Stepwise Reduction of MeNC to Me_2NH on a Metallaborane Substrate: an Interesting Reaction Sequence and the Molecular Structure of [μ-6,9-(NMe_2)-10-(PMe_2Ph)-5-(η^6-C_6Me_6)-*arachno*-5-RuB_9H_{10}]

Evert J. Ditzel, Xavier L. R. Fontaine, Norman N. Greenwood, John D. Kennedy, Zhu Sisan, and Mark Thornton-Pett

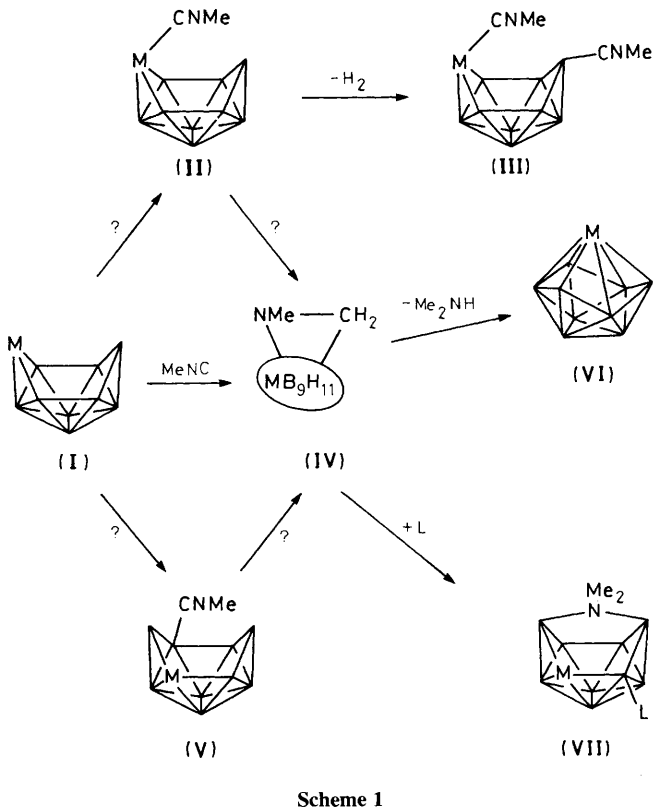
School of Chemistry, University of Leeds, Leeds LS2 9JT, U.K.

Reaction of MeNC with [6-(η^6-C_6Me_6)-*nido*-5-RuB_9H_{13}] (**1**) yields an unstable –$NMeCH_2$-bridged intermediate of empirical formula [(C_6Me_6)Ru(NMe_2CH_2)B_9H_{11}] (**2**); this reacts with PMe_2Ph to give the –NMe_2-bridged species [μ-6,9-(NMe_2)-10-(PMe_2Ph)-5-(η^6-C_6Me_6)-*arachno*-5-RuB_9H_{10}] (**4**), but in the absence of PMe_2Ph it decomposes to give Me_2NH and [1-(η^6-C_6Me_6)-*isocloso*-1-RuB_9H_9] (**3**).

There is interest in, and some investigation of, the use of polyhedral metallaboranes and metallacarbaboranes as catalysts, for example in hydrogenation.[1] We here report the facile stepwise (though non-catalytic) reduction of MeNC *via* {$MeNCH_2$–} and {MeN(Me)–} to MeNHMe using [6-(η^6-C_6Me_6)-*nido*-6-RuB_9H_{13}] (**1**). The reaction, which has the overall stoicheiometry of equation (**1**), is potentially of relevance to an understanding and development of metallaborane-catalysed reductions.

$$MeNC + [(C_6Me_6)RuB_9H_{13}] \rightarrow MeNHMe + [(C_6Me_6)RuB_9H_9] \quad (1)$$

We have previously reported that reaction of MeCN with [6-(η^5-C_5Me_5)-*nido*-6-RhB_9H_{13}] [structure (**I**) in Scheme 1] yields an *arachno*-bis(MeNC) species (**III**) with loss of dihydrogen,[2] probably *via* an *arachno*-type mono(MeNC) adduct [structure (**II**)]. We now find that the reaction of MeNC with the ostensibly analogous [6-(η^6-C_6Me_6)-*nido*-6-RuB_9H_{13}] [compound (**1**) structure (**I**)] in toluene at room temperature for <10 min yields, instead, an unstable yellow adduct [compound (**2**), structure (**IV**)] in essentially quantitative yield (by integrated NMR spectroscopy; isolable yield 63%). So far, in our hands, (**2**) decomposes too rapidly in solution at room temperature (*ca.* 3 h) for crystallization and characterization by single-crystal *X*-ray diffraction analysis. However, the results of NMR spectroscopy† show that (**2**) is a



