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# Coordination of the *nido*-carboranyldiphosphine ligand to ruthenium(II): the first example of the tricoordinating capacity of the 7,8-$(PPh_2)_2$-7,8-$C_2B_9H_{10}$ moiety†

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**Reaction of [RuH(AcO)$(PPh_3)_3$] and [$NMe_4$][7,8-$(PPh_2)_2$-7,8-$C_2B_9H_{10}$] in methanol yields [RuH(7,8-$(PPh_2)_2$-7,8-$C_2B_9H_{10}$)$(PPh_3)_2$] (1). The reaction of [$RuCl_2(PPh_3)_3$] and [$NMe_4$][7,8-$(PPh_2)_2$-7,8-$C_2B_9H_{10}$] in a 1 : 1 or 1 : 2 ratio in methanol yields [RuX(7,8-$(PPh_2)_2$-7,8-$C_2B_9H_{10}$)$(PPh_3)_2$] (X = Cl, H) (2). NMR spectroscopic analyses of 1 and 2 indicate that the centers have an octahedral geometry and the carborane acts as a tricoordinating ligand to ruthenium(II) by means of P–Ru, B(11)–H→Ru and B(2)–H→Ru agostic bonds. A chloride or hydride and two $PPh_3$ ligands complete the coordination sphere of the metal. The formation of two B–H→Ru agostic bonds rather than a second P–Ru bond appears to be due to steric factors. Reaction of [$NMe_4$][7,8-$(PPh_2)_2$-7,8-$C_2B_9H_{10}$] with [$RuCl_2(PMePh_2)_4$] in ratios of 1 : 1 and 2 : 1 in methanol yields complexes [Ru(7,8-$(PPh_2)_2$-7,8-$C_2B_9H_{11})_2$] (3) and [RuH(7,8-$(PPh_2)_2$-7,8-$C_2B_9H_{11})_2$] (4) respectively, which incorporate two *nido*-carboranylphosphine ligands. Copyright © 2003 John Wiley & Sons, Ltd.**

**KEYWORDS:** metallacarboranes; phosphines; ruthenium complexes; carboranes

## INTRODUCTION

*nido*-Carboranylmonophosphines [7-$PR_2$-8-R′-7,8-$C_2B_9H_{10}]^-$ (Fig. 1a) have been shown to be tridentate when they are bonded to ruthenium(II), forming octahedral species such as [RuCl(7-$PPh_2$-8-Me-7,8-$C_2B_9H_{10}$)$(PPh_3)_2$].[1,2] Coordination takes place by means of the exo-cluster $PPh_2$ group plus the boron atoms B(2) and B(11) through two B–H→Ru agostic bonds. The *S*-aryl substituted *nido*-carboranylmonothioethers act in the same way as the *nido*-carboranylmonophosphines.[3] The dithioether derivatives of the 7,8-dicarba-*nido*-undecaborate anion have been shown to possess a high ligand capacity for a wide variety of transition metals,[4–7] and the study of their chemistry has been mainly confined to *S*-alkyl[4–9] and *S*-aryl[3] derivatives. These ligands have been shown to be tricoordinating towards ruthenium(II). In the *S*-alkyl dithioethers, coordination takes place by means of the two sulfur atoms and B(3) through a B–H→Ru agostic bond, whereas in the *S*-aryl dithioethers the coordination occurs via S–Ru and two B–H→Ru bonds. Other similar B–H→Ru bonds have been observed, for example by Fehlner and coworkers, in other metallacarboranes obtained by reaction of mono- and poly-boranes with ruthenium(II).[10–16]

The diphosphino derivatives of the 7,8-dicarba-*nido*-undecaborate (−1) (Fig. 1b) act as bidentate ligands for square-planar-demanding transition metal ions (copper, gold, rhodium, palladium). The coordination sites are provided by the two phosphorus atoms, and no participation of the cluster has been observed.[17–22]

The reactivity of *nido*-carboranyldiphosphines with octahedrally demanding transition metal ions such as ruthenium(II) has not yet been tested. In this paper, the synthesis and characterization of the first ruthenium complexes of [7,8-$(PPh_2)_2$-7,8-$C_2B_9H_{10}]^-$ are described and their coordination features are discussed with reference to those of *nido*-carboranylmonophosphines and *nido*-carboranyldithioethers.

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†Dedicated to Professor Thomas P. Fehlner on the occasion of his 65th birthday, in recognition of his outstanding contributions to organometallic and inorganic chemistry.

