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Highlights

- Triple-decker complex with a bridging rhodacyclopentadienyl ligand was described.
- Triple-decker complexes effectively catalyze coupling of benzoic acid with alkynes.
- Catalytic selectivity is determined by terminal ligands in triple-decker structure.

Graphical abstract



μ-Borole triple-decker complexes as catalysts for oxidative coupling of benzoic acid with alkynes. Structure of hybrid rhodacyclopentadienyl/borole triple-decker complex

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Dedicated to 70th anniversary of Prof. Georgiy B. Shul'pin in recognition of his great contribution to the development of the metal-complex catalyzed C–H activation.

Abstract

Reaction of dimethylamine adduct of 1-methyl-3-borolene with $[(C_2H_4)_2RhCl]_2$ gives the triple-decker complex (η -C₄H₄BMe)Rh(μ - η : η -C₄H₄BMe)Rh(η -C₄H₄BMe)(**1a**) in 62% yield and trace amount (<1%) of the hybrid rhodacyclopentadienyl/borole triple-decker complex (η -C₄H₄BMe)Rh(μ - η : η -C₄H₄Rh {(μ - η : η -C₄H₄BMe)Rh(η -C₄H₄BMe)})Rh(η -C₄H₄BMe) (**2**). The structure of **2** was determined by X-ray diffraction. In the presence of Cu(OAc)₂, **1a** and (η -C₄H₄BPh)Rh(μ - η : η -C₄H₄BPh)Rh(η -C₄H₄BPh) (**1b**) catalyze the oxidative coupling of benzoic acid with diphenylacetylene selectively giving 1,2,3,4-tetraphenylnaphtalene in 50–90% yields. Analogous reactions of benzoic acid with 1-phenyl-1-butyne catalyzed by **1a** and [CpRhI₂]₂ regioselectively give 1,4-diethyl-2,3-diphenylnaphtalene. The related dicationic triple-decker complexes [(9-SMe₂-7,8-C₂B₉H₁₀)Rh(μ - η : η -C₄H₄BPh)Rh(μ - η : η -C₄H₄BPh)Rh(μ - η : η -C₄H₄BPh)IrCp*]²⁺ (**4**) were also tested as catalysts.

Keywords: C-H activation; Rhodium; Metal complex catalysis; Triple-decker complexes

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1. Introduction

The metal-catalyzed C–H functionalization of organic compounds is of great significance in synthetic chemistry.¹ In particular, the catalytic coupling reactions of aromatic compounds with alkynes give a number of oxygen- and nitrogen-containing heterocycles. Extensive investigations in this area have revealed that the cyclopentadienyl complexes $[Cp*MCl_2]_2$ (M = Rh, Ir) can effect regioselective arene C–H bond activation under chelation-assistance of an appropriate directing group (e.g., COOR, OH, C(O)NR₂ substituents).² Satoh and Miura have shown that these complexes catalyze the oxidative coupling of benzoic acids with internal alkynes giving isocoumarins (M = Rh) and naphthalenes (M = Ir; Scheme 1).³ Recently, we have demonstrated that the selectivity depends not only on the nature of the metal, but also on the ligand. Thus, use of carborane-containing complexes $[(C_2B_9H_{11})M(C_6H_6)]^+$ instead of cyclopentadienyl derivatives dramatically changes the selectivity of oxidative coupling giving naphthalenes for Rh and isocoumarins for Ir.⁴



Scheme 1. Reaction of oxidative coupling of benzoic acids with internal alkynes.

Triple-decker complexes of transition metals are well known.⁵ They have unique structure in which two metal atoms are located between three cyclic frames. In 1972, Werner and Salzer have synthesized the first representative of such complexes, *viz.*, the nickel derivative $[CpNi(\mu-\eta;\eta-Cp)NiCp]^+$ containing cyclopentadienyl ligand in a bridging position.⁶ Boron-containing heterocycles possess the highest ability for the bifacial bonding with two metal atoms.⁷ In particular, borole ligand C₄H₄BR was used for the synthesis of numerous triple-decker complexes.⁸ However, the complexes of this class have not yet been applied in catalysis.

