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Journal of Organometallic Chemistry 536–537 (1997) 115–121

Journal of Organometallic Chemistry

Organotransition-metal metallacarboranes 45. [1] Synthesis and structure of hydridoruthenacarborane double-decker and triple-decker sandwich complexes

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Received 8 May 1996; revised 2 July 1996

Abstract

The reaction of the $Et_2C_2B_4H_5^-$ monoanion with $(Cp^*RuCl)_4$ in THF gave pale yellow, air-stable, crystalline $Cp^*RuH(Et_2C_2B_4H_4)$ (**1H**), which was characterized via NMR, IR, UV–visible, and mass spectroscopy and X-ray diffraction. The hydride ligand on ruthenium is monohapto, with an Ru–H bond distance of 1.55(8) Å, and is protonic in character, being easily removed on treatment with t-butyllithium to afford the $Cp^*Ru(Et_2C_2B_4H_4)^-$ monoanion (**1**). In an attempt to prepare an Ru–Me derivative, **1** was reacted with methyl triflate, but the only isolable product, unexpectedly, was a B-methylated species, $Cp^*Ru^{II}H(Et_2C_2B_4H_3\text{-}5\text{-}Me)$ (**2**), obtained as a colorless air-stable solid and characterized via multinuclear, IR, UV–visible, and mass spectroscopy. Treatment of the cobaltcarborane monoanion $Cp^*Co(Et_2C_2B_3H_4)^-$ with $(Cp^*RuCl)_4$ in THF gave the heterobimetallic triple-decker sandwich $Cp^*Co(Et_2C_2B_3H_3)RuHCp^*$ (**4**), a dark green diamagnetic crystalline solid, characterized spectroscopically as in the cases of the preceding compounds. Crystal data for **1H**: space group $P2_1/c$; $a = 12.598(3)$ Å, $b = 8.674(2)$ Å, $c = 16.772(6)$ Å, $\beta = 100.29(3)°$, $Z = 4$; $R = 0.043$ for 2462 independent reflections having $I > 3\sigma(I)$. © 1997 Elsevier Science S.A.

Keywords: Carborane; Boron; Cluster; Ruthenium; Group 8; Agostic

1. Introduction

The chemistry of small metallacarborane sandwich complexes based on the $RR'C_2B_4H_4^{2-}$ and $RR'C_2B_3H_5^{2-}$ ligands (R, R′ = alkyl or $SiMe_3$), whose metal sandwich complexes are readily derivatized via introduction of substituents at one or more ring boron atoms [2,3], has evolved into an area of considerable scope (for recent reviews see Refs. [4–6]). These carboranes can be employed together with aromatic hydrocarbon rings as interchangeable construction units in building molecular sandwiches of two to six decks that incorporate a range of metals and metal oxidation states [1,4–6].

The versatility of this chemistry is extended still further by incorporating metal-bound protons. As illustrated in Scheme 1 for double-decker systems, suitable combinations of $RR'C_2B_4H_4^{2-}$, $RR'C_2B_3H_5^{2-}$, arene, Cp or Cp* ligands ($Cp^* = \eta^5\text{-}C_5Me_5$), and protons can stabilize metal oxidation states from +1 to +4 in neutral compounds.

The metal-protonated species are obtained from *nido*-$RR'C_2B_4H_5^-$ carborane *mono* anions having acidic B–H–B hydrogens, which characteristically undergo two types of reaction in THF solution: reversible intermolecular proton transfer to form the neutral carborane and the dianion, and/or complexation with a metal ion with retention of the 'extra' proton. As shown in Scheme 2, both processes often take place competitively, generating both metal-protonated and unprotonated metallacarborane products [1,5](a)[6–10].

Thus, in the chemistry of iron and cobalt double-decker, triple-decker, and multidecker complexes of the

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[1] For part 44 see Ref. [1]. Dedicated to the memory of Professor Yu.T. Struchkov in recognition of his outstanding contributions to structural organometallic chemistry.

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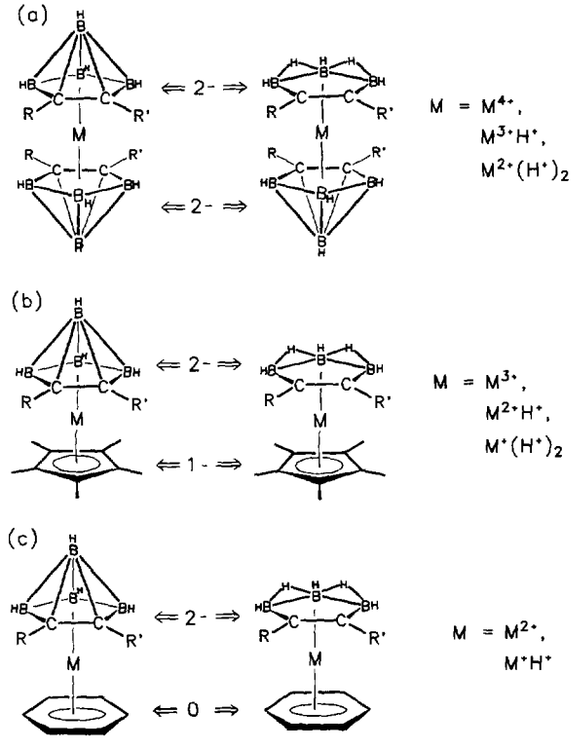
PII S0022-328X(96)06645-4



