Synthesis and Reactivity of Ruthenatetraboranes: Molecular Structure of [RuH(B_3H_8)(CO)(PPh_3)$_2$]

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The reactions of [RuClH(CO)(PPh_3)$_3$] and [RuH(CO)(NCMe)$_2$(PPh_3)$_2$]ClO_4 with [NMe_4][B_3H_8] provide the ruthenatetraborane [RuH(B_3H_8)(CO)(PPh_3)$_2$] [crystallographically characterized: monoclinic crystals of space group $P2_1/c$ ($Z = 4$), in a unit cell of dimensions $a = 14.424$ (5) Å, $b = 10.628$ (4) Å, $c = 22.987$ (9) Å, and $\beta = 97.86$ (3)°]. The integrity of the RuB_3 moiety is retained in the reactions with *N*-halosuccinimides, leading to the halo derivatives [RuX(B_3H_8)(CO)(PPh_3)$_2$] (X = Cl, Br, I); however, reaction of the bromo derivative with Na[S_2CNMe_2] leads to rupture of the metallatetraborane and formation of [Ru(S_2CNMe_2)$_2$(CO)(PPh_3)].

Introduction

Despite the early interest in the synthesis of metallatetraboranes,[1] a review[2] makes the following observation: "In view of the substantial preparative effort into the investigation of the metal octahydrotriborates, the lack of extensive further chemistry is disappointing."

We were interested recently in the hydroruthenation of alkynes and diynes[3] and were intrigued by the possibility of employing, in these reactions, a hydridoruthenium complex which also bore other types of active element–hydrogen bonds. Such a complex, [RuH(B_3H_8)(CO)(PPh_3)$_2$] (**1**), was prepared previously;[4] however, no subsequent reactions were described and the characterization was based on spectroscopic data. We report herein an improved preparation of complex **1**, its structural characterization, and preliminary reactivity studies, specifically regarding its conversion to stable halometallatetraboranes, [RuX(B_3H_8)(CO)(PPh_3)$_2$] (X = Cl, Br, I).

Experimental Section

General Procedures. All manipulations were routinely carried out under an atmosphere of prepurified dinitrogen using conventional Schlenk-tube techniques. Solvents were purified by distillation from an appropriate drying agent (ethers, paraffins, benzene, and toluene from sodium/potassium alloy with benzophenone as indicator; halocarbons and acetonitrile from CaH_2). ^1H, ^{11}B, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker WH-400 or Perkin-Elmer R34 NMR spectrometer and calibrated against internal Me_4Si (^1H), internal $CDCl_3$ (^{13}C), external $BF_3{\cdot}OEt_2$ (^{11}B), or external H_3PO_4 (^{31}P). The assistance of O. W. Howarth and the University of Warwick NMR service is gratefully acknowledged. Infrared spectra were recorded using a Perkin-Elmer 1720-X FT-IR spectrometer. FAB mass spectrometry was carried out with a Kratos MS80 mass spectrometer using nitrobenzyl alcohol as matrix. Petroleum ether refers to that fraction boiling at 40–60 °C. Elemental microanalyses were carried out by Medac Ltd., Reading, U.K. The complex [RuClH(CO)(PPh_3)$_3$][5] and the salt [RuH(CO)(NCMe)$_2$(PPh_3)$_2$]ClO_4[6] have been described elsewhere. [NMe_4][B_3H_8] was obtained commercially (Strem), and [NBu_4][B_3H_8] was prepared according to a published procedure.[7] Data for the complexes are collected in Tables IV, V, and VIII.

Preparations. [RuH(B_3H_8)(CO)(PPh_3)$_2$]. (a) A solution of [RuClH(CO)(PPh_3)$_3$] (5.00 g, 5.25 mmol) in dichloromethane (150 cm^3) was treated with [NBu_4][B_3H_8] (1.49 g, 5.25 mmol), and the mixture was stirred for 2 h (monitored by solution IR) until the reaction was complete. Ethanol (75 cm^3) was added and the suspension filtered through Kieselguhr to remove [NBu_4]Cl. The filtrate was concentrated to ca. 15 cm^3, and the complex [RuH(B_3H_8)(CO)(PPh_3)$_2$] was isolated by filtration and recrystallized from dichloromethane/ethanol. Yield: 3.41 g (93%). Crystals suitable for X-ray diffractometry were obtained by slow diffusion of ethanol vapor into a saturated solution of the complex in dichloromethane.