Herein we report unexpected formation of the hybrid rhodacyclopentadienyl/borole triple-decker complex $(\eta-C_4H_4BMe)Rh(\mu-\eta:\eta-C_4H_4Rh\{(\mu-\eta:\eta-C_4H_4BMe)Rh(\eta-C_4H_4BMe)\})Rh(\eta-C_4H_4BMe)$ (2) as byproduct in reaction of dimethylamine adduct of 1-methyl-3-borolene C₄H₆BMe·NMe₂H with bis(ethylene)rhodium complex $[(C_2H_4)_2RhCl]_2$ as well as study of the catalytic activity of μ -borole triple-decker complexes $(\eta-C_4H_4BR)Rh(\mu-\eta:\eta-C_4H_4BR)Rh(\mu-\eta:\eta-C_4H_4BR)Rh(\mu-\eta:\eta-C_4H_4BR)Rh(\eta-C_4H_4BR)$ (1a: R = Me, 1b: R = Ph),⁹ $[(9-SMe_2-7,8-C_2B_9H_{10})Rh(\mu-\eta:\eta-\eta-2H_4BR)Rh(\mu-\eta:\eta-2H_4BR)Rh(\mu-\eta)Rh($

 $C_4H_4BPh)Rh(9-SMe_2-7,8-C_2B_9H_{10})]^{2+}$ (3)¹⁰ and $[Cp*Rh(\mu-\eta:\eta-C_4H_4BPh)IrCp*]^{2+}$ (4)¹¹ in oxidative coupling of benzoic acid with internal alkynes.

2. Results and discussion

2.1. Reaction of dimethylamine adduct of 1-methyl-3-borolene with $[(C_2H_4)_2RhCl]_2$

Herberich et al. have previously shown that reaction of borolenes C_4H_6BR with $[(C_2H_4)_2RhCl]_2$ is an effective method for the synthesis of triple-decker complexes with a bridging borole ligand $(\eta-C_4H_4BR)Rh(\mu-\eta:\eta-C_4H_4BR)Rh(\eta-C_4H_4BR)$ (**1a**: R = Me, **1b**: R = Ph).⁹ In present work we found that the analogous reaction of complex $C_4H_6BMe\cdotNMe_2H$ with $[(C_2H_4)_2RhCl]_2$ results in the formation of the hybrid rhodacyclopentadienyl/borole triple-decker complex $(\eta-C_4H_4BMe)Rh(\mu-\eta:\eta-C_4H_4Rh\{(\mu-\eta:\eta-C_4H_4BMe)Rh(\eta-C_4H_4BMe)\})Rh(\eta-C_4H_4BMe)$ (**2**) as a minor product (<1%) along with the main product **1a** (Scheme 2).



Scheme 2. Reaction of $C_4H_6BMe \cdot NMe_2H$ with $[(C_2H_4)_2RhCl]_2$.

The ¹H spectral data for **2** are consistent with the expected structure. The proton signals related to the Rh-cycle are observed at $\delta = 5.19 (\alpha$ -H) and 6.84 (β -H) ppm; they are very close to the signals previously reported for rhodium complexes with the C₄H₄Rh ring (5.58–6.86 ppm).^{12,13} The signals of the bridging borole ring protons are upfield-shifted ($\Delta \delta = 0.15$ –0.31 ppm) as compared to the corresponding signals for the terminal borole ring.

The structure of **2** was investigated by X-ray diffraction study (Fig. 1). It is the first crystallographically characterized triple-decker complex with bridging rhodacyclopentadienyl

ligand. Earlier, Müller and co-workers¹² have described complexes $(\eta^4$ -diene)(μ -H)Rh(μ - η : η -C₄R₄Rh{ η^4 -diene})Rh(η^4 -diene) containing diene ligands in terminal positions, however, their structure was not confirmed by X-ray diffraction.



