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An unprecedented intramolecular coupling of *o*-carboranyl and cyclopentadienyl. Synthesis and structural characterization of a ruthenium complex containing a novel doubly-bridged cyclopentadienyl-carboranyl ligand†

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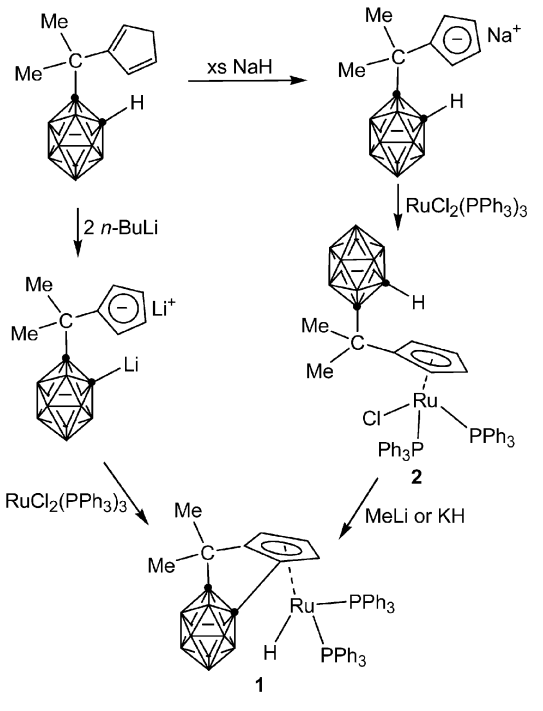
A novel ruthenium-mediated coupling reaction of a carboranyl with a cyclopentadienyl was discovered for the first time, leading to a brand new doubly-bridged cyclopentadienyl-carboranyl ligand bearing two five-membered rings and to a new type of chiral ruthenium complex.

Carboranes are finding many applications in catalysis,[1] boron neutron capture therapy,[2] siloxane-linked polymers,[3] solvent extraction of radionuclides,[4] and ceramics.[5] Thus their functionalizations become an important subject in this area of research. C,C′-linked *o*-carboranes are usually prepared *via* (1) salt metathesis reactions of $Li_2C_2B_{10}H_{10}$ with dihalides,[6] (2) fluoride ion promoted intramolecular cycloaddition of *o*-carboranes bearing carbonyl groups,[7] and (3) intermolecular cycloaddition of 1,2-dehydro-*o*-carborane with dienes.[8] We have recently developed a new class of linked cyclopentadienyl-carboranyl compounds that are widely used as versatile ligands in organometallic chemistry,[9] and would like to extend this singly-bridged system to a doubly-bridged one as a convenient way to introduce a planar chirality into η^5-cyclopentadienyl metal complexes. It is found, however, that the above three commonly used methods are not applicable to the doubly-bridged cyclopentadienyl-carboranyl system. We then attempted to prepare this class of compounds from the reactions of $Li_2[Me_2A(C_5H_4)(C_2B_{10}H_{10})]$ (A = C, Si) with Me_2SiCl_2 under various reaction conditions, but all failed. To our surprise, in an attempt to synthesize $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ru(PPh_3)_2$, it was unprecedentedly discovered that the ruthenium can mediate the intramolecular coupling of an *o*-carboranyl and a cyclopentadienyl, leading to the formation of a novel doubly-bridged ligand. This new finding is reported in this communication.

Treatment of $Li_2[Me_2C(C_5H_4)(C_2B_{10}H_{10})]$[9] with one equivalent of $RuCl_2(PPh_3)_3$ in THF gave, after recrystallization, $[\eta^5\text{-}Me_2C(C_5H_3)(C_2B_{10}H_{10})]RuH(PPh_3)_2{\cdot}0.5THF$ (**1**·0.5THF) as yellow crystals in 80% yield (Scheme 1). It is soluble in most organic solvents and sparely soluble in hot hexane. The most salient spectroscopic features are the observation in the ^1H NMR spectrum of a hydride at −10.86 ppm (dd, J_{HP} = 39.3 and 31.2 Hz), of three pseudo singlets for the cyclopentadienyl protons at 4.83, 3.70, 3.65 ppm, and of aromatic protons in the range 7.60–6.81 ppm, as well as the observation in the ^{31}P NMR spectrum of two singlets at 71.9 and 65.2 ppm consistent with the planar chirality of the complex. The IR spectrum shows a characteristic terminal B–H absorption at around 2568 cm^{-1},[9] and the frequency of Ru–H stretch at 1970 cm^{-1}.[10]

The molecular structure of **1**·0.5THF is confirmed by a single-crystal X-ray analysis and shown in Fig. 1.‡ The Ru(II) ion is



Scheme 1 Syntheses of complexes **1** and **2**.