(b) A solution of [RuH(CO)(NCMe)$_2$(PPh_3)$_2$]ClO_4 (0.25 g, 0.30 mmol) in dichloromethane (30 cm^3) was treated with [NMe_4][B_3H_8] (0.040 g, 0.35 mmol), and the mixture was stirred for 10 h (monitored by solution IR) until the reaction was complete. Hexane (20 cm^3) was added and the suspension filtered through Kieselguhr to remove [NMe_4]Cl. The filtrate was concentrated to ca. 15 cm^3, and the complex [RuH(B_3H_8)(CO)(PPh_3)$_2$] was isolated by filtration and recrystallized from dichloromethane/ethanol. Yield: 0.18 g (87%). Anal. Calcd for $C_{37}H_{39}B_3OP_2Ru$: C, 63.9; H, 5.7. Found: C, 63.8; H, 5.7. The complex was also characterized by comparison of spectroscopic data (^1H, ^{31}P, and ^{11}B NMR and IR) with those previously published, in addition to FAB mass spectroscopy: 695, [M]$^+$; 655, [M – B_3H_7]$^+$; 625, [M – B_3H_8 – CO – H]$^+$; 548, [M – B_3H_8 – CO – C_6H_6]$^+$.

[RuCl(B_3H_8)(CO)(PPh_3)$_2$]. (a) A solution of [RuH(B_3H_8)(CO)(PPh_3)$_2$] (0.50 g, 0.72 mmol) and *N*-chlorosuccinimide (0.096 g, 0.72 mmol) in dichloromethane (30 cm^3) was stirred for 6 h, and the solvent was removed under reduced pressure. The residue was crystallized from dichloromethane/ethanol. Yield: 0.41 g (78%). Anal. Calcd for $C_{37}H_{38}B_3ClOP_2Ru$: C, 61.0; H, 5.3. Found: C, 60.9; H, 5.2.

(b) A mixture of [RuH(B_3H_8)(CO)(PPh_3)$_2$] (0.10 g, 0.14 mmol) and PhSeCl (30 mg, 0.16 mmol, 1.1 equiv) in dichloromethane (20 cm^3) was stirred for 72 h, and the reaction was monitored by solution infrared spectroscopy (CH_2Cl_2). The solvent was removed in vacuo, and the residue was crystallized from a mixture of dichloromethane and ethanol and characterized as [RuCl(B_3H_8)(CO)(PPh_3)$_2$] by comparison of spectroscopic data with those obtained for an authentic sample. Yield: 30 mg (29%).

[RuBr(B_3H_8)(CO)(PPh_3)$_2$]. A solution of [RuH(B_3H_8)(CO)(PPh_3)$_2$] (0.30 g, 0.43 mmol) and *N*-bromosuccinimide (0.82 g, 0.50 mmol) in dichloromethane (30 cm^3) was stirred for 2 h, and the solvent was removed under reduced pressure. The residue was crystallized from dichloromethane/ethanol. Yield: 0.28 g (83%). Satisfactory elemental microanalytical data could not be obtained.

[RuI(B_3H_8)(CO)(PPh_3)$_2$]. A solution of [RuH(B_3H_8)(CO)(PPh_3)$_2$] (0.50 g, 0.72 mmol) and *N*-iodosuccinimide (0.16 g, 0.71 mmol) in

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Table I. Atomic Coordinates (Å × 10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for $[RhH(B_3H_8)(CO)(PPh_3)_2]$