Figure 1. Structure of complex **2**. Atoms are represented by 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Rh2–Rh3 2.6500(5), Rh2–Rh4 2.6299(5), Rh1–C1 2.183(5), Rh1–C2 2.150(5), Rh1–C3 2.122(5), Rh1–C4 2.170(5), Rh1–B1 2.267(5), Rh1–C6 2.245(5), Rh1–C7 2.198(4), Rh1–C8 2.219(4), Rh1–C9 2.221(4), Rh1–B2 2.287(5), Rh2–C6 2.223(4), Rh2–C7 2.229(4), Rh2–C8 2.200(4), Rh2–C9 2.255(5), Rh2–B2 2.322(5), Rh2–C21 2.024(4), Rh2–C24 2.020(4), Rh3–C16 2.191(5), Rh3–C17 2.131(5), Rh3–C18 2.131(5), Rh3–C19 2.166(5), Rh3–B3 2.288(5), Rh3–C21 2.233(4), Rh3–C22 2.205(4), Rh3–C23 2.199(4), Rh3–C24 2.270(4), Rh4–C11 2.177(5), Rh4–C12 2.136(4), Rh4–C13 2.159(4), Rh4–C14 2.180(5), Rh4–B4 2.282(5), Rh4–C21 2.290(4), Rh4–C22 2.234(4), Rh4–C23 2.188(4), Rh4–C24 2.227(4), C21–C22 1.434(6), C22–C23 1.467(6), C23–C24 1.449(6), C21–Rh2–C24 78.39(18), C1–B1–C4 102.7(4), C6–B2–C9 100.6(4), C16–B3–C19 100.9(4), C11–B4–C14 100.9(4).

Complex **2** consists of two triple-decker fragments: $(\eta$ -C₄H₄B)Rh(μ - η : η -C₄H₄Rh)Rh(η -C₄H₄B) and $(\eta$ -C₄H₄B)Rh(μ - η : η -C₄H₄B)Rh. In both cases the planes of the cyclic ligands are almost parallel (dihedral angles C₄H₄Rh/C₄H₄B = 3.9 and 5.1°; C₄H₄B/C₄H₄B = 3.8°). Commonly, the heterocyclic ligands in sandwich compounds are folded along the axis C_a···C_a, with the heteroatom being deviated from the C₄ plane away from the metal atom. For example, the folding angle[†] and the deviation of the Rh atom from the C₄ plane for (η^4 -nbd)Rh(η -C₄Me₂H₂Rh{ η^4 -nbd}PMe₃) (nbd – norbornadiene) are 17.1° and 0.47 Å, respectively.¹² In contrast, the bridging rings C₄H₄Rh and C₄H₄B in **2** are almost planar (folding angles are 0.7 and 1.2°). The C₄H₄Rh ring is strongly distorted pentagon owing to great difference of the C–C and Rh–C bond lengths (av. 1.450 and 2.022 Å, respectively); the angle C21–Rh2–C24 (78.39(18)°) is considerably smaller than 108° (typical of a regular pentagon).