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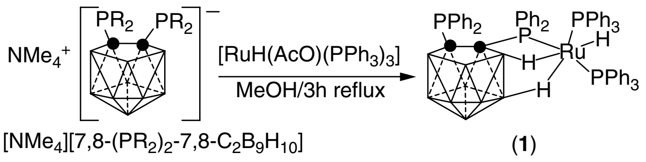
$[7\text{-}PR_2\text{-}8\text{-}R'\text{-}7,8\text{-}C_2B_9H_{10}]^-$ (a)

$[7,8\text{-}(PR_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ (b)

**Figure 1.** Graphical representation of *nido*-carboranylmonophosphines and *nido*-carboranyldiphosphines.

## RESULTS AND DISCUSSION

Reflux of $[RuH(AcO)(PPh_3)_3]$ and $[NMe_4][7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]$ in methanol for 3 h yields a yellow solid $[RuH(7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10})(PPh_3)_2]$ (**1**; Scheme 1). The $^1H$ NMR spectrum of **1** displays a tetraplet at −1.81 ppm ($^1J_{BH}$ = 107 Hz) (B*H*Ru) and broad resonances at −2.67 (B*H*B), −6.55 (B*H*Ru) and −13.78 ppm (Ru*H*), indicating the presence of two agostic B–H–Ru bonds. The $^1H\{^{11}B\}$ NMR spectrum shows that the broad resonance at −6.55 ppm is a doublet ($^2J_{PH}$ = 28.8 Hz) and is assigned to a B–H trans to a $PPh_3$; the resonance at −13.78 ppm is a triplet of doublets ($^2J_{PH}$ = 20 Hz, $^2J_{HH}$ = 8 Hz) and is attributed to the hydride. The $^{31}P\{^1H\}$ NMR spectrum reveals four sets of resonances, indicating the presence of four different phosphorus atoms in the molecule (see Fig. 2ii). The doublet at higher field (1.60 ppm, $^3J_{PP}$ = 12 Hz) is due to an exo-cluster $PPh_2$ group, which is not coordinated to the metal. The doublet of doublets of doublets at 48.97 ppm ($^2J_{PPtrans}$ = 248 Hz, $^2J_{PPcis}$ = 38 Hz and $^3J_{PPcis}$ = 12 Hz) is assigned to the second exo-cluster $PPh_2$ group coordinated to the metal and the two doublets of doublets, at 53.61 ($^2J_{PPtrans}$ = 248 Hz and $^2J_{PPcis}$ = 27 Hz) and 66.28 ppm ($^2J_{PPcis}$ = 38 Hz and $^2J_{PPcis}$ = 27 Hz), are assigned to two $PPh_3$ ancillary ligands. The $J_{PP}$ coupling constants indicate that two phosphorus atoms are in a trans position, and the third one is in a cis disposition. The $^{11}B$ NMR spectrum shows a 1 : 1 : 1 : 1 : 1 : 3 : 1 pattern, and the elemental analysis is in agreement with the stoichiometry $[RuH(7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10})(PPh_3)_2]$.



