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Functionalized Ruthenatricarbadecaborane via Selective Cage Iodination and Sonogashira Coupling Reactions

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Abstract: Selective iodination of the cyclopentadienylruthenium tricarbadecaboranyl complexes 1 (η5 C5H5) 2 Ph closo 1,2,3,4 RuC3B7H9 (1) and 1 (η5 C5(CH3)5) 2 Ph closo-1,2,3,4-RuC3B7H8 (2) to form their mono-iodo derivatives, 1 (η5 C5H5)-2 Ph-6 I-closo 1,2,3,4-RuC3B7H8 (3) and 1 (η5 C5(CH3)5) 2 Ph 6 I closo 1,2,3,4 RuC3B7H8 (4), was achieved in 90% yields by their reactions with ICl in CH2Cl2 solution. Also isolated in trace amounts from the reaction with 2 was the diiodo 1 (η5 C5(CH3)5) 2 Ph 6,11 I2-closo 1,2,3,4 RuC3B7H7, (5) complex. The sonication promoted Sonogashira coupling reaction of 3 with terminal acetylenes catalyzed by Pd(dppf)2Cl2/CuI yielded the functionalized ruthenatricarbadecaboranyl complexes 1 (η5 C5H5) 2 Ph 6 (Ph-C≡C) closo 1,2,3,4-RuC3B7H8 (6), 1 (η5 C5H5) 2 Ph 6 [CH3CH2C(O)OCH2 C≡C] closo 1,2,3,4 RuC3B7H8 (7), 1 (η5 C5H5) 2 Ph 6 [(η5 C5H5)Fe(η5 C5H4) C≡C] closo 1,2,3,4 RuC3B7H8 (8) and 1 (η5 C5H5) 2 Ph 6 [(CH3)3Si C≡C] closo 1,2,3,4 RuC3B7H8 (9). These reactions thus provide a versatile, systematic pathway for the syntheses of a wide variety of new types of functionalized ruthenatricarbadecaboranyl complexes.

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Larry G. Sneddon
Blanchard Professor of Chemistry

April 15, 2012

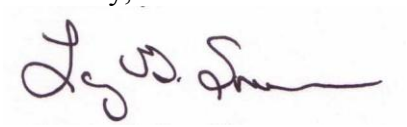
Professor Richard Adams, Editor in Chief
Journal of Organometallic Chemistry

Dear Rick,

We wish to submit the attached article **Functionalized Ruthenatricarbadecaboranes via Selective Cage Iodination and Sonogashira Coupling Reactions** for publication in the special issue of the *Journal of Organometallic Chemistry* dedicated to Tom Fehlner.

The paper describes the general routes to boron-functionalized metallatricarbadecaboranyl complexes, via selective cage-iodination and palladium-catalyzed Sonogashira coupling steps. This method should now allow the syntheses of a wide variety of derivatives for potential uses in medical and/or optical and electronic applications. This work will be of interest to main-group, organometallic and materials chemists, particularly those interested in the complimentary properties of metallocene and metallacarborane complexes. Given Tom's interests in both organometallic and metallacarborane chemistry, we feel this paper is especially appropriate for this special issue.

Sincerely,



Larry G. Sneddon
Blanchard Professor of Chemistry

Abstract

Selective iodination of the cyclopentadienylruthenium tricarbadecaboranyl complexes 1-(η^5-C_5H_5)-2-Ph-*closo*-1,2,3,4-$RuC_3B_7H_9$ (**1**) and 1-(η^5-$C_5(CH_3)_5$)-2-Ph-*closo*-1,2,3,4-$RuC_3B_7H_8$ (**2**) to form their mono-iodo derivatives, 1-(η^5-C_5H_5)-2-Ph-6-I-*closo*-1,2,3,4-$RuC_3B_7H_8$ (**3**) and 1-(η^5-$C_5(CH_3)_5$)-2-Ph-6-I-*closo*-1,2,3,4-$RuC_3B_7H_8$ (**4**), was achieved in 90% yields by their reactions with ICl in CH_2Cl_2 solution. Also isolated in trace amounts from the reaction with **2** was the diiodo 1-(η^5-$C_5(CH_3)_5$)-2-Ph-6,11-I_2-*closo*-1,2,3,4-$RuC_3B_7H_7$, (**5**) complex. The sonication-promoted Sonogashira coupling reaction of **3** with terminal acetylenes catalyzed by $Pd(dppf)_2Cl_2$/CuI yielded the functionalized ruthenatricarbadecaboranyl complexes 1-(η^5-C_5H_5)-2-Ph-6-(Ph-C≡C)-*closo*-1,2,3,4-$RuC_3B_7H_8$ (**6**), 1-(η^5-C_5H_5)-2-Ph-6-[$CH_3CH_2C(O)OCH_2$-C≡C]-*closo*-1,2,3,4-$RuC_3B_7H_8$ (**7**), 1-(η^5-C_5H_5)-2-Ph-6-[(η^5-C_5H_5)Fe(η^5-C_5H_4)-C≡C]-*closo*-1,2,3,4-$RuC_3B_7H_8$ (**8**) and 1-(η^5-C_5H_5)-2-Ph-6-[$(CH_3)_3$Si-C≡C]-*closo*-1,2,3,4-$RuC_3B_7H_8$ (**9**). These reactions thus provide a versatile, systematic pathway for the syntheses of a wide variety of new types of functionalized ruthenatricarbadecaboranyl complexes.

*Graphical abstract: pictogram (for review)

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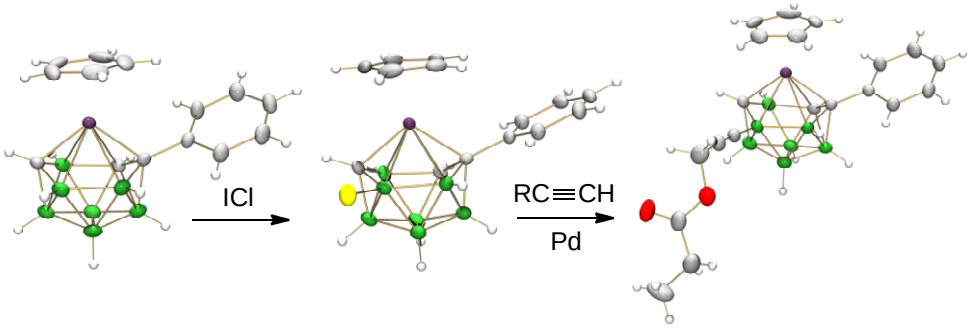
Graphic for Table of Contents



***Graphical abstract: synopsis (for review)**

Synposis

A versatile, systematic pathway for the syntheses of a wide variety of new types of functionalized ruthenatricarbadecaboranyl has been developed based on selective B-iodination followed by palladium catalyzed Sonogashira coupling reactions.

Highlights

- A synthetic strategy of selective B-iodination followed by palladium catalyzed Sonogashira coupling reactions has provided a versatile, systematic pathway to functionalized ruthenatricarbadecaboranyl complexes.
- Selective mono-iodination of cyclopentadienylruthenium tricarbadecaboranyl complexes was achieved in 90% yields by their reactions with ICl.
- Sonication-promoted Sonogashira coupling reactions with terminal acetylenes catalyzed by $Pd(dppf)_2Cl_2$/CuI yielded a wide variety of new types of alkynyl-linked functionalized ruthenatricarbadecaboranes.