atom	*x*	*y*	*z*	U^a
Ru(1)	2447.7 (2)	1678.4 (3)	1342.4 (1)	29 (1)
P(1)	2537.9 (8)	1759.0 (10)	2380.1 (5)	29 (1)
P(2)	2575.9 (8)	2232.3 (11)	360.7 (5)	30 (1)
O(1)	774 (3)	3351 (4)	1302 (2)	68 (2)
B(1)	3200 (4)	−347 (5)	1233 (3)	43 (2)
B(2)	2650 (6)	−1498 (6)	1648 (3)	54 (2)
B(3)	1993 (4)	−530 (6)	1090 (3)	44 (2)
C(1)	1436 (3)	2749 (5)	1312 (2)	42 (2)
C(111)	3272 (3)	623 (4)	2831 (2)	36 (1)
C(112)	2942 (4)	−42 (5)	3284 (2)	47 (2)
C(113)	3552 (5)	−888 (5)	3621 (3)	60 (2)
C(114)	4441 (5)	−1055 (6)	3500 (3)	64 (2)
C(115)	4764 (4)	−403 (6)	3050 (3)	56 (2)
C(116)	4174 (3)	433 (5)	2713 (2)	46 (2)
C(121)	1410 (3)	1661 (4)	2655 (2)	34 (1)
C(122)	790 (4)	714 (6)	2443 (3)	58 (2)
C(123)	−55 (4)	583 (7)	2642 (3)	74 (3)
C(124)	−333 (4)	1428 (6)	3030 (3)	61 (2)
C(125)	260 (4)	2378 (6)	3239 (2)	52 (2)
C(126)	1129 (3)	2492 (5)	3054 (2)	40 (2)
C(131)	3024 (3)	3255 (4)	2685 (2)	34 (1)
C(132)	2724 (4)	4378 (4)	2419 (2)	44 (2)
C(133)	3109 (5)	5511 (5)	2643 (3)	61 (2)
C(134)	3799 (4)	5527 (6)	3116 (3)	64 (2)
C(135)	4096 (4)	4433 (6)	3375 (3)	56 (2)
C(136)	3716 (3)	3284 (5)	3170 (2)	42 (2)
C(211)	3756 (3)	2419 (4)	153 (2)	33 (1)
C(212)	3939 (4)	3313 (6)	−247 (3)	67 (2)
C(213)	4819 (4)	3432 (7)	−407 (3)	75 (3)
C(214)	5533 (4)	2641 (6)	−168 (3)	59 (2)
C(215)	5357 (4)	1774 (6)	227 (3)	59 (2)
C(216)	4479 (4)	1657 (5)	393 (3)	49 (2)
C(221)	2067 (3)	3789 (5)	153 (2)	37 (1)
C(222)	2271 (4)	4794 (5)	518 (3)	56 (2)
C(223)	1912 (5)	5976 (6)	369 (3)	73 (3)
C(224)	1332 (5)	6135 (6)	−152 (3)	76 (3)
C(225)	1109 (5)	5147 (6)	−525 (3)	76 (3)
C(226)	1487 (4)	3969 (5)	−375 (3)	54 (2)
C(231)	2010 (3)	1170 (4)	−203 (2)	33 (1)
C(232)	2492 (3)	456 (5)	−550 (2)	45 (2)
C(233)	2041 (4)	−426 (6)	−941 (3)	57 (2)
C(234)	1086 (4)	−579 (6)	−982 (2)	56 (2)
C(235)	594 (4)	152 (6)	−630 (3)	58 (2)
C(236)	1045 (3)	1004 (5)	−244 (2)	47 (2)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

dichloromethane (30 cm^3) was stirred for 1 h, and the solvent was removed under reduced pressure. The residue was crystallized from dichloromethane/ethanol. Yield: 0.50 g (84%). Satisfactory elemental microanalytical data could not be obtained.

$[Ru(CO)(PPh_3)(S_2CNMe_2)_2]$. A suspension of $[RuBr(B_3H_8)(CO)(PPh_3)_2]$ (250 mg, 0.32 mmol) in methanol (30 cm^3) was treated with $[Me_2NCS_2]Na \cdot 2H_2O$ (58 mg, 0.32 mmol), and the mixture was irradiated by ultrasound for ca. 15 min and then stirred for 5 d. The reaction was monitored by solution infrared spectroscopy (MeOH) and TLC. The reaction mixture was concentrated in vacuo and the product separated from $[RuBr(B_3H_8)(CO)(PPh_3)_2]$ by column chromatography (silica gel, 20 × 5 cm^3, 25 °C), eluting with dichloromethane. The second fraction was concentrated under reduced pressure, and the residue was crystallized from dichloromethane/ethanol and characterized as $[Ru(CO)(PPh_3)(S_2CNMe_2)_2]$ by comparison of spectroscopic data with those reported previously.[8] Yield: 55 mg (27%).

Crystal and Molecular Structure Determination of $[RuH(B_3H_8)(CO)(PPh_3)_2]$. Selected bond lengths and bond angles are given in Tables I and II, and experimental details are contained in Table III. Listings of anisotropic thermal parameters, located and calculated hydrogen positions, complete bond lengths, and complete bond angles have been deposited in the supplementary material.