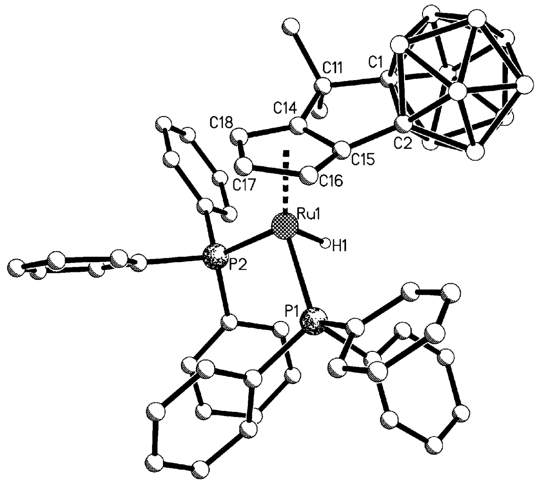


Fig. 1 Molecular structure of **1** (the solvated THF molecule is not shown). Selected bond distances (Å) and angles (°): Ru1–Cent = 1.910 [1.916], Ru1–H1 = 1.54(1) [1.55(1)], Ru1–C14 = 2.255(2) [2.276(2)], Ru1–C15 = 2.240(2) [2.256(2)], Ru1–C16 = 2.276(2) [2.266(2)], Ru1–C17 = 2.293(2) [2.286(2)], Ru1–C18 = 2.253(2) [2.248(2)], Ru1–P1 = 2.291(1) [2.289(1)], Ru1–P2 = 2.282(1) [2.283(1)], C1–C2 = 1.671(2) [1.674(2)], C2–C15 = 1.490(2) [1.482(2)], C15–C14 = 1.442(2) [1.422(2)], C14–C11 = 1.516(2) [1.539(2)], C11–C1 = 1.571(2) [1.569(2)], P1–Ru1–P2 = 95.9(1) [96.5(1)], C1–C11–C14 = 101.1(1) [100.9(2)], C15–C2–C1 = 102.5(1) [102.5(1)], C2–C1–C11 = 109.1(1) [108.7(2)]. Distances and angles in brackets are those of a second molecule.

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† Electronic supplementary information (ESI) available: Experimental details. See http://www.rsc.org/suppdata/cc/b4/b409772f/

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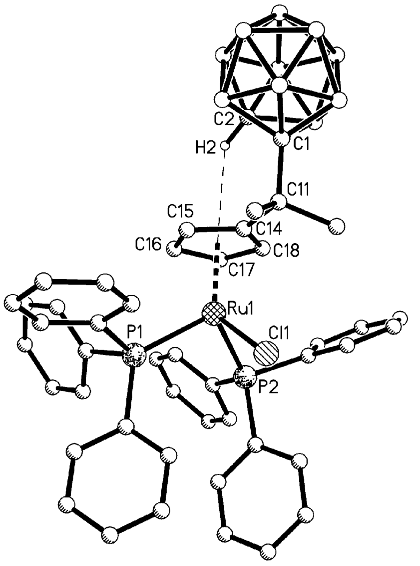
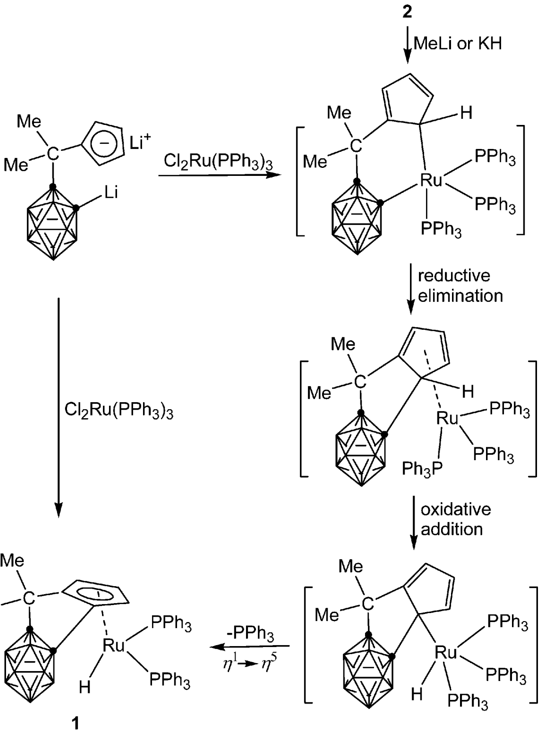


