanium and zirconium complexes [7]. However, it now appears that 1,4 dicouplings are promoted by an initial ketone coupling, which leads to an alkoxide ligand which can serve as a 5 electron donor [8]. In fact, NMR spectroscopic data for the imine coupling product, particularly the observation of two signals for protons on the central carbon atoms of the original diene ligands, suggested that a 1,5 dicoupling

process has occurred, involving a single dmch ligand, the product complex then being **4**.



4

A single crystal structural study of **4** has been carried out (Table 2, Fig. 2). One can see that one ligand has indeed undergone two couplings, thereby demonstrating that for the mono(coupling) intermediate **5**, it is the diene ligand which is more reactive. This is in accord with other results [9], and reflects the fact that the formal diene fragment in **5** is expected to be more appropriately described as an enediyl ligand, **6**, with nearly a full negative charge on the diene/enediyl termini [10].



5

The structural result also confirms the product to be an uncommon example of a high ($\geq +4$) valent η^5 -pentadienyl metal complex [11]. Such species generally

Table 2
Selected bond distances (Å) and angles ($^\circ$) for $\text{Zr}(6,6\text{-dmch})_2(\text{PMe}_3)_2$

Bond distances (Å)			
Zr–P1	2.7349(5)	Zr–P2	2.7418(5)
Zr–C1	2.4758(16)	Zr–C9	2.4833(17)
Zr–C2	2.4669(16)	Zr–C10	2.4614(17)
Zr–C3	2.5210(17)	Zr–C11	2.5209(17)
Zr–C4	2.5251(16)	Zr–C12	2.5254(17)
Zr–C5	2.5114(16)	Zr–C13	2.5209(17)
C1–C2	1.404(2)	C9–C10	1.406(3)
C2–C3	1.415(3)	C10–C11	1.415(3)
C3–C4	1.395(3)	C11–C12	1.397(3)
C4–C5	1.410(2)	C12–C13	1.409(3)
Bond angles ($^\circ$)			
C1–C2–C3	118.76(16)	C9–C10–C11	118.52(18)
C2–C3–C4	118.94(16)	C10–C11–C12	119.08(18)
C3–C4–C5	120.87(16)	C11–C12–C13	120.83(17)
C4–C5–C6	116.09(15)	C12–C13–C14	116.18(18)
C1–C6–C5	103.71(14)	C9–C14–C13	103.49(15)
C2–C1–C6	118.68(16)	C10–C9–C14	118.89(17)
P1–Zr–P2	88.683(16)		

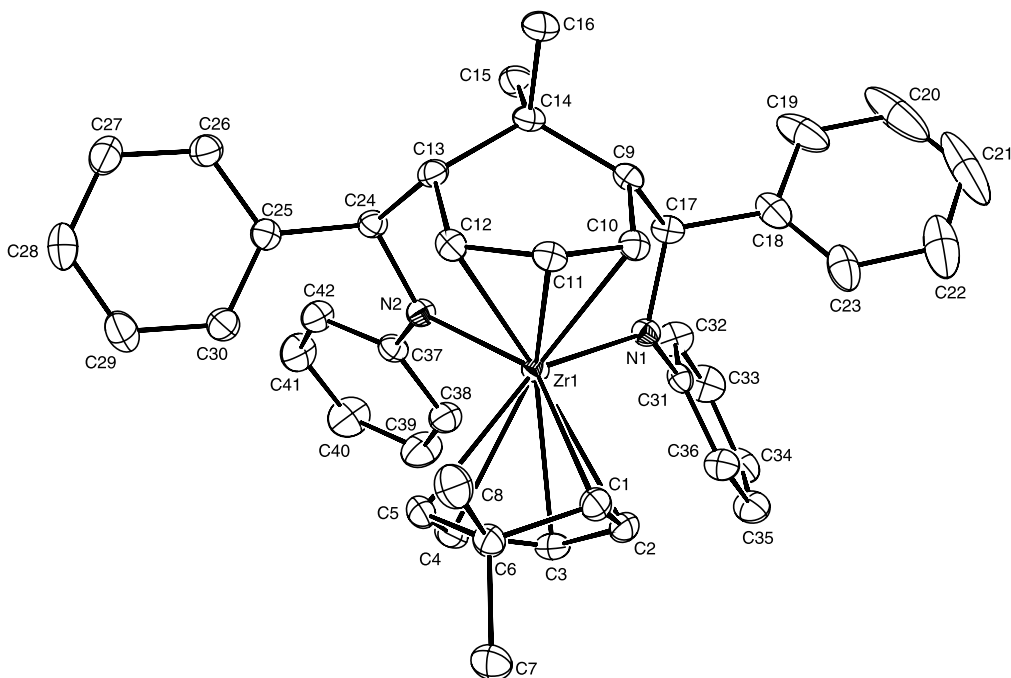
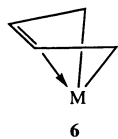