Functionalized Ruthenatricarbadecaboranes via Selective Cage Iodination and Sonogashira Coupling Reactions

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Dedicated to our friend Tom Fehlner on the occasion of his 75th birthday

Abstract

Selective iodination of the cyclopentadienylruthenium tricarbadecaboranyl complexes 1-(η^5-C_5H_5)-2-Ph-*closo*-1,2,3,4-$RuC_3B_7H_9$ (**1**) and 1-(η^5-$C_5(CH_3)_5$)-2-Ph-*closo*-1,2,3,4-$RuC_3B_7H_8$ (**2**) to form their mono-iodo derivatives, 1-(η^5-C_5H_5)-2-Ph-6-I-*closo*-1,2,3,4-$RuC_3B_7H_8$ (**3**) and 1-(η^5-$C_5(CH_3)_5$)-2-Ph-6-I-*closo*-1,2,3,4-$RuC_3B_7H_8$ (**4**), was achieved in 90% yields by their reactions with ICl in CH_2Cl_2 solution. Also isolated in trace amounts from the reaction with **2** was the diiodo 1-(η^5-$C_5(CH_3)_5$)-2-Ph-6,11-I_2-*closo*-1,2,3,4-$RuC_3B_7H_7$, (**5**) complex. The sonication-promoted Sonogashira coupling reaction of **3** with terminal acetylenes catalyzed by $Pd(dppf)_2Cl_2$/CuI yielded the functionalized ruthenatricarbadecaboranyl complexes 1-(η^5-C_5H_5)-2-Ph-6-(Ph-C≡C)-*closo*-1,2,3,4-$RuC_3B_7H_8$ (**6**), 1-(η^5-C_5H_5)-2-Ph-6-[$CH_3CH_2C(O)OCH_2$-C≡C]-*closo*-1,2,3,4-$RuC_3B_7H_8$ (**7**), 1-(η^5-C_5H_5)-2-Ph-6-[(η^5-C_5H_5)Fe(η^5-C_5H_4)-C≡C]-*closo*-1,2,3,4-$RuC_3B_7H_8$ (**8**) and 1-(η^5-C_5H_5)-2-Ph-6-[$(CH_3)_3$Si-C≡C]-*closo*-1,2,3,4-$RuC_3B_7H_8$ (**9**). These reactions thus provide a

versatile, systematic pathway for the syntheses of a wide variety of new types of functionalized ruthenatricarbadecaboranyl complexes.

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Keywords: tricarbaborane, metallatricarbaborane, carborane, Sonogashira coupling, iodination, boron halogenation

1. Introduction

The key to the utilization of polyhedral boranes/carboranes and metalla-boranes/carboranes in many applications is the development of efficient methods for the systematic syntheses of functional derivatives. One method that has now proven to be especially useful for the boron-functionalization of a variety of carborane [1] and metallacarborane [2] clusters has employed the palladium catalyzed cross-coupling reactions of their B-iodo derivatives. We recently [3] employed this strategy to enable the functionalization of ferratricarbadecaboranes by a sequence involving a selective B-halogenation reaction followed by palladium catalyzed Sonogashira couplings. In this paper, we further demonstrate the utility of this route by achieving, in even higher yields than those found for the iron complexes, the efficient functionalization of ruthenatricarbadecaboranes.

2. Experimental Section

2.1 General Procedures and Materials

Unless otherwise noted, all reactions and manipulations were performed in dry glassware under a nitrogen atmosphere using the high-vacuum or inert-atmosphere techniques described by Shriver [4]. The Li^+[6-Ph-*nido*-5,6,9-$C_3B_7H_9^-$] [5,6] and 1-(η^5-$C_5(CH_3)_5$)-2-Ph-*closo*-1,2,3,4-$RuC_3B_7H_9$ (**2**) [7] were prepared by the reported methods. Iodine monochloride, aluminum chloride, phenylacetylene, ethynylferrocene, propargyl propionate, and diethyl amine (Aldrich); trimethylsilylacetylene (Lancaster); bis(diphenylphosphino)ferrocene, palladium(II) chloride, tris(acetonitrile)cyclopentadienylruthenium(II) hexafluorophosphate and copper iodide (Strem); spectrochemical grade dichloromethane and hexanes (Fisher) were used as received. Glyme was freshly distilled from sodium-benzophenone ketyl and carbon disulfide (Fisher) was

freshly distilled from calcium hydride prior to use. All other solvents were used as received unless noted otherwise.

The ^{11}B NMR at 128.4 MHz and ^{1}H NMR at 400.1 MHz were obtained on a Bruker DMX-400 spectrometer equipped with appropriate decoupling accessories. All ^{11}B chemical shifts are referenced to external $BF_3{\cdot}O(C_2H_5)_2$ (0.0 ppm) with a negative sign indicating an upfield shift. All ^{1}H chemical shifts were measured relative to internal residual protons in the lock solvents and are referenced to Me_4Si (0.0 ppm). High- and low-resolution mass spectra employing chemical ionization with negative ion detection were obtained on a Micromass AutoSpec high-resolution mass spectrometer. IR spectra were obtained on a Perkin-Elmer Spectrum 100 FT-IR spectrometer. Elemental analyses were carried out at either Robertson Microlit Laboratories in Madison, NJ or at the MicroAnalytical Facility at UC Berkeley, CA. Melting points were determined using a standard melting point apparatus and are uncorrected.

*2.2 1-(η^5-C_5H_5)-2-Ph-closo-1,2,3,4-$RuC_3B_7H_9$ (**1**)*

A glyme solution of Li^+[6-Ph-*nido*-5,6,9-$C_3B_7H_9^-$] (1.65 mL of a 0.35 M solution, 0.57 mmol) was added dropwise to a stirring glyme (20 mL) solution of (η^5-C_5H_5)$Ru(CH_3CN)_3PF_6$ (250 mg, 0.57 mmol) under N_2. After stirring for 24 h at 50 ^{o}C, the reaction mixture was exposed to air and filtered through a short silica gel plug using CH_2Cl_2 and ether as eluents. The solvent was vacuum evaporated and the oily orange residue was redissolved in 5 mL of CH_2Cl_2 and eluted through a silica gel column using 2:1 hexanes/CH_2Cl_2 as the eluent to give **1**: 62% yield (130 mg, 0.35 mmol); orange; mp 139-141 ^{o}C. Anal. calcd.: C 46.19, H 5.26; fd. C 46.03, H 5.21. HRMS: *m/z* for $C_{14}H_{19}B_7Ru^-$: calcd. 368.1210; fd. 368.1217. ^{11}B NMR (128.4 MHz, CD_2Cl_2, ppm, *J* = Hz): 3.9 (d, 156, 1B), 1.7 (d, 166, 1B), -11.1 (d, 148, 1B), -12.3 (d, 156, 1B),

-30.0 (d, ~160, 1B), -30.8 (d, ~100, 1B), -31.5 (d, ~100, 1B). ^{1}H NMR (400.1 MHz, CD_2Cl_2, ppm, *J* = Hz): 7.42-7.33 (m, Ph), 5.88 (s, C3*H*), 4.74 (s, Cp), 2.54 (s, C4*H*). IR (KBr, cm^{-1}): 2961 (m), 2924 (s), 2853 (m), 2606 (m), 2577 (s), 2525 (vs), 1493 (m), 1446 (m), 1415 (m), 1261 (s), 1105 (vs, br), 1021 (vs, br), 936 (m), 797 (vs, br), 737 (m), 725 (m), 693 (s), 525 (m).

*2.3 1-(η^5-C_5H_5)-2-Ph-6-I-closo-1,2,3,4-$RuC_3B_7H_8$ (**3**)*

A CH_2Cl_2 solution of ICl (0.42 mL of a 1 M solution, 0.42 mmol) was added dropwise to a stirring CH_2Cl_2 solution of **1** (102 mg, 0.33 mmol) under N_2. Stirring was continued at room temperature for 1 h. The solvent was vacuum evaporated and the dark orange residue was redissolved in 20 mL of CH_2Cl_2 and shaken 2 times with 20 mL of a $Na_2S_2O_3$ solution (0.6 M in H_2O), then twice with 20 mL of H_2O. The organic layer was collected and dried over $MgSO_4$, then filtered through a short silica gel plug using CH_2Cl_2 as the eluent. The solvent was vacuum evaporated to yield orange crystals of **3**: 90% yield (129 mg, 0.30 mmol); orange; mp 176-177 ^{o}C. Anal. calcd. C 34.32, H 3.70; fd. C 34.50, H 3.59. HRMS *m/z* for $C_{14}H_{18}B_7IRu^{-}$: calcd. 492.0148; fd. 492.0131. ^{11}B NMR (128.4 MHz, CD_2Cl_2, ppm, *J* = Hz): 5.4 (d, 163, 1B), 2.6 (d, 163, 1B), -8.9 (d, 154, 1B), -22.9 (s, 1B), -27.9 (d, 163, 1B), -28.5 (d, 100, 1B), -30.5 (d, 163, 1B). ^{1}H NMR (400.1 MHz, CD_2Cl_2, ppm, *J* = Hz): 7.48-7.39 (Ph), 6.02 (s, C3*H*), 4.85 (s, Cp), 2.73 (s, C4*H*). IR (KBr, cm^{-1}): 3084 (m), 3044 (m), 2924 (m), 2852 (m), 2545 (vs), 2558 (vs), 1595 (w), 1578 (w), 1495 (s), 1444 (s), 1413 (s), 1308 (w), 1261 (m), 1208 (m), 1105 (vs), 1044 (s), 1002 (s), 934 (s), 838 (vs), 792 (vs), 749 (vs), 691 (vs), 617 (m), 521 (m).

