

The synthesis and structural characterization of phenyl tris(3-*t*-butylpyrazolyl)borato alkyl complexes of magnesium and zinc, [PhTp^{Bu^t}]MgR (R = Me, Et) and [PhTp^{Bu^t}]ZnMe

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Dedicated to Al Cotton on the occasion of his 70th birthday.

Abstract

Magnesium and zinc alkyl complexes supported by the phenyltris(3-*t*-butylpyrazolyl)borato ligand, [PhTp^{Bu^t}]MgR (R = Me, Et) and [PhTp^{Bu^t}]ZnEt, have been synthesized by reaction of [PhTp^{Bu^t}]Tl with R₂M (M = Mg, Zn). Comparison of the structures of [PhTp^{Bu^t}]MMe with those of [Tp^{Bu^t}]MMe indicates that the phenyl substituent on boron has an almost negligible effect on the Mg–C and Zn–C bond lengths. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Tris(pyrazolyl)hydroborato ligands [1,2] have recently been used to stabilize alkyl complexes of a variety of metals from each of the s-, p-, d-, and f-blocks. Representative examples include: [Tp^{Bu^t}]BeMe [3], [Tp^{RR}]MgR [4], [Tp^{RR}]ZnR [5,6], [Tp^{Bu^t,Me}]CdMe [7], [Tp^{Me₂}]CdR [8], [Tp^{Bu^t,Me}]CrR (R = Et, Ph, CH₂SiMe₃) [9], [PhTp^{Bu^t}]FeMe [10], [Tp^{Prⁱ}]FeR (R = Et [11], CH₂CHCH₂ [12], CH₂-*p*-Tol^{1,2}), [Tp^{Bu^t}]CoMe [13], [Tp^{Bu^t,Me}]CoR (R = Me, Et, Buⁿ) [13], [Tp^{Prⁱ}]CoEt [11] and [Tp^{Bu^t,Me}]YbCH(SiMe₃)₂ [14]. The majority of ligands used for this purpose incorporate a hydrogen substituent on boron. For certain applications, however, the presence of a B–H bond as a potential site of reactivity may prove problematic, and so we have turned our attention to ligands that incorporate a phenyl, rather than a hydrogen, substituent on boron [15]. In this paper we report the synthesis and characterization of the magnesium and zinc alkyl complexes, [PhTp^{Bu^t}]MgR (R = Me, Et) and [PhTp^{Bu^t}]ZnMe, with

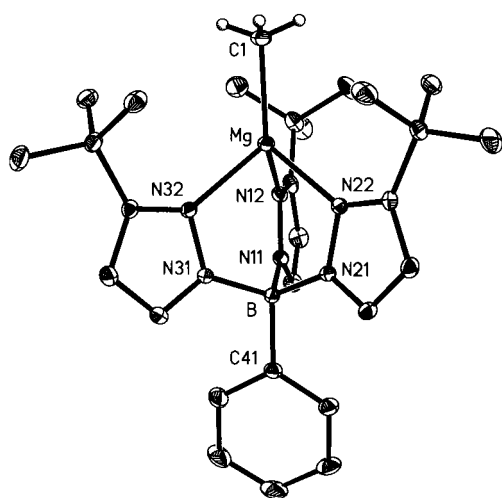
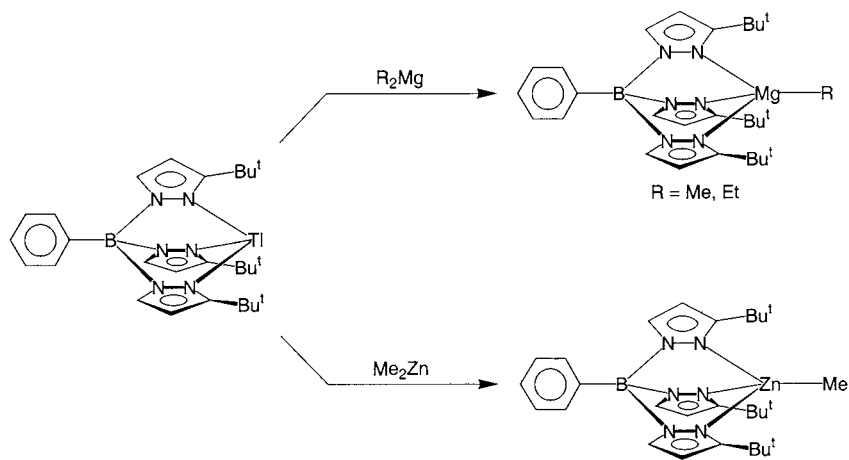
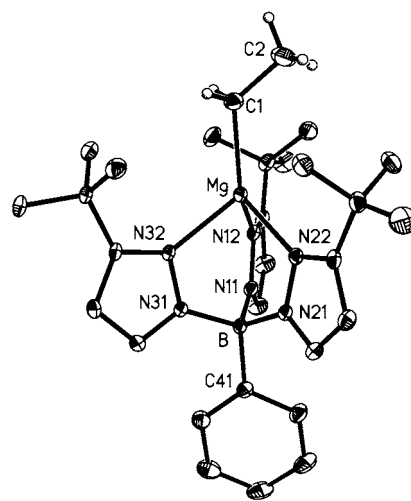
the intention of assessing the structural impact at the metal center created by a phenyl substituent on boron.

