Preliminary communication

The preparation of the metal-rich ruthenaborane, $Ru_3(CO)_9BH_5$: a case of isomerisation involving *endo*-hydrogen migration.

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Abstract

The synthesis and spectroscopic characterisation of the new metal-rich ruthenaborane, $Ru_3(CO)_9BH_5$, are reported. Variable temperature ^{1}H NMR spectral data reveal that the compound exists in two isomeric forms, which differ only in the location of the *endo*-hydrogen atoms. The two isomers are equally favoured at room temperature. The fluxional processes involving the *endo*-hydrogens in each isomer, and the equilibrium between the two isomers, are examined.

Many transition metal clusters exhibit tetrahedral cores, and within this class of compound is a variety of neutral clusters containing a triangular frame of metal atoms capped by a main group element, X. Where *endo*-hydrogen atoms are present, their location on the M_3X tetrahedral core is a function of both M and X. For instance, of those neutral clusters which contain Group 8 metals, $H_3M_3(CO)_9CR$ (M = Fe, Ru, R = alkyl [1–6]; M = Os, R = H [7]), $H_2M_3(CO)_9PR$ (M = Ru, Os; R = Ph [8,9]), $H_2M_3(CO)_9NR$ (M = Ru, R = H, Me, Ph [10–15]; M = Os, R = Ph [16]), $H_3M_3(CO)_9Bi$ (M = Fe, Ru) [17,18], $HFe_3(CO)_9SR$ (R = C_3H_7, C_6H_{11}) [19, 20], and $H_2Os_3(CO)_9S$ [21], all exhibit *endo*-H atoms bridging M–M edges. In contrast, the boron-capped cluster $HFe_3(CO)_9BH_4$, possesses three Fe–B and one Fe–Fe bridging hydrogen atoms [22]. Other boron capped examples are confined to systems with a 2-electron donor on boron; in $H_3Os_3(CO)_9BR$ (R = CO [23], PMe_3 [24]), all *endo*-hydrogen atoms are metal–metal bridging, while in $H_3Os_3(CO)_9$-($B=CH_2$), the introduction of a borylidene cap gives rise to an *endo*-hydrogen atom rearrangement with one Os–Os and two Os–B bonds bridged [25]. On the other hand, in $H_2Fe_3(CO)_9(C=CH_2)$, Fe–H–Fe bridges again predominate [26]. Several theoretical investigations of the bonding within M_3X type clusters have been presented [27], and the location of *endo*-H atoms has been found to depend on a subtle balance of electronic effects [27c].

We have now extended the experimental methodology for the preparation of metal-rich ruthenaboranes [28*], and present here a report on the cluster

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* Reference number with asterisk indicates a note in the list of references.

$Ru_3(CO)_9BH_5$. This compound serves to fill gaps both in periodic and metal-triad trends of M_3X compounds, and gives further insight into the problem of partitioning the effects of metal and main group atoms in these clusters.

$Ru_3(CO)_{12}$ reacts with $BH_3 \cdot HF$ in the presence of $[Et_3BH]Li$ in hexane solution at room temperature. After acidification, followed by thin layer chromatography, yellow $Ru_3(CO)_9BH_5$ [29*] is obtained in $\cong 10\%$ yield as the 3rd band. The ^{11}B NMR spectrum of the new compound shows two resonances which, at room temperature, are present in a ratio of approximately 1/1. The variable temperature ^1H NMR spectrum of the compound is shown in Fig. 1. $Ru_3(CO)_9BH_5$ exhibits two independent fluxional processes, consistent with the presence of two isomers, I and II. The spectral properties of I are reminiscent of those of $Fe_3(CO)_9BH_5$. There is a ^1H NMR signal at δ +3.5 (terminal BH) which is temperature invariant, and the resonances assigned to the endo-hydrogen atoms follow the same qualitative behavioural pattern as those in $Fe_3(CO)_9BH_5$. Thus, structure I is proposed. The interaction of the boron atom with one terminal and three M–H–B bridging hy-