*2.4 1-(η^5-$C_5(CH_3)_5$)-2-Ph-6-I-closo-1,2,3,4-$RuC_3B_7H_8$ (**4**) and 1-(η^5-$C_5(CH_3)_5$)-2-Ph-6,11-I_2-closo-1,2,3,4-$RuC_3B_7H_7$ (**5**)*

A CH_2Cl_2 solution of ICl (0.24 mL of a 1 M solution, 0.24 mmol) was added dropwise to a stirring CH_2Cl_2 solution of **2** (50 mg, 0.12 mmol) and $AlCl_3$ (3 mg, 0.02 mmol) under N_2. Stirring was continued at room temperature for 1.5 h. The solvent was vacuum evaporated and the dark orange residue was redissolved in 20 mL of CH_2Cl_2 and shaken 2 times with 25 mL of a $Na_2S_2O_3$ solution (0.6 M in H_2O), then twice with 20 mL of H_2O. The organic layer was collected and dried over $MgSO_4$ and then filtered through a short silica gel plug using CH_2Cl_2 as the eluent. The solvent was vacuum evaporated and the resulting orange crystals were then chromatographed on silica gel plates using 3:1 hexanes/CH_2Cl_2 as eluent to give the major product **4**: 92% yield (62 mg, 0.10 mmol); orange; mp 231-232 ^oC. Anal. calcd. C 40.75, H 5.04; fd. C 40.65, H 5.09. HRMS: *m/z* for $C_{19}H_{28}B_7IRu^-$: calcd. 564.0997; fd. 564.0747. ^{11}B NMR (128.4 MHz, CD_2Cl_2, ppm, *J* = Hz): 3.8 (d, 162, 1B), 1.9 (d, 169, 1B), -9.5 (d, 155, 1B), -20.9 (s, 1B), -26.6 (d, 155, 1B), -28.0 (d, 155, 1B), -28.7 (d, 162, 1B). ^1H NMR (400.1 MHz, CD_2Cl_2, ppm, *J* = Hz): 8.10-7.15 (m, Ph), 4.89 (s, C3*H*), 2.85 (s, C4*H*), 1.50 (s, Cp*). IR (KBr, cm^{-1}): 3041 (m), 2908 (m), 2605 (m), 2563 (vs), 2549 (vs), 1596 (w), 1495 (m), 1476 (m), 1446 (m), 1383 (s), 1209 (w), 1103 (m), 1085 (m), 1028 (s), 935 (m), 864 (m), 789 (s), 695 (s).

Also isolated from the reaction were trace amounts of **5**: 2% yield (~3 mg, 0.003 mmol); orange; mp 235-237 ^oC. Anal. calcd. C 33.27, H 3.97; fd. C 33.1, H 3.89. HRMS *m/z* for $C_{19}H_{27}B_7I_2Ru^-$: calcd. 689.9908; fd. 689.9839. ^{11}B NMR (128.4 MHz, CD_2Cl_2, ppm, *J* = Hz): 5.1 (d, 166, 1B), 2.6 (d, 166, 1B), -8.4 (d, 145, 1B), -19.4 (s, 1B), -26.2 (d, 155, 1B), -27.4 (d, ~125, 1B), -29.1 (s, 1B). ^1H NMR (400.1 MHz, CD_2Cl_2, ppm, *J* = Hz): 8.06-7.11 (m, Ph), 4.87 (s, C3*H*), 2.61 (s, C4*H*), 1.64 (s, Cp). IR (KBr, cm^{-1}): 3026 (w), 2918 (m), 2618 (m), 2563 (s), 1493 (m), 1470 (m), 1446 (m), 1378 (s), 1261 (m), 1200 (m), 1099 (s, br), 1017 (s), 856 (m), 814 (s), 795 (s), 767 (s), 696 (s).

*2.5 1-(η^5-C_5H_5)-2-Ph-6-[C_6H_5-C≡C]-closo-1,2,3,4-$RuC_3B_7H_8$ (**6**)*

A mixture of **3** (50 mg, 0.10 mmol), Pd(dppf)Cl_2 (16.3 mg, 0.02 mmol) and CuI (3.4 mg, 0.02 mmol) was dissolved in Et_2NH (5 mL). Phenyl acetylene (0.13 mL, 1.17 mmol) was added to the flask via syringe and the solution was placed in a sonication bath for 2 h at ~43 °C, after which it was filtered through a short silica gel plug. The solvent was vacuum evaporated and the oily residue then chromatographed on silica gel plates using 2:1 hexanes:CH_2Cl_2 as eluent to yield orange crystals of **6**: 42% yield (18 mg, 0.042 mmol); R_f (0.38), orange; mp 135-138 °C. Anal. calcd.: C 56.93, H 4.99; fd. C 58.12, H 4.84. NCI HRMS *m/z* for $C_{22}H_{23}B_7Ru^-$: calcd. 468.1500; fd. 468.1531. ^{11}B NMR (128.4 MHz, CD_2Cl_2, ppm, *J* = Hz): 5.4 (d, 116, 1B), 2.9 (d, 161, 1B), -9.6 (d, 161, 1B), -13.3 (s, 1B), -29.2 (d, 141, 2B), -32.1 (d, 180, 1B). ^{1}H NMR (400.1 MHz, CD_2Cl_2, ppm, *J* = Hz): 7.70-7.37 (m, Ph), 5.99 (s, C3*H*), 4.83 (s, Cp), 2.64 (s, C4*H*). IR (KBr, cm^{-1}): 2960 (m), 2925 (m), 2598 (s), 2556 (vs), 1727 (s, br), 1594 (m), 1488 (s), 1445 (m), 1260 (s, br), 1122 (s), 843 (s), 757 (vs), 690 (vs), 521 (m).

*2.6 1-(η^5-C_5H_5)-2-Ph-6-[$CH_3CH_2C(O)OCH_2$-C≡C]-closo-1,2,3,4-$RuC_3B_7H_8$ (**7**)*

A mixture of **3** (50 mg, 0.10 mmol), Pd(dppf)Cl_2 (16.3 mg, 0.02 mmol) and CuI (3.4 mg, 0.02 mmol) was dissolved in Et_2NH (5 mL). Propargyl propionate (0.14 mL, 1.1 mmol) was added to the flask via syringe and the solution was placed in a sonication bath for 15 h at ~43 °C, after which the solution was filtered through a short silica gel plug. The solvent was vacuum evaporated and the oily residue then chromatographed on silica gel plates using 2:1 hexanes:CH_2Cl_2 as eluent to yield orange crystals of **7**: 21% yield (10 mg, 0.02 mmol); R_f (0.55), orange; mp 184-186 °C. Anal. calcd C 50.66, H 5.31; fd. C 50.65, H 5.26. NCI HRMS

m/z for $C_{20}H_{25}B_7O_2Ru^-$: calcd. 476.2106; fd. 476.2123. ^{11}B NMR (128.4 MHz, CD_2Cl_2, ppm, *J* = Hz): 1.6 (d, 164, 1B), -1.7 (d, 156, 1B), -10.0 (d, 148, 1B), -13.5 (s, 1B), -29.2 (d, 140, 2B), -31.9 (d, 164, 1B). ^{1}H NMR (400.1 MHz, CD_2Cl_2, ppm, *J* = Hz): 7.70-7.32 (m, Ph), 5.84 (s, C3*H*), 4.77 (s, Cp), 4.61 (s, CH_2), 2.63 (s, C*H*), 2.34 (q, 7.5, CH_2), 1.12 (t, 8, CH_3). IR (KBr, cm^{-1}): 3107 (m), 2939 (m), 2623 (m), 2547 (vs), 1729 (vs), 1494 (m), 1447 (m), 1412 (m), 1372 (m), 1337 (m), 1257 (m), 1173 (vs), 1076 (s), 999 (m), 946 (m), 931 (m), 849 (s), 742 (m), 697 (s).