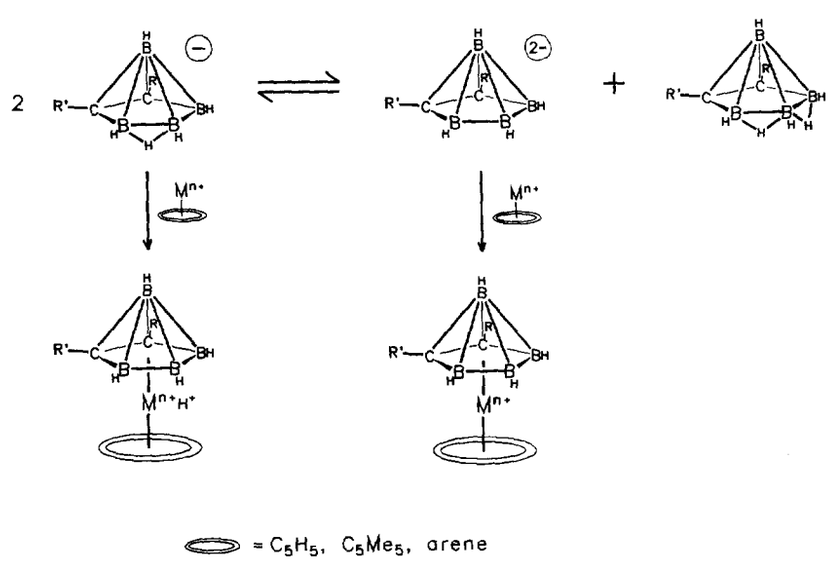
Scheme 1.

monoanions, one frequently finds species containing formal $[Fe^{II}H]^{3+}$ or $[Co^{III}H]^{4+}$ units.

While the designation of these metal-associated hydrogens as protonic rather than hydridic may appear unusual to some readers, this situation is well established in metallacarborane chemistry generally [4]. In the M–H species we have studied, the protonic character of the hydrogens is evident from their Brønsted acidity toward nucleophilic reagents such as butyllithium, and is further supported by NMR, ESR, and other spectroscopic evidence that distinguishes, for example, diamagnetic Co^{III} from paramagnetic Co^{II} or Co^{IV} [1,7]. In a collaborative study of mono- and dinuclear iron complexes in our laboratory, redox processes involving the Fe^{II}/Fe^{III} couple as well as protonation at the metal centers were both found to be completely reversible, allowing the synthesis and study of numerous diamagnetic and paramagnetic species by manipulation of the metal oxidation states and proton sources [10].

In the small metallacarborane area, metal hydride chemistry has thus far been confined to first-row transition metal complexes. Icosahedral MC_2B_9 clusters featuring Ru–H bonds have been investigated by Hawthorne and coworkers [11] and Stone and coworkers [12], and the former group has extensively studied the properties of 11- and 12-vertex hydridometallacarboranes of Ru, Rh, and Ir, some of which are catalyst precursors in olefin and alkyne hydrogenation and other reactions [11,13]. A 10-vertex monocarbon arachno-carborane RuH complex has been structurally characterized by Wallbridge and coworkers [14]. Several (arene)$Ru^{II}(R_2C_2B_4H_4)$ complexes (lacking Ru-bound hydrogens) have also been reported from this laboratory [3,8,15,16].

The present study extends our exploration of FeH and CoH small carborane complexes to ruthenium, and reports a structural characterization of a ruthenacarborane (the first example of an RuC_2B_4 cluster) that contains a well-defined η^1-H ligand bound to ruthenium, as well as an unexpected new route to B-alkylation of the carborane ligand.



Scheme 2.