**Scheme 1.** Formation of $[RuH(7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10})(PPh_3)_2]$ (**1**).

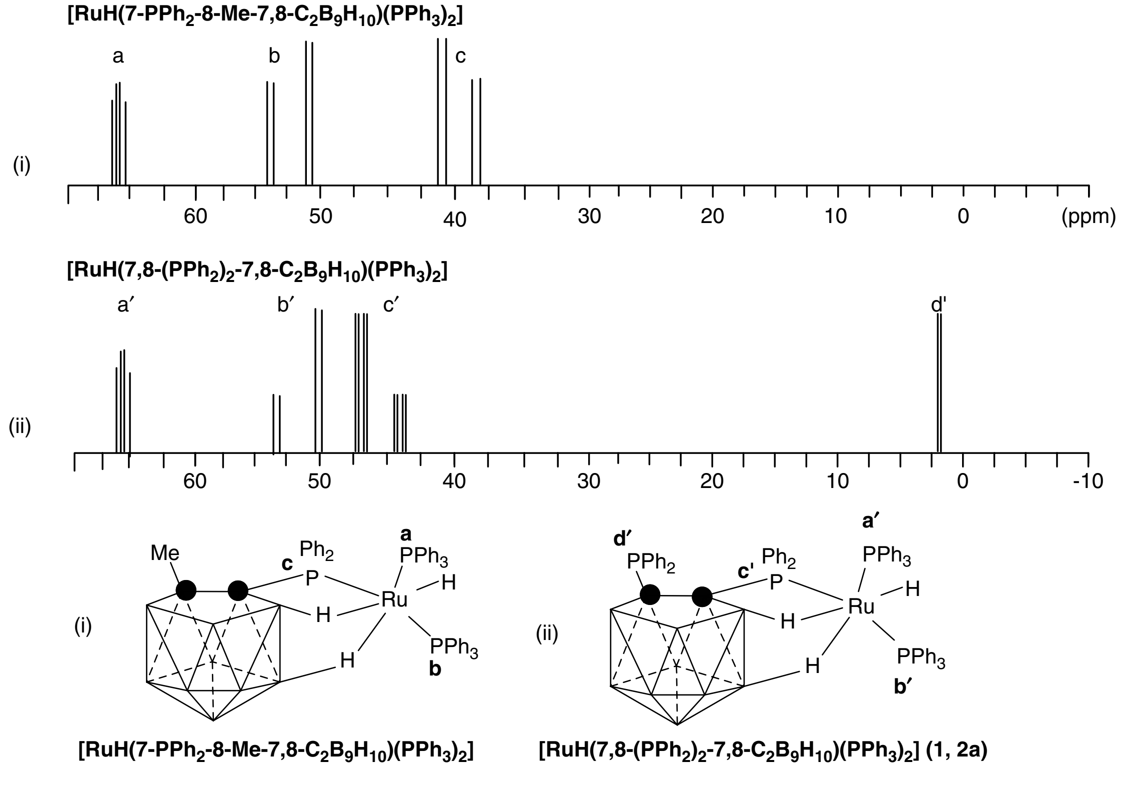


**Figure 2.** Schematic representation of the $^{31}P\{^1H\}$ NMR spectra of $[RuH(7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10})(PPh_3)_2]$ (**1 = 2a**) and $[RuH(7\text{-}PPh_2\text{-}8\text{-}Me\text{-}7,8\text{-}C_2B_9H_{10})(PPh_3)_2]$.

Taking into account the NMR data, we propose a structure where the *nido*-carboranyldiphosphine ligand is tricoordinating to the metal, like the *nido*-carboranylmonophosphine (see Fig. 2i),[2] through an exo-cluster $PPh_2$ group and two B–H→Ru agostic bonds. Two $PPh_3$ ligands and one hydride complete the coordination sphere of the metal. Three isomers are compatible with this $[RuH(7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10})(PPh_3)_2]$ stoichiometry, which are indicated schematically in Fig. 3 as motifs A, B, and C. The all *cis*-P–P disposition shown in motif B is excluded due to the large trans coupling constant ($^2J_{PP}$ 292 Hz)[23,24] found in the $^{31}P\{^1H\}$ NMR spectrum of **1**. The A and C motifs have only one BH group trans to a $PPh_3$ and are difficult to differentiate, since both possess a B–H trans to a metal hydride, an exo-cluster $PPh_2$ trans to a $PPh_3$, and a B–H trans to a $PPh_3$. A comparison of the $^1H$, $^{11}B$ and $^{31}P$ NMR spectra displayed for **1** with those observed for the analogous previously characterized complex $[RuH(7\text{-}PPh_2\text{-}8\text{-}Me\text{-}7,8\text{-}C_2B_9H_{10})(PPh_3)_2]$ (Fig. 2i),[2] shows a very similar set of resonances, suggesting that compound **1** corresponds to configuration C.

