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Preparation of some Carbonyl Rhenium and Rhodium Hydroundecaborates from $Na_2B_{11}H_{13}$

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Metallic derivatives can be obtained from hydroborates by various mechanisms, some of them bringing about a change in the number of vertices of the original cage. A simple way of producing new species with a B11 cage is via cation exchange from easily available salts. Excluding monoatomic cations, no successful syntheses were reported until the studies of Zhang Lun *et al.* appeared [1–4]. The production of such compounds is not straightforward, necessitating the reaction of MCl_4^- derivatives of the exchanged cation with the hydroborate $Et_4NB_{11}H_{14}$. All the compounds described contained at least one cyclopentadienyl ligand bonded to the metal. When reacted with a suitable metallic ligand, hydroborates containing eleven boron atoms can also be expected to form derivatives with an icosahedral structure. Many examples of such polyhedral expansion reactions have been described with the parent carboranes, phosphaboranes and thiaboranes [5–10]. However, only two metallaboranes of this type have been prepared from a cage containing eleven boron atoms, the nickelaborane $CpNiB_{11}H_{11}$ obtained by Hawthorne *et al.* in 1975 [11] and $\{B_{11}H_{11}AlCH_3\}Na_2$ recently obtained by Shore and Getman [12].

In the present work we have studied reactions involving the hydroborates $Na_2B_{11}H_{13}$ or $NaB_{11}H_{14}$ and the bromides $[Re(CO)_5Br]$, $[Re(CO)_4]_2$ or $[RhCO(PPh_3)_2Br]$. Conductivity measurements have been made in THF solution with the aim of explaining the different reactivities of these salts. The conversion of the new ionic species into metallaboranes has also been attempted.

Results and Discussion

Reactions involving the sodium hydroborates $NaB_{11}H_{14}$ or $Na_2B_{11}H_{13}$ and $[Re(CO)_5Br]$ or $[Re(CO)_4Br]_2$ have been attempted in THF because the reagents are soluble and the sodium halide may be easily removed by crystallization. No reaction occurred between $NaB_{11}H_{14}$ and either $[Re(CO)_5Br]$ or $[Re(CO)_4Br]_2$. In the case of the reaction between $Na_2B_{11}H_{13}$ and $[Re(CO)_5Br]$, the crystallization of NaBr was very slow, only one sodium cation being involved. During the reaction, a mixture of $B_{11}H_{14}^-$ and $B_{11}H_{13}^{2-}$ anions were characterized by NMR spectroscopy. After solvent removal, a crude orange product was obtained from which two new species were isolated by use of appropriate solvents and sublimation of excess carbonyl bromide.

The most stable compound, a light brown solid, was extracted with methylene chloride from the crude solid phase with a 20% yield. The $^{11}B[^1H]$ NMR is consistent with the presence of $B_{11}H_{14}^-$, having one singlet with a chemical shift of −36.7 ppm, with reference to $B(OMe)_3$, and a coupling constant of $J = 155$ Hz. These data can be compared (Table 1) with those measured with the same anion associated with other cations. The IR spectrum of the THF solution shows a strong B–H absorption at 2525 cm^{-1}, further confirming the presence of the $B_{11}H_{14}^-$ anion. The cationic part has been identified as a rhenium pentacarbonyl from its strong C–O absorptions at 2045 and 1987 cm^{-1} [13, 14], showing that no carbonyl group is lost during the reaction. In general, the IR spectra were measured in solution since this gave sharper bands than when measured as solids. However, it is worth noting that there was a significant change in the C–O stretching frequencies on changing from solid to solution.

TABLE 1. NMR data for $[Re(CO)_5]Br_{11}H_{14}$, $NaB_{11}H_{14}$ and $Me_3NHB_{11}H_{14}$ in THF with reference to $B(OMe)_3$

Compound	δ ^{11}B (ppm)	J(B–H) (Hz)
$[Re(CO)_5]B_{11}H_{14}$	−36.7	155
$NaB_{11}H_{14}$	−34.8	150
$Me_3NHB_{11}H_{14}$	−32.2	155

A second component was isolated from the residue by crystallization from a THF solution with a 35% yield. The $^{11}B[H]$ NMR spectrum shows two singlets of chemical shifts −35.2 ppm and −48.2 ppm, having an intensity ratio of 10:1, which are assigned to $B_{11}H_{13}^{2-}$. These values appear in Table 2 together with results for $Na_2B_{11}H_{13}$ for comparison. The product has been identified as $Na[Re(CO)_5]B_{11}H_{13}$ after conversion into $Cs[Re(CO)_5]B_{11}H_{13}$.