2. Results and discussion

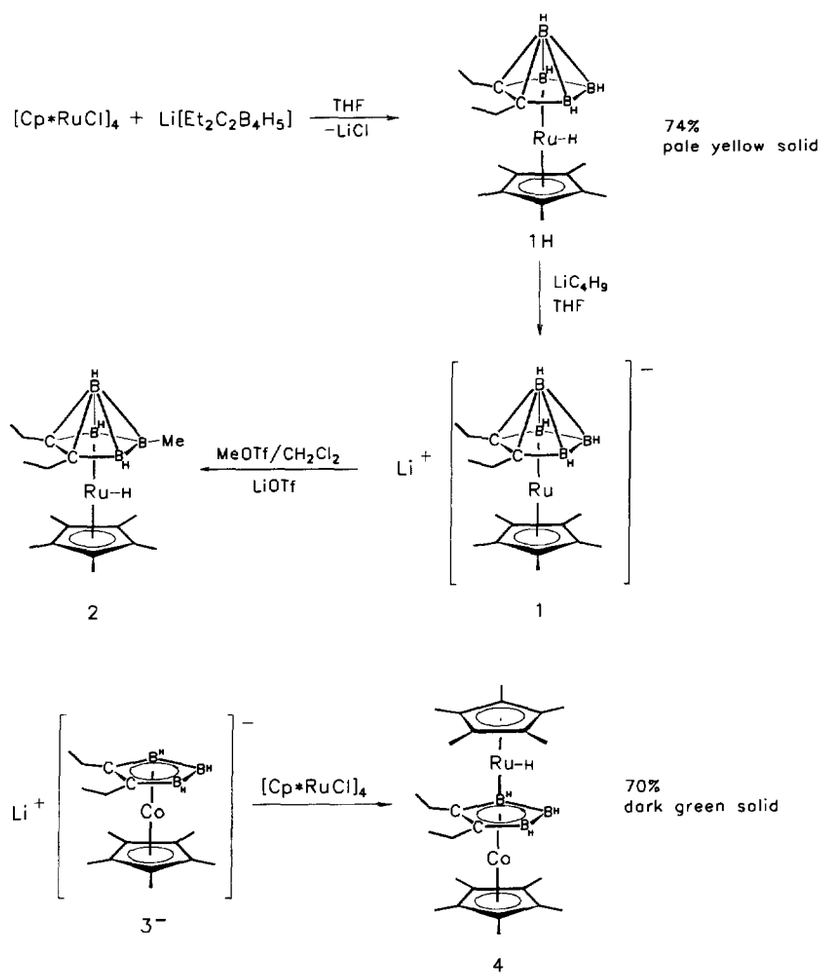
2.1. Synthesis and structure of a hydridoruthenacarborane

The lithium salt of the $Et_2C_2B_4H_5^-$ monoanion reacted with $[Cp^*RuCl]_4$ in THF solution to give a red solution. Following work-up in air, elution on a silica column, and recrystallization from hexanes at −78 °C, pale yellow $Cp^*RuH(Et_2C_2B_4H_4)$ (**1H**) was isolated in ca. 74% yield and characterized via multinuclear NMR and mass spectroscopy (Scheme 3).

The mass spectrum of **1H** exhibits a strong parent group, and the NMR data (Section 3) indicate mirror symmetry and are consistent with the structure depicted. The presence of a hydrogen ligand on ruthenium is supported by the observation of a high-field proton NMR signal at δ −9.5 (vs. TMS) which is diagnostic for M–H groups where M is a late transition metal. Moreover, the diamagnetism of **1H** is consistent with the assignment of Ru^{II} (d^6) with an attached H^+, which balances the dinegative carborane and mononegative Cp^* ligands. However, the spectroscopic data cannot clearly distinguish between a monohapto η^1-H^+ ligand and other possible bonding modes in which the proton bridges an M–B edge or an M–B–B triangular face (see below).

These and other structural details were elucidated by an X-ray crystal structure determination on **1H** (Fig. 1 and Tables 1–3), which confirmed the sandwich geometry and established that the hydrogen ligand [H(1)] is of the monohapto type, bound only to Ru.

The Ru–H distance is 1.55(8) Å, and the shortest H(1)–boron vector [1.87 Å to B(4)] is clearly nonbonding. This situation closely resembles that in a recently reported [1] Co_5 hexadecker sandwich containing a crystallographically defined Co–(η^1-H) group in which the metal-bound hydrogen is 1.6 Å from the nearest boron atom. However, it differs from other metallacarborane sandwich complexes having trihapto hydrogens that cap M–B–B triangular faces, e.g. the cobalt triple-decker $Cp^*Co(Et_2C_2B_3H_2Me)CoH(Et_2C_2B_3H_5)$ [7] and the ferracarborane dimer $[(Et_2C_2B_4H_4)FeH(C_5Me_4]_2C_6H_4$ [10]; in these two



Scheme 3.

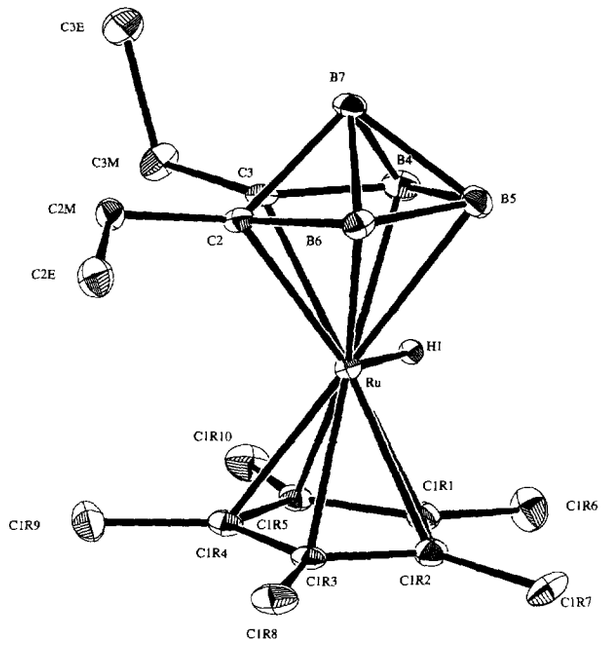


Fig. 1. Molecular structure of 1,2,3-Cp*Ru(H)($Et_2C_2B_4H_4$) (**1H**), drawn with 30% thermal ellipsoids.

species the B–H_{metal} distances are shorter than 1.5 Å and are comparable to (or less than) the M–H bond length. As yet, we have no simple rationale that can account for the different modes of metal–hydrogen binding that we have observed in closely related systems. As structural data are collected on additional hydridometallacarboranes, it is possible that clearer trends may emerge.