The reaction of $[RuCl_2(PPh_3)_3]$ and $[NMe_4][7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]$ in refluxing methanol in a 1 : 1 ratio (method I) or 1 : 2 ratio (method II) affords an orange solid. The $^1H$ and $^{31}P\{^1H\}$ NMR spectra indicated a mixture of two species, which we were unable to separate due to their instability. However, we were able to characterize tentatively species **2a** and **2b** by NMR spectroscopy. The ratio of the two species was estimated by the integrated intensity of the peaks in the $^1H\{^{11}B\}$ NMR spectrum. Method I yields 64% of **2a** and 37% of **2b**, whereas 40% of **2a** and 60% of **2b** are achieved using method II. The $^1H$ NMR spectrum of **2** displays resonances at −14.80, −13.78, −6.55, −3.27, −2.67 and −1.81 ppm, which are indicative of B–H–B and B–H→Ru bonds.[8,9,25] The signal at −1.81 ppm is a tetraplet ($^1J_{BH} = 106$ Hz) and the others are broad signals. When the $^1H\{^{11}B\}$ NMR spectrum was recorded, the broad resonances at −3.27 and −6.55 ppm were shown to be doublets due to coupling to $^{31}P$ ($^2J_{PH} = 38.9\ H_3$ and 28.8 Hz respectively) and are assigned to B–H trans to $PPh_3$; the resonance at −13.78 ppm was a triplet of doublets and the resonances at −1.81, −2.67 and −14.80 ppm sharpened to singlets. The areas allowed us to attribute the resonances observed at −1.81, −2.67, −6.55 and −13.78 ppm to species **2a** and the resonances displayed at −2.67, −3.27 and −14.80 ppm to species **2b**. Typical signals in the aromatic region, 6.5–7.5 ppm, corroborated the presence of the phenyl groups. The $^{31}P\{^1H\}$ NMR spectrum of the solid is in agreement with the presence of two species featuring two sets of resonances. The first set of resonances is comprised as follows: a doublet of doublets at 66.28 ppm ($^2J_{PPcis} = 38$ Hz and $^2J_{PPcis} = 27$ Hz), a doublet of doublets at 53.61 ppm ($^2J_{PPtrans} = 248$ Hz and $^2J_{PPcis} = 27$ Hz), a doublet of doublets of doublets at 48.97 ppm ($^2J_{PPtrans} = 248$ Hz, $^2J_{PPcis} = 38$ Hz and $^3J_{PP} = 12$ Hz) and a doublet at 1.60 ppm ($^3J_{PP} = 12$ Hz) are associated, by their coupling constants, to one species (**2a**). The second set of resonances is comprised as follows: a doublet of doublets at 45.84 ppm ($^2J_{PPcis} = 34$ Hz and $^2J_{PPcis} = 26$ Hz), a doublet of doublets at 28.28 ppm ($^2J_{PPtrans} = 292$ Hz, $^2J_{PPcis} = 26$ Hz), a doublet of doublets of doublets at 24.27 ppm ($^2J_{PPtrans} = 292$ Hz, $^2J_{PPcis} = 34$ Hz, and $^3J_{PP} = 14$ Hz) and a doublet at 0.68 ppm ($^3J_{PP} = 14$ Hz) belong to the second species (**2b**).

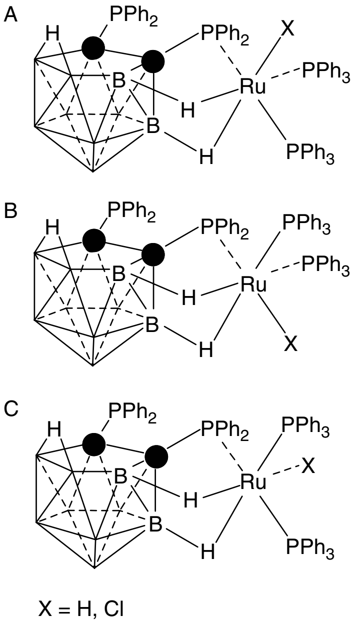
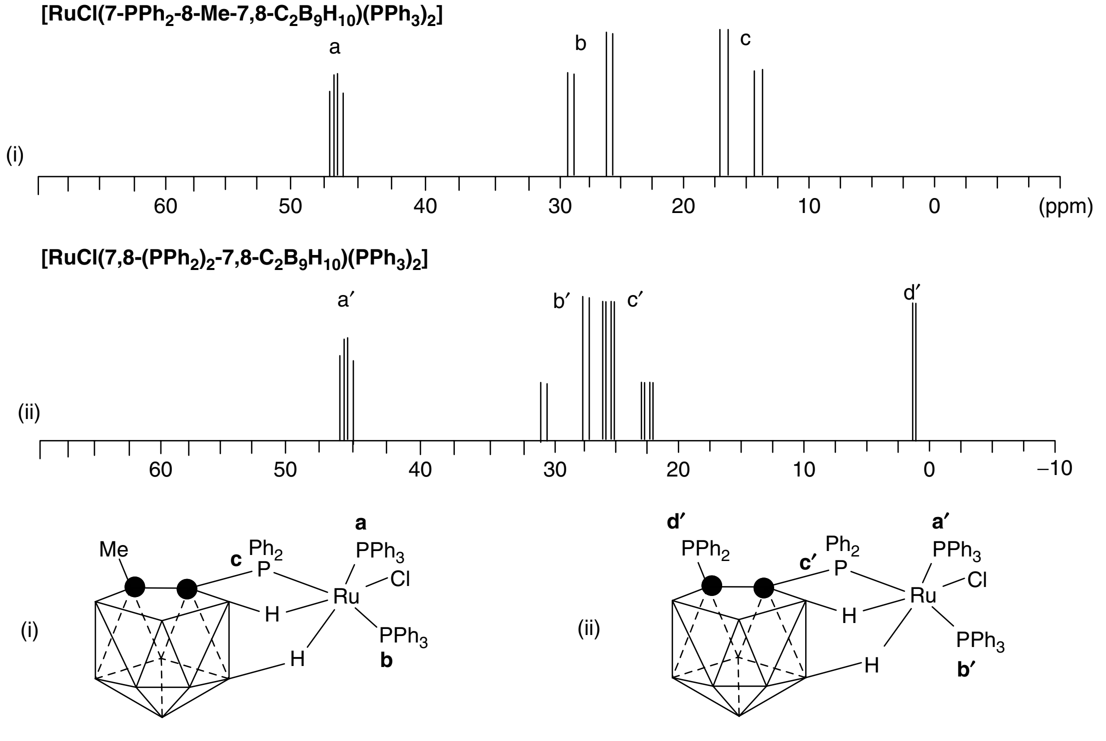


