Unexpectedly facile isomerisation of [7,10-Ph_2-7,10-*nido*-$C_2B_{10}H_{10}$]$^{2-}$ to [7,9-Ph_2-7,9-*nido*-$C_2B_{10}H_{10}$]$^{2-}$ †

Sergey Zlatogorsky, David Ellis, Georgina M. Rosair and Alan J. Welch*

Received (in Cambridge, UK) 19th December 2006, Accepted 5th February 2007
First published as an Advance Article on the web 1st March 2007
DOI: 10.1039/b618556h

The 2e-reduction of 1,12-Ph_2-1,12-*closo*-$C_2B_{10}H_{10}$ followed by oxidation or metallation gives products that arise from [7,9-Ph_2-7,9-*nido*-$C_2B_{10}H_{10}$]$^{2-}$, formed by unexpectedly facile isomerisation of the kinetic 7,10-isomer: the 4,1,6-MC_2B_{10} compounds which result are progressively isomerised to 4,1,8- and 4,1,12-isomers for *M* = {CpCo} but to an equilibrium mixture of 4,1,8- and 4,1,12-isomers for *M* = {(arene)Ru}.

Reduction of the icosahedral carborane $C_2B_{10}H_{12}$ or its derivatives is a necessary first step in the major synthetic route to supraicosahedral carboranes and heterocarboranes. The addition of transition metal fragments[1] or main group cations[2] to reduced 12-vertex carboranes leads to 13-vertex metallacarboranes, whilst the addition of boron fragments leads to 13-vertex carboranes.[3] Reduction of both 1,2-*closo*-$C_2B_{10}H_{12}$ (ortho carborane) and 1,7-*closo*-$C_2B_{10}H_{12}$ (meta carborane) affords the same dianion, [7,9-*nido*-$C_2B_{10}H_{12}$]$^{2-}$,[4] whilst reduction of 1,12-*closo*-$C_2B_{10}H_{12}$ (para carborane) yields [7,10-*nido*-$C_2B_{10}H_{12}$]$^{2-}$ (Fig. 1).[5] Oxidation of [7,9-*nido*-$C_2B_{10}H_{12}$]$^{2-}$ gives ortho carborane,[6] whilst oxidation of [7,10-*nido*-$C_2B_{10}H_{12}$]$^{2-}$ gives meta carborane.[7] Reduction of the *C*,*C*-diphenyl derivatives of both ortho and meta carborane also gives a common product, whilst reduction of 1,12-Ph_2-1,12-*closo*-$C_2B_{10}H_{10}$ affords a species with a different ^{13}C NMR spectrum.[8] We now report evidence that, surprisingly, this reduced form of diphenyl para carborane easily transforms to the same [7,9-Ph_2-7,9-*nido*-$C_2B_{10}H_{10}$]$^{2-}$ dianion that is afforded by reduction of its ortho and meta analogues. We show that, similarly, [7,10-*nido*-$C_2B_{10}H_{12}$]$^{2-}$ can be transformed to [7,9-*nido*-$C_2B_{10}H_{12}$]$^{2-}$ under THF reflux and that 4,1,6-RuC_2B_{10} species formed by metallation of [7,9-*nido*-C_2B_{10}]$^{2-}$ anions will isomerise if sufficiently heated, but that the ultimate result of such isomerisation is an equilibrium mixture of 4,1,8- and 4,1,12- forms.

Compound **1**, 1,12-Ph_2-1,12-*closo*-$C_2B_{10}H_{10}$, has been known for a considerable time[9] but, surprisingly, its solid-state structure has not previously been reported.‡ Two, practically superimposable, independent molecules of **1** are found but only one is shown in Fig. 2.§ Both molecules have crystallographically-imposed C_i symmetry which requires the Ph rings on each carborane to be co-parallel.

We prepared **1** in the expectation of being able to synthesise, from it, *C*,*C*-diphenyl derivatives of 4,1,10-MC_2B_{10} metallacarboranes,[5] which, following thermal isomerisation to equivalent 4,1,12-species, we planned to use as precursors to *C*,*C*-diphenyl 14-vertex $M_2C_2B_{10}$[11] and, ultimately, higher polyhedra.