Fig. 2 Molecular structure of **2** (the solvated CH_2Cl_2 molecules are not shown). Selected bond distances (Å) and angles (°): Ru1–Cent = 1.872, H2–Cent = 2.539, Ru1–Cl1 = 2.448(2), Ru1–C14 = 2.310(5), Ru1–C15 = 2.246(6), Ru1–C16 = 2.171(6), Ru1–C17 = 2.180(6), Ru1–C18 = 2.235(6), Ru1–P1 = 2.342(2), Ru1–P2 = 2.317(2), C1–C2 = 1.690(10), C15–C14 = 1.431(8), C14–C11 = 1.520(8), C11–C1 = 1.593(9), H2–Cent–Ru1 = 167.9, P1–Ru1–P2 = 99.0(1), C1–C11–C14 = 108.4(5), C2–C1–C11 = 118.9(5).

η^5-bound to a cyclopentadienyl ring and σ-bound to a hydrogen atom and two phosphorus atoms in a three-legged piano stool geometry. The Ru–H distance (1.55(1) or 1.54(1) Å) is within the range reported for other Ru–H complexes.[10,11] It is noteworthy that the newly formed five-membered ring (C2C1C11C14C15) is almost planar, and the dihedral angle between two five-membered ring planes is 18.8°.

1 was also prepared from the reaction of $[\eta^5\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{11})]RuCl(PPh_3)_2$ (**2**) (Fig. 2); with one equivalent of MeLi or KH in THF in 70–80% yields.† It is proposed that the formation of **1** may result from the same intermediate $[\eta^1\text{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ru(PPh_3)_3$, followed by reductive elimination, oxidative addition, and η^1–η^5 rearrangement, as shown in Scheme 2. Steric factors may play an important role in this coupling reaction.



Scheme 2 Proposed reaction mechanism for the formation of **1**.

In summary, a novel Ru mediated coupling reaction of a carboranyl with a cyclopentadienyl was discovered for the first time, leading to a brand new doubly-bridged cyclopentadienyl-carboranyl ligand bearing two five-membered rings and to a new type of metal complex with a planar chirality brought by a linked cyclopentadienyl-carboranyl ligand. We are currently exploring the generality of this coupling reaction and the potential of linked organic-carboranyl ligands as provider of chiral planarity.

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Notes and references

‡ *Crystal data*: for **1**·0.5THF: $C_{48}H_{54}B_{10}O_{0.5}P_2Ru$, M = 910.02, triclinic, space group $P\bar{1}$, a = 13.317(3), b = 16.389(3), c = 23.527(5) Å, α = 93.51(3), β = 100.28(3), γ = 109.95(1)°, V = 4707.8(2) Å^3, D_c = 1.284 g cm^{-3}, Z = 4, $2\theta_{max}$ = 50°, R_1 = 0.048 ($I > 2.0\sigma(I)$), wR_2 = 0.136 on F^2. For **2**·1.5CH$_2$Cl$_2$: $C_{47.5}H_{54}B_{10}Cl_4P_2Ru$, M = 1037.82, triclinic, space group $P\bar{1}$, a = 11.468(1), b = 11.832(1), c = 20.344(2) Å, α = 83.52(1), β = 79.26(1), γ = 74.80(1)°, V = 2611.1(3) Å^3, D_c = 1.320 g cm^{-3}, Z = 2, $2\theta_{max}$ = 50°, R_1 = 0.067 ($I > 2.0\sigma(I)$), wR_2 = 0.205 on F^2. Data were collected at 293 K on a Bruker SMART 1000 CCD diffractometer using Mo-Kα radiation. An empirical absorption correction was applied using the SADABS program.[12] All structures were solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms by full-matrix least squares calculations on F^2 using the SHELXTL program package.[13] CCDC 243739–243740. See http://www.rsc.org/suppdata/cc/b4/b409772f/ for crystallographic data in .cif or other electronic format.

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