2.7 1-(η^5-C_5H_5)-2-Ph-6-[(η^5-C_5H_5)Fe(η^5-C_5H_4)-C≡C]-closo-1,2,3,4-$RuC_3B_7H_8$ ***(8)***

A mixture of **3** (50 mg, 0.10 mmol), Pd(dppf)Cl_2 (16.3 mg, 0.02 mmol), CuI (3.4 mg, 0.02 mmol) and ethynylferrocene (21 mg, 0.1 mmol) was dissolved in Et_2NH (5 mL) and the solution was placed in a sonication bath for 24 h at ~43 ^{o}C, after which the solution was filtered through a short silica gel plug. The solvent was vacuum evaporated and the oily residue then chromatographed on silica gel plates using 2:1 hexanes:CH_2Cl_2 as eluent to yield orange crystals of **8**: 19% yield (11 mg, 0.02 mmol); R_f (0.29), orange, mp >300 ^{o}C. Anal. Calcd. for **8**·$(CH_2Cl_2)_{1.5}$: C 47.22, H, 4.32 ; fd. 47.92 H 4.39. ^{11}B NMR (128.4 MHz, CD_2Cl_2, ppm, *J* = Hz): 4.5 (d, 161, 1B), 0.4 (d, 161, 1B), -10.6 (d, 149, 1B), -13.4 (s, 1B), -30.2 (d, 143, 2B), -33.3 (d, 155, 1B). ^{1}H NMR (400.1 MHz, CD_2Cl_2, ppm, *J* = Hz): 7.72-7.44 (m, Ph), 5.90 (s, C3*H*), 4.79 (s, Cp, 5H), 4.33 (s, Cp, 2H), 4.13 (s, Cp, 7H), 2.54 (s, C4*H*). IR (KBr, cm^{-1}): 3191 (w), 3101 (w), 2967 (w), 2919 (w), 2611 (m), 2570 (vs), 2175 (s), 1495 (m), 1457 (m), 1445 (m), 1412 (m), 1264 (m), 1138 (m), 1106 (m), 1058 (m), 998 (m), 819 (vs), 695 (s).

*2.8 1-(η^5-C_5H_5)-2-Ph-6-[$(CH_3)_3$Si-C≡C]-closo-1,2,3,4-$RuC_3B_7H_8$ (**9**)*

A mixture of **3** (50 mg, 0.10 mmol), Pd(dppf)Cl_2 (16.3 mg, 0.02 mmol) and CuI (3.4 mg, 0.02 mmol) was dissolved in Et_2NH (5 mL). Trimethylsilane acetylene (0.1 mL, 1.2 mmol) was added to the flask via syringe and the solution was placed in a sonication bath for 2 h at ~43 ^oC, after which it was filtered through a short silica gel plug. The solvent was vacuum evaporated and the oily residue then chromatographed on silica gel plates using 2:1 hexanes:CH_2Cl_2 as eluent to yield orange crystals of **9**: 40% yield (18 mg, 0.04 mmol); R_f (0.32), orange, mp 195 ^oC. Anal. calcd. C 49.58, H 5.91; fd. C 49.80, H 5.81. NCI HRMS *m/z* for $C_{19}H_{27}B_7RuSi^-$: calcd. 462.1577; fd. 462.1573. ^{11}B NMR (128.4 MHz, CD_2Cl_2, ppm, *J* = Hz): 5.3 (d, 155, 1B), 1.6 (d, 155, 1B), -9.5 (d, 149, 1B), -13.3 (s, 1B), -29.2 (d, 149, 2B), -32.1 (d, 161, 1B). ^1H NMR (400.1 MHz, CD_2Cl_2, ppm, *J* = Hz): 7.70-7.34 (m, Ph), 5.85 (C3*H*), 4.75 (s, Cp), 2.51 (s, C4*H*), 0.12 (s, (CH_3)$_3$). IR (KBr, cm^{-1}): 3428 (m, br), 3086 (m), 2956 (m), 2572 (vs), 2130 (m), 1496 (m), 1446 (m), 1415 (m), 1246 (s), 1154 (s), 1032 (m), 1003 (m), 857 (vs, br), 840 (vs, br), 755 (s), 692 (s).

2.10 Crystallographic Procedures

Single crystals of all compounds were grown through slow solvent evaporation from dichloromethane solutions in air or through vapor-liquid diffusion of pentane into a dichloromethane solution. X-ray intensity data for **1** (Penn3318), **3** (Penn3317), **4** (Penn3306), **5** (Penn3305), **6** (Penn3319), **7** (Penn 3324), **8** (Penn3332) and **9** (Penn 3329) were collected on a Rigaku Mercury CCD area detector employing graphite-monochromated Mo-K_α radiation (λ=0.71073 Å) at a temperature of 143(1) K. Rotation frames were integrated using CrystalClear [8], producing a list of unaveraged F^2 and σ(F^2) values that were then passed to the Crystal

Structure [9] package for further processing and structure solution on a Dell Pentium 4 computer. The intensity data were corrected for Lorentz and polarization effects and for absorption using SADABS [10].

The structures were solved by direct methods (SIR97) [11]. Refinement was by full-matrix least squares based on F^2 using SHELXL-97 [12]. All reflections were used during refinement (values of F^2 that were experimentally negative were replaced with $F^2 = 0$). All non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined isotropically.

Crystal and refinement data are given in **Table 1**. Selected bond distances and angles are given in the corresponding figure captions.

3. Results and Discussion

The 1-(η^5-C_5H_5)-2-Ph-*closo*-1,2,3,4-$RuC_3B_7H_9$ (**1**) analog of the previously known 1-(η^5-$C_5(CH_3)_5$)-2-Ph-*closo*-1,2,3,4-$RuC_3B_7H_9$ (**2**) [6] complex was synthesized in a straight-forward manner via the reaction of the Li^+[6-Ph-*nido*-5,6,9-$C_3B_7H_9^-$] salt [5, 6] with (η^5-C_5H_5)$Ru(CH_3CN)_3PF_6$. The crystallographic determination of **1** that is depicted in **Figure 1** confirmed the sandwich structure of the complex with the ruthenium η^5-coordinated to the cyclopentadienyl ring and bonded in an η^6-fashion to the tricarbadecaboranyl cage. The ruthenium is approximately centered over the face of the tricarbadecaboranyl fragment with its most significant bonding interactions with the C2 and C3 carbons that are puckered toward the metal. In keeping with their *closo* skeletal electron counts, the RuC_3B_7 fragments in both **1** and **2** adopt octadecahedral cage structures.

3.1 Iodination Reactions

As summarized in **Scheme 1**, iodination of **1** and **2** was readily achieved by their reactions with ICl in CH_2Cl_2 solutions to give the mono-iodo derivatives, 1-(η^5-C_5H_5)-2-Ph-6-I-*closo*-1,2,3,4-$RuC_3B_7H_8$ (**3**) and 1-(η^5-$C_5(CH_3)_5$)-2-Ph-6-I-*closo*-1,2,3,4-$RuC_3B_7H_8$ (**4**), in 90% yields. The reaction with **1** gave excellent yields without the need of added $AlCl_3$, but the reaction with **2** required this catalyst in order to achieve high yields. Also isolated in minor amounts from the reaction with **2** was the di-iodo 1-(η^5-$C_5(CH_3)_5$)-2-Ph-6,11-I_2-*closo*-1,2,3,4-$RuC_3B_7H_7$, (**5**) derivative.

The ^{11}B NMR spectra of **3**-**5** exhibit doublet resonances in the chemical shift ranges of those observed for **1** and **2**. However, consistent with their formulations as B-substituted mono- and di-iodo derivatives, the spectra of **3** and **4** (**Figure 4**, middle) each show one singlet near -21

ppm, while the spectrum of **5** (**Figure 4**, top) exhibits two singlets, one at -19.4 ppm and the other at -29.1 ppm. The ^{1}H NMR spectra of **1**-**5** each show two characteristic cage C-H resonances, with C4-H occurring at higher-field (3.09-2.17 ppm) and the C3-H at lower-field (6.02-4.87 ppm) [13].

The crystallographic determinations of **3** and **4** depicted in **Figures 3** and **4** (top) confirmed, as previously observed for the 1-(η^5-C_5H_5)-2-Ph-*closo*-1,2,3,4-$FeC_3B_7H_9$ complexes [3], that halogenation of **1** and **2** occurred at the B6 cage position. However, the ICl reactions with **1** and **2** exhibited much higher reactivities than those of 1-(η^5-C_5H_5)-2-Ph-*closo*-1,2,3,4-$FeC_3B_7H_9$ where the B6 mono-iodinated derivative could only be obtained in 58% yield.