2. Results and discussion

The magnesium and zinc alkyl complexes [PhTp^{Bu^t}]MgR (R = Me, Et) and [PhTp^{Bu^t}]ZnMe are conveniently obtained by reaction of the thallium reagent [PhTp^{Bu^t}]Tl¹⁵ with R₂M (Scheme 1). Due to the instability of [TlR], these reactions are accompanied by the deposition of elemental thallium, which thereby provides an effective driving force for the formation of [PhTp^{Bu^t}]MR. The molecular structures of [PhTp^{Bu^t}]MgR (R = Me, Et) and [PhTp^{Bu^t}]ZnMe have been determined by X-ray diffraction, as illustrated in Figs. 1–3. Selected bond lengths and angles are listed in Table 1, from which it is evident that the coordination geometries may be described as trigonally distorted tetrahedral, with N–M–C and N–M–N bond angles of approximately 125 and 90°, respectively. For the ethyl complex, the Mg–C–C bond angle in [PhTp^{Bu^t}]MgEt is 127.2(1)°, which is greater than the mean value of 119° for compounds listed in the Cambridge Structural Database [16], presumably due to the sterically de-

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Fig. 1. Molecular structure of $[\text{PhTp}^{\text{Bu}^t}]\text{MgMe}$.Fig. 2. Molecular structure of $[\text{PhTp}^{\text{Bu}^t}]\text{MgEt}$.

manding environment provided by the three *t*-butyl groups. It is also worth noting that the M–C and B–C bonds in these complexes are not colinear, as indicated by the respective C–M⋯B and M–B⋯C bond angles listed in Table 1.

For purposes of comparison, the M–C bond lengths for $[\text{PhTp}^{\text{Bu}^t}]\text{MgR}$ (R = Me, Et), $[\text{PhTp}^{\text{Bu}^t}]\text{ZnMe}$ and related $[\text{Tp}^{\text{RR}'}]\text{MR}$ complexes are summarized in Table 2, thereby demonstrating that the Mg–C bonds in the magnesium complexes are ca. 0.14 Å longer than the Zn–C bond in corresponding zinc derivatives [17]. Furthermore, the Mg–C and Zn–C bond lengths in these complexes are comparable to the mean values for structurally characterized complexes listed in the Cambridge Structural Database: Mg (2.147 Å) and Zn (1.974) [16]. Finally, comparison of the M–C bond lengths in $[\text{PhTp}^{\text{Bu}^t}]\text{MMe}$ (M = Mg, Zn) with the corresponding values for $[\text{Tp}^{\text{Bu}^t}]\text{MMe}$ indicates that the phenyl sub-