Results and Discussion

It has been previously shown[4] that the reaction of $[RuClH(CO)(PPh_3)_3]$ with $Tl[B_3H_8]$ provides the ruthenatetraborane

Table II. Selected Molecular Dimensions of $[RuH(B_3H_8)(CO)(PPh_3)_2]$

	Bond Lengths (Å)		
Ru(1)–P(1)	2.373 (1)	Ru(1)–P(2)	2.364 (1)
Ru(1)–B(1)	2.439 (6)	Ru(1)–B(3)	2.484 (6)
Ru(1)–C(1)	1.844 (5)	B(1)–B(2)	1.802 (10)
B(1)–B(3)	1.738 (9)		
	Bond Angles (deg)		
P(1)–Ru(1)–P(2)	161.8 (1)	P(1)–Ru(1)–B(1)	99.9 (2)
P(2)–Ru(1)–B(1)	91.5 (2)	P(1)–Ru(1)–B(3)	104.2 (2)
P(2)–Ru(1)–B(3)	93.7 (2)	B(1)–Ru(1)–B(3)	41.3 (2)
P(1)–Ru(1)–C(1)	87.2 (1)	P(2)–Ru(1)–C(1)	88.6 (2)
B(1)–Ru(1)–C(1)	154.3 (2)	B(3)–Ru(1)–C(1)	113.0 (2)
Ru(1)–B(1)–B(2)	108.0 (4)	Ru(1)–B(1)–B(3)	70.7 (3)
B(2)–B(1)–B(3)	61.4 (4)	B(1)–B(2)–B(3)	57.6 (3)
Ru(1)–B(3)–B(1)	67.9 (3)	Ru(1)–B(3)–B(2)	106.0 (3)
B(1)–B(3)–B(2)	61.0 (4)	Ru(1)–C(1)–O(1)	175.7 (5)

Table III. Crystal Data and Data Collection and Solution and Refinement Details for $[RuH(B_3H_8)(CO)(PPh_3)_2]$

	Crystal Data
empirical formula	$C_{37}H_{39}B_3OP_2Ru$
M_r	695
a, *b*, *c*	14.424 (5), 10.628 (4), 22.987 (9) Å
α, *β*, *γ*	90, 97.86 (3), 90°
V	3491 (2) Å^3
space group	$P2_1/c$ (No. 14)
Z	4
D_{calcd}	1.32 g cm^{-3}
F(000)	1432
μ	0.56 mm^{-1}
crystallization	diffusion of ethanol into a dichloromethane solution
crystal size	ca. 0.20 × 0.40 × 0.15 mm
	Data Collection
T	ambient
diffractometer	Nicolet $P2_1$
scan type	ω–2θ ($3 \le 2\theta \le 50°$)
check reflns	(3,0,−2), (2,0,4), (3,4,−11); measured every 200 reflns
abs cor	analytical; complete definition of crystal morphology using the program CRYSPLANES
no. of data	6794 unique; ($0 \le h \le 17$), ($0 \le k \le 12$), ($-27 \le l \le 27$); 4592 with $F \ge 4\sigma(F)$ retained
	Solution and Refinement
method	heavy atom and difference Fourier
program	SHELXTL-PLUS[18]
scattering factors	ref 19
coordinates	refined, all non-H, H(1)–H(9); calculated, all remaining H
thermal params	refined: anisotropic, all non-H fixed: isotropic, remaining H (8 × 10^4 Å^2)
weighting	*w* = 0.004 75
residuals	*R* = 0.047, R_w = 0.052 e density max = 1.31, min = −1.17 e Å^{-3}

$[RuH(B_3H_8)(CO)(PPh_3)_2]$ in good yield. We were eager to investigate the subsequent reactivity of the complex and have accordingly developed a more expedient procedure for large-scale preparations which avoids the use of large quantities of toxic thallous salts. Reaction of the hydrido complex with tetraalkylammonium salts of the $[B_3H_8]^-$ anion ($[NBu_4]^+$ [7] or $[NMe_4]^+$, Strem) in dichloromethane leads to smooth conversion to the ruthenatetraborane over a period of 2–5 h (Scheme I). The reaction is easily monitored by solution infrared spectroscopy, and the product may be isolated in yields in excess of 90%. Since $Tl[B_3H_8]$ is usually prepared from the tetraalkylammonium salts, this procedure also eliminates one step. Spectroscopic data obtained for the complex were identical to those reported previously;[4] however, we wished to firmly establish the identity of the complex prior to subsequent study and have carried out a single-crystal X-ray diffraction analysis which confirms the