The distance Rh3…Rh4 (3.654 Å) in **2** exceeds the sum of the covalent radii Rh–Rh (av. 2.92 Å)¹⁴ suggesting the absence of the direct Rh–Rh bond in this case. At the same time the Rh2–Rh3 and Rh2–Rh4 bonds (2.6500(5) and 2.6299(5) Å) are shorter than the corresponding bond in sandwich complex (η^4 -nbd)Rh(η -C₄Me₂H₂Rh{ η^4 -nbd}PMe₃) (2.704 Å).¹² Although these bonds are considerably longer than the Rh1–B2 bond (2.267(5) Å), the metal-to-ring distances for bridging rings Rh3…C₄H₄Rh2, Rh4…C₄H₄Rh2 and Rh1…C₄H₄B2 are practically the same (1.825, 1.828 and 1.830 Å, respectively). It is noteworthy that these values are very close to the corresponding distances in the related μ -borole triple-decker complexes (η -C₄H₄BPh)Rh(μ - η : η -C₄H₄BPh)Rh(μ - η : η -C₄H₄BPh)Rh(μ - $G_{4}H_{4}BPh$)Rh(μ - η : η -C₄H₄BPh)Rh(μ - $G_{5}R_5$) (1.826–1.845 Å, av. 1.835 Å).¹⁵ The Rh…C₄H₄B distances in **2** for the terminal borole ligands (1.780–1.788 Å, av. 1.784 Å) are shorter than for the bridging one (1.830 Å) that is in accordance with general tendency for triple-decker complexes.¹⁶

A supposed pathway of the reaction of dimethylamine adduct of 1-methyl-3-borolene with $[(C_2H_4)_2RhC]_2$ is illustrated in Scheme 3. Probably, dehydrogenation of the borolene and its subsequent coordination mainly produce the chloride complex $[(\eta-C_4H_4BMe)RhCl]_4$ (A). Similar iodides $[(n-C_4H_4BR)RhI]_4$ (R = Me, Ph) have been described and structurally characterized earlier.¹⁷ Further transformation of **A** leads to the formation of the triple-decker complex 1a (the main product of the reaction). Side reaction takes place in such a way that at the first stage, the removal of boron atom from the starting borolene occurs. The subsequent reaction with $[(C_2H_4)_2RhCl]_2$ affords the rhodacyclopentadienyl derivative $(C_2H_4)_2Rh(\eta C_4H_4Rh(H)_2(C_2H_4)_2$) (**B**). Related intermediates have been suggested earlier by Müller and coworkers¹² in reactions of $[(\eta^4-nbd)MCl]_2$ with magnesium butadiene (C₄H₆Mg). Possibly the

[†] Folding angle is dihedral angle between C–X–C and C₄ planes, where X is heteroatom.

coordinated amine, NMe₂H, acts as the basic agent to facilitate removal of the boron atom. Subsequent reaction of **B** with **A** and C₄H₆BMe·NMe₂H finally gives the minor product **2**.



Scheme 3. A supposed pathway for the formation of 2.

2.2. Oxidative coupling of benzoic acid with alkynes

It is known that the triple-decker complexes easily undergo nucleophilic degradation.¹⁸ For example, Herberich has shown that complexes **1a**,**b** react with CpNa giving two sandwich compounds CpRh(η -C₄H₄BR) and [Rh(η -C₄H₄BR)₂]^{-,9b} Similar reaction of **1a**,**b** with I₂ affords iodine derivatives $[(\eta - C_4H_4BR)RhI]_4$ and $Rh(\eta - C_4H_4BR)_2I$.¹⁷ Taking into account this reactivity, we examined **1a**,**b** as well as the related μ -borole triple-decker complexes [(9-SMe₂-7,8- $C_{2}B_{9}H_{10}$)Rh(μ - η : η - $C_{4}H_{4}BPh$)Rh(9-SMe₂-7,8- $C_{2}B_{9}H_{10}$)]²⁺ $(3)^{10}$ and $[Cp*Rh(\mu-\eta:\eta-\eta)]$ $C_4H_4BPh)IrCp^{*}l^{2+}$ (4)¹¹ as catalysts for the oxidative coupling of benzoic acid with diphenylacetylene in refluxing o-xylene (Scheme 4). This reaction has two possible pathways giving either isocumarin 5a or naphthalene 5b. Copper acetate and silver carbonate were used as co-catalysts (necessary for oxidation of M^I to M^{III}). We hypothesized that the triple-decker complexes would be cleaved by benzoic acid, giving the catalytically active species (n- C_4H_4BR , R, (9-SMe₂-7,8- $C_2B_9H_{10}$)Rh or Cp*M (M = Rh, Ir), which may act as catalysts of C-H activation in aromatic compounds.