**Figure 3.** Isomers compatible with the formulation $[RuX(7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10})(PPh_3)_2]$ (X = H, Cl).

The $^1H\{^{11}B\}$ and $^{31}P\{^1H\}$ resonances (see Fig. 4ii) assigned to species **2b** are very similar to those observed in the previously reported ruthenium(II) complexes obtained with *nido*-carboranylmonophosphines $[RuCl(7\text{-}PR_2\text{-}8\text{-}R'\text{-}7,8\text{-}C_2B_9H_{10})(PPh_3)_2]$ (Fig. 4i).[2] For these, an X-ray diffraction study allowed us to confirm that isomer C of Fig. 3 was formed, and thus, by comparison of the NMR data for both types of complex, we may confirm that **2b** also corresponds to isomer C of stoichiometry $[RuCl(7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10})(PPh_3)_2]$. If we compare the behavior of the *nido*-carboranyldiphosphines towards ruthenium(II) with that observed for the *nido*-carboranyldithioethers, we find that the latter form both isomers, A and C, of stoichiometry $[RuCl(7,8\text{-}(SPh)_2\text{-}7,8\text{-}C_2B_9H_{10})(PPh_3)_2]$.[3] Thus, the second species (**2a**) could correspond to the other isomer, A. However, two other points have to be considered. First, the ruthenium complexes containing *nido*-carboranyldithioethers show very similar B–H→Ru chemical shifts in $^1H\{^{11}B\}$ NMR spectra for both isomers (−2.09, −14.74 and −2.22 ppm, and −13.71 ppm for A and C respectively), whereas species **2a** and **2b** display a dissimilar number of resonances with very different chemical shifts. Second, it may be noted that all the $^1H$ and $^{31}P$ NMR chemical shifts of **2a** are identical to those observed and described for complex **1**. This suggests that both compounds, **1** and **2a**, are the ruthenium-hydride



**[RuCl(7-PPh$_2$-8-Me-7,8-C$_2$B$_9$H$_{10}$)(PPh$_3$)$_2$]** **[RuCl(7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$)(PPh$_3$)$_2$] (2b)**

**Figure 4.** Schematic representation of the $^{31}$P{$^1$H} NMR spectra of [RuCl(7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$)(PPh$_3$)$_2$] (**2b**) and [RuCl(7-PPh$_2$-8-Me-7,8-C$_2$B$_9$H$_{10}$)(PPh$_3$)$_2$].