The iodinations of **1** and **2** with ICl should proceed through an electrophilic mechanism, where I^+ attacks the most electronegative boron. The selectivity observed for the B6 position is consistent with the established trend [14] for electrophilic cage halogenations in metallacarboranes to occur at borons that are both most separated from the cage-carbons and adjacent to the metal center.

A structural study of the di-iodo derivative **5**, **Figure 4** (bottom), confirmed that the second iodination took place, again as previously found for the 1-(η^5-C_5H_5)-2-Ph-*closo*-1,2,3,4-$FeC_3B_7H_9$ complexes, at the B11 boron. This boron is also opposite the C2 and C4 carbons, but is not adjacent to the ruthenium.

The iodine substitutions in **3**-**5** appear to have little effect on the cage bonding as their intracage bond distances and angles, as well as the Ru-cage and Ru-$Cp_{centroid}$ distances are essentially unchanged from the values in **1** and **2**. The B6-I1 distances, 2.189(3) Å (**3**), 2.194(3) Å (**4**), and 2.184(4) Å (**5**), and the B11-I2 distance, 2.178(4) Å (**5**) are consistent with the B-I distances observed in other iodinated metallacarboranes [15] and are significantly longer than in

BI_3, 2.1251(3) Å [16] suggesting little π donation of a halogen lone pair to an orbital on the 6-boron.

3.2 Sonogashira Coupling Reactions

Palladium-catalyzed Sonogashira cross-coupling reactions have been shown to provide an effective route to the synthesis of substituted alkynes [17] with the highest reactivity generally found for iodinated substrates. The high yield-synthesis of the iodinated derivative **3** made it an ideal substrate for the exploration of the Sonogashira-type coupling reactions depicted in **Scheme 2**.

The sonicated reaction of **3** with phenylacetylene in the presence of 20 mol% Pd[dppf]Cl_2/CuI using diethylamine as both a base and solvent afforded the phenylacetylene-functionalized product 1-(η^5-C_5H_5)-2-Ph-6-(Ph-C≡C)-*closo*-1,2,3,4-$RuC_3B_7H_8$ (**6**) in 42% yield. Utilizing these conditions, alkynyl derivatives were obtained containing terminal ester 1-(η^5-C_5H_5)-2-Ph-6-[$CH_3CH_2C(O)OCH_2$-C≡C]-*closo*-1,2,3,4-$RuC_3B_7H_8$ (**7**), ferrocene 1-(η^5-C_5H_5)-2-Ph-6-[(η^5-C_5H_5)Fe(η^5-C_5H_4)-C≡C]-*closo*-1,2,3,4-$RuC_3B_7H_8$ (**8**) and trimethylsilane 1-(η^5-C_5H_5)-2-Ph-6-[$(CH_3)_3$Si-C≡C]-*closo*-1,2,3,4-$RuC_3B_7H_8$ (**9**) functional groups. Greatly decreased yields for **6** (16%), **7** (18%) and **9** (<5%) and much longer reaction times (24 h instead of 2-4 h) were observed if these reactions were carried out at room (or even reflux) temperature without sonication. The synthesis of **8** could only be achieved with the sonication conditions.

In each reaction, only one product was observed and **6-9** were easily isolated using thin layer plate chromatography as air and moisture stable orange solids that were soluble in a wide variety of both polar and nonpolar organic solvents.

As shown in the example in **Figure 5**, the ^{11}B NMR spectra of **6-9** are similar to that of **3**, but the singlet resonance observed for **3** at -22.9 ppm was replaced by a new downfield singlet resonance near -13 ppm. This shift was largely unaffected by the terminal functionality of the acetylene linker. The ^{1}H NMR spectra of these compounds each show two cage CH resonances occurring in their normal higher-field (3.09-1.27 ppm, C4-H) and lower-field (6.02-4.87 ppm, C3-H) ranges, as well as the resonances expected for their organic and organometallic substituents.

As shown in **Figures 6-9**, crystallographic determinations of **6-9** confirmed the formation of the alkynyl-linked derivatives having C≡C distances (average C≡C, 1.203(5) Å) and B6-$C_{acetylene}$ distances similar to those found in the analogous cyclopentadienyl iron tricarbadecaboranyl complexes [3] and other alkynyl-functionalized carboranes [1d, 1l] and metallacarboranes [2, 3].

In conclusion, the above results again further illustrate both the importance and utility of palladium catalyzed cross coupling reactions of iodo-carboranes/metallacarboranes as a means of functionalizing these boron cluster compounds. The ability of the Sonogashira reaction to produce complexes containing either π-conjugated linkages (e.g. **6** and **8**) or chemically active units that can undergo further modification (e.g. **7** and **9**) should prove valuable in realizing the potential metallocene-like biomedical and/or materials applications of the metallatricarbadecaboranes.

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Appendix. Supplementary Material

CCDC 873728, 873729, 873730, 873731, 873732, 873733, 873734 and 873735 contain the supplementary crystallographic data for the structures of **1** and **3**-**9** in this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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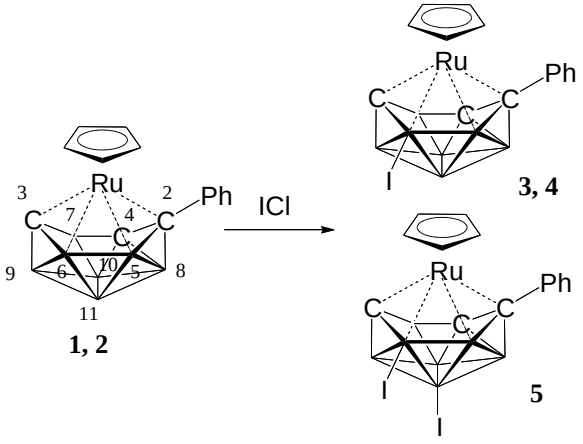
Table 1. Crystallographic Data Collection and Structure Refinement Information

	1	**3**	**4**	**5**
empirical formula	$C_{14}B_7H_{19}Ru$	$C_{14}B_7H_{18}IRu$	$C_{19}B_7H_{28}IRu$	$C_{19}B_7H_{27}I_2Ru$
formula weight	364.03	489.92	560.05	685.95
crystal class	Triclinic	Monoclinic	Triclinic	Orthorhombic
space group	$P\bar{1}$ (#2)	$P2_1/n$ (#14)	$P\bar{1}$ (#2)	Pbca (#61)
Z	2	4	2	8
a, Å	6.6641(10)	12.1493(8)	8.7379(10)	11.6451(8)
b, Å	8.1495(10)	10.6633(7)	8.8013(10)	19.8644(13)
c, Å	15.5911(16)	14.1142(10)	15.0767(18)	20.4269(14)
α, deg	76.043(12)		100.043(3)	
β, deg	85.135(14)	104.558(2)	98.688(3)	
γ, deg	74.323(10)		92.426(3)	
V, $Å^3$	791.0(2)	1769.8(2)	1125.8(2)	4725.2(6)
D_{calc}, g/cm^3	1.528	1.839	1.652	1.928
μ, cm^{-1}	9.76	26.19	20.70	32.81
λ, Å (Mo-$K_α$)	0.71073 Å	0.71073	0.71073 Å	0.71073 Å
crystal size, mm	0.32x0.25x0.01	0.32x0.18x0.04	0.42x0.22x0.20	0.42x0.30x0.05
F(000)	364	936	548	2608
2*θ* angle, deg	5.34-54.84	5.10-54.94	5.08-54.96	5.30-54.96
temperature, K	143(1)	143(1)	143(1)	143(1)
hkl collected	$-8 \le h \le 8$ $-10 \le k \le 9$ $-18 \le l \le 20$	$-15 \le h \le 15$ $-13 \le k \le 11$ $-18 \le l \le 17$	$-11 \le h \le 9$ $-11 \le k \le 11$ $-19 \le l \le 19$	$-12 \le h \le 15$ $-21 \le k \le 25$ $-20 \le l \le 26$