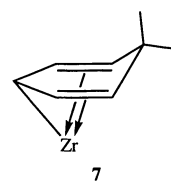
Fig. 2. Perspective view of the bis(imine) coupling product, 4.

appear to be unstable due to the strong δ acidities of pentadienyl ligands [2]. Indeed, most of the known higher valent pentadienyl complexes incorporate potentially π -donating nitrogen centers, which should enhance δ backbonding by making the metal center more electron rich. However, two tetravalent zirconium pentadienyl complexes without π -donating ligands have been reported, one incorporating the 6,6-dmch ligand, the other 2,4- C_7H_{11} (C_7H_{11} = dimethylpentadienyl) [3]. A common structural observation for these species is a particularly short Zr–C bond for the central dienyl carbon atom. In this case, the Zr–C3 distance is 2.439(2) Å, which may be compared to the progressively longer average Zr–C(2,4) and Zr–C(1,5) distances, 2.524 and 2.775 Å. This is consistent with early calculations which indicated that negative charge in a dienyl anion would be greatest for the central carbon atom [12]. As would be expected from a strong M–C3 interaction, one observes substantially shorter distances for the external dienyl C–C bonds (average 1.364(2) Å) versus the internal ones (average 1.423(2) Å), in accord with 7.



The strong Zr–C3 interaction also leads to an otherwise usual pattern of substituent tilts. The tilts for H(1,2,4,5) follow the usual pattern, ranging from 11.3 to 13.3° (average, 12.3°), toward the metal center [13]. In contrast, that for H3 is 3.6°, away from the

metal center. Such a tilt would be in accord with a partial sp^3 hybridization on C3. In contrast, a far different pattern was observed for $Zr(6,6\text{-dmch})_2(PMe_3)_2$, in which the tilts for the formally charged carbon atoms (1,3,5 positions) averaged 1.5° away from the metal center, while those for the 2 and 4 positions averaged 5.4° toward the metal center. The generally substantially greater tilts for the tetravalent complex likely reflect the smaller size of Zr(IV) compared to Zr(II).



Although the allyl coordination is asymmetric, it is clear that the Zr–C distances for the terminal carbon atoms are shorter than that for the formally uncharged central carbon atom. Such a trend is opposite that seen for transition metal complexes in general [14], but consistent with the presence of a more ionic interaction. As with the dienyl ligand, the substituents are displaced out of the allyl plane, the tilts for H10–12 being 7.4, 15.2, and 9.2°, all toward the metal center, while C9 and C13 experience tilts of 25.0 and 27.2°, respectively, in the opposite direction. The Zr–N coordination is also somewhat asymmetric, at least in the solid state. The angles about each nitrogen atom are consistent with formal sp^2 hybridization, indicating π -amide donation and a formal 18 electron configuration for zirconium.

3. Conclusions

Despite the generally greater steric demands of 6,6-dmch compared to the 2,4-C₇H₁₁ ligand, attempts to prepare an edge-bridged open zirconocene lead to the 18 electron Zr(6,6-dmch)₂(PMe₃)₂, rather than to a 16 electron mono(phosphine) complex. This species reacts with PhCH=NPh, resulting in the incorporation of two equivalents of the imine. Each imine coupled to one end of the same 6,6-dmch ligand, thereby leading to a still uncommon example of a higher valent metal pentadienyl complex. Structural parameters, particularly Zr–C bond distances and dienyl substituent tilts, differ dramatically from those exhibited by lower valent complexes, reflecting in part apparently poorer overlap between the dienyl ligand and the contracted metal orbitals. Notably, Zr(6,6-dmch)₂(PMe₃)₂ has also been found to serve as a useful precursor to a number of other Zr(IV) complexes of the general type Zr(6,6-dmch)₂(X)₂ [15], which are allowing for the first studies of the chemistry of pentadienyl analogues of the ubiquitous M(C₅H₅)₂X₂ complexes.