complex [RuH(7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$)(PPh$_3$)$_2$]. This would require a chloride ligand replacement by hydride during the course of the reaction. In this regard, it is known that some ruthenium-chloride systems may be converted into hydride or deuteride in the presence of a base in MeOH, e.g. CpRuL$_2$Cl and Cp*RuL$_2$Cl can be easily converted into CpRuL$_2$(H/D) and Cp*RuL$_2$(D) in methanol-*d*$_4$–sodium methoxide-*d*$_3$ at reflux or at room temperature respectively.[26,27] The latter occurs at room temperature, apparently due to the better electron donating properties of Cp* versus Cp, which further labilizes the chlorides toward heterolytic dissociation. On the other hand, complexes containing the carborane cluster as ligand, such as [3,3-(PPh$_3$)$_2$-3-H-3,1,2-RhC$_2$B$_9$H$_{10}$],[28] are directly obtained by the oxidative addition reaction of the ligand [Me$_3$NH][7,8-C$_2$B$_9$H$_{12}$] with [RhCl(PPh$_3$)$_3$] in alcoholic solutions. Thus, taking into account that the *nido*-carboranyldiphosphine is an electron-donating carborane ligand, we could propose that the formation of the ruthenium-hydride complex **2a** = **1** occurs after the partial conversion of the chloride species **2b**, under these reaction conditions (MeOH at reflux).

On comparing the $^{31}$P{$^1$H} chemical shifts for the hydride and chloride complexes with *nido*-carboranyldiphosphine, (Table 1), we observe that in the hydride species all the resonances have been shifted 20–25 ppm to low field with respect to the chloride one. A similar shift is observed for complexes formed with *nido*-carboranylmonophosphines (Table 2), suggesting that the influence of the exo-cluster group bonded to the second cluster carbon vertex is very poor.

To obtain a better understanding of the behavior of these ligands towards ruthenium(II), the anion [7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$]$^-$ was allowed to react with [RuCl$_2$(PMePh$_2$)$_4$] in 1 : 1 and 2 : 1 ratios to yield complex **3** and **4** respectively. The $^1$H NMR spectrum of **3** displays only one broad resonance at high field, −1.96 ppm, assigned to the B–H–B bridge, plus resonances in the aromatic region. Only one peak at $\delta$ 17.64 ppm is observed in the $^{31}$P{$^1$H} NMR spectrum,

**Table 1.** $^{31}$P{$^1$H} chemical shift for ruthenium-hydride and -chloride complexes containing the *nido*-carboranyldiphosphine ligand

| | [RuH(7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$)(PPh$_3$)$_2$] (**1** = **2a**) | [RuCl(7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$)(PPh$_3$)$_2$] (**2b**) | $\Delta\delta$ |
|---|---|---|---|
| a′ | 66.28 | 45.84 | 20.44 |
| b′ | 53.61 | 28.28 | 25.33 |
| c′ | 48.97 | 24.27 | 24.70 |
| d′ | 1.60 | 0.68 | 0.92 |

**Table 2.** $^{31}P\{^1H\}$ chemical shifts for ruthenium-hydride and -chloride complexes containing the *nido*-carboranylmonophosphine ligand

| | $[RuH(7\text{-}Me\text{-}8\text{-}PPh_2\text{-}7,8\text{-}C_2B_9H_{10})(PPh_3)_2]$ | $[RuCl(7\text{-}Me\text{-}8\text{-}PPh_2\text{-}7,8\text{-}C_2B_9H_{10})(PPh_3)_2]$ | $\Delta\delta$ |
|---|---|---|---|
| a′ | 66.87 | 46.17 | 20.70 |
| b′ | 53.98 | 27.34 | 26.64 |
| c′ | 39.49 | 14.34 | 25.15 |

and the $^{11}B$ NMR spectra show resonances in the range −8.2 to −33.6 ppm that integrate nine boron atoms. The elemental analysis indicates the existence of two *nido*-carboranyldiphosphine ligands and one ruthenium atom in the molecule. Assuming an octahedral geometry around the ruthenium(II) center, and considering the spectroscopic data above, we propose that each *nido*-carboranyldiphosphine ligand coordinates ruthenium through the phosphorus atoms in a chelating fashion. Although the $^1H$ NMR data of **3** in solution show no evidence of B–H→Ru interactions, we believe they exist in the solid state, as was previously reported for $[Rh(7\text{-}PPh_2\text{-}8\text{-}Me\text{-}7,8\text{-}C_2B_9H_{10})(cod)]$.[29] Thus, a structure with two *nido*-carboranyldiphosphine ligands, in which each ligand is tricoordinating the ruthenium(II) center through two Cc–PPh$_2$ groups and one B–H→Ru interaction is proposed. Geometrically, the B–H→Ru interaction is most probably formed by the B(3)–H bond (Fig. 5), similar to the structure reported for $[RuCl(7,8\text{-}\mu\text{-}7,8\text{-}(SCH_2{-}CH_2S)\text{-}7,8\text{-}C_2B_9H_{10})_2]$.[9]