However, in our hands 2e-reduction (either Na in liq. NH_3 or Na in THF) of **1** followed by subsequent oxidation or metallation did not afford products that derive from [7,10-Ph_2-7,10-*nido*-$C_2B_{10}H_{10}$]$^{2-}$, but instead gave products that derive from [7,9-Ph_2-7,9-*nido*-$C_2B_{10}H_{10}$]$^{2-}$. Thus (i) aerial re-oxidation of the reduced

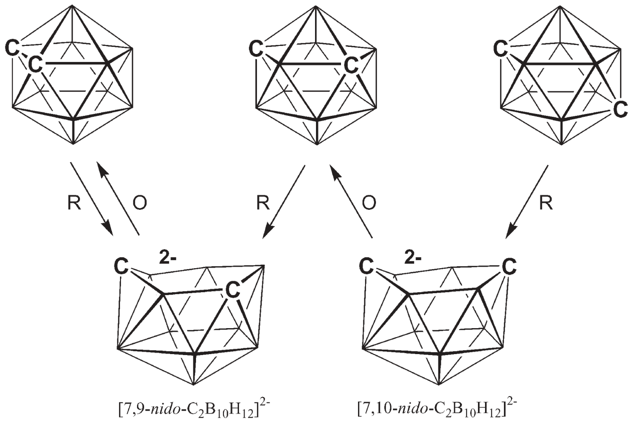

Fig. 1 Reduction (R) and subsequent oxidation (O) of ortho-, meta- and para-carborane.

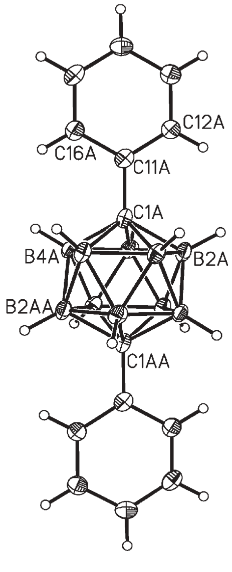

Fig. 2 Perspective view of molecule A of **1** (50% probability ellipsoids). Average interatomic distances (Å): C–B 1.725(8), B–B (tropical) 1.777(6), B–B (equatorial) 1.761(6).¶

School of Engineering & Physical Sciences, Heriot-Watt University, Edinburgh, UK EH14 4AS. E-mail: a.j.welch@hw.ac.uk; Fax: +44 131 451 3180; Tel: +44 131 451 3217

† Electronic supplementary information (ESI) available: Experimental procedure and isomerisations. See DOI: 10.1039/b618556h

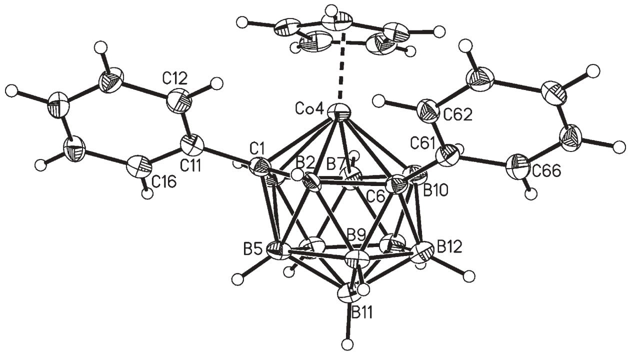

Fig. 3 Perspective view of **3** (50% probability ellipsoids). Selected interatomic distances (Å): Co4–C1 2.038(3), Co4–B2 2.193(4), Co4–C6 2.187(3), Co4–B10 2.124(4), Co4–B7 2.183(4), Co4–B3 2.196(4), Co4–C(Cp) 2.031(4)–2.082(3), B5–C1 1.772(5), B5–B2 1.988(5), B5–B9 1.903(6), B5–B11 1.802(6), B5–B8 1.898(6), B5–B3 2.028(6), C1–C11 1.500(4), C6–C61 1.516(4).

species yields only 1,2-Ph_2-1,2-*closo*-$C_2B_{10}H_{10}$ (by ^{11}B NMR spectroscopy) and (ii) metallation of the reduced species with [Ru(*p*-cymene)Cl_2]$_2$ affords 1,6-Ph_2-4-(*p*-cymene)-4,1,6-*closo*-$RuC_2B_{10}H_{10}$ (**2**) which we have previously prepared from metallation of reduced 1,2-Ph_2-1,2-*closo*-$C_2B_{10}H_{10}$ and fully characterised.[12] We have confirmed that **2** is also afforded by reduction and metallation of 1,7-Ph_2-1,7-*closo*-$C_2B_{10}H_{10}$.