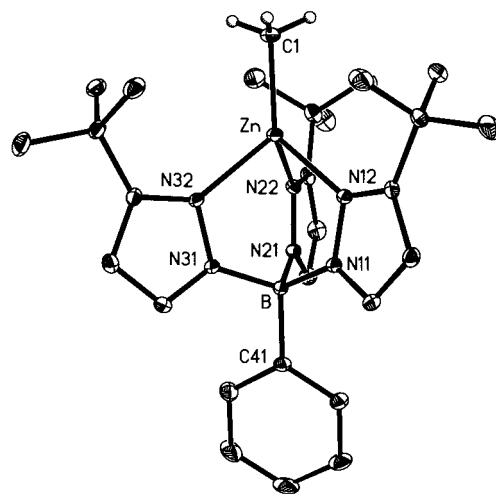
Fig. 3. Molecular structure of $[\text{PhTp}^{\text{Bu}^t}]\text{ZnMe}$.

Table 1
Selected bond lengths (Å) and angles (°) for [PhTp^{Bu}]⁺MgR (R = Me, Et) and [PhTp^{Bu}]⁺ZnMe

	[PhTp ^{Bu}] ⁺ MgMe	[PhTp ^{Bu}] ⁺ MgEt	[PhTp ^{Bu}] ⁺ ZnMe
<i>Bond lengths</i>			
M–C1	2.136(2)	2.163(2)	1.994(2)
M–N12	2.103(1)	2.114(1)	2.124(1)
M–N22	2.148(1)	2.138(1)	2.074(1)
M–N32	2.134(1)	2.170(1)	2.107(1)
<i>Bond angles</i>			
C1–M–N12	124.34(6)	123.23(7)	125.40(6)
C1–M–N22	126.16(5)	130.08(7)	125.29(7)
C1–M–N32	124.81(6)	122.76(6)	124.72(6)
N12–M–N22	88.91(4)	91.68(5)	89.04(5)
N12–M–N32	91.52(4)	89.06(5)	90.21(5)
N22–M–N32	90.24(4)	88.38(5)	91.28(5)
C1–M···B	179.4	175.2	179.1
M–B···C41	172.9	172.7	172.9

Table 2
Comparison of M–C bond lengths (Å) in [Tp^{RR}]⁺MR complexes (M = Mg, Zn)

	Mg	Zn
[PhTp ^{Bu}] ⁺ MMe	2.136(2) 2.118(11) ^a	1.994(2) 1.971(4) ^b
[Tp ^{Ph}] ⁺ MMe	–	1.950(4) ^c
[Tp ^{Me₂}] ⁺ MMe	–	1.981(8) ^d
[PhTp ^{Bu}] ⁺ Met	2.163(2) 2.182(8) ^a	– –
[Tp ^{Bu}] ⁺ MCH ₂ SiMe ₃	2.096(9) ^a	–

^a R. Han, G. Parkin, *Organometallics* 10 (1991) 1010–1020.

^b K. Yoon, G. Parkin, *J. Am. Chem. Soc.* 113 (1991) 8414–8418.

^c R. Alsfasser, A.K. Powell, S. Trofimenko, H. Vahrenkamp, *Chem. Ber.* 126 (1993) 685–694.

^d A. Looney, R. Han, I.B. Gorrell, M. Cornebise, K. Yoon, G. Parkin, A.L. Rheingold, *Organometallics* 14 (1995) 274–278.