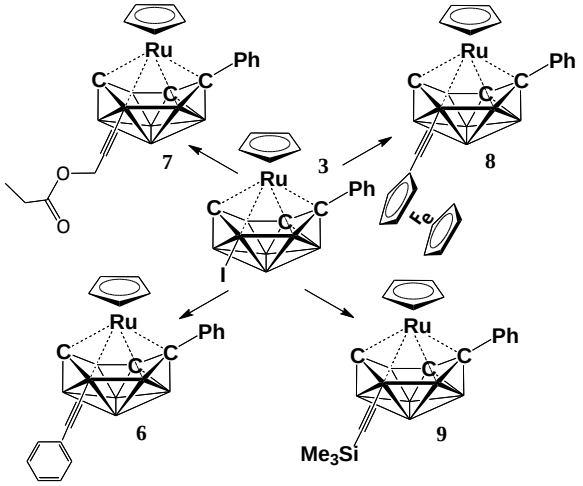
no. of reflns measured	11618	11056	9708	28551
no. of unique reflns	3574	4013	5033	5393
no. of observed reflns ($F > 4\sigma$)	3264	3555	4698	5014
no. of reflns used in refinement	3574	4013	5033	5393
no. parameters	263	281	259	268
R^a indices ($F>4\sigma$)	R_1=0.0317 wR_2=0.0675	R_1=0.0253 wR_2=0.0600	R_1=0.0229 wR_2=0.059	R_1=0.0312 wR_2=0.0761
R^a indices (all data)	R_1=0.0359 wR_2=0.0703	R_1=0.0290 wR_2=0.0628	R_1=0.0249 wR_2=0.0603	R_1=0.0345 wR_2=0.0780
GOF[b]	1.101	1.110	1.090	1.147
final difference peaks, e/Å^3	+1.467, -1.379	0.955, -0.881	+0.808, -0.825	+0.843, -1.658

	6	**7**	**8**	**9**
empirical formula	$C_{22}B_7H_{23}Ru$	$C_{20}B_7H_{25}O_2Ru$	$C_{26}B_7H_{27}FeRu$	$C_{19}B_7H_{27}SiRu$
formula weight	464.14	474.14	572.07	460.24
crystal class	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic
space group	$P2_1/c$ (#14)	C2/c (#15)	Pbca (#61)	Pbcn (#60)
Z	8	8	8	8
a, Å	17.4033(13)	26.683(3)	13.2824(13)	23.4967(17)
b, Å	10.8743(8)	8.0688(7)	16.0857(16)	11.0206(5)
c, Å	24.3877(19)	21.029(2)	22.727(2)	17.3871(9)
α, deg				
β, deg	109.630(3)	110.410(2)		
γ, deg				
V, Å^3	4347.1(6)	4243.3(7)	4855.8(8)	4502.4(4)
D_{calc}, g/cm^3	1.418	1.484	1.565	1.358
μ, cm^{-1}	7.28	7.54	12.34	7.52
λ, Å (Mo-K_α)	0.71073	0.71073	0.71073	0.71073
crystal size, mm	0.38x0.12x0.01	0.38x0.32x0.22	0.26x0.18x0.12	0.38x0.25x0.08
F(000)	1872	1920	2304	1872
2θ angle, deg	5.04-50.10	5.3-54.92	5.06-54.98	5.58-50.12
temperature, K	143(1)	143(1)	143(1)	143(1)
hkl collected	$-20 \le h \le 20$ $-12 \le k \le 12$ $-29 \le l \le 26$	$-34 \le h \le 34$ $-10 \le k \le 8$ $-19 \le l \le 27$	$-17 \le h \le 15$ $-20 \le k \le 20$ $-28 \le l \le 29$	$-27 \le h \le 20$ $-13 \le k \le 13$ $-20 \le l \le 20$

no. of reflns measured	26095	13307	31425	31081
no. of unique reflns	26095	4779	5521	3993
no. of observed reflns ($F > 4\sigma$)	20830	4279	4942	3678
no. of reflns used in refinement	26095	4779	5521	3993
no. parameters	543	372	349	257
R^a indices ($F>4\sigma$)	R_1=0.0616 wR_2=0.1430	R_1=0.0359 wR_2=0.0810	R_1=0.0455 wR_2=0.1153	R_1=0.0416 wR_2=0.1107
R^a indices (all data)	R_1=0.0834 wR_2=0.1519	R_1=0.0403 wR_2=0.0855	R_1=0.0512 wR_2=0.1200	R_1=0.0449 wR_2=0.1139
GOF[b]	1.150	1.098	1.075	1.124
final difference peaks, e/Å^3	1.099, -1.011	1.560, -0.893	1.621, -0.971	1.314, -1.016



Scheme 1. Iodination reactions of 1-(η^5-C_5H_5)-2-Ph-*closo*-1,2,3,4-$RuC_3B_7H_9$ (**1**) and 1-(η^5-$C_5(CH_3)_5$)-2-Ph-*closo*-1,2,3,4-$RuC_3B_7H_7$ (**2**) with ICl to yield their 1-(η^5-C_5H_5)-2-Ph-6-I-*closo*-1,2,3,4-$RuC_3B_7H_8$ (**3**), 1-(η^5-$C_5(CH_3)_5$)-2-Ph-6-I-*closo*-1,2,3,4-$RuC_3B_7H_8$ (**4**) and 1-(η^5-$C_5(CH_3)_5$)-2-Ph-6,11-I_2-*closo*-1,2,3,4-$RuC_3B_7H_7$ (**5**) derivatives, respectively.



Scheme 2. Sonogashira cross-coupling reactions of **3**

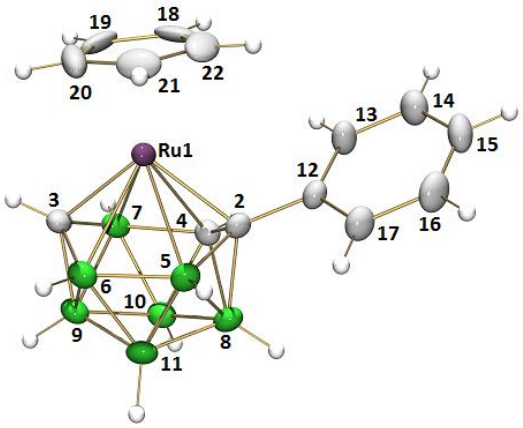


Figure 1. Crystallographically determined structure of 1-(η^5-C_5H_5)-2-Ph-*closo*-1,2,3,4-$RuC_3B_7H_9$ (**1**). Selected distances (Å) and angles (deg): Ru1-C2, 2.093(2); Ru1-C3, 2.067(3); Ru1-C4, 2.352(3); Ru1-B5, 2.336(3); Ru1-B6, 2.339(3); Ru1-B7, 2.372(3); Ru1-$Cp_{Centroid}$, 1.8169(2); C2-B5, 1.596(4); B5-B6, 1.863(4); C3-B6, 1.588(4); C3-B7, 1.582(4); C4-B7, 1.786(4); C2-C4, 1.510(4); C2-C12, 1.496(4); B6-B9, 1.828(5); B6-B11, 1.815(4); C3-Ru1-C2, 106.10(10); C12-C2-Ru1, 121.89(17)

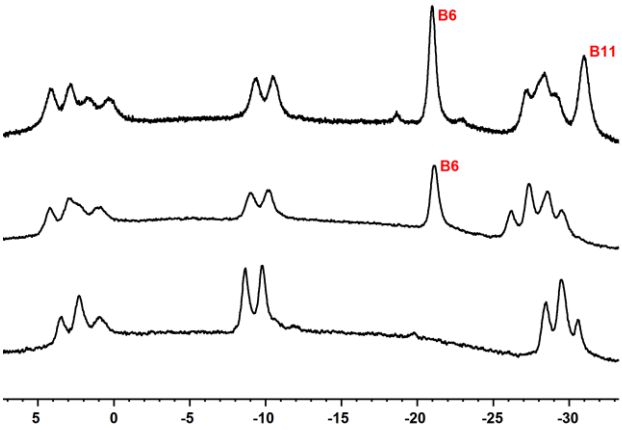


Figure 2. Comparison of the ^{11}B NMR spectra of (bottom) 1-(η^5-$C_5(CH_3)_5$)-2-Ph-*closo*-1,2,3,4-$RuC_3B_7H_8$ (**2**); (middle) 1-(η^5-$C_5(CH_3)_5$)-2-Ph-6-I-*closo*-1,2,3,4-$RuC_3B_7H_8$ (**4**); (top) 1-(η^5-$C_5(CH_3)_5$)-2-Ph-6,11-I_2-*closo*-1,2,3,4-$RuC_3B_7H_8$ (**5**).