Scheme 1

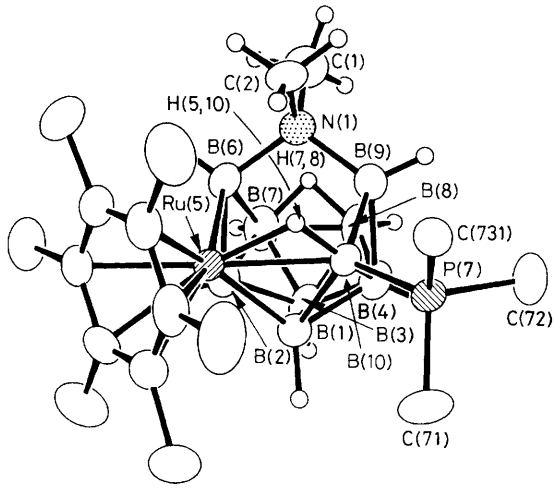


Figure 1. Drawing of the molecular structure of [μ-6,9-(NMe_2)-10-(PMe_2Ph)-5-(η^6-C_6Me_6)-*arachno*-5-RuB_9H_{10}], (**4**).‡ Distances from Ru(5) are: to B(1) 221.2(5), to B(2) 217.8(5), to B(6) 230.0(5), to B(10) 231.9(5), to C_{ring} (mean) 224.5(4), and to H(5,10) 166.3(27) pm. Distances from N(1) are: to C(1) 153.2(6), to C(2) 150.6(6), to B(6) 162.5(6), and to B(9) 161.5(6) pm. Other selected interatomic distances are: B(6)–B(7) 198.4(7), B(7)–B(8) 183.7(7), B(8)–B(9) 196.4(7), B(9)–B(10) 184.9(6), B(7)–H(7,8) 126.2(34), B(8)–H(7,8) 130.4(34), and B(10)–P(7) 192.3(5) pm.

† NMR *Spectroscopic data* for [(C_6Me_6)RuB_9H_{11}(CH_2NMe)] (**2**): in CD_2Cl_2 solution at 294—297 K, ordered as δ(^{11}B) [δ(^{1}H)]: +65.7 [+7.30], +26.1 [+4.30], +10.2 [+3.19], *ca.* −0.6 [+2.35], *ca.* −0.6 [+2.16], −8.5 [+1.95], −13.9 [+0.31], −22.3 [+1.52], and −25.6 [+1.00]; plus δ(^{1}H)(bridged) at −2.17 and −10.81, δ(^{1}H)(C_6Me_6) at 2.04, δ(^{1}H)(NMe) at +2.26, and δ(^{1}H)(CH_2) at +1.84 and +1.69 [^2J(^{1}HC^{1}H) 9.8 Hz]. δ(^{11}B) in p.p.m. to low field (high frequency) of [$BF_3(OEt_2)$].

For [(C_6Me_6)RuB_9H_9] (**3**) in $CDCl_3$ solution at 294 K (*cf.* ref. 4), ordered as assignment, δ(^{11}B) [δ(^{1}H)]: BH(2,4,6) +93.2 [+8.65]; BH(3,5,7) −13.6 [+0.02]; and BH(8,9,10) +26.8 [+3.98].

For [(C_6Me_6)RuB_9H_{10}(NMe_2)(PMe_2Ph)] (**4**) in CD_2Cl_2 solution at 294—297 K, ordered as δ(^{11}B) [δ(^{1}H)]: +11.4 [+1.90], +10.4 [+2.16], +5.5 [+4.02], +2.9 [+3.50], +0.5 [+2.41], −3.0 [+2.54], −9.7 [+1.52], −23.50 [no ^{1}H attached; δ(^{31}P) *ca.* +0.04 at 223 K; ^1J(^{31}P–^{11}B) *ca.* 130 Hz], −37.7 [+0.19]; plus δ(^{1}H)(bridge) at −3.62 and −13.76, δ(^{1}H)(C_6Me_6) at +1.87, δ(^{1}H)(MeNMe) at +2.34 and +2.67; δ(^{1}H)(PMe_2) at +1.63 [^2J(^{31}P–^{1}H) 11.2 Hz] and +1.70 [^2J(^{31}P–^{1}H) 11.6 Hz]; and δ(^{1}H)(PPh) centred at *ca.* +7.85 and +7.53 (both multiplets). δ(^{31}P) in p.p.m. to low field of H_3PO_4 (85%).

compound of formulation [$(C_6Me_6)RuB_9H_{11}(CH_2NMe)$] with *nido/arachno* ten-vertex {RuB_9} character and, unusually, a cluster-bound exocyclic –$NMeCH_2$– moiety resulting from the reductive capture of one MeNC molecule. This product could form *via* an MeNC adduct of formulation (**II**) or possibly of formulation (**V**) for which there is also some[3] structural precedent in a related rhodium system.