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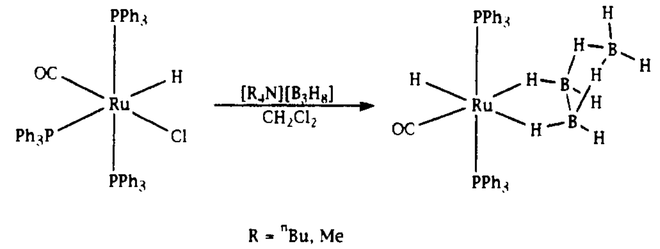
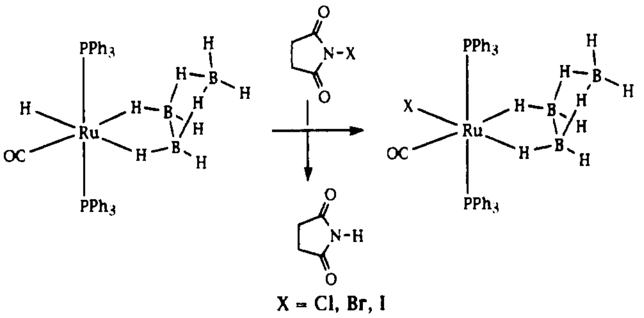
Scheme I



Scheme II



originally proposed structure. The structural aspects of this complex will be discussed later (vide infra).

The complex $[RuH(B_3H_8)(CO)(PPh_3)_2]$ is unusual in having two types of "hydride" substituents, i.e., ruthenium and boron hydrides. This property is only shared with the complexes $[FeH(B_3H_8)(CO)_3]$,[9] $[OsH(B_3H_8)(CO)(PPh_3)_2]$, and $[IrH_2(B_3H_8)(PPh_3)_2]$,[4] which clearly show isoelectronic relationships with the ruthenatetraborane.

In an attempt to establish the relative reactivity of the two element–hydrogen bonds, the reactions of $[RuH(B_3H_8)(CO)(PPh_3)_2]$ with *N*-halosuccinimides were investigated. We have previously employed these reagents for the smooth conversion of ruthenium hydrides to the corresponding halides[10] for compounds which are stable with respect to chloroform and thus not suitable for the normal haloform oxidation approach. Halometallatetraboranes presented themselves as worthwhile synthetic goals. First, they are rare, the only known example being the "half-sandwich" complex $[RuCl(B_3H_8)(\eta\text{-}C_6Me_6)]$ prepared from $[Ru_2Cl_2(\mu\text{-}Cl)_2(\eta\text{-}C_6Me_6)_2]$ and $Tl[B_3H_8]$.[11] Second, while rare, they are almost certainly crucial intermediates in the reactions of metal halides with $[B_3H_8]^-$ which lead to heptahydrometallatetraborane or "borallyl" complexes, e.g., in the synthesis of $[Pt(B_3H_7)(PMePh_2)_2]$ from $[PtCl_2(PMePh_2)_2]$, $[B_3H_8]^-$, and NEt_3.[12]

We find that it is in fact the ruthenium hydride which is oxidized in preference to a B–H bond. Thus, for example, reaction of $[RuH(B_3H_8)(CO)(PPh_3)_2]$ with *N*-bromosuccinimide leads to clean conversion to the bromide complex $[RuBr(B_3H_8)(CO)(PPh_3)_2]$ in high yield (Scheme II). The reaction is accompanied by the disappearance of the high-field triplet ^1H NMR signal due to the ruthenium hydride; however, the RuB_3H_8-derived resonances remain essentially unchanged. The carbonyl peak in the infrared spectrum moves upon reaction to the higher energy value of 2000 cm^{-1} (CH_2Cl_2), and this feature facilitates monitoring of the reaction by solution infrared spectroscopy. Similar reactions ensure for the *N*-chloro- and *N*-iodosuccinimides to provide the chloride and iodide derivatives, both in high yields. Succinimide is the only other significant side product of these reactions and is easily removed.