Similar results have been obtained using the rhodium complex *trans*-$[RhCO(PPh_3)_2Br]$. However, the lability of the phosphine ligand bonded to the metal [15] did not allow good characterization of $Cs[RhCO(PPh_3)_2]B_{11}H_{13}$. $[RhCO(PPh_3)_2]B_{11}H_{14}$ has been obtained by protonation of this salt. The ^{11}B NMR shows the presence of the $B_{11}H_{14}^-$ anion (δ $^{11}B = -34.5$ ppm, $J = 132$ Hz). The IR spectrum recorded on a solid sample shows characteristic bands of terminal B–H groups at 2525 cm^{-1}, C–O at

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TABLE 2. NMR data for $Na[Re(CO)_5]B_{11}H_{13}$ and $Na_2B_{11}H_{13}$ in THF with reference to $B(OMe)_3$

Compound	Main peak (intensity 10)		Weak peak (intensity 1)	
	δ ^{11}B (ppm)	J(B–H) (Hz)	δ ^{11}B (ppm)	J(B–H) (Hz)
$Na[Re(CO)_5]B_{11}H_{13}$	−35.2	135	−48.2	150
$Na_2B_{11}H_{13}$	−39.4	120	−50.5	130

2090 and 1920 cm^{-1} and phosphine at 750 and 690 cm^{-1}, the organometallic moiety maintaining a *trans* configuration. These ^{11}B NMR data have been obtained at 32.1 MHz and the resolution is not sufficient to differentiate the boron atoms of the cage, as has been observed at 96.3 MHz [16].

The presence of the rhenium and rhodium derivatives of $B_{11}H_{14}^-$ in the reaction medium is due to a protonation of the parent $B_{11}H_{13}^{2-}$ derivative since $NaB_{11}H_{14}$ is unreactive. The protonation may be due to the presence of traces of water, the synthesis being carried out on small amounts of product over 12 h. It also seems probable that THF plays a role in this protonation, which does not occur readily in the presence of water.

During the reaction, the crystallization of NaBr from THF solution does not proceed through a simple mechanism involving free ions, since $NaB_{11}H_{14}$ (which is much more dissociated than $Na_2B_{11}H_{13}$) does not react. At 298 K, the conductivity of a THF solution of $Na_2B_{11}H_{13}$ containing 0.22 mol l^{-1} of sodium was only 0.08 Ω^{-1} cm, whereas with the same sodium concentration a conductivity of 1.80 Ω^{-1} cm was measured for $NaB_{11}H_{14}$. In the reaction with the metal bromide, $Na_2B_{11}H_{13}$ behaves very probably as an ion pair. This interpretation is consistent with the low reaction rate observed, since most reactions between free ions take place with extreme rapidity [17].

Conversion of $[Re(CO)_5]B_{11}H_{14}$ to the hypothetical $[Re(CO)_4]B_{11}H_{11}$ has been attempted without success, reaction under oxidative conditions producing boric acid by rupture of the boron cage.

Experimental

All syntheses, filtrations and solvent removals were carried out in a glove box filled with dried argon. The solvents were distilled and the reagents dried according to the standard conditions used for air-sensitive compounds [18].

Starting Materials

$NaB_{11}H_{14}$ was prepared from $NaBH_4$ and Et_2OBF_3 [19]. It was dissolved in water and converted to $Me_3NHB_{11}H_{14}$ by addition of Me_3NHCl to the solution. After purification of $Me_3NHB_{11}H_{14}$ by crystallization from acetone, sodium hydride was used to obtain very dry $NaB_{11}H_{14}$ and $Na_2B_{11}H_{13}$ by displacement of trimethylamine from $Me_3NHB_{11}H_{14}$ and subsequent deprotonation as described in the synthesis of the dicarbollid anion $C_2B_9H_{11}^{2-}$ [9].

$[Re(CO)_5Br]$ was prepared from $[Re_2(CO)_{10}]$ (Johnson-Matthey) and Br_2 [12] and purified by sublimation. $[Re(CO)_4Br]_2$ was obtained after refluxing a cyclohexane solution of $[Re(CO)_5Br]$ [13]. $[RhCO(PPh_3)_2Br]$ was used as supplied by Johnson-Matthey.