Table 1
Experimental X-ray diffraction parameters and crystal data for **1H**

Formula	$RuC_{16}B_4H_{30}$
Formula weight	366.72
Crystal color, habit	yellow plate
Crystal dimensions (mm^3)	0.24×0.18×0.41
Space group	$P2_1/c$
a (Å)	12.598(3)
b (Å)	8.674(2)
c (Å)	16.772(6)
β (deg)	100.29(3)
V ($Å^3$)	1803
Z	4
μ(Mo Kα) (cm^{-1})	8.41
Transmission factors	0.80–1.00
D(calcd) ($g\,cm^{-3}$)	1.351
$2\theta_{max}$ (deg)	50.0
Reflections measured	3408
Reflections observed [$I > 3\sigma(I)$]	2462
Temperature (°C)	−100
R	0.043
R_w	0.059
Largest peak in final diff. map (e^- $Å^3$)	0.75
Goodness of fit	1.70

Table 2
Atomic coordinates for **1H**

Atom	x	y	z
Ru	0.30014(3)	0.17818(4)	0.14576(2)
C(2M)	0.0788(4)	−0.0518(6)	0.1321(3)
C(2)	0.1561(4)	0.0675(6)	0.1748(3)
C(2E)	0.1250(5)	−0.2138(7)	0.1332(4)
C(3M)	0.0382(4)	0.2926(6)	0.1027(3)
C(3)	0.1366(4)	0.2338(6)	0.1605(3)
C(3E)	−0.0627(5)	0.2979(7)	0.1410(4)
C(1R1)	0.4171(4)	0.3104(6)	0.0919(3)
C(1R2)	0.4618(4)	0.1627(6)	0.1144(3)
C(1R3)	0.3942(4)	0.0484(6)	0.0692(3)
C(1R4)	0.3062(4)	0.1268(6)	0.0192(3)
C(1R5)	0.3202(4)	0.2890(6)	0.0326(3)
C(1R6)	0.4665(5)	0.4636(7)	0.1192(4)
C(1R7)	0.5670(4)	0.1351(7)	0.1705(4)
C(1R8)	0.4157(5)	−0.1224(6)	0.0714(4)
C(1R9)	0.2194(5)	0.0526(7)	−0.0410(3)
C(1R10)	0.2511(5)	0.4158(7)	−0.0082(4)
B(4)	0.2149(5)	0.3400(7)	0.2194(4)
B(5)	0.2929(5)	0.2188(7)	0.2832(4)
B(6)	0.2471(5)	0.0348(7)	0.2489(4)
B(7)	0.1557(5)	0.1815(7)	0.2623(4)
H(1)	0.312(5)	0.36(1)	0.148(4)

The C_5 and C_2B_3 rings in **1H** are planar within experimental error, and are located 1.82 Å and 1.80 Å respectively from the Ru atom. These planes are not quite parallel, with a dihedral angle of 9.9°, and are bent

Table 3
Bond distances and selected bond angles for **1H**

Bond distances (Å)			
Ru–C(2)	2.183(5)	C(3)–B(4)	1.566(8)
Ru–C(3)	2.173(5)	C(3)–B(7)	1.743(8)
Ru–C(1R1)	2.186(5)	C(1R1)–C(1R2)	1.423(7)
Ru–C(1R2)	2.196(5)	C(1R1)–C(1R5)	1.443(7)
Ru–C(1R3)	2.205(5)	C(1R1)–C(1R6)	1.503(7)
Ru–C(1R4)	2.184(5)	C(1R2)–C(1R3)	1.432(7)
Ru–C(1R5)	2.183(5)	C(1R2)–C(1R7)	1.502(8)
Ru–B(4)	2.263(6)	C(1R3)–C(1R4)	1.437(7)
Ru–B(5)	2.349(6)	C(1R3)–C(1R8)	1.505(7)
Ru–B(6)	2.323(6)	C(1R4)–C(1R5)	1.430(8)
C(2M)–C(2)	1.511(7)	C(1R4)–C(1R9)	1.494(8)
C(2M)–C(2E)	1.520(8)	C(1R5)–C(1R10)	1.491(8)
C(2)–C(3)	1.476(7)	B(4)–B(5)	1.685(9)
C(2)–B(6)	1.560(8)	B(4)–B(7)	1.777(9)
C(2)–B(7)	1.772(8)	B(5)–B(6)	1.758(9)
C(3M)–C(3)	1.518(7)	B(5)–B(7)	1.732(9)
C(3M)–C(3E)	1.524(8)	B(6)–B(7)	1.758(8)
Ru–H(1)	1.55(8)		
Selected bond angles (deg)			
Ru–C(2)–C(2M)	133.4(4)	C(2)–C(3)–C(3M)	121.7(5)
C(2M)–C(2)–C(3)	121.2(4)	C(2)–C(3)–C(4)	113.9(4)
C(2M)–C(2)–B(6)	125.0(4)	C(3M)–C(3)–B(4)	123.8(5)
C(2M)–C(2)–B(7)	132.7(4)	C(3M)–C(3)–B(7)	131.8(4)
C(3)–C(2)–B(6)	112.6(4)	C(3)–B(4)–B(5)	105.3(4)
Ru–C(3)–C(3M)	133.2(4)	B(4)–B(5)–B(6)	103.8(4)
C(2)–B(6)–B(5)	104.3(4)		

away from H(1). Comparison of the structure with those of previously characterized RuC_2B_3M 7-vertex clusters [8,15,17] shows that the Ru–B, B–C, B–B, and C–C bond lengths in **1H** are within normal ranges.