4. Experimental

All reactions were carried out under a nitrogen atmosphere in Schlenk apparatus. Ether and hydrocarbon solvents were distilled from sodium-benzophenone under a nitrogen atmosphere. Published procedures were used for the synthesis of 6,6-dimethyl-1,3-cyclohexadiene [16]. K(6,6-dmch) was prepared according to a general method for pentadienyl anions [5a,17]. Elemental analyses were obtained from E&R Microanalytical Laboratories and Desert Analytics.

4.1. Zr(η⁵-dmch)₂(PMe₃)₂ (3)

To a slurry of ZrCl₄ (1.60 g, 6.87 mmol) in 30 ml THF cooled to –78° was added PMe₃ (1.40 ml, 13.7 mmol) and the mixture was stirred for 5 min. K(6,6-dmch) (4.00 g, 27.5 mmol) in 30 ml THF was added dropwise via a pressure equalizing addition funnel. The reaction mixture turned dark red immediately and was slowly warmed to room temperature, and thereafter allowed to stir for 2 h. Next, the solvent was removed in vacuo to give a black–red solid. Extraction of the solid with ca. 220 ml of hexanes and filtration through a Celite pad on a medium frit gave a red filtrate. Concentration in vacuo of the filtrate to ca. 15 ml and cooling to –30° overnight gave 1.90 g (60%) of an air-sensitive red solid.

¹H-NMR (benzene-*d*₆, ambient): δ 5.59 (tt, 2H, H_{3,11}), 5.10 (t, 4H, H_{2,4,10,12}, *J* = 6.9 Hz), 3.11 (dd, 4H, H_{1,5,9,13}, *J* = 1.2 Hz, 6.3 Hz), 1.33 (s, 6H, endo CH₃), 0.66 (s, 6H, exo CH₃), 0.60 (d, 18H, 2 PMe₃, *J* = 3.9 Hz).

¹³C-NMR (benzene-*d*₆, ambient): δ 103.1 (dt, 2C, C_{3,11}, *J* = 160, 7 Hz), 94.3 (dd, 4C, C_{2,4,10,12}, *J* = 158, 7 Hz), 68.7 (d, 4C, C_{1,5,9,13}, *J* = 158 Hz), 36.3 (q, 2C, endo CH₃, *J* = 127 Hz), 33.0 (s, 2C, quaternary), 30.7 (q, 2C, exo CH₃, *J* = 124 Hz), 10.1 (q, 6C, 2PMe₃, *J* = 132 Hz).

Anal. Calc. for C₂₂H₄₀P₂Zr: C, 57.73; H, 8.81. Found: C, 57.55; H, 8.64%.

4.2. Zr(η⁵-dmch) {η³-dmch-[PhC(H)NPh]₂} (4)

To a solution of Zr(6,6-dmch)₂(PMe₃)₂ (260 mg, 0.568 mmol) in 20 ml of hexane was added PhC(H)NPh (0.200 g, 1.14 mmol). The mixture was stirred overnight. The solvent of the resulting orange solution was removed in vacuo. The crude product was extracted using ca. 40 ml of hexane. The solution was filtered through a Celite pad on a medium frit. The product was crystallized by concentration of the filtrate to ca. 15 ml and slowly evaporating the solvent (313 mg, 55% yield).

¹H-NMR (benzene-*d*₆, ambient): δ 7.14–7.25 (m, 8H, NPh), 7.02 (t, 2H_{35,40}, NPh), 6.91 (t, 2H_{21,28}, CHPh, *J* = 8.0 Hz), 6.60–6.69 (m, 8H, CHPh), 6.32 (t, 1H₃, *J* = 8.3 Hz), 5.96 (m, 2H_{2,4}), 5.53 (s, 2H_{17,24}), 5.25 (m, 3H_{10,11,12}), 4.14 (dd, 2H_{1,5}, *J* = 1.2 Hz, 6.6 Hz), 2.97 (d, 2H_{9,13}, *J* = 6.6 Hz), 1.40 (s, 3H₇, endo CH₃), 1.11 (s, 3H₁₅, endo CH₃), 0.67 (s, 3H₈, exo CH₃), 0.59 (s, 3H₁₆, exo CH₃).

