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Preliminary communication

HEXAMETHYLBENZENE-RUTHENABORANE AND -OSMABORANE CHEMISTRY

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Summary

An extensive suite of polyhedral metalloborane structural types is readily synthesizable by the reactions of $[(\eta^6\text{-}C_6Me_6)RuCl_2]_2$ with polyhedral borane anions, and preliminary indications are that the osmium analogue $[(\eta^6\text{-}C_6Me_6)OsCl_2]_2$, prepared by a route analogous to that used for $[(\eta^6\text{-}C_6Me_6)RuCl_2]_2$, is an equally versatile metallaborane synthon.

One of the more fascinating though frequently frustrating challenges in metallaborane chemistry is the problem of identifying convenient metal-containing starting materials that will react with a wide variety of borane species to yield, in turn, a variety of structural types each of which contains the same metal centre as one of the cluster vertices. Such a suite of polyhedral metallaboranes can then be used to establish structural, mechanistic, and spectroscopic systematics by facilitating intercomparisons and reducing interpretational ambiguities. We here report preliminary results for a variety of reactions undergone by the areneruthenium dimer $[(\eta^6\text{-}C_6Me_6)RuCl_2]_2$ which fulfils this role in that it readily yields a diverse suite of new ruthenaborane cluster compounds of which each incorporates the $\{(\eta^6\text{-}C_6Me_6)Ru\}$ moiety as a cluster vertex.

Compounds identified so far include *arachno- nido-* and *closo*-type clusters and include examples with four, five, six, ten, and eleven vertices as summarized in Scheme 1. Interestingly, *nido*-$B_5H_8^-$ and *closo*-$B_{12}H_{12}^{2-}$ were the only two common polyhedral borane anions that were found not to react to give isolable metallaborane products in significant yield. In addition to the products indicated in Scheme 1, some of the reactions also yield further as yet unidentified metallaborane products which consequently promise further novelty.

All products illustrated in the Scheme were isolated by preparative HPLC or by TLC in air, and were characterized by mass spectroscopy, by comprehensive multielement, multiple resonance, and multidimensional NMR spectroscopy, and

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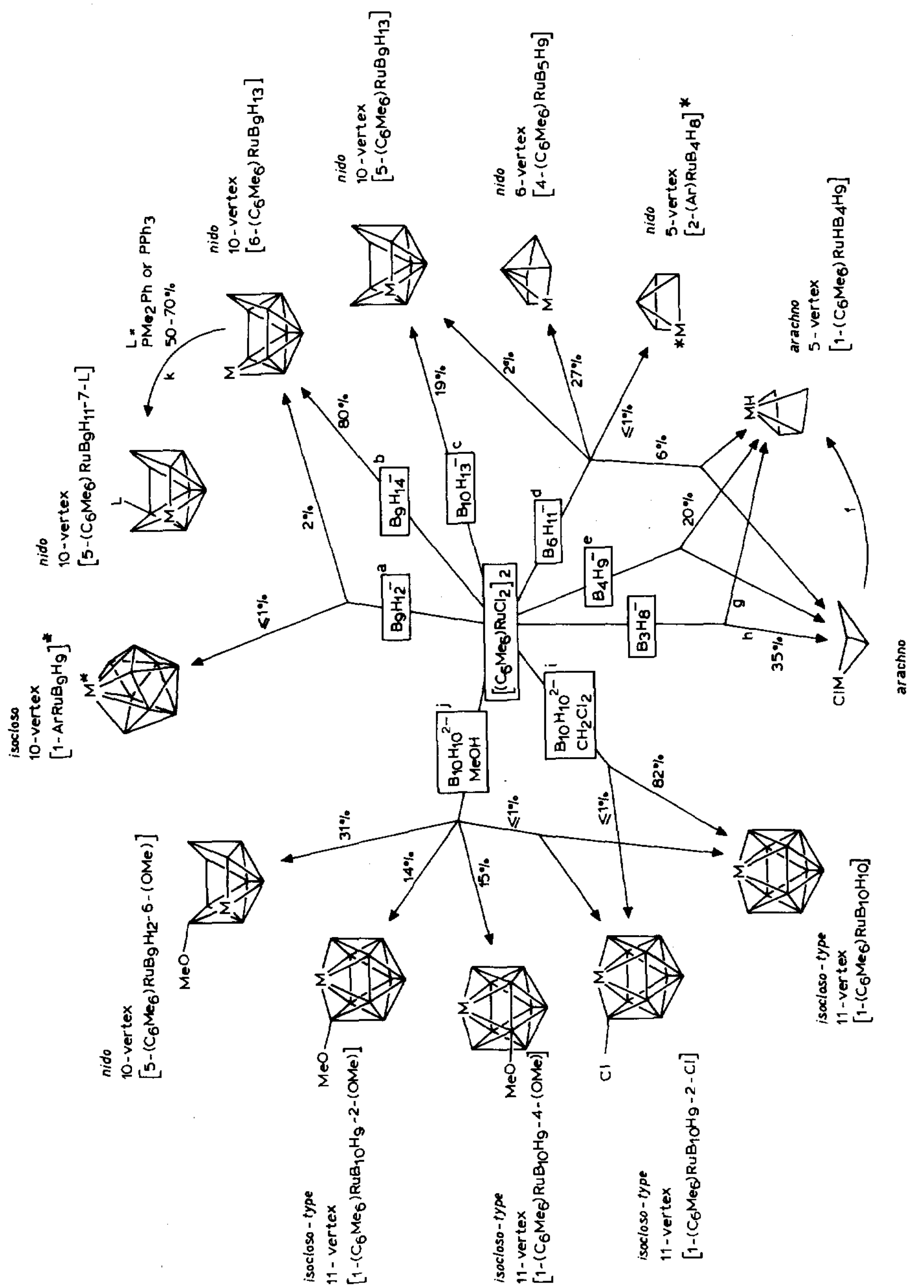