Similarly, addition of $CoCl_2$ and NaCp to the product of reduction of **1** affords, following $Co^{II} \rightarrow Co^{III}$ oxidation on work-up, the new cobaltacarborane 1,6-Ph_2-4-Cp-4,1,6-*closo*-$CoC_2B_{10}H_{10}$ (**3**) (see ESI†). Compound **3** was fully characterised by mass spectrometry, ^{11}B NMR spectroscopy and single-crystal X-ray diffraction.§ RT NMR spectra of **3** imply a molecule with C_s symmetry but the fluctional process by which this is achieved is well understood.[1,12] A perspective view of a single molecule is shown in Fig. 3.

In a manner similar to that established for the non-arylated analogues 4-Cp-4,1,6-*closo*-$CoC_2B_{10}H_{12}$[1] and 4-Cp*-4,1,6-*closo*-$CoC_2B_{10}H_{12}$,[13] **3** can easily be progressively isomerised by heat, first to the 4,1,8-isomer (**4**) then to the target 4,1,12-isomer (**5**), both of which were fully characterised (see ESI†).§ However, we have already noted that the 4,1,6-RuC_2B_{10} species **2** does not similarly isomerise even in refluxing toluene.[12] Thus whilst we had managed to prepare a *C,C*-diphenyl 4,1,12-cobaltacarborane, we appeared to be doubly frustrated in our attempts to prepare the analogous ruthenacarborane: its logical precursor,‖ the 4,1,10-isomer, is not obtained by metallation of reduced 1,12-Ph_2-1,12-*closo*-$C_2B_{10}H_{10}$, and what is formed (the 4,1,6-isomer) appears itself to be resistant to thermal isomerisation.

However, raising the temperature to *ca.* 180 °C, in tetra(ethylene glycol) dimethyl ether, successfully isomerises **2** to the new ruthenacarboranes 1,8-Ph_2-4-(*p*-cymene)-4,1,8-*closo*-$RuC_2B_{10}H_{10}$ (**6**) and 1,12-Ph_2-4-(*p*-cymene)-4,1,12-*closo*-$RuC_2B_{10}H_{10}$ (**7**).** Compound **6** and **7** were characterised both spectroscopically (see ESI†) and crystallographically,§ and views of single molecules are given in Fig. 4 and Fig. 5, respectively.

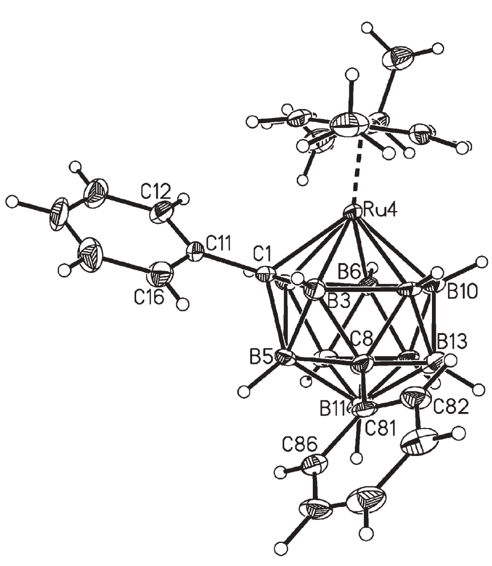

Fig. 4 Perspective view of **6** (50% probability ellipsoids). Selected interatomic distances (Å): Ru4–C1 2.168(6), Ru4–B2 2.309(7), Ru4–B6 2.308(7), Ru4–B10 2.266(7), Ru4–B7 2.242(7), Ru4–B3 2.280(7), Ru4–C(cymene) 2.206(6)–2.290(6), B5–C1 1.724(9), B5–B2 2.042(10), B5–B9 1.876(10), B5–B11 1.814(10), B5–C8 1.887(10), B5–B3 1.969(11), C1–C11 1.512(8), C8–C81 1.525(8).