The major identified product of the decomposition of unstable (**2**) is the ten-vertex *isocloso*-species [1-(η^6-C_6Me_6)-*isocloso*-RuB_9H_9] [compound (**3**), schematic structure (**VI**)] that would result from the complete reduction of MeNC and the consequent extrusion of MeNHMe from the polyhedral cluster [equation (1)].† The MeNHMe was tentatively identified in solution by NMR spectroscopy.

An attempt to elucidate the structure of the intermediate (**2**) [structure (**IV**)] by the addition of the stronger ligand PMe_2Ph resulted in the formation of the air-stable orange adduct [μ-6,9-(NMe_2)-10-(PMe_2Ph)-5-(η^6-C_6Me_6)-*arachno*-5-RuB_9H_{10}] (**4**) characterized by NMR spectroscopy† and single-crystal *X*-ray diffraction analysis‡ [Figure 1 and structure (**VII**)]. Compound (**4**) exhibits several interesting features, in particular (a) a {μ-6,9-NMe_2} bridging moiety that is reasonably presumed to represent another of the two-electron transfer steps in the overall four-electron reduction of MeNC to MeNHMe, and (b) an *arachno* ten-vertex 5-metalla polyhedral borane for which there is little precedent.[5]

The various structural implications, together with the stepwise redox pedigree[6] implied by the various structural types in the sequence (**I**) → (**II**)/(**V**) → (**IV**) → (**VII**) → (**VI**) suggest much interesting further chemistry which we are currently investigating.

We thank the S.E.R.C. for financial support, the Leeds/Fudan (Shanghai) exchange scheme for a grant (to Z. S.) and Dr. B. Štíbr for helpful discussions.

Received, 28th July 1989; Com. 9/03210J

‡ *Crystal data* for $C_{22}H_{45}B_9NPRu$: M = 552.95, monoclinic, a = 899.1(2), b = 1951.9(4), c = 1647.2(3) pm, β = 101.18(2)°, U = 2.836(1) nm^3, Z = 4, space group $P2_1/n$, D_c = 1.29 g cm^{-3}, μ = 5.49 cm^{-1}, $F(000)$ = 1152. $R(R_W)$ = 0.0333 (0.0364) for refinement of 4572 unique absorption-corrected reflections with $I > 2.0\sigma(I)$ and $4.0 \leqslant 2\theta \leqslant 50.0°$.

All crystallographic measurements were made on a Nicolet P3/F diffractometer operating in the ω–2θ scan mode using graphite monochromated *X*-ray radiation. The structure was determined *via* standard heavy-atom methods and refined by full-matrix least-squares. All non-hydrogen atoms were refined with aniosotropic thermal parameters. The methyl hydrogen atoms were included in calculated positions and assigned to an overall isotropic thermal parameter. The borane hydrogen atoms were located in a Fourier difference synthesis and were refined with isotropic thermal parameters. The weighting scheme $w = [\sigma^2(F_o) + 0.0002(F_o)^2]^{-1}$ was used at the end of refinement. Atomic co-ordinates, interatomic distances and bond angles, and thermal parameters have been deposited at the Cambridge Crystallographic Centre. See Notice to Authors, Issue No. 1.

References

1 J. A. Walker, C. B. Knobler, and M. F. Hawthorne, *Inorg. Chem.*, 1985, **24**, 2688, and references cited therein.
2 X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy, P. MacKinnon, and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1988, 2809.
3 X. L. R. Fontaine, H. Fowkes, N. N. Greenwood, J. D. Kennedy, and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1987, 1431; E. J. Ditzel, X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy, and M. Thornton-Pett, *J. Chem. Soc., Chem. Commun.*, 1989, 1262.
4 M. Bown, Ph.D. Thesis, University of Leeds, 1989, and other unpublished work from this laboratory by M. Bown, E. J. Ditzel, X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy, and M. Thornton-Pett.
5 J. Briguglio and L. G. Sneddon, *Organometallics*, 1986, **5**, 327.
6 K. Baše, Abstract CA10, VI International Meeting on Boron Chemistry, Bechyně, Czechoslovakia, 22—26 June 1987, p. 49.