Notes

A High Yield Route to Ruthenaboranes

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*Summary: The versatility and synthetic potential of the novel tris-acetonitrile-substituted cluster $Ru_3(CO)_9(MeCN)_3$ (**3**) for the formation of ruthenaboranes in unprecedently high yields are illustrated. Reaction of **3** with $[Me_4N][B_3H_8]$ yields $HRu_3(CO)_9B_2H_5$ (65%) and with $BH_3{\cdot}THF$ yields $HRu_6B(CO)_{17}$ (60%).*

Introduction

Part of the strategy for controlled synthesis of cluster carbonyl complexes is the preparation of stable intermediates that allow displacement of ligands under relatively mild conditions. This avoids the extreme temperatures and pressures normally required for direct substitution of carbonyl groups.[1] Acetonitrile has been used as a labile ligand,[2] the mono- and bis-acetonitrile-substituted clusters $Ru_3(CO)_{11}(MeCN)$ (**1**) and $Ru_3(CO)_{10}(MeCN)_2$ (**2**) being used very widely in cluster chemistry for over 10 years.[3,4] Recently, the synthesis of the tris-acetonitrile-substituted complex $Ru_3(CO)_9(MeCN)_3$ (**3**) has been reported,[5,6] but its synthetic potential has not been explored, except in the case of its reactions with alkynes.[7] In this note, we show that **3** acts as a good starting material for the synthesis of heterometallic boride clusters much more efficiently and in significantly higher yields than previously reported.

Results and Discussion

Reaction of $Ru_3(CO)_9(MeCN)_3$ (**3**) with $[Me_4N][B_3H_8]$ under reflux for 20 min followed by acidification leads to the formation of the metal-rich ruthenaborane $HRu_3(CO)_9B_2H_5$ (**4**) in 65% yield together with some decomposition. The ^1H and $^{11}B\{^1H\}$ NMR spectra of **4** are indicative of a structure where the di-boron unit caps the Ru_3 triangle showing that it is a structural analogue of pentaborane[9] with the isolobal replacement of three BH units by three $Ru(CO)_3$ fragments. The ^1H NMR spectrum of **4** shows evidence for one terminal hydrogen atom per boron and four bridging hydrides in three environments (one B−H−B, two Ru−H−B, and one Ru−H−Ru). The schematic structure of **4** is shown in Scheme 1.

The synthesis of **4** from **3** represents a great improvement on previous preparative routes to this complex. Compound **4** was first observed as a product of the thermolysis of $NaBH_4$ with $Ru_3(CO)_{12}$ (**5**) being recovered in approximately 5% yield.[8] A higher yield (≤20%) of **4** has been obtained from the reaction of $[Me_4N][B_3H_8]$ with **2** but only after leaving the reaction mixture stirring for around 3 days.[9] The reason **3** is such a good starting material for the synthesis of **4** may have its roots in the fact that **3** is essentially a source of an "$Ru_3(CO)_9$" fragment, and hence no decarbonylation, CO scavenging, or cluster rearrangement is necessary to form **4**.

The hydride cluster **4** is readily deprotonated by reaction with Na_2CO_3 to yield $[Ru_3(CO)_9B_2H_5]^-$ (**6**), the Ru−H−Ru hydrogen being removed.[9] Reaction of this anion with **3** at room temperature leads to the formation of the hexanuclear cluster anions $[Ru_6B(CO)_{17}]^-$ (**7**) and $[H_2Ru_6B(CO)_{18}]^-$ (**8**) in 15% and 20% yields, respectively. This result is similar to that reported for the reaction of **6** with **2**,[10] the exception being that yields are higher when **3** is used.

The anion **7** is isoelectronic with $Ru_6C(CO)_{17}$, and as expected, both clusters adopt a similar, octahedral, geometry, the boron and carbon atoms occupying an interstitial position in the two respective cases.[11] The $^{11}B\{^1H\}$ NMR spectrum of **7** shows a single peak at δ 195 ppm, this being significantly downfield shifted from the signals in **4** and similar to that observed in the related anion $[Fe_4Rh_2(CO)_{16}B]^-$ (δ 211 ppm).[12] Cluster **8** adopts a trigonal prismatic geometry, the single peak in the $^{11}B\{^1H\}$ NMR spectrum observed at δ 206 ppm,