I   II
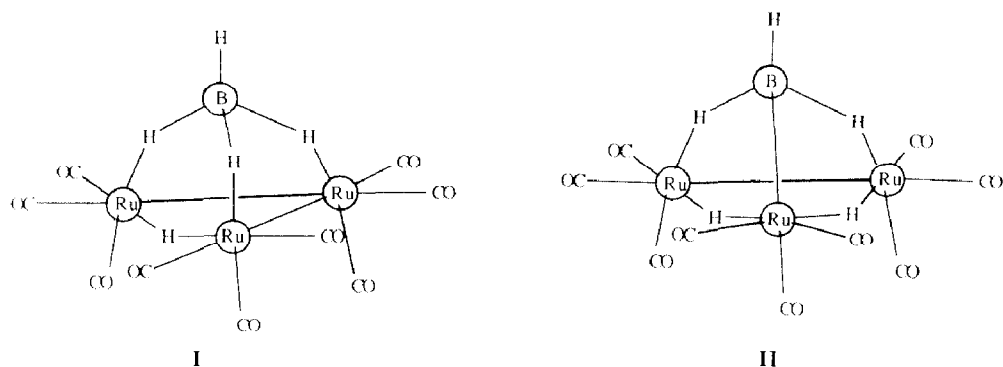
drogens is supported by an ^{11}B chemical shift at δ +2.8 in I compared to δ +1.8 in the iron analogue [30*]. The second isomer is assigned structure II on the basis of possessing a terminal H (δ +4.0), two Ru–H–B protons (δ −11.3), and two Ru–H–Ru protons (δ −18.4). Again, the ^{11}B NMR chemical shift is in accordance with this assignment; a shift to lower field is indicative of fewer B–H, and more direct Ru–B interactions (viz. the change from I to II).

Over the temperature range 233 to 293 K, I and II are not interconverting on the 250 MHz NMR time scale; relative hydride intensities suggest that I is slightly preferred over II at lower temperatures. In I, equivalence of the three Ru–H–B bridging hydrogen atoms is observed at 293 K. Between 333 and 373 K, the metal hydride resonances in each isomer collapse, and the signals in the Ru–H–B region broaden and merge together (Fig. 1). This is consistent with rapid interconversion of I and II. Complete equivalence of all the bridging-hydrogen atoms is not attained by 373 K on the 250 MHz time scale. An equilibrium between I and II is supported by variable temperature FT-IR studies; studies of the infrared spectra in various solvents indicate that this equilibrium does not depend significantly on the solvent [31*].
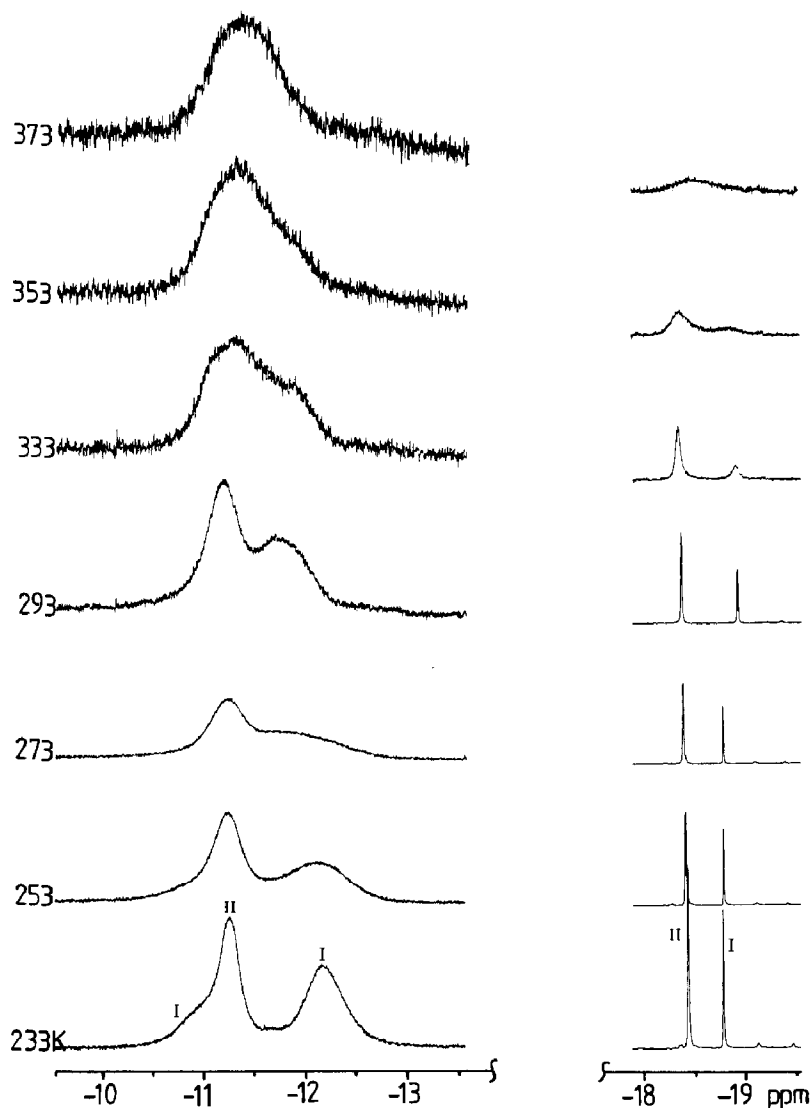
Fig. 1. 250 MHz ^{1}H NMR variable temperature spectrum for $Ru_3(CO)_9BH_5$.