Table 3
NMR spectroscopic data

Assignment	[PhTp ^{Bu}] ⁺ MgMe	[PhTp ^{Bu}] ⁺ MgEt	[PhTp ^{Bu}] ⁺ ZnMe
¹ H (C ₆ D ₆)			
C(CH ₃) ₃	1.46, s	1.45, s	1.45, s
C ₃ N ₂ H ₂	5.84, d, ³ J _{H–H} = 2	5.83, d, ³ J _{H–H} = 2	5.87, d, ³ J _{H–H} = 2
	7.42, d, ³ J _{H–H} = 2	7.41, d, ³ J _{H–H} = 2	7.43, d, ³ J _{H–H} = 2
C ₆ H ₅	7.23–7.83	7.23–7.83	7.23–7.86
MCH _n	0.08, s (n = 3)	0.67, q, ³ J _{H–H} = 8 (n = 2)	0.59, s (n = 3)
CH ₂ CH ₃	–	2.02, t, ³ J _{H–H} = 8	–
¹³ C (C ₆ D ₆)			
C(CH ₃) ₃	31.0, q, ¹ J _{C–H} = 126	31.0, q, ¹ J _{C–H} = 128	30.8, q, ¹ J _{C–H} = 126
C(CH ₃) ₃	32.1, s	32.1, s	32.1, s
C ₃ N ₂ H ₂	102.1, d, ¹ J _{C–H} = 174	102.0, d, ¹ J _{C–H} = 173	102.0, d, ¹ J _{C–H} = 174
	137.2, d, ¹ J _{C–H} = 181	137.2, d, ¹ J _{C–H} = 184	136.3, ¹ J _{C–H} = 181
	166.0, s	166.0, s	164.8, s
BC ₆ H ₅ ^a	137.2, d, ¹ J _{C–H} = 159 (2C)	135.8, d, ¹ J _{C–H} = 157 (2C)	135.7, d, ¹ J _{C–H} = 158 (2C)
MCH ₃	–2.9, q, ¹ J _{C–H} = 108		–0.7, q, ¹ J _{C–H} = 119
MCH ₂ CH ₃		7.3, t, ¹ J _{C–H} = 113	
MCH ₂ CH ₃		14.1, q, ¹ J _{C–H} = 128	

^a C_{ipso} not observed and other phenyl resonances are obscured by solvent.

stituent exerts an almost negligible effect, with the M–C bonds in [PhTp^{Bu}]⁺MMe being only ca. 0.02 Å longer than those in [Tp^{Bu}]⁺MMe. The fact that the steric perturbation is minimal is of interest, since it may have been expected to be more significant; indeed, intraligand steric interactions between 5-R' substituents and the B–H in {[Tp^{RR'}]⁺M} derivatives is known to influence the binding mode of poly(pyrazoly)borate complexes [18].

3. Experimental

3.1. General considerations

All manipulations were performed using a combination of glovebox, high-vacuum or Schlenk techniques [19]. Solvents were purified and degassed by standard procedures. Commercially available reagents were used as received. All glassware was oven dried prior to use. ¹H and ¹³C chemical shifts are reported in ppm relative to SiMe₄ (δ = 0) and were referenced internally with respect to the protio solvent impurity or the ¹³C resonances, respectively. All coupling constants are reported in Hertz. C, H and N elemental analyses were measured using a Perkin–Elmer 2400 CHN elemental analyzer.

3.2. Synthesis of [PhTp^{Bu}]⁺MgMe

Me₂Mg (100 mg, 1.84 mmol) was added to [PhTp^{Bu}]⁺Tl (226 mg, 0.34 mmol) in benzene and the gray suspension was heated at 50°C for 2 days. The mixture was filtered and the solvent was removed from the filtrate in vacuo. The resulting white powder was