2.2. Deprotonation and methylation of 1H

As anticipated from studies of hydridometallacarborane clusters of cobalt and iron mentioned earlier, the Ru-bound hydrogen in **1H** is protonic and is easily removed on reaction with t-butyllithium in THF (Scheme 3). The lithium salt of the deprotonated $Cp^*Ru(Et_2C_2B_4H_4)^-$ anion (**1**) is a pale yellow *very* air-sensitive solid. Treatment with methyl triflate followed by separation of the product on a silica plate in air generated a colorless, air-stable solid product **2** whose mass spectrum and elemental analysis are consistent with a monomethyl derivative of **1H**. However, instead of the expected Ru-methylated complex $Cp^*Ru^{IV}Me(Et_2C_2B_4H_4)$, it is apparent that **2** is in fact a B-methyl species, $Cp^*Ru^{II}H(Et_2C_2B_4H_3\text{-}5\text{-}Me)$ (Scheme 3). The structure of **2** is apparent from (1) the ^{11}B NMR spectrum, which contains a singlet area-1 resonance corresponding to a B-alkyl group, (2) the retention of the Ru–H signal (integrated area corresponding to 1 H) near δ −9.6 in the ^1H spectrum, and (3) the diamagnetism of the compound, which supports a formal Ru(II) oxidation state.

The isolation of a B–Me rather than an Ru–Me product from this reaction is surprising and interesting. There can be little doubt that the hydrogen on **1H** initially removed by t-butyllithium is the metal-bound proton, since terminal B–H groups in MC_2B_4 carborane clusters exhibit no acidic behavior whatever toward nucleophiles [4–10]. Consequently, a likely scenario is that there is an agostic B · · · H · · · Ru interaction in the anion **1**, probably involving H(5) (but not necessarily excluding H(4) and H(6)) which effects a partial transfer of that proton from B to Ru. The observed formation of the B-methyl product **2** on reaction with methyl triflate is understandable on a thermodynamic basis, since a covalent B–C single bond should be far more stable than an Ru–C link.

In small metallacarborane chemistry, intramolecular metal–H–B interactions involving *terminal* B–H hydrogens on the carborane ligand in a monomeric species have not been described to our knowledge. However, precedents for agostic B–H–metal binding in 12-vertex icosahedral metallacarboranes can be found in a recently reported $[Cp^*Hf(Me)(C_2B_9H_{11})]_2$ dimer [18], in several complexes of Rh, Ir, and Al prepared earlier (see refs. [12–14] in Ref. [18]), and in a tungsten–carborane alkylidyne complex containing a B–H–Ru group in which the ruthenium atom is external to the icosahedral cage [12]. B–H–Ru bridging is also well known in polyhedral ruthenaborane chemistry [19]. In the case of **2**, the proposed agostic interaction has not been directly observed, and other methylation pathways are conceivable. However, it is clear from NMR spectra of the reaction mixture that **2** is present in solution prior to work-up and isolation.

Alkylation at metal centers in small metallacarborane clusters has been demonstrated. In recent work in this laboratory, treatment of *neutral* $Cp^*MCl_2(Et_2C_2B_4H_4)$ (M = Ta, Nb) and $Cp^*TaCl_2(Et_2C_2B_3H_3)CoCp^*$ with methyl Grignards and other alkylating agents gave mono- and dimethylated derivatives in which Cl atoms are replaced by CH_3 [20]. Methylation occurs exclusively at the metal in these reactions, which involve nucleophilic substitution at early transition metal centers and are very different in kind from the preparation of **2** described here. It remains to be seen whether the B-methylation of **1** will prove to have general applicability as a synthetic route to B-alkyl metallacarboranes.

2.3. Synthesis and characterization of a hydridoruthenium triple-decker complex

In a process analogous to the formation of **1H** from the carborane anion, the reaction of the cobaltacarborane monoanion [15] $Cp^*Co(Et_2C_2B_3H_4)^-$ (**3**$^-$) with $(Cp^*RuCl)_4$ in THF gave the heterobimetallic triple-decker sandwich $Cp^*Co(Et_2C_2B_3H_3)RuHCp^*$ (**4**), which was isolated in air as a dark green diamagnetic solid (Scheme 3). Although X-ray quality crystals are not yet available, the proposed structure is supported by NMR and mass spectra, and the presence of an Ru–H group is signaled by the proton NMR resonance at δ −9.3. Complex **4** is an isoelectronic analogue of a previously prepared ruthenium–cobalt triple-decker, $CpCo(Et_2C_2B_3H_3)Ru(Me_2CHC_6H_4Me)$ (**5**) whose structure was established by X-ray crystallography [15]. Both **4** and **5** are diamagnetic 30-valence electron (ve) sandwiches containing formal Co(III) and Ru(II) centers; the $Cp^*Ru^{II}(H^+)$ group in **4** is equivalent to the (cymene)Ru moiety in **5**. Oxidation of **5** produces a 29 ve cation that has been shown to be a Class III (fully delocalized) mixed-valence species in which the unpaired electron occupies a molecular orbital extending over both metals [21], and the same property was found in the isoelectronic dicobalt cation $[Cp^*Co(Et_2C_2B_3H_3)CoCp^*]^+$. It will be of interest to determine whether similar behavior extends to hydridoruthenium species such as **4**.