Table IV. Infrared Data (cm^{-1}) for the Complexes $[RuX(B_3H_8)(CO)(PPh_3)_2]$ [X = H, Cl, Br, I; {Ru} = "$Ru(B_3H_8)(CO)(PPh_3)_2$"]

complex	CH_2Cl_2 $\nu(CO)$	Nujol $\nu(CO)$	Nujol $\nu(BH)/\nu(B_2H)$
{Ru}H[a]	1977	1978	2520, 2491, 2464, 2162[a]
{Ru}Cl	2002	2007	2539, 2519, 2476, 2167
{Ru}Br	2000	2006	2540, 2521, 2474, 2167
{Ru}I	1994	1985	2537, 2470, 2162

[a] $\nu(RuH)$ 2098 (Nujol).

Spectroscopic data for the three halide complexes indicate that they are isostructural. All three complexes give rise to AB quartet resonances in the ^{31}P NMR spectrum with comparable $J(P_AP_B)$ coupling constants which are somewhat larger than that observed for the hydrido derivative and typical of a *trans*-P–Ru–P arrangement. Furthermore, the appearance of two ^1H NMR resonances attributable to the Ru–H–B bridging hydrides indicates that these are chemically inequivalent for the three complexes and that one of these is trans to the halide ligand which is changed throughout the series. Thus, even the iodo derivative, which might have been expected to favor a *cis*–bis(phosphine) arrangement, also adopts the same trans arrangement. Data for the complexes are collected in Tables IV and V. Most conspicuous among the ^1H NMR data for the series of complexes is the effect of the halide ligand on the chemical shift of the B–H–Ru bridging proton trans to it. Thus, the position of this resonance moves smoothly from δ −17.08 to −9.41 ppm within the series Cl < Br < I < H. In contrast, the signal due to the B–H–Ru bridging hydride trans to the carbonyl is only very slightly variant within the series.

The reaction of $[RuH(B_3H_8)(CO)(PPh_3)_2]$ with phenylselenenyl chloride was investigated in the hopes that a phenylselenolato complex might be isolable; however, in all attempts the only metallaborane complex obtained was the chloro derivative $[RuCl(B_3H_8)(CO)(PPh_3)_2]$. Presumably, if the desired complex $[Ru(SePh)(B_3H_8)(CO)(PPh_3)_2]$ was to form, subsequent rapid reaction with further PhSeCl could produce diphenyl diselenide, which would ultimately be replaced by the chloride ion. Clearly, a milder source of "$PhSe^+$" is required.

Despite the implied intermediacy of $[PtCl(B_3H_8)(PMePh_2)_2]$ in the synthesis of $[Pt(B_3H_7)(PMePh_2)_2]$, the ruthenium halide complexes do not readily dehydrohalogenate in the presence of base (Et_3N or the nonnucleophilic base 1,5-diazabicyclo[4.3.0]non-5-ene) to provide a metallaborane. While a slow reaction does ensue, if the as yet hypothetical heptahydrometallatetraborane $[Ru(B_3H_7)(CO)(PPh_3)_2]$ is formed, it is unstable under the reaction conditions. The complex $[Ru(B_3H_7)(CO)(PPh_3)_2]$ would be isoelectronic with $[Pt(B_3H_7)(PMePh_2)_2]$; however, the increased tendency of ruthenium to complete its EAN requirements relative to platinum would render this former species considerably more reactive.

The cleavage of the triborane fragment from the ruthenium coordination sphere was a feature of many test reactions carried out on the hydride and halide complexes. Thus, e.g., reaction of $[RuBr(B_3H_8)(CO)(PPh_3)_2]$ with sodium dimethyldithiocarbamate leads only to the slow formation of the previously reported

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Table V. NMR Data for the Complexes [$RuX(B_3H_8)(CO)(PPh_3)_2$] [X = H, Cl, Br, I; {Ru} = "$Ru(B_3H_8)(CO)(PPh_3)_2$"][a]