¹³C-NMR (benzene-*d*₆, ambient): δ, 154.7 (t, 2C, Ph, *J* = 9 Hz), 147.8 (s, 2C, Ph), 127.2–130.2 (m, 16C, Ph), 126.5 (t, 2C, Ph, *J* = 7 Hz), 119.4 (dt, 2C_{17,24}, *J* = 179, 7 Hz), 119.1 (dd, 2C, Ph, *J* = 158, 7 Hz), 103.1 (d, 1C₁₁, *J* = 162 Hz), 94.7 (dt, 2C_{2,4}, *J* = 171, 8 Hz), 92.0 (dq, 2C_{1,5}, *J* = 164, 8 Hz), 72.0 (d, 2C_{10,12}, *J* = 136 Hz), 58.3 (d, 2C_{9,13}, *J* = 133 Hz), 40.4 (q, 1C₈, endo CH₃, *J* = 123 Hz), 35.4 (s, 1C₁₄), 33.9 (q, 1C₇, exo CH₃, *J* = 125 Hz), 30.7 (s, 1C₆), 27.5 (q, 1C₁₆, endo CH₃, *J* = 129 Hz), 25.7 (q, 1C₁₅, exo CH₃, *J* = 127 Hz).

Anal. Calc. for C₄₂H₄₄N₂Zr: C, 75.52; H, 6.64; N, 4.19. Found: C, 75.55; H, 6.74; N, 3.90%.

4.3. X-ray diffraction studies

Crystal, data collection, and refinement parameters are contained in Table 1. Suitable crystals of each compound were examined under Paratone oil, and transferred to a Nonius–Kappa CCD diffractometer, where they were immediately cooled with a nitrogen stream. Both structures were solved using direct methods and difference Fourier maps. Subsequent least-squares refinements were carried out with anisotropic thermal parameters for the nonhydrogen atoms, while the hydrogen atoms were successfully refined isotropically. Pertinent bonding parameters are presented in Tables 2 and 3.

Table 3
Selected bond distances (Å) and angles (°) for $Zr(\eta^5\text{-dmch})\{\eta^3\text{-dmch-}[\text{PhC(H)NPh}]_2\}$ (**4**)

Bond distances (Å)			
Zr–C1	2.787(2)	Zr–N1	2.1014(17)
Zr–C2	2.536(2)	Zr–N2	2.1415(17)
Zr–C3	2.439(2)	C1–C2	1.366(3)
Zr–C4	2.511(2)	C2–C3	1.421(3)
Zr–C5	2.763(2)	C3–C4	1.425(3)
Zr–C10	2.409(2)	C4–C5	1.363(3)
Zr–C11	2.481(2)	C10–C11	1.387(3)
Zr–C12	2.466(2)	C11–C12	1.394(3)
Bond angles (°)			
C1–C2–C3	121.0(2)	C9–C10–C11	120.6(2)
C2–C3–C4	116.4(2)	C10–C11–C12	121.1(2)
C3–C4–C5	120.5(2)	C11–C12–C13	120.8(2)
C4–C5–C6	120.4(2)	C12–C13–C14	112.5(2)
C1–C6–C5	102.8(2)	C9–C14–C13	116.3(2)
C2–C1–C6	119.8(2)	C10–C9–C14	112.1(2)
Zr–N1–C17	111.94(13)	C17–N1–C31	112.97(16)
Zr–N1–C31	132.38(13)	C24–N2–C37	115.60(17)
Zr–N2–C24	117.54(13)	N1–Zr–N2	96.71(7)
Zr–N2–C37	126.75(14)		

5. Supplementary materials available

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 201586 and 201587 for compound **3** and **4**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