Synthesis

In a typical reaction, $[Re(CO)_5Br]$ (11.2 mmol), dissolved in the minimum volume of THF (approximately 25 cm^3), was mixed at room temperature and under vigorous stirring with 15 cm^3 of a THF solution containing the stoichiometric amount (11.2 mmol) of $Na_2B_{11}H_{13}$. A white solid characterized by X-ray diffraction as very pure NaBr crystallized slowly. The reaction reached completion after 12 h and the theoretical amount of NaBr was recovered by filtration (starting the reaction with an excess of $[Re(CO)_5Br]$ did not change the amount of NaBr recovered). The solvent was removed by vacuum distillation and a yellow solid was collected and dried at room temperature at 5×10^{-4} Torr for 12 h. During this operation, unreacted $[Re(CO)_5Br]$ was removed by sublimation. $[Re(CO)_5]B_{11}H_{14}$ was extracted from the crude solid by CH_2Cl_2 and this solvent was removed by distillation under low pressure. The solid was purified by recrystallization from CH_3CN solution by addition of a 1:1 mixture of toluene and hexane. $[Re(CO)_5]B_{11}H_{14}$ was collected as a light brown hygroscopic powder. In the laboratory atmosphere, the protonation of the solid occurred slowly, but this reaction was accompanied by some degradation of the boron cage giving boric acid. The protonation was more rapid and easier to control using a $THF-CH_2Cl_2$ solution of $Na[Re(CO)_5]B_{11}H_{13}$ which was stirred under atmospheric conditions for 24 h.

The conversion of $Na[Re(CO)_5]B_{11}H_{13}$ or $[Re(CO)_5]B_{11}H_{14}$ to a metallaborane has been attempted under various conditions without success: (a) refluxing a benzene suspension of $NaRe(CO)_5B_{11}H_{13}$ in contact with air; (b) reaction of $FeCl_3$ with $[Re(CO)_5]B_{11}H_{14}$ in a CH_3CN-H_2O mixture; (c) irradiation of a hexane suspension of $[Re(CO)_5]B_{11}H_{14}$

with a mercury lamp; (d) use of sodium amalgam as catalyst.

The conductivity of the solutions was measured in a hermetic thermostated cell fitted with an electrode having a constant of 0.843 using a C.D. 810 Tacussel instrument. The conductivity was determined at 250 Hz, 4 KHz, 10 KHz and 1 MHz. Except for the lowest frequency, the conductivity was not frequency dependent and it increased reversibly with the temperature of the solution.

Characterization

$Na[Re(CO)_5]B_{11}H_{13}$: the main IR bands of the THF solution were (in cm^{-1}) 2475(vs), 2045(s) and 1987(s). The IR bands of the solid (Nujol mull) were: 2480(vs), 2090(m), 1980(vs), 1200(vw), 1035(s), 920(s), 840(vw), 815(vw), 780(w), 730(w), 590(m), 580(w), 565(vw), 505(w) and 470(w). The sodium cation was exchanged for caesium by adding $Na[Re(CO)_5]B_{11}H_{13}$ to a stirred aqueous solution of CsF. $Cs[Re(CO)_5]B_{11}H_{13}$ was recovered as a light brown solid precipitate and its IR spectrum was similar to that of the sodium salt. The product was free from solvent but contained some CsF. The rhenium/boron ratio of 1.65 (required 1.56) and rhenium/carbon of 3.13 (required 3.10) were obtained by elemental analysis.

$[Re(CO)_5]B_{11}H_{14}$: the main IR bands of the THF solution were (in cm^{-1}) 2525(vs), 2045(s) and 1987(s). The following bands have been observed for the solid (Nujol mull): 2525(vs), 2090(s), 2030(sh), 1995(s), 1935(m), 1920(m), 1150(w), 1070(vw), 1035(vw), 970(w), 815(w), 720(m) and 420(s).

$[RhCO(PPh_3)_2]B_{11}H_{14}$: the IR spectrum of the solid (Nujol mull) showed the following bands: 2490(s), 1995(s), 1590(w), 1570(w), 1310(vw), 1120(w), 1090(m), 1070(w), 1030(m), 1000(m), 745(m), 720(vs), 690(s), 545(s), 530(w), 520(w), 510(w) and 485(w).

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