	^{31}P		^{11}B	^{1}H
complex	δ	$J(P_AP_B)$, Hz	δ	δ
{Ru}H	49.8	248	0.21	−9.41, −7.22 [s(br) × 2, 2 H, Ru*H*B]
	44.2		−36.6	−9.14 [t, 1 H, Ru*H*, *J*(PH) = 21 Hz]
			−38.6	−1.35, −0.51, 0.50 [m(br) × 3, 4 H, B*H*B and B*H*]
				1.91, 2.61 [s(br) × 2, wingtip BH_2]
{Ru}Cl	32.72	301	2.0	−17.08, −6.03 [s(br) × 2, 2 H, Ru*H*B]
	32.37		−35.9 [2 B]	−1.08, −0.44 [s(br) × 2, 4 H, B*H*B and B*H*]
				2.16, 2.48 [s(br) × 2, wingtip BH_2]
{Ru}Br	33.06	302	3.2	−16.15, −6.65 [s(br) × 2, 2 H, Ru*H*B]
	31.86		−32.7	−0.81, −0.61 [s(br) × 2, 4 H, B*H*B and B*H*]
			−35.3	2.20, 2.63 [s(br) × 2, wingtip BH_2]
{Ru}I	33.92	293	3.34	−14.20, −7.92 [s(br) × 2, 2 H, Ru*H*B]
	31.14		−34.6 [2 B]	−0.88, −0.60 [s(br) × 2, 4 H, B*H*B and B*H*]
				2.21, 2.78 [s(br) × 2, wingtip BH_2]

[a] From saturated solutions of the complex in $CDCl_3$ at ambient temperature. Chemical shifts are reported relative to external H_3PO_4 (^{31}P), external $BF_3 \cdot OEt_2$ (^{11}B), or internal $SiMe_4$ (^{1}H). Resonances due to PPh_3 are omitted.

Table VI. Selected Interatomic Distances for Structurally Characterized Monometallatetraboranes

	bond lengths, Å					
complex	M–B(1)	M–B(3)	M–B(2)	B(1)–B(3)	B(1)–B(2)	B(2)–B(3)
[$RuH(B_3H_8)(CO)(PPh_3)_2$]	2.439 (6)	2.484 (6)		1.738 (9)	1.80 (1)	1.808 (9)
[$Mn(B_3H_7Br)(CO)_4$][13]	2.356 (9)	2.356 (9)		1.75 (2)	1.71 (2)	1.71 (2)
[$Mn(B_3H_8)(CO)_3$][9]	2.281 (7)	2.273 (7)	2.316 (7)	1.748 (9)	1.713 (9)	1.737 (9)
[$WH_3(B_3H_8)(PMe_3)_3$][14]	2.520 (7)	2.491 (8)		1.81 (1)	1.76 (1)	1.82 (2)
[$Nb(B_3H_8)(\eta\text{-}C_5H_5)_2$][15]	2.555 (6)	2.566 (6)		1.727 (8)	1.804 (9)	1.79 (1)
[$Cu(B_3H_8)(PPh_3)_2$][16]	2.30 (1)	2.30 (1)		1.76 (1)	1.81 (2)	1.83 (2)
[$Cr(B_3H_8)(CO)_4$]$^-$ [17]	*a*	*a*		1.78 (1)	1.82 (1)	1.82 (1)

[a] Not available.

Table VII. Selected Intermolecular Bond Angles for Structurally Characterized Monometallatetraboranes

	interbond angles, deg		
complex	B(1)–M–B(3)	B(1)–B(2)–B(3)	B(1)–M–B(3)/ B(1)–B(2)–B(3) (dihedral)
[$RuH(B_3H_8)(CO)(PPh_3)_2$]	41.3 (2)	57.6 (3)	124.4
[$Mn(B_3H_7Br)(CO)_4$]	43.5 (4)	61.5 (8)	127
[$Mn(B_3H_8)(CO)_3$]	45.1 (2)	60.9 (4)	78.3
[$WH_3(B_3H_8)(PMe_3)_3$]	42.4 (3)	60.8 (5)	127.98
[$Nb(B_3H_8)(\eta\text{-}C_5H_5)_2$]	39.4 (2)	61.6 (4)	124.93
[$Cu(B_3H_8)(PPh_3)_2$]	*a*	*a*	119.3
[$Cr(B_3H_8)(CO)_4$]$^-$	*a*	*a*	118.5

[a] Not given.