When a 2 : 1 ratio is used the orange solid **4** is obtained. The $^{11}B\{^1H\}$ NMR spectrum of this solid shows ill-defined resonances that overlap in the region 0 to −20 ppm integrating 14B and two bands at −31.9 (2B) and −37.8 ppm (2B). The $^1H\{^{11}B\}$ NMR spectrum reveals a resonance at −2.25 ppm due to the B–H–B bridge proton, a quintuplet at higher field (−28.68 ppm, $J_{PH} = 18$ Hz) attributed to a terminal metal hydride, and resonances between 6.63 and 7.31 ppm that corroborate the presence of phenyl groups. The $^{31}P\{^1H\}$ NMR spectrum displays two singlet resonances, at 90.06 and 17.64 ppm.

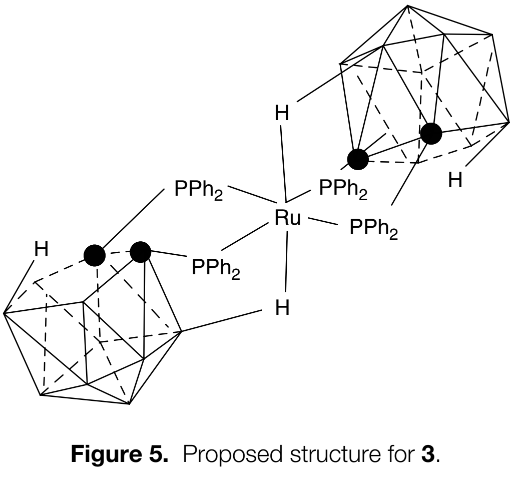


**Figure 5.** Proposed structure for **3**.

Additionally, the $^1H\{^{31}P\}$ NMR spectra and dynamic $^{31}P\{^1H\}$ NMR spectra in the range between 25 and −60 °C using dichloromethane as a solvent have been recorded.

When the phosphorus resonance at 90.06 ppm was selectively irradiated, the high-field quintuplet signal in the $^1H$ NMR spectrum sharpened to a single resonance. However, the $^1H$ NMR signal multiplicity was not modified when the irradiated resonance was the one at 17.64 ppm in the $^{31}P$ NMR. This study indicates that the hydride is only coupled to the phosphorus at 90.06 ppm (see Fig. 6).

On cooling **4** in $CD_2Cl_2$ it was found that the resonance at 90.06 ppm decoalesced at −20 °C and two different resonances were clearly seen at −60 °C, which indicate that two different sets of phosphorus atoms, with two phosphorus atoms in each set, exist in the molecule (see Fig. 7). Other minor phosphorus resonances observed could be due to the presence of rotational isomers.

Matrix-assisted laser desorption/ionization (MALDI)[30–32] is widely used for mass spectrometry (MS) analysis of large, non-volatile biomolecules, e.g. peptides, proteins, oligonucleotides, and oligosaccharides.[33–35] The orange solid **4** has been studied by MALDI-MS in negative ion mode not using matrices. The lack of matrices could help in interpretation of the peaks. Figure 8 shows the MALDI time-of-flight (TOF) MS spectrum of **4**. Typical patterns associated to boron clusters are observed for the highest peak, being found at $m/z = 1105$ corresponding to either **3** or **4** proposed

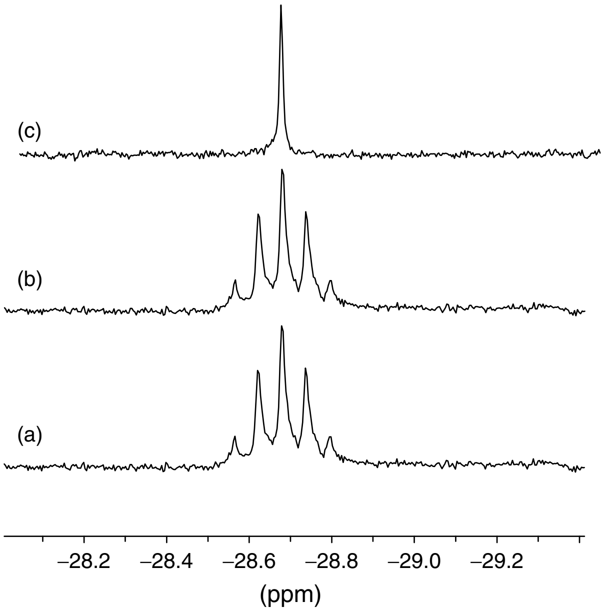


**Figure 6.** Fragment of $^1H$ NMR spectrum corresponding to the hydride region of **4**: (a) without phosphorus decoupling; (b) $^1H\{^{31}P\}$ NMR spectrum when the phosphorus resonance at 17.64 ppm was irradiated; (c) $^1H\{^{31}P\}$ NMR spectrum when the phosphorus resonance at 90.06 ppm was irradiated.