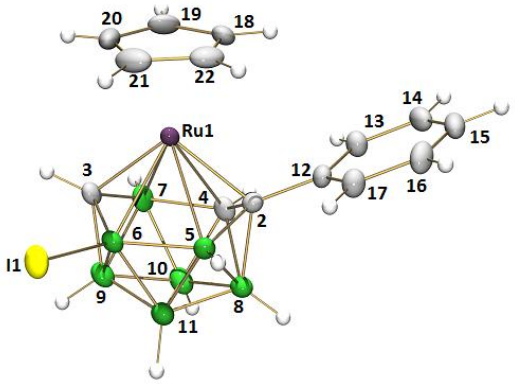


Figure 3. Crystallographically determined structure of 1-(η^5-C_5H_5)-2-Ph-6-I-*closo*-1,2,3,4-$RuC_3B_7H_8$ (**3**). Selected distances (Å) and angles (deg), **3**: Ru1-C2, 2.076(2); Ru1-C3, 2.074(2); Ru1-C4, 2.352(3); Ru1-B5, 2.333(3); Ru1-B6, 2.304(3); Ru1-B7, 2.373(3); Ru1-$Cp_{Centroid}$, 1.8227(3); C2-B5, 1.609(3); B5-B6, 1.855(4); C3-B6, 1.583(3); C3-B7, 1.585(4); C4-B7, 1.776(4); C2-C4, 1.508(3); C2-C12, 1.491(3); B6-B9, 1.824(4); B6-B11, 1.801(4); B6-I1, 2.189(3); C3-Ru1-C2, 106.53(10); C12-C2-Ru1, 121.7(2).

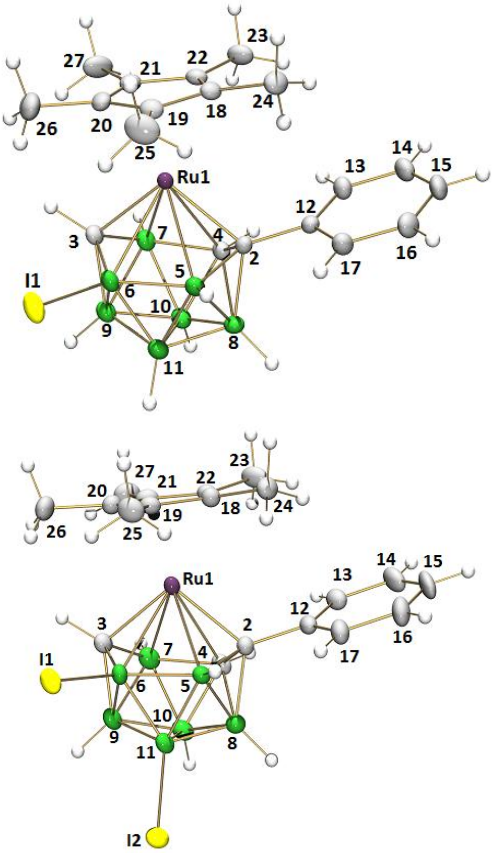


Figure 4. Crystallographically determined structure of (top) 1-(η^5-$C_5(CH_3)_5$)-2-Ph-6-I-*closo*-1,2,3,4-$RuC_3B_7H_8$ (**4**) and (bottom) 1-(η^5-$C_5(CH_3)_5$)-2-Ph-6,11-I,I-*closo*-1,2,3,4-$RuC_3B_7H_8$ (**5**). Selected distances (Å) and angles (deg), **4**: Ru1-C2, 2.103(2); Ru1-C3, 2.072(2); Ru1-C4, 2.379(2); Ru1-B5, 2.338(2); Ru1-B6, 2.329(2); Ru1-B7, 2.392(2); Ru1-$Cp_{Centroid}$, 1.8360(1); C2-B5, 1.606(3); B5-B6, 1.859(4); C3-B6, 1.580(3); C3-B7, 1.590(3); C4-B7, 1.768(3); C2-C4, 1.503(3); C2-C12, 1.491(3); B6-B9, 1.825(3); B6-B11, 1.799(3); B6-I1, 2.194(3); C3-Ru1-C2, 105.30(8); C12-C2-Ru1, 124.91(14). **5**: Ru1-C2, 2.102(3); Ru1-C3, 2.087(3); Ru1-C4, 2.400(3); Ru1-B5, 2.324(4); Ru1-B6, 2.335(4); Ru1-B7, 2.408(4); Ru1-$Cp_{Centroid}$, 1.8388(2); C2-B5, 1.616(5); B5-B6, 1.867(5); C3-B6, 1.584(5); C3-B7, 1.589(6); C4-B7, 1.772(5); C2-C4, 1.503(4); C2-C12, 1.497(4); B6-B9, 1.827(5); B6-B11, 1.796(5); B6-I1, 2.184(4); B11-I2, 2.178(4); C3-Ru1-C2, 105.02(13); C12-C2-Ru1, 125.1(2).

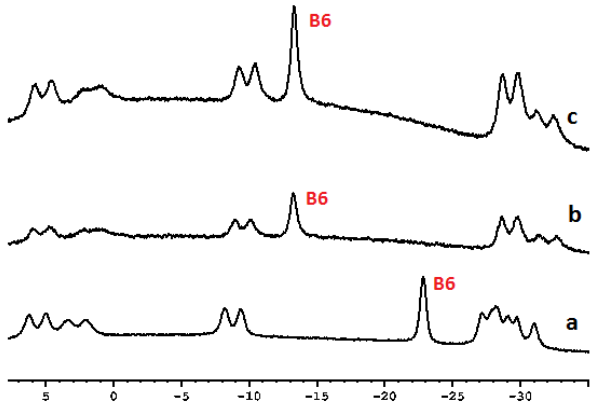


Figure 5. Comparison of the ^{11}B NMR spectra of (a) 1-(η^5-C_5H_5)-2-Ph-6-I-*closo*-1,2,3,4-$RuC_3B_7H_8$ (**3**); (b) 1-(η^5-C_5H_5)-2-Ph-6-(Ph-C≡C)-*closo*-1,2,3,4-$RuC_3B_7H_8$ (**6**); (c) 1-(η^5-C_5H_5)-2-Ph-6-[$(CH_3)_3$Si-C≡C]-*closo*-1,2,3,4-$RuC_3B_7H_8$ (**9**).

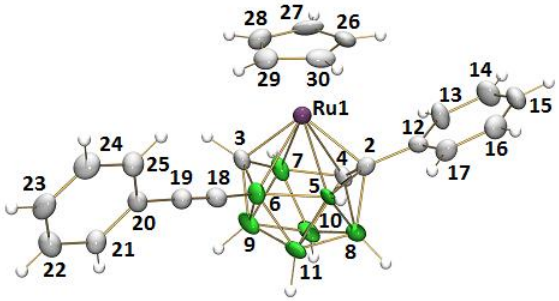


Figure 6. Crystallographically determined structure of 1-(η^5-C_5H_5)-2-Ph-6-(Ph-C≡C)-*closo*-1,2,3,4-$RuC_3B_7H_8$ (**6**). Selected distances (Å) and angles (deg): Ru1-C2, 2.096(4); Ru1-C3, 2.079(4); Ru1-C4, 2.410(5); Ru1-B5, 2.309(5); Ru1-B6, 2.339(6); Ru1-B7, 2.428(5); Ru-$Cp_{Centroid}$, 1.8353(3); C2-B5, 1.631(7); B5-B6, 1.891(7); C3-B6, 1.614(7); C3-B7, 1.588(7); C4-B7, 1.765(7); C2-C4, 1.521(6); C2-C12, 1.490(6); B6-C18, 1.543(7); C18-C19, 1.215(7); C19-C20, 1.438(6); B6-B9, 1.816(8); B6-B11, 1.811(8); C3-Ru1-C2, 106.0(2); C12-C2-Ru1, 120.3(3); C18-C19-C20, 177.2(6); B6-C18-C19, 176.0 (5).