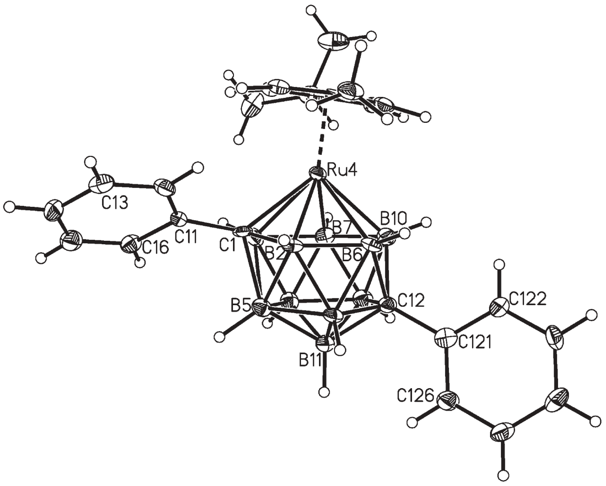

Fig. 5 Perspective view of **7** (50% probability ellipsoids). Selected interatomic distances (Å): Ru4–C1 2.186(6), Ru4–B2 2.288(7), Ru4–B6 2.245(7), Ru4–B10 2.247(7), Ru4–B7 2.281(7), Ru4–B3 2.307(7), Ru4–C(cymene) 2.190(6)–2.310(6), B5–C1 1.784(9), B5–B2 2.037(9), B5–B9 1.886(9), B5–B11 1.760(10), B5–B8 1.891(10), B5–B3 2.037(10), C1–C11 1.514(8), C12–C121 1.516(8).

In contrast, however, to the sequential 4,1,6 → 4,1,8 → 4,1,12 isomerisation of both the *C,C*-arylated and non-arylated forms of the 13-vertex cobaltacarborane, isomerisation of the ruthenacarborane **2** affords an equilibrium mixture of **6** and **7**. After 6 h at 180 °C the ratio is *ca.* 2 : 1, respectively. Heating either pure **6** or pure **7** separately at 180 °C ultimately yields a 1 : 5 ratio of **6** and **7** after *ca.* 24 h.

All five new metallacarboranes (compounds **3–7**) have docosahedral MC_2B_{10} cages similar to that of the archetypal 13-vertex species 4-Cp-4,1,6-*closo*-$CoC_2B_{10}H_{12}$[1,15] featuring relatively long connectivities involving the degree-6 vertex B5. B5–B3 is particularly long, *ca.* 2 Å.

The formation of 1,2-Ph_2-1,2-*closo*-$C_2B_{10}H_{10}$ by the oxidation of reduced **1**, and the isolation of 4,1,6-MC_2B_{10} species from the metallation of reduced **1**, could be interpreted in one of two ways.

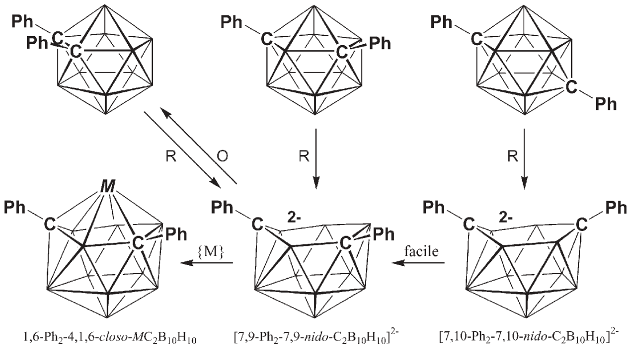

Fig. 6 Reduction (R), oxidation (O) and metallation ({M}) of the *C*,*C*-diphenyl derivatives of ortho-, meta- and para-carborane.