Scheme 4. Oxidative coupling of benzoic acid with diphenylacetylene.

As can be seen from Table 1, complexes 1a,b selectively catalyze the oxidative coupling to give naphthalene **5b** as a sole product in 50–90% yields. The turnover number (TON) is ca. 20–45. The phenyl-substituted complex **1b** reveals higher catalytic activity than the methyl derivative **1a**, which may be explained by better stabilization of catalytic intermediates by phenyl substituent. It is interesting to note that the rhodium complex [Cp*RhCl₂]₂ predominantly gives isocumarin **5a** instead of **5b**.³

The triple-decker complex **3** having two carborane ligands in terminal positions catalyzes the oxidative coupling reaction giving the naphthalene **5b** as the major product in moderate yield (40%). Earlier we have shown that chloride (η -9-SMe₂-7,8-Me₂-C₂B₉H₈)RhCl₂ reacts in the same manner,^{4a} and suggested that the key catalytic species is (η -9-SMe₂-7,8-C₂B₉H₈R₂)Rh (R = H, Me). This leads to the conclusion that the selectivity of the oxidative coupling is mainly determined by the nature of the terminal ligands in the triple-decker structure.

Taking into account the different selectivity of rhodium and iridium cyclopentadienyl complexes³ we have assumed that the use of the heterometallic RhIr triple-decker complex **4** with different co-catalysts (Cu(OAc)₂ or Ag₂CO₃) may lead to different products. However, in both cases the reaction predominantly gives isocoumarin **5a**, suggesting that the selectivity is determined by direction of nucleophilic degradation of **4**. Usually, the bonding in triple-decker complexes between bridging ligand and rhodium atom is weaker compared to iridium. Therefore the most probable catalytic particle in these reactions is Cp*Rh.

Table 1. Catalytic activity of triple-decker complexes **1a**,**b**, **3** and **4** as well as halides $[CpRhI_2]_2$, $[Cp*RhCl_2]_2$ and $(\eta-9-SMe_2-7,8-Me_2-C_2B_9H_8)RhCl_2$ in the oxidative coupling of benzoic acid with diphenylacetylene.

Catalyst	Co-catalyst	Yield, % ^a	
		5a	5b
1a	Cu(OAc) ₂	-	51
1b	Cu(OAc) ₂	-	91
3	Cu(OAc) ₂	3	40

4	Cu(OAc) ₂	54	17
4	Ag ₂ CO ₃	60	29
[CpRhI ₂] ₂ ^b	Cu(OAc) ₂	-	91
[Cp*RhCl ₂] ₂ ^c	Cu(OAc) ₂	82	12
$(\eta-9-SMe_2-7,8-Me_2-C_2B_9H_8)RhCl_2^{b}$	$Cu(OAc)_2$	-	32

^aYield is based on the amount of benzoic acid used; the ratio of **5a** and **5b** in product mixture was determined by ¹H NMR. ^bRef.^{4a c}Ref.³

The reaction of benzoic acid with 1-phenyl-1-butyne catalyzed by **1a** regioselectively gives 1,4diethyl-2,3-diphenylnaphthalene (**6**) in 54% yield (Scheme 5). The (cyclopentadienyl)rhodium complex [CpRhI₂]₂ catalyzes this reaction in a similar way to give **6** in 81% yield. In accordance with the mechanism proposed by Satoh and Miura,³ the formation of naphthalenes in oxidative coupling reactions proceeds via rhodacycle intermediate **C**. The observed regioselectivity is explained by better stabilization of α -carbon atoms in **C** by phenyl substituent.¹⁹



Scheme 5. Oxidative coupling of benzoic acid with 1-phenyl-1-butyne.