Table 4
Crystal, intensity collection and refinement data

	[PhTp ^{Bu'}]MgMe	[PhTp ^{Bu'}]MgEt	[PhTp ^{Bu'}]ZnMe
Lattice	Monoclinic	Monoclinic	Monoclinic
Formula	C ₂₈ H ₄₁ BN ₆ Mg	C ₂₉ H ₄₃ BN ₆ Mg	C ₂₈ H ₄₁ BN ₆ Zn
Formula weight	496.79	510.81	537.85
Space group	<i>P</i> 2 ₁ / <i>n</i> (No. 14)	<i>P</i> 2 ₁ / <i>n</i> (No. 14)	<i>P</i> 2 ₁ / <i>n</i> (No. 14)
<i>a</i> (Å)	10.4522(5)	9.8893(5)	10.4897(5)
<i>b</i> (Å)	17.4856(8)	18.1302(9)	17.4573(8)
<i>c</i> (Å)	16.2264(8)	16.4333(8)	16.1071(8)
α (°)	90	90	90
β (°)	93.499(1)	93.282(1)	93.203(1)
γ (°)	90	90	90
<i>V</i> (Å ³)	2960.1(2)	2941.6(3)	2945.0(2)
<i>Z</i>	4	4	4
Temperature (K)	203	203	203
Radiation (λ , Å)	0.71073	0.71073	0.71073
<i>D</i> _{calc} (g cm ⁻³)	1.115	1.153	1.213
μ (Mo–K α) (mm ⁻¹)	0.086	0.088	0.860
θ max (°)	28.3	28.3	28.3
No. of data	6890	6700	6898
No. of parameters	336	345	336
<i>R</i> ₁	0.0458	0.0520	0.0315
<i>wR</i> ₂	0.1042	0.1275	0.0738
GOF	1.064	0.942	1.038

extracted into pentane (ca. 3 ml), filtered, and cooled to –15°C. Colorless crystals of [PhTp^{Bu'}]MgMe were deposited over a period of 5 days (129 mg, 76%). Anal. Calc. for [PhTp^{Bu'}]MgMe: C, 67.7; H, 8.3; N, 16.9. Found: C, 66.4; H, 8.1; N, 16.8%. NMR spectroscopic data are listed in Table 3. [PhTp^{Bu'}]MgEt was obtained by a similar procedure from Et₂Mg and [PhTp^{Bu'}]Ti.

3.3. Synthesis of [PhTp^{Bu'}]ZnMe

A solution of Me₂Zn in toluene (0.5 ml of 1.0 M, 0.50 mmol) was added to [PhTp^{Bu'}]Ti (220 mg, 0.33 mmol) in benzene (ca. 3 ml). A black precipitate formed upon addition and the resulting dark suspension was stirred at room temperature for 20 min. The mixture was filtered and the solvent was removed from the filtrate in vacuo. The resulting white powder was extracted into pentane (ca. 3 ml), filtered, and allowed to stand at –15°C. Colorless crystals of [PhTp^{Bu'}]ZnMe were deposited over a period of 4 days (46 mg, 26%). Anal. Calc. for [PhTp^{Bu'}]ZnMe: C, 62.5; H, 7.7; N, 15.6. Found: C, 61.9; H, 7.6; N, 15.4%. NMR spectroscopic data are listed in Table 3.

3.4. X-ray structure determinations

Crystallographic data for [PhTp^{Bu'}]MgR (R = Me, Et) and [PhTp^{Bu'}]ZnMe were collected on a Bruker P4 diffractometer equipped with a SMART CCD detector. The structures were solved using direct methods and standard difference map techniques, and were refined by full-matrix least-squares procedures using SHELXTL [20]. Hydrogen atoms on carbon were included in calculated positions. Systematic absences for all structures were consistent uniquely with *P*2₁/*n* (No. 14). Crystal data, data collection and refinement parameters for all structures are summarized in Table 4.

4. Summary

In conclusion, X-ray diffraction studies on [PhTp^{Bu'}]MgMe and [PhTp^{Bu'}]ZnMe indicate that the Mg–C bond is ca. 0.14 Å longer than the corresponding Zn–C bond and comparisons between [PhTp^{Bu'}]MMe and [Tp^{Bu'}]MMe (M = Mg, Zn) indicate that incorporation of a phenyl substituent on boron exerts an almost negligible effect on the M–C bond length.

5. Supplementary material

Atomic coordinates for [PhTp^{Bu'}]MgMe (CCDC no. 127830), [PhTp^{Bu'}]MgEt (CCDC no. 127829), and [PhTp^{Bu'}]ZnMe (CCDC no. 127831) have been deposited with the Cambridge Crystallographic Data Centre. 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; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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