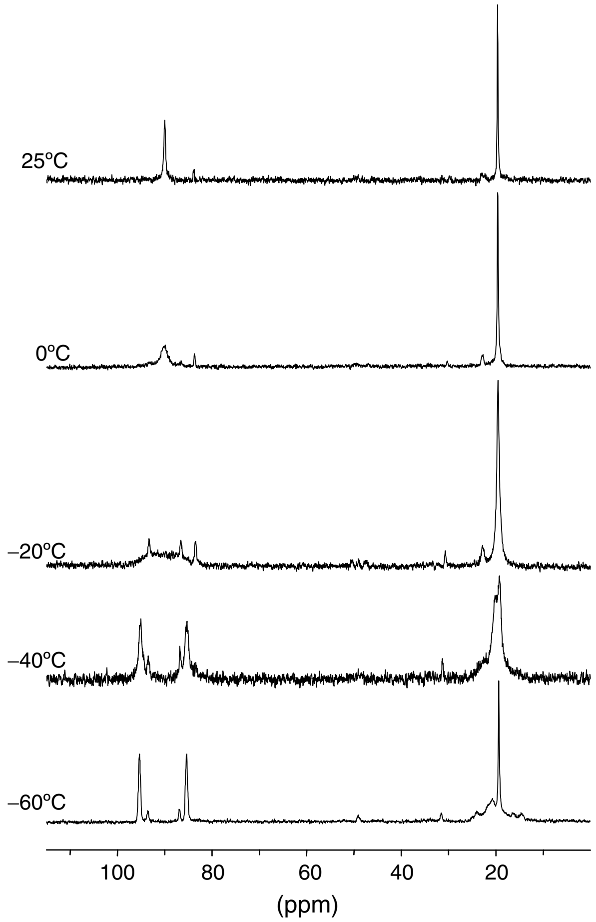


**Figure 7.** Variable-temperature $^{31}$P NMR spectra of **4**.

compounds. A comparison of the experimental (E) and theoretical (T) envelopes for the two peaks is included in Fig. 8.

Thus, we propose that **4** is a mixture of two geometrical isomers in the ratio of 57% to 43% according to the $^{31}$P NMR spectrum. The less abundant isomer (**4a**) corresponds to a species in fast equilibrium with a similar one. This is shown in Fig. 9. Lowering the temperature freezes out the two species in equilibrium and two sets of resonances with the same area are observed in the $^{31}$P NMR (see Fig. 7). The second species corresponds to compound **3**. The fact that comparable Kharasch catalytic activity is found for **3** and **4** may suggest that **3** and **4** interconvert easily, or alternatively that the catalytic species is only **3**.

Work is under way to isolate and crystallize the two compounds present in the orange solid **4**.

## CONCLUSIONS

These results indicate that the *nido*-carboranyldiphosphine ligand possesses a large coordinating capacity, since it is able to displace ligands from the coordination sphere of the starting $[RuH(CH_3COO)(PPh_3)_2]$, $[RuCl_2(PPh_3)_3]$ and $[RuCl_2(PMePh_2)_4]$ complexes. However, the *nido*-carboranyldiphosphine behavior depends on the starting ruthenium complex. With $[RuCl_2(PPh_3)_4]$, the *nido*-carboranyldiphosphine behaves as a monophosphine, showing a comparable behavior to that found for the *nido*-carboranyldithioether $[7,8\text{-}(SPh)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$. In both compounds, the formation of two B–H→Ru bonds was preferred to a second P–Ru or S–Ru bond, probably to release steric energy, as revealed by a molecular models study.[3] With respect to $[RuCl_2(PMePh_2)_4]$, the *nido*-carboranyldiphosphine displaces all initial ligands from the starting ruthenium(II) coordination sphere. Interestingly, two geometrical isomers are obtained from this reaction. One has an Ru–H and the other does not.

All these ruthenium complexes have been shown to be very efficient catalysts in radical reactions, such as Kharasch addition of $CCl_4$