3. Conclusion

The formation of a minor product, the hybrid rhodacyclopentadienyl/borole triple-decker complex **2**, caused by the coordinated amine, was observed in the reaction of $C_4H_6BMe\cdot NMe_2H$ with $[(C_2H_4)_2RhCl]_2$. To our knowledge, this is the first example of a crystallographically characterized triple-decker complex with a bridging rhodacyclopentadienyl ligand. The main product of this reaction is the triple-decker complex **1a**. X-ray data for **2** suggest that the bonding of rhodium with the rhodacyclopentadienyl ligand C_4H_4Rh is very close to that with borole C_4H_4B .

The triple-decker complexes with a bridging borole ligand were shown to be effective catalysts for the oxidative coupling of benzoic acid with alkynes. For instance, complexes **1a**,**b** exhibit notable catalytic activity in reactions of benzoic acid with alkynes in the presence of Cu(OAc)₂, giving exclusively naphthalenes. The observed catalytic selectivity is determined by

the direction of the nucleophilic degradation of triple-decker structure and the nature of terminal ligands.

4. Experimental

General

The reactions were carried out under an inert atmosphere in dry degassed solvents. The isolation of products was conducted in air. Starting complex $[Rh(C_2H_4)_2Cl]_2$ was prepared as described.²⁰ Complex C₄H₆BMe·NMe₂H was synthesized from C₄H₆BNMe₂ and LiMe in a similar manner as C₄H₆BPh·NMe₂H.²¹ The ¹H, ¹¹B and ¹³C NMR spectra (δ in ppm) were recorded with a Bruker Avance-400 spectrometer operating at 400.13, 128.38 and 100.61 MHz, respectively.

$(\eta - C_4 H_4 BMe) Rh(\mu - \eta; \eta - C_4 H_4 BMe) Rh(\eta - C_4 H_4 BMe)$ (1a)

The 50 ml of THF was added to the mixture of $[Rh(C_2H_4)_2Cl]_2$ (1.94 g, 5 mmol) and $C_4H_6BMe \cdot NMe_2H$ (3.13 g, 25 mmol). The reaction mixture was stirred for 48 h at ambient temperature. The solvent was removed in a high vacuo and the residue was subjected to column chromatography (aluminium oxide activity grade II; 3 × 10 cm). Elution first with hexane led to a brown band, which was discarded. The further elution with hexane/CH₂Cl₂ mixture (1/1) gave the second dark-orange band, which was evaporated till 20 ml, crystallized at –78 °C and held for 4 h in a high vacuo. Yield of **1a** is 1.05 g (3.12 mmol; 62%). Orange solid, which has 99% purity according to NMR. ¹H NMR (CDCl₃) δ : 5.21 (m, 4H, β -H, η -C₄H₄B); 4.77 (m, 2H, β -H, μ - η : η -C₄H₄B); 4.05 (m, 4H, α -H, η -C₄H₄B); 3.86 (m, 2H, α -H, μ - η : η -C₄H₄B); 0.63 (s, 3H, μ - η : η -C₄H₄B), 10.1 (broad, 1B, μ - η : η -C₄H₄B). ¹³C {¹H} NMR (CDCl₃) δ : 88.55 (d, *J*(C-Rh) = 9 Hz, β -C, η -C₄H₄B), -3.71 (broad, Me) (cf.^{9b}). Found (%): C, 40.80; H, 4.64; B, 7.37; Rh, 46.46. Calc. for C₁₅H₂₁B₃Rh₂ (%): C, 40.99; H, 4.82; B, 7.38; Rh, 46.82.