Either reduction of **1** proceeds differently to that of 1,12-*closo*-$C_2B_{10}H_{12}$ (in contrast to previously published reports[8]) or the [7,10-Ph$_2$-7,10-*nido*-$C_2B_{10}H_{10}$]$^{2-}$ anion formed converts to the 7,9-form before oxidation or metallation takes place. To investigate this we reduced 1,12-*closo*-$C_2B_{10}H_{12}$ and heated the [7,10-*nido*-$C_2B_{10}H_{12}$]$^{2-}$ anion known to form[5] at THF reflux. Subsequent metallation with [Ru(*p*-cymene)Cl$_2$]$_2$ yields the known compound 4-(*p*-cymene)-4,1,6-*closo*-Ru$C_2B_{10}H_{12}$.[11] This suggests that reduction of **1** does indeed produce [7,10-Ph$_2$-7,10-*nido*-$C_2B_{10}H_{10}$]$^{2-}$, but that this is only a kinetic form and easily transforms (at or below room temperature) to the 7,9-isomer, ultimately captured by oxidation or metallation (Fig. 6). The reasons for the apparent thermodynamic preference of [7,9-*nido*-C_2B_{10}]$^{2-}$ over [7,10-*nido*-C_2B_{10}]$^{2-}$ dianions are not intuitively obvious, and will be the subject of future investigation.[14]

We thank the ORSAS and Heriot-Watt University (S. Z.) and the EPSRC (D. E.) for support, Dr A. S. F. Boyd for NMR spectroscopy, Mr G. P. Smith for mass spectrometry and Ms C. Graham for microanalysis.

Notes and references

‡ However the structure has been previously determined. See ref. 1 of Fox *et al.*[10] We thank Mark Fox for details of his unpublished work.

§ *Crystal data*: for **1**: $C_{14}H_{20}B_{10}$, *M* = 296.40, monoclinic, $P2_1/c$, *a* = 11.560(3), *b* = 7.3833(17), *c* = 19.199(4) Å, *β* = 93.339(12)°, *V* = 1635.9(7) Å^3, *Z* = 4 (2 independent half-molecules), D_c = 1.203 Mg m^{-3}, *μ* = 0.059 mm^{-1}, *F*(000) = 616. Data to θ_{max} = 26.37° collected at 100(2) K on a Bruker X8 diffractometer using Mo-Kα radiation. 3328 out of 26728 independent reflections, R_1 = 0.0957, wR_2 = 0.2614, *S* = 1.099 for data with $I > 2\sigma(I)$.

For **3**: $C_{19}H_{25}B_{10}Co$, *M* = 420.42, monoclinic, $P2_1/n$, *a* = 7.9865(15), *b* = 16.119(3), *c* = 15.593(2) Å, *β* = 96.559(7)°, *V* = 1994.3(6) Å^3, *Z* = 4, D_c = 1.400 Mg m^{-3}, *μ* = 0.865 mm^{-1}, *F*(000) = 864. Data collection as for **1** except θ_{max} = 23.37°. 2878 out of 22792 independent reflections, R_1 = 0.0387, wR_2 = 0.0681, *S* = 1.036 for data with $I > 2\sigma(I)$.

For **4**: $C_{19}H_{25}B_{10}Co\cdot\frac{1}{2}C_6H_{14}$, *M* = 463.50, monoclinic, $P2_1/c$, *a* = 8.782(3), *b* = 19.357(7), *c* = 15.252(5) Å, *β* = 101.266(16)°, *V* = 2543.0(15) Å^3, *Z* = 4, D_c = 1.211 Mg m^{-3}, *μ* = 0.684 mm^{-1}, *F*(000) = 964. Data collection as for **1** except θ_{max} = 20.68°. 2566 out of 20710 independent reflections, R_1 = 0.0829, wR_2 = 0.2108, *S* = 1.170 for data with $I > 2\sigma(I)$.

For **5**: $C_{19}H_{25}B_{10}Co$, *M* = 420.42, monoclinic, $P2_1/n$, *a* = 12.0447(8), *b* = 12.6676(8), *c* = 13.8241(8) Å, *β* = 104.129(16)°, *V* = 2045.4(2) Å^3, *Z* = 4, D_c = 1.365 Mg m^{-3}, *μ* = 0.843 mm^{-1}, *F*(000) = 864. Data collection as for **1** except θ_{max} = 30.73°. 6327 out of 30880 independent reflections, R_1 = 0.0468, wR_2 = 0.0985, *S* = 0.972 for data with $I > 2\sigma(I)$.