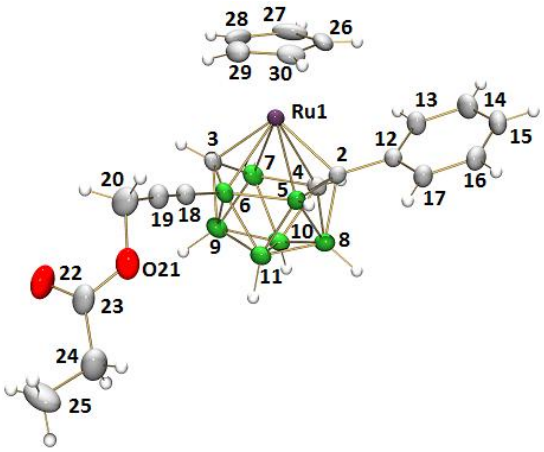


Figure 7. Crystallographically determined structure of 1-(η^5-C_5H_5)-2-Ph-6-[$CH_3CH_2C(O)OCH_2$-C≡C]-*closo*-1,2,3,4-$RuC_3B_7H_8$ (**7**). Selected distances (Å) and angles (deg): Ru1-C2, 2.092(2); Ru1-C3, 2.065(2); Ru1-C4, 2.388(3); Ru1-B5, 2.309(3); Ru1-B6, 2.309(3); Ru1-B7, 2.389(3); Ru-$Cp_{Centroid}$, 1.8303(1); C2-B5, 1.608(4); B5-B6, 1.878(4); C3-B6, 1.601(4); C3-B7, 1.574(4); C4-B7, 1.776(4); C2-C4, 1.499(3); C2-C12, 1.491(3); B6-C18, 1.545(4); B6-B9, 1.836(4); B6-B11, 1.818(4); C18-C19, 1.192(4); C19-C20, 1.465(4); C3-Ru1-C2, 105.92(10); C12-C2-Ru1, 122.7(2); C18-C19-C20, 177.3(3); B6-C18-C19, 174.0(3).

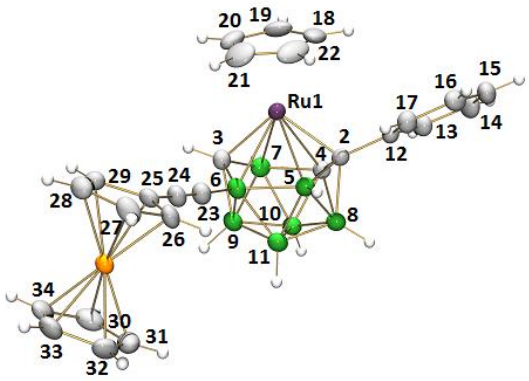


Figure 8. Crystallographically determined structure of 1-(η^5-C_5H_5)-2-Ph-6-[(η^5-C_5H_5)Fe(η^5-C_5H_4)-C≡C]-*closo*-1,2,3,4-$RuC_3B_7H_8$ (**8**). Selected distances (Å) and angles (deg): Ru1-C2, 2.086(3); Ru1-C3, 2.076(3); Ru1-C4, 2.375(3); Ru1-B5, 2.308(3); Ru1-B6, 2.329(3); Ru1-B7, 2.392(3); Ru1-$Cp_{Centroid}$, 1.8206(2); C2-B5, 1.601(4); B5-B6, 1.879(5); C3-B6, 1.604(5); C3-B7, 1.577(5); C4-B7, 1.783(5); C2-C4, 1.496(4); C2-C12, 1.493(4); B6-B9, 1.837(5); B6-B11, 1.821(5); B6-C23, 1.540(5); C23-C24, 1.195(4); C24-C25, 1.427(4); C3-Ru1-C2, 106.08(12); C12-C2-Ru1, 122.1(2); C23-C24-C25, 176.2(3); B6-C23-C25, 174.0(3).

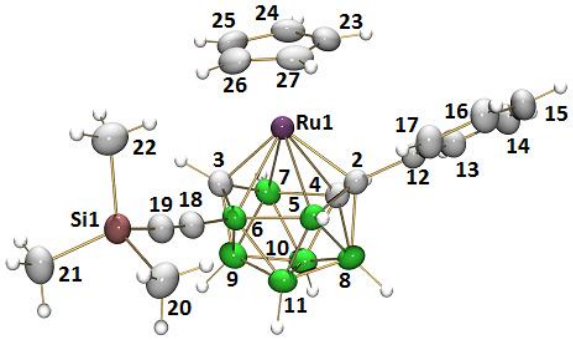
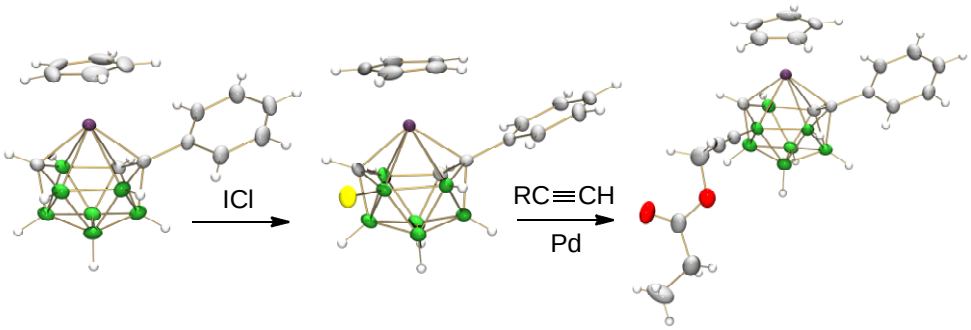


Figure 9. Crystallographically determined structure of 1-(η^5-C_5H_5)-2-Ph-6-[$(CH_3)_3$Si-C≡C]-*closo*-1,2,3,4-$RuC_3B_7H_8$ (**9**). Selected distances (Å) and angles (deg): Ru1-C2, 2.085(3); Ru1-C3, 2.071(3); Ru1-C4, 2.381(3); Ru1-B5, 2.322(3); Ru1-B6, 2.323(3); Ru1-B7, 2.387(3); Ru1-$Cp_{Centroid}$, 1.8385(2); C2-B5, 1.605(4); B5-B6, 1.875(5);

C3-B6, 1.599(4); C3-B7, 1.570(5); C4-B7, 1.766(5); B6-B9, 1.819(5); B6-B11, 1.830(4); C2-C4, 1.508(4); C2-C12, 1.493(4); B6-C18, 1.535(4); C18-C19, 1.211(4); C19-Si1, 1.835(3); C3-Ru1-C2, 105.73(12); C12-C2-Ru1, 122.00(19); C18-C19-Si1, 174.1(3); B6-C18-C19, 173.6(3).

Graphic for Table of Contents



Synposis

A versatile, systematic pathway for the syntheses of a wide variety of new types of functionalized ruthenatricarbadecaboranyl has been developed based on selective B-iodination followed by palladium catalyzed Sonogashira coupling reactions.

Highlights

- A synthetic strategy of selective B-iodination followed by palladium catalyzed Sonogashira coupling reactions has provided a versatile, systematic pathway to functionalized ruthenatricarbadecaboranyl complexes.
- Selective mono-iodination of cyclopentadienylruthenium tricarbadecaboranyl complexes was achieved in 90% yields by their reactions with ICl.
- Sonication-promoted Sonogashira coupling reactions with terminal acetylenes catalyzed by $Pd(dppf)_2Cl_2$/CuI yielded a wide variety of new types of alkynyl-linked functionalized ruthenatricarbadecaboranes.

Vitae: picture

Ariane Perez-Gavilan was born and raised in Mexico, but she received her undergraduate education in the United States at Notre Dame University. Her first exposure to polyhedral borane chemistry was in Dr. Thomas Fehlner's General Chemistry course at Notre Dame. She carried out her graduate studies in Larry Sneddon's group at the University of Pennsylvania on the development of systematic methods for the functionalization of metallatricarbadecaboranyl complexes that would facilitate their uses in bio and materials related applications. She completed her Ph.D. in 2012 and has now assumed a faculty position at Maastricht University in The Netherlands.

Patrick Carroll received his B.S. in Chemistry from King's College (PA) in 1970, the Ph.D. in Inorganic Chemistry from Temple University in 1978 and served as a post-doctoral research associate at the University of Maryland in S. O. Grim's laboratory (1978-1979). He has been director of the X-ray Crystallography Facility in the Department of Chemistry at the University of Pennsylvania since 1980.

Larry Sneddon received his B.S. at Centenary College of Louisiana before carrying out his graduate studies in boron hydride chemistry with Riley Schaffer at Indiana University. After obtaining his Ph.D. in 1971, he held postdoctoral appointments at the University of Virginia and the Massachusetts Institute of Technology. He moved to the University of Pennsylvania in 1974 and established a research program focused on the syntheses and properties of a wide range of molecular, polymeric and solid-state materials. He was appointed Professor in 1984 and Department Chair for 2002-2005. He presently holds appointment as *Blanchard Professor of Chemistry* at Penn.