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References

- [1] I. Hyla-Kryspin, T.E. Waldman, E. Meléndez, W. Trakarnpruk, A.M. Arif, M.L. Ziegler, R.D. Ernst, R. Gleiter, *Organometallics* 14 (1995) 5030.
- [2] R.D. Ernst, *Comments Inorg. Chem.* 21 (1999) 285.
- [3] (a) V. Kulsomphob, B.G. Harvey, A.M. Arif, R.D. Ernst, *Inorg. Chim. Acta* 334 (2002) 17; (b) V. Kulsomphob, A.M. Arif, R.D. Ernst, *Organometallics* 21 (2002) 3182.
- [4] (a) T.E. Waldman, L. Stahl, D.R. Wilson, A.M. Arif, J.P. Hutchinson, R.D. Ernst, *Organometallics* 12 (1993) 1543; (b) R.W. Gedridge, A.M. Arif, R.D. Ernst, *J. Organometal. Chem.* 501 (1995) 95.
- [5] (a) P.T. DiMauro, P.T. Wolczanski, *Organometallics* 6 (1987) 1947; (b) V. Kulsomphob, R. Tomaszewski, G.P.A. Yap, L.M. Liable-Sands, A.L. Rheingold, R.D. Ernst, *J. Chem. Soc. Dalton Trans.* (1999) 3995.
- [6] T.E. Waldman, A.L. Rheingold, R.D. Ernst, *J. Organometal. Chem.* 503 (1995) 29.
- [7] (a) A.M. Wilson, F.G. West, A.L. Rheingold, R.D. Ernst, *J. Am. Chem. Soc.* 117 (1995) 8490; (b) A.M. Wilson, F.G. West, A.L. Rheingold, R.D. Ernst, *Inorg. Chim. Acta* 300–302 (2000) 65; (c) R. Basta, A.M. Arif, R.D. Ernst, unpublished results.
- [8] R. Tomaszewski, A.M. Arif, R.D. Ernst, *J. Chem. Soc. Dalton Trans.* (1999) 1883.
- [9] V. Kulsomphob, Ph.D. Thesis, University of Utah, 1999.
- [10] (a) H. Yasuda, A. Nakamura, *Angew. Chem. Int. Ed. Engl.* 26 (1987) 723; (b) G. Erker, C. Krüger, G. Müller, *Adv. Organomet. Chem.* 24 (1985) 1.
- [11] (a) S. Feng, J. Klosin, W.J. Kruper, Jr., M.H. McAdon, D.R. Neithamer, P.N. Nickias, J.T. Patton, D.R. Wilson, K.A. Abboud, C.L. Stern, *Organometallics* 18 (1999) 1159; (b) S. Pillet, G. Wu, V. Kulsomphob, B.G. Harvey, R.D. Ernst, P. Coppens, *J. Am. Chem. Soc.*, 125 (2003) 1937.; (c) A. Gutierrez, G. Wilkinson, B. Hussain-Bates, M.B. Hursthouse, *Polyhedron* 9 (1990) 2081; (d) J. Gavenonis, T.D. Tilley, *J. Am. Chem. Soc.* 124 (2002) 8536; (e) J. Gavenonis, T.D. Tilley, *Organometallics* 21 (2002) 5549.
- [12] (a) R.B. Bates, D.W. Gosselink, J.A. Kaczynski, *Tetrahedron Lett.* (1967) 199; (b) A. Brickstock, J.A. Pople, *Trans. Faraday Soc.* 50 (1954) 901.
- [13] (a) R.D. Ernst, *Struct. Bond. (Berlin)* 57 (1984) 1; (b) R.D. Ernst, *Chem. Rev.* 88 (1988) 1255.
- [14] J.A. Kaduk, A.T. Poulos, J.A. Ibers, *J. Organometal. Chem.* 127 (1977) 245.
- [15] R. Basta, R.D. Ernst, unpublished results.
- [16] (a) C. Walling, A.A. Zavitsas, *J. Am. Chem. Soc.* 85 (1963) 2084; (b) B.R. Davis, P.D. Woodgate, *J. Chem. Soc. Sect. C* (1966) 2006; (c) S. Yao, M. Johannsen, R.G. Hazell, K.A. Jørgensen, *J. Org. Chem.* 63 (1998) 118.
- [17] D.R. Wilson, L. Stahl, R.D. Ernst, *Organomet. Synth.* 3 (1986) 136.