3. Experimental details

3.1. Instrumentation

^1H NMR spectra (300 MHz), ^{13}C NMR spectra (75.5 MHz), and ^{11}B NMR spectra (115.8 MHz) were

recorded on GE QE-300 and Nicolet NT-360 spectrometers respectively. Unit resolution mass spectra were obtained on a Finnegan MAT 4600 GC/MS spectrometer using perfluorotributylamine (FC43) as a calibration standard. Infrared spectra were recorded as thin films on a Mattson Cygnus FTIR spectrometer. Visible–ultraviolet spectra were recorded on a Hewlett-Packard 8452A diode array with an HP Vectra computer interface. In each case, a strong parent envelope was observed and the observed and calculated unit-resolution intensity patterns were in close agreement. Elemental analyses were conducted on a Perkin–Elmer 2400 CHN Analyzer using 2,4-dinitrophenylhydrazone as a standard.

3.2. Materials and procedures

All manipulations were carried out under an inert atmosphere using standard Schlenk techniques. Work-up of products was generally carried out in air using bench-top procedures. Solvents were distilled from appropriate drying agents under an inert atmosphere. $(Cp^*RuCl)_4$ [22] and $Cp^*Co(Et_2C_2B_4H_4)$ [15] were prepared by literature methods, and all other chemicals were reagent grade and used without further purification. We thank the Johnson-Matthey Corporation for a generous loan of $RuCl_3 \cdot (H_2O)_x$.

3.3. Synthesis of $Cp^*RuH(Et_2C_2B_4H_4)$ (1H)

A solution of $Li[(Et_2C_2B_4H_4)]$ was prepared from 0.509 g (3.87 mmol) of $Et_2C_2B_4H_6$ and 2.23 ml of 1.7 M LiBu in a 100 ml Schlenk flask. This solution was added via cannula to a suspension of $(Cp^*RuCl)_4$ (1.05 g, 0.97 mmol) in 50 ml of THF in a 250 ml Schlenk flask, and the resulting red homogeneous solution was stirred for 2 h. The solvent was removed in vacuo, leaving a dark red residue which was extracted with 50 ml of hexanes and eluted through 3 cm of silica gel to give an essentially colorless solution. Removal of the solvent under vacuum afforded **1H** as a pale yellow solid which was recrystallized from hexanes at −78 °C. Yield: 1.052 g, 74%. Found: C, 51.84; H, 9.09. $RuC_{16}B_4H_{30}$ requires C, 52.40; H, 8.25. CIMS (CH_4): *m/e* 367 (M). ν_{max} cm^{-1}: 2971 (vs, Et), 2923 (vs, Et), 2865 (vs, Et), 2558 (vvs, BH), 1453, 1384, 1273, 1030, 739. Visible–UV (λ_{max}, nm, CH_2Cl_2): 240 (100%), 316 (7%); $\epsilon_{240} = 7730\,l\,mol^{-1}\,cm^{-1}$. δ ^1H NMR ($CDCl_3$): 2.35 (m, Et CH_2), 2.20 (m, Et CH_2), 1.84 (s, Cp*), 1.18 (t, Et CH_3, $J_{H-H} = 7.3$ Hz), −9.54 (s, RuH). δ $^{13}C\{H\}$ ($CDCl_3$): 10.89 (q, Cp* CH_3, $J_{C-H} = 60.3$ Hz), 15.26 (q, Et CH_3, $J_{C-H} = 63.5$ Hz), 22.15 (t, Et CH_2, $J_{C-H} = 58.5$ Hz), 88.84 (s, Cp* ring carbons), 112 (s br, carborane carbons). δ ^{11}B ($CDCl_3$): −0.3 (d, 1B, $J_{B-H} = 156$ Hz), −8.1 (d, 2B, $J_{B-H} = 150$ Hz), −17.5 (d, 1B, $J_{B-H} = 146$ Hz).