SCHEME 1. Summary of products so far identified [M = {(η^6-Ar)Ru}] from a series of reactions undergone by $[(\eta^6\text{-}C_6Me_6)RuCl_2]_2$ with a variety of anionic binary borane species on a 300 μmol scale. Reaction conditions were as follows (ambient temperature unless otherwise specified): (a) $[NBu^n_4][B_9H_{12}]$ in CH_2Cl_2, 17 h; (b) $[NEt_4][B_9H_{14}]$ in CH_2Cl_2, 18 h; (c) $B_{10}H_{14}$ plus $C_{10}H_6(NMe_2)_2$ in CH_2Cl_2, 5 h; (d) $K[B_6H_{11}]$ in CH_2Cl_2/THF at −25°C, 2 h; (e) $K[B_4H_9]$ in CH_2Cl_2/THF at −35°C, 8 h; (f) $Tl[B_3H_8]$ in CH_2Cl_2, 4 days; (g) $Tl[B_3H_8]$ in CH_2Cl_2, 4 days; (h) $Tl[B_3H_8]$ in CH_2Cl_2, 1 h; (i) $[NEt_3H]_2[B_{10}H_{10}]$ in CH_2Cl_2, 0.5 h; (j) $[NEt_3H]_2[B_{10}H_{10}]$ in MeOH, reflux 1–16 h; and (k) in CH_2Cl_2, reflux 2–4 h. *In these two compounds the C_6Me_6 ligand has possibly undergone some modification, possibly chlorination, as is also the case with a variety of other low-yield products (not included in the scheme) that have been isolated from some of the above reactions.

also by elemental analysis when the isolated amounts of material were sufficiently high.

Of particular interest are the "*isocloso*" ten- and eleven-vertex species that pose interesting questions for the development of electron-counting rules and cluster-bonding theory [1], and the novel *arachno* five-vertex species $[(C_6Me_6)RuHB_4H_9]$ which has an *endo* hydrogen atom on the Ru(1)-position just like the one [2] on B(1) in B_5H_{11} itself. Also of interest are the high yields of some of the products, particularly *isocloso*-$[1\text{-}(C_6Me_6)RuB_{10}H_{10}]$, *nido*-$[6\text{-}(C_6Me_6)RuB_9H_{13}]$, and *nido*-$[5\text{-}(C_6Me_6)RuB_9H_{11}\text{-}7\text{-}(PMe_2Ph)]$, since their ready synthesis will better facilitate the generation of further metallaborane chemistry.

A number of interesting structural rearrangements and degradations are also evident. In addition, the aufbau conversion of *arachno* four-vertex $[2\text{-}(C_6Me_6)\text{-}ClRuB_3H_8]$ to *arachno* five-vertex $[1\text{-}(C_6Me_6)RuHB_4H_9]$ is unusual, and may well have relevance to the mechanism of formation of *nido*-$[(CO)_3FeB_4H_8]$ from *arachno*-$[(CO)_3HFeB_3H_8]$ [3] and to other hitherto puzzling cluster aufbau-processes.

We have also been able to synthesize the previously unreported osmium analogue $[(\eta^6\text{-}C_6Me_6)OsCl_2]_2$ * in a yield (as yet unoptimized) of 26% using a route analogous to that [4] available for $[(\eta^6\text{-}C_6Me_6)RuCl_2]_2$. Preliminary results suggest that this complex is equally useful as a new osmaborane synthon. For example, the eleven-vertex *isocloso*-type species $[1\text{-}(\eta^6\text{-}C_6Me_6)OsB_{10}H_{10}]$ is obtained in 52% yield from the reaction with *closo*-$[B_{10}H_{10}]^{2-}$, the four-vertex *arachno* species $[2\text{-}(\eta^6\text{-}C_6Me_6)ClOsB_3H_8]$ in 70% yield from the reaction with Tl[*arachno*-B_3H_8], and the ten-vertex *nido* species $[6\text{-}(\eta^6\text{-}C_6Me_6)OsB_9H_{13}]$ in 21% yield from the reaction with *arachno*-$[B_9H_{14}]^-$.

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* Analytical and spectroscopic data are fully consistent with this formulation of the mustard-coloured product.