For **6**: $C_{24}H_{34}B_{10}Ru$, *M* = 531.68, monoclinic, $P2_1$, *a* = 9.3596(8), *b* = 8.7670(9), *c* = 15.4785(15) Å, *β* = 96.803(5)°, *V* = 1261.2(2) Å^3, *Z* = 2, D_c = 1.400 Mg m^{-3}, *μ* = 0.635 mm^{-1}, *F*(000) = 544. Data collection as for **1** except θ_{max} = 24.32°. 3972 out of 20080 independent reflections, R_1 = 0.0388, wR_2 = 0.0895, *S* = 1.058, *x* = −0.02(5) for data with $I > 2\sigma(I)$.

For **7**: $C_{24}H_{34}B_{10}Ru$, *M* = 531.68, monoclinic, *C*2/*c*, *a* = 21.144(4), *b* = 13.209(2), *c* = 18.065(3) Å, *β* = 100.439(8)°, *V* = 4961.6(15) Å^3, *Z* = 8, D_c = 1.424 Mg m^{-3}, *μ* = 0.645 mm^{-1}, *F*(000) = 2176. Data collection as for **1** except θ_{max} = 23.34°. 3583 out of 27682 independent reflections, R_1 = 0.0425, wR_2 = 0.0924, *S* = 0.963 for data with $I > 2\sigma(I)$.

CCDC 631512–631517. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b618556h

¶ E.s.d.s of the mean of *N* independent observations given by the expression $\sigma^2 = \{\sum_{i=1}^{i=N}(\chi_i - \;)^2\}/(N - 1)$ where χ_i is the i^{th} and the mean value. Tropical B–B distances are those between B atoms connected to the same C atom, whilst equatorial B–B distances are between B atoms connected to different C atoms.

|| The compound 4-(*p*-cymene)-4,1,10-*closo*-Ru$C_2B_{10}H_{12}$ isomerises quantitatively to 4-(*p*-cymene)-4,1,12-*closo*-Ru$C_2B_{10}H_{12}$ in refluxing toluene. See ref. 5.

** The non-phenylated analogue of compound **2**, 4-(*p*-cymene)-4,1,6-*closo*-Ru$C_2B_{10}H_{12}$, similarly isomerises at 180 °C.[14]

1 G. B. Dunks, M. M. McKown and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1971, **93**, 2541.
2 R. Khattar, C. B. Knobler and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1990, **112**, 4962; K. Chui, H.-W. Li and Z. Xie, *Organometallics*, 2000, **19**, 7447; N. M. M. Wilson, D. Ellis, A. S. F. Boyd, B. T. Giles, S. A. Macgregor, G. M. Rosair and A. J. Welch, *Chem. Commun.*, 2002, 464.
3 A. Burke, D. Ellis, B. T. Giles, B. E. Hodson, S. A. Macgregor, G. M. Rosair and A. J. Welch, *Angew. Chem., Int. Ed.*, 2003, **42**, 225.
4 G. B. Dunks, R. J. Wiersema and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1973, **95**, 3174.
5 D. Ellis, M. E. Lopez, R. McIntosh, G. M. Rosair, A. J. Welch and R. Quenardelle, *Chem. Commun.*, 2005, 1348.
6 L. I. Zakharkin, V. N. Kalinin and L. S. Podvisotskaya, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1966, 1444.
7 V. I. Stanko, Yu. V. Gol'tyapin and V. A. Brattsev, *J. Gen. Chem. USSR*, 1969, 1142.
8 L. I. Zakharkin, V. N. Kalinin, V. A. Antonovich and E. G. Rys, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1976, 1009.
9 L. I. Zakharkin and A. I. Kovredov, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1974, 710.
10 M. A. Fox, J. A. H. MacBride, R. J. Peace and K. Wade, *J. Chem. Soc., Dalton Trans.*, 1998, 401.
11 D. Ellis, M. E. Lopez, R. McIntosh, G. M. Rosair and A. J. Welch, *Chem. Commun.*, 2005, 1917.
12 A. Burke, D. Ellis, D. Ferrer, D. L. Ormsby, G. M. Rosair and A. J. Welch, *Dalton Trans.*, 2005, 1716.
13 A. Burke, R. McIntosh, D. Ellis, G. M. Rosair and A. J. Welch, *Collect. Czech. Chem. Commun.*, 2002, **67**, 991.
14 S. Zlatogorsky, D. Ellis and A. J. Welch, to be published.
15 M. R. Churchill and B. G. DeBoer, *J. Chem. Soc., Chem. Commun.*, 1972, 1326.