3.4. Deprotonation and methylation of $Cp^*RuH(Et_2C_2B_4H_4)$ (1H)

A solution of 0.136 g (0.37 mmol) of **1H** in 25 ml of THF at 0 °C was treated with 0.26 ml of 1.7 M t-butyllithium (0.44 mmol), and the solution was stirred for 1 h, during which it warmed to room temperature. The solvent was removed in vacuo, and the residue was redissolved in 25 ml of CH_2Cl_2. This solution was cooled to 0 °C and 0.13 ml (1.11 mmol) of $CF_3SO_3CH_3$ was added. After the solution was stirred for 1 h at room temperature, the solvent was removed, the residue was taken up in a minimum volume of CH_2Cl_2, and the solution was eluted on a silica TLC plate in 4:1 hexane–CH_2Cl_2. Two colorless bands were obtained, the first of which was characterized as colorless, air-stable $Cp^*Ru^{II}H(Et_2C_2B_4H_3\text{-}5\text{-}Me)$ (**2**), and the second was identified as **1H** (21 mg, 0.057 mmol). Yield of **2**: 43 mg (0.11 mmol), 36% based on **1H** consumed. Found: C, 54.01; H, 9.29. $RuC_{17}B_4H_{32}$ requires C, 53.63; H, 8.47. CIMS (CH_4): *m/e* 382 (M). ν_{max} cm^{-1}: 2972 (vs, Et), 2902 (vs, Et), 2871 (m, Et), 2576 (m, BH), 2560 (vs, BH), 2525 (s, BH), 2505 (vs, BH), 1467, 1386, 1273, 1030, 895. Visible–UV (λ_{max}, nm, CH_2Cl_2): 242 (100%), 322 (7%); $\epsilon_{242} = 8270\,l\,mol^{-1}\,cm^{-1}$. δ ^1H NMR ($CDCl_3$): 2.29 (m, Et CH_2), 2.18 (m, Et CH_2), 1.84 (s, Cp*), 1.17 (t, Et CH_3, 0.38 (s, B-CH_3), −9.61 (s, RuH). δ ^{13}C ($CDCl_3$): 10.98 (s, Cp* CH_3), 15.40 (s, Et CH_3), 22.37 (s, Et CH_2), 88.07 (Cp* ring carbons). δ ^{11}B ($CDCl_3$): −0.2 (d, 1B, $J_{B-H} = 117$ Hz, B[7]), −5.4 (s, 1B, B[5]), −8.9 (d, 2B, $J_{B-H} = 225$ Hz, B[4,6]).

3.5. Synthesis of $Cp^*Co(Et_2C_2B_3H_3)RuHCp^*$ (4)

A solution of $Li[Cp^*Co(Et_2C_2B_3H_4)]$ was prepared from 0.20 g (0.64 mmol) of $Cp^*Co(Et_2C_2B_3H_5)$, 0.4 ml of 1.6 M LiBu, and 20 ml of THF in a 100 ml Schlenk flask. This solution was added to a suspension of $(Cp^*RuCl)_4$ (0.18 g, 0.16 mmol) in 30 ml of THF in a 250 ml flask, and the resulting dark green homogeneous solution was stirred for 5 h under argon. The solvent was removed in vacuo, leaving a dark green residue which was extracted with 50 ml of hexanes and eluted through 2 cm of silica gel to give a dark green solution. Removal of the solvent under vacuum gave **4** as a dark green solid. Yield: 245 mg, 70%. Found: C, 56.41 H, 8.86. $RuCoC_{26}B_3H_{44}$ requires C, 56.88; H, 8.08. CIMS (CH_4): *m/e* 550 (M). δ ^1H NMR ($CDCl_3$): 2.35 (m, Et CH_2), 2.18 (m, Et CH_2), 1.650 (s, Cp*), 1.637 (s, Cp*), 1.38 (t, Et CH_3), −9.31 (s, RuH). δ $^{13}C\{^1H\}$ ($CDCl_3$): 9.83 (s, Cp* CH_3), 10.64 (s, Cp* CH_3), 15.40 (s, Et CH_3), 24.21 (s, Et CH_2), 82.14 (s, Cp* ring carbons), 89.64 (s, Cp* ring carbons), 110 (s br, carborane carbons). ν_{max} cm^{-1}: 2955 (s, Et), 2897 (s, Et), 2479 (m, BH), 1463, 1384 (s), 1024 (s), 807 (s).

Visible–UV (λ_{max}, nm, CH_2Cl_2): 238 (67%), 282 (56%), 320 (100%), 370 (36%), 590 (4%); $\epsilon_{320} = 18\,570\,l\,mol^{-1}\,cm^{-1}$.

3.6. X-ray structure determination on 8

Diffraction data were collected on a Rigaku AFC6S diffractometer at −100 °C using Mo K α radiation (λ = 0.71069 Å). Details of the data collection and structure determination are listed in Table 1. Calculations were performed on a VAX station 3520 computer employing the TEXSAN 5.0 crystallographic software package [23], and in the later stages on a Silicon Graphics Personal Iris 4D35 computer using the texsan 1.7 package [24]. The unit cell dimensions were determined by least squares refinement of the setting angles of 25 high-angle reflections. The intensities of three standard reflections, monitored throughout, showed no significant variation. Empirical absorption corrections were applied following Ψ scanning of several high-angle reflections (transmission factors are reported in Table 1). The structure was solved by direct methods in SIR88 [25], and full-matrix least squares refinement with anisotropic thermal displacement parameters was carried out for all nonhydrogen atoms. The hydrogen atoms were located from difference Fourier maps, and H(1) was refined with an isotropic temperature factor; the remaining hydrogen atoms were included in the calculations without further refinement. The final difference Fourier map was featureless.