The cluster $Ru_3(CO)_9BH_5$ provides an example of isomerisation via *endo*-hydrogen migration. Although isomer formation in itself is not uncommon, the observation of two, *favoured*, isomers for a system of type M_3X is an extremely unusual feature. For carbon capped, neutral trimetal clusters, the *endo*-hydrogen atoms prefer to bridge the M–M edges [32*,33*], although in the case of iron, a minor isomer, which exhibits C–H–M bridges and is the kinetic product of protonation of the conjugate base, has been observed [34]. Along the series $Fe_3(CO)_9XH_n$ (X = B, C, N) *endo*-hydrogen atoms tend from being Fe–H–X toward Fe–H–Fe bridging, but in each case, only one structure is predominant. In going from $Fe_3(CO)_9BH_5$ to $Ru_3(CO)_9BH_5$ we have exemplified migration of *endo*-hydrogen atoms towards the metal atom. This may be rationalised in terms of the increased metal–hydrogen bond strength (i.e. $E(Ru–H) > E(Fe–H)$). Alternatively, the

migration may be linked with an optimisation of metal to main group atom bonding [27c]; as the metal triangle increases in size (viz. $Fe_3(CO)_9BH_5$ to $Ru_3(CO)_9BH_5$), the orbital lobes on each metal atom should tilt inwards to enhance their overlap with the $2s$ and $2p$ AO's of the boron atom. (This is akin to the deformations described in cyclic hydrocarbon π-donor ligands, C_nH_n) [35]. A direct consequence of this orbital tilt, will be a carbonyl ligand reorientation, and a redistribution of *endo*-hydrogen atoms. Obviously, in the case of ruthenium, since the observed energy difference between isomers I and II is a small one, the balance between Ru–Ru and Ru–B bonding must be a delicate one.

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29 $Ru_3(CO)_9BH_5$: $m/e\ P^+$ 573 (isotopic pattern agrees with simulated pattern) with sequential loss of 9CO molecules from parent ion; IR [29] ($\nu(CO)$, CH_2Cl_2) 2110w, 2106w, 2078vs, 2053s, 2034s, 2020m cm^{-1}; I: ^{11}B (CD_2Cl_2; 298 K) δ +2.8(br, m); ^1H (CD_2Cl_2, 233 K) δ +3.5(1H), −11.0(1H),

$-12.2(2H)$, $-18.8(1H)$; II: ^{11}B (CD$_2$Cl$_2$; 298 K) δ $+21.0$(br, m); ^1H (CD$_2$Cl$_2$, 233 K) δ $+4.0(1H)$, $-11.3(2H)$, $-18.4(2H)$.

30 ^{11}B NMR chemical shifts are sensitive to B–H vs. B–M interactions. For structurally related systems, $\delta(^{11}B)$ values are expected to be similar.

31 Solvents chosen varied in polarity; basic solvents, such as methanol, however, lead to cluster deprotonation and were therefore not included.

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