Table VIII. FAB-MS Data for the Complexes [$RuX(B_3H_8)(CO)(PPh_3)_2$] [X = H, Cl, Br, I; {Ru} = "$Ru(B_3H_8)(CO)(PPh_3)_2$"][a]

complex	*m/z*, assignment
{Ru}H	695, $[M]^+$; 655, $[M - B_3H_7]^+$; 6.25, $[Ru(PPh_3)_2]^+$; 548, $[M - B_3H_8 - C_6H_6 - CO]$
{Ru}Cl	689, $[M - B_3H_8]^+$; 613, $[M - B_3H_8 - C_6H_5]^+$
{Ru}Br	733, $[M - B_3H_8]^+$, 692, $[M - Br]^+$; 654, $[M - B_3H_8 - Br]^+$; 625, $[Ru(PPh_3)_2]^+$; 576, $[M - Br - B_3H_8 - C_6H_5]^+$; 547, $[M - Br - B_3H_8 - CO - C_6H_5]^+$; 363, $[RuPPh_3]^+$
{Ru}I	654, $[M - I - B_3H_8]^+$; 576 $[M - I - B_3H_8 - C_6H_5]^+$; 548, $[M - B_3H_8 - I - CO - C_6H_5]^+$; 363, $[RuPPh_3]^+$

[a] Data obtained from nitrobenzyl alcohol matrices.

complex [$Ru(S_2CNMe_2)_2(CO)(PPh_3)_2$],[8] with no carbonyl-containing metallaborane intermediates being detected (solution IR). Finally, our original interest in the complex [$RuH(B_3H_8)(CO)(PPh_3)_2$] had been as a potential reagent for the hydroruthenation or hydroboration of alkynes. However, treating the complex with simple or activated alkynes does not lead to any identifiable hydrometalation products in our hands under mild reaction conditions and under more forcing conditions only intractable mixtures have so far been obtained.

Description of the Molecular Structure of [$RuH(B_3H_8)(CO)(PPh_3)_2$]. The molecular structure of [$RuH(B_3H_8)(CO)(PPh_3)_2$]

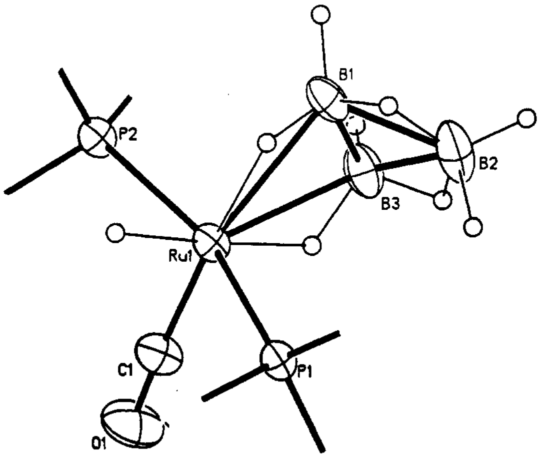

Figure 1. Molecular geometry of [$RuH(B_3H_8)(CO)(PPh_3)_2$]. Phenyl groups have been omitted for clarity.

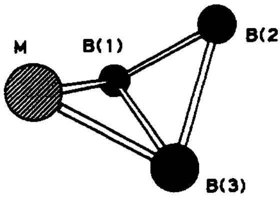

Figure 2. Atom labeling for Tables VI and VII.

is depicted in Figure 1, and selected bond lengths and angles are collected in Table II, whilst Tables VI and VII summarize pertinent data for the previous structural characterizations of monometallatetraboranes.

The complex is monomeric as a crystal, with a distorted octahedral environment about the ruthenium center. The primary distortion arises from the inequivalent steric congestion associated with the exo and endo sites for phosphine coordination to the RuB_3 butterfly. The phosphine coordinated in the endo position [based on P(1)] is clearly distorted away from the butterfly moiety, while the remaining ligands at ruthenium all have interligand angles approaching 90°. The dihedral angle between the Ru–B(1)–B(3) and B(1)–B(2)–B(3) planes is somewhat larger than values for complexes where steric pressures are less important, and the Ru–P(1) bond is marginally longer than that between Ru and P(2). These ground-state distortions are certainly not large, and the molecule is known to be fluxional in solution above room temperature.

A further distortion from ideal pseudooctahedral geometry is apparent in the bonding between ruthenium and the triborane. Thus, the bond between ruthenium and the BH unit trans to the hydride is longer than that trans to the carbonyl ligand. This is presumably a reflection of the relative trans influence of hydride and carbonyl ligands.

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Supplementary Material Available: Tables of anisotropic thermal parameters, hydrogen coordinates, and complete bond lengths and angles (4 pages). Ordering information is given on any current masthead page.