Tables of atomic coordinates (including hydrogen atom positions), anisotropic thermal parameters, bond angles, and calculated mean planes have been deposited at the Cambridge Crystallographic Data Centre.

Acknowledgements

This work was supported by the US Army Research Office, Grant No. DAAH04-95-1-0145 and the National Science Foundation, Grant No. CHE 9322490.

References

[1] X. Wang, M. Sabat and R.N. Grimes, Part 44, *J. Am. Chem. Soc., 117* (1995) 12227.
[2] (a) K.W. Piepgrass and R.N. Grimes, *Organometallics, 11* (1992) 2397. (b) K.W. Piepgrass, K.E. Stockman, M. Sabat and R.N. Grimes, *Organometallics, 11* (1992) 2404.
[3] K.E. Stockman, D.L. Garrett and R.N. Grimes, *Organometallics, 14* (1995) 4661.
[4] R.N. Grimes, in E. Abel, F.G.A. Stone and G. Wilkinson (eds.), *Comprehensive Organometallic Chemistry II*, Vol. 1, Pergamon, Oxford, 1995, Chapter 9, pp. 373–430.
[5] (a) R.N. Grimes, in G.W. Kabalka (ed.), *Current Topics in the Chemistry of Boron*, Royal Society of Chemistry, London, 1994, p. 269. (b) N.S. Hosmane and J.A. Maguire, *J. Cluster Sci., 4* (1993) 297. (c) A.K. Saxena and N.S. Hosmane, *Chem. Rev., 93* (1993) 1081.
[6] R.N. Grimes, *Coord. Chem. Rev., 43* (1995) 71.
[7] X. Wang, M. Sabat and R.N. Grimes, *J. Am. Chem. Soc., 117* (1995) 12218.
[8] P. Greiwe, M. Sabat and R.N. Grimes, *Organometallics, 14* (1995) 3683.
[9] X. Meng, M. Sabat and R.N. Grimes, *J. Am. Chem. Soc., 115* (1993) 6143.
[10] M. Stephan, J.H. Davis, Jr., X. Meng, K.J. Chase, J. Hauss, U. Zenneck, H. Pritzkow, W. Siebert and R.N. Grimes, *J. Am. Chem. Soc., 114* (1992) 5214.
[11] (a) T.B. Marder, R.T. Baker, J.A. Long, J.A. Doi and M.F. Hawthorne, *J. Am. Chem. Soc., 103* (1981) 2988. (b) P.E. Behnken and M.F. Hawthorne, *Inorg. Chem., 23* (1984) 3420.
[12] M. Green, J.A.K. Howard, A.N. de M. Jelfs, O. Johnson and F.G.A. Stone, *J. Chem. Soc. Dalton Trans.*, (1987) 73.
[13] (a) E.H. Wong and M.F. Hawthorne, *Inorg. Chem., 17* (1978) 2863. (b) C.W. Jung and M.F. Hawthorne, *J. Am. Chem. Soc., 102* (1980) 3024.
[14] N.W. Alcock, M.J. Jasztal and M.G.H. Wallbridge, *J. Chem. Soc. Dalton Trans.*, (1987) 2793.
[15] J.H. Davis, Jr., E. Sinn and R.N. Grimes, *J. Am. Chem. Soc., 111* (1989) 4776.
[16] (a) M.D. Attwood, J.H. Davis, Jr. and R.N. Grimes, *Organometallics, 9* (1990) 1177. (b) M.A. Benvenuto and R.N. Grimes, *Inorg. Chem., 31* (1992) 3897.
[17] (a) K.W. Piepgrass, X. Meng, M. Hölscher, M. Sabat and R.N. Grimes, *Inorg. Chem., 31* (1992) 5202. (b) J.H. Davis, Jr., E. Sinn and R.N. Grimes, *J. Am. Chem. Soc., 111* (1989) 4784. (c) K.E. Stockman, M. Sabat, M.G. Finn and R.N. Grimes, *J. Am. Chem. Soc., 114* (1992) 8733.
[18] D.C. Crowther, D.C. Swenson and R.F. Jordan, *J. Am. Chem. Soc., 117* (1995) 10403.
[19] J.D. Kennedy, *J. Chem. Soc. Dalton Trans.*, (1993) 2545 and references cited therein.
[20] K.E. Stockman, K.L. Houseknecht, E.A. Boring, M. Sabat, M.G. Finn and R.N. Grimes, *Organometallics, 14* (1995) 3014.
[21] J. Merkert, J.H. Davis, Jr., W. Geiger and R.N. Grimes, *J. Am. Chem. Soc., 114* (1992) 9846.
[22] P.J. Fagan, W.S. Mahoney, J.C. Calabrese and I.D. Williams, *Organometallics, 9* (1990) 1843.
[23] TEXSAN 5.0: *Single Crystal Structure Analysis Software*, 1989, Molecular Structure Corporation, The Woodlands, TX 77381.
[24] texsan 1.7: *Single Crystal Structure Analysis Software*, 1995, Molecular Structure Corporation, The Woodlands, TX 77381.
[25] M.C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, G. Polidori, R. Spagna and D. Viterbo, SIR88, *J. Appl. Crystallogr., 22* (1989) 389.