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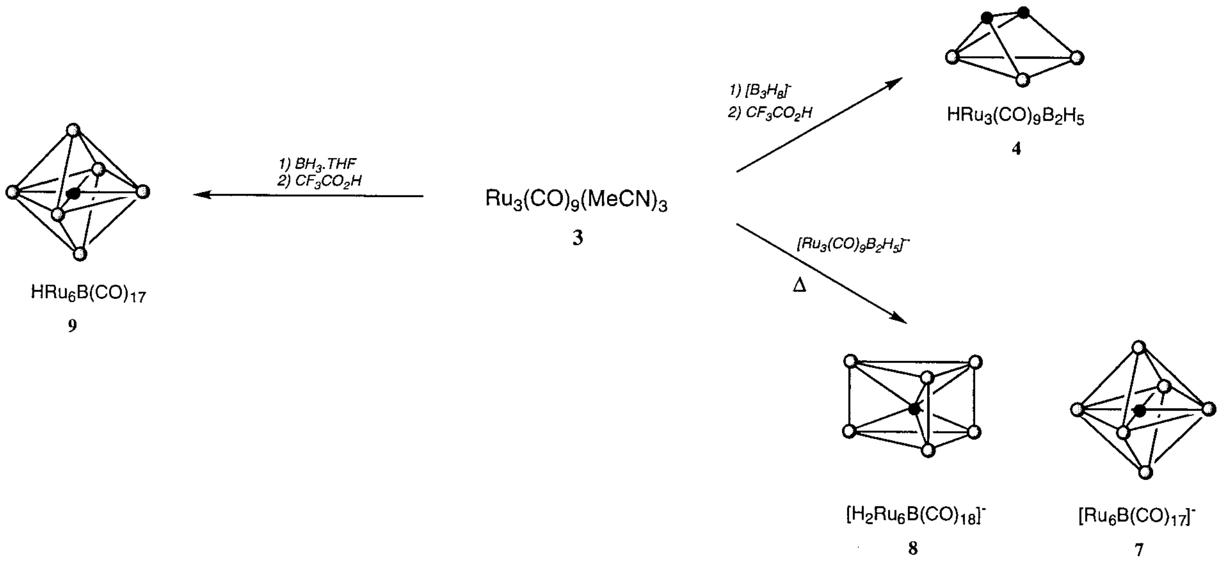
Scheme 1



indicating that the boron again occupies an interstitial site.[10] It is of interest that both these compounds are formed in the same reaction, and this confirms the postulation made previously that the choice of trigonal prismatic (in the case of **8**) or octahedral (in the case of **7**) geometry is not determined by the size of the interstitial atom.[10] The schematic structures of **7** and **8** are shown in Scheme 1.

We have found that a much more efficient route to **7** is by reaction of **3** with BH_3·THF under reflux for 40 min, the yield of **7** being 60%. This represents a significant improvement over any of the previously reported synthetic routes. The cluster was first prepared, in less than 10% yield, by thermolysis of a toluene solution of **5** with BH_3·THF.[13] More recently, more synthetic routes have been developed including photolysis of $Ru_3(CO)_9(BH_5)$[14] and reaction of $H_2Ru_6(CO)_{17}$ with $BH_3S(CH_3)_2$[15] but none of these are as selective or high yielding as that reported here. The anion **7** is readily acidified to yield $HRu_6B(CO)_{17}$ (**9**).

In all the reactions undertaken, there is some degree of decomposition in addition to product formation. This may be attributed to reaction of the boron reagents with the small amount of water in the solvents (even after rigorous dehydration) yielding $B(OH)_3$, which may subsequently attack **3**. This assertion has been confirmed by the controlled addition of microliter volumes of water to the reaction mixture, the result being greatly increased decomposition of **3**.

The results presented here illustrate clearly the selectivity and versatility of **3** as a reagent for the synthesis of metalloboranes. We feel that it will be possible to form other known, and novel, homo- and heterometallic compounds efficiently and in high yield, using **3** as a starting material, and work is currently under way to confirm this assertion.

Experimental Section

General Comments. The boron reagents used and intermediates formed in this investigation are sensitive to oxygen and moisture, so all syntheses were performed under an inert atmosphere of dry nitrogen using standard Schlenk techniques. Routine separation of products was performed by thin-layer chromatography (TLC), using commercially prepared glass plates, precoated to a thickness of 0.25 mm with Merck Kieselgel 60 F_{254} as supplied by Merck. Alternatively laboratory-prepared glass plates, coated to a thickness of 1.0 mm with Merck Kieselgel 60 F_{254}, were used.