After recrystallization of **1a** by slow evaporation of its hexane solution, orange admixture crystals (<1%) of $(\eta$ -C₄H₄BMe)Rh(μ - η : η -C₄H₄Rh{(μ - η : η -C₄H₄BMe)Rh(η -C₄H₄BMe)})Rh(η -C₄H₄BMe))})Rh(η -C₄H₄BMe) (**2**) were selected. ¹H NMR (CDCl₃) for **2**, δ : 6.84 (m, 2H, β -H, μ - η : η -C₄H₄Rh), 5.26

(m, 2H, β -H, η -C₄H₄B), 5.19 (m, 2H, α -H, μ - η : η -C₄H₄Rh), 5.18 (m, 4H, β -H, η -C₄H₄B), 4.95 (m, 2H, β -H, μ - η : η -C₄H₄B), 4.21 (m, 4H, α -H, η -C₄H₄B), 4.10 (m, 2H, α -H, η -C₄H₄B), 3.95 (m, 2H, α -H, μ - η : η -C₄H₄B), 0.67 (s, 3H, μ - η : η -C₄H₄BMe), 0.44 (s, 3H, η -C₄H₄BMe), 0.27 (s, 6H, η -C₄H₄BMe).

Oxidative coupling of benzoic acid with alkynes (general procedure)

A mixture of benzoic acid (31 mg, 0.25 mmol), alkyne (0.5 mmol), catalyst (0.005 mmol), *o*-xylene (2 ml), and Cu(OAc)₂ (182 mg, 1.00 mmol) or Ag₂CO₃ (138 mg, 0.5 mmol) was refluxed with vigorous stirring for 6 h. The solvent was removed in vacuo, and the residue was extracted with diethyl ether. The extract was chromatographed on a silica column (1×15 cm). Unreacted alkyne was washed off with petroleum ether. Then the yellow band was collected using diethyl ether as the eluent. After the removal of the solvent in vacuo, isocumarin **5a** or naphthalenes **5b** and **6** were obtained as yellow oils.

5a, ¹H NMR (CDCl₃) δ : 8.44 (d, 1H, *J* = 8.0 Hz); 7.67 (m, 1H); 7.55 (m, 1H); 7.44 (m, 3H), 7.35 (m, 2H), 7.20–7.30 (m, 6H) (cf.³).

5b, ¹H NMR (CDCl₃) δ: 7.76–7.78 (m, 2H); 7.47–7.49 (m, 2H); 7.32–7.34 (m, 10H); 6.95–6.97 (m, 10H) (cf.²²).

6, ¹H NMR (CDCl₃) δ : 8.30 (m, 2H); 7.68 (m, 2H); 7.11–7.24 (m, 10H); 2.98 (q, 4H, J = 10.0 Hz), 1.30 (t, 6H, J = 10.0 Hz) (cf.²³).

X-ray crystallography

Crystals of **2** were grown by slow evaporation of hexane solution of crude **1a**. Crystals of **2** (C₂₄H₃₂B₄Rh₄, M = 775.37) are triclinic, space group P-1, at 120 K: a = 10.6545(9), b = 10.9399(9), c = 11.9022(10) Å, α = 89.571(2), β = 85.811(2), γ = 61.680(2)°, V = 1217.42(18) Å³, Z = 2, d_{calc} = 2.115 gcm⁻³, μ (MoK α) = 26.75 cm⁻¹, F(000) = 752. Intensities of 15185 reflections were measured with a Bruker APEX2 DUO diffractometer using graphite monochromated Mo-K α radiation (λ = 0.71073 Å, ω -scans, 2 θ < 58°), and 6460 independent reflections [R_{int} 0.0536] were used in further refinement. The structure was solved by direct method and refined by the full-matrix least-squares against F² in anisotropic approximation for non-hydrogen atoms. The positions of hydrogen atoms were calculated, and they were refined in isotropic approximation in riding model. The refinement converged to wR₂ = 0.0855 and GOF = 1.006 for all the independent reflections (R₁ = 0.0359 was calculated against F for 5224 observed

reflections with I>2 σ (I)). All calculations were performed using the SHELXTL PLUS 5.0 software. ²⁴

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Appendix A. Supplementary material

CCDC 1473095 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <u>www.ccdc.cam.ac.uk/data_request/cif....</u>

Graphical Abstract

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