All reagents were purchased from commercial sources and used as received unless noted otherwise. The binary metal carbonyl $Ru_3(CO)_{12}$ (**5**) was prepared from $RuCl_3$·H_2O, and $Ru_3(CO)_9(MeCN)_3$ (**3**) was prepared from **5** by literature methods.[16,17]

Physical Measurements. Infrared (IR) spectra were recorded using NaCl solution cells (path length 0.5 mm), and all values are quoted are in wavenumbers (cm^{-1}). The ^1H and $^{11}B\{^1H\}$ NMR spectra are reported using the chemical shift scale in units of ppm relative to $SiMe_4$ ($\delta = 0$) in the case of ^1H NMR and relative to BF_3·OEt_2 ($\delta = 0$) in the case of ^{11}B NMR spectra. All downfield chemical shifts are positive. Fast atom bombardment (FAB) mass spectra were recorded using either 3-nitrobenzyl alcohol or thioglycerol as a matrix and CsI as calibrant.

Reaction of $Ru_3(CO)_9(MeCN)_3$ (3) with $[Me_4N][B_3H_8]$. To an acetonitrile solution of **3** (100 mg in 100 mL) was added $[Me_4N][B_3H_8]$ (34 mg) in acetonitrile (50 mL), and the reaction mixture refluxed for 20 min then acidified with trifluoroethanoic acid. Purification of the reaction mixture by TLC (1:1 dichloromethane/hexane as eluent) gave yellow $HRu_3(CO)_9(B_2H_5)$ (**4**) (60 mg, 65% yield) together with some decomposition.

4. IR(CH_2Cl_2) ν_{BH}: 2355(w), 2305(w); ν_{CO}: 2106(w), 2084(s), 2065(m), 2053(vs), 2041(m), 2033(m), 2014(w) cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.3(br, 1H), −1.2(br, 2H), −12.3(br, 2H), − 19.0(s, 1H) ppm. $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ 17(br) ppm. *m/z*: 584 (calc 583 using ^{101}Ru).

Reaction of $Ru_3(CO)_9(MeCN)_3$ (3) with $[Ru_3(CO)_9(B_2H_5)]^-$ (6). To an acetonitrile solution of **3** (50 mg in 50 mL) was

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added **6** (50 mg) in acetonitrile (50 mL), and the reaction mixture refluxed for 40 min. Purification of the reaction mixture by TLC (1:1 dichloromethane/hexane as eluent) gave brown $[Me_4N][Ru_6B(CO)_{17}]$ (**7**) (15 mg, 15% yield) and brown $[Me_4N][H_2Ru_6B(CO)_{18}]$ (**8**) (20 mg, 20% yield) together with some uncharacterized deep brown products.

7. IR(CH_2Cl_2) ν_{CO}: 2078(s), 2063(vs), 2045(s), 2024(s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.34(s, 12H) ppm. $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ 195(s) ppm. m/z: 1167 (calc 1166 using ^{101}Ru).

8. IR(CH_2Cl_2) ν_{CO}: 2043(w), 228(s), 2011(w), 1985(m) cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.34(s, 12H), −17.1(s, 2H) ppm. $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ 206(s) ppm. m/z: 1197 (calc 1196 using ^{101}Ru).

Reaction of $Ru_3(CO)_9(MeCN)_3$ 3 with $BH_3{\cdot}THF$. To an acetonitrile solution of **3** (100 mg in 50 mL) was added $BH_3{\cdot}THF$ (2 mg) in THF (10 mL), and the reaction mixture refluxed for 40 min then acidified with trifluoroethanoic acid. Purification of the reaction mixture by TLC (1:1 dichloromethane/hexane as eluent) gave brown $HRu_6B(CO)_{17}$ (**9**) (18 mg, 60% yield) with some decomposition.

$HRu_6B(CO)_{17}$. IR(CH_2Cl_2) ν_{CO}: 2079(s), 2065(vs), 2047(s), 2027(s) cm^{-1}. ^1H NMR ($CDCl_3$): δ −17.8(s, 1H) ppm. $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ 194(s) ppm. m/z: 1095 (calc 1094 using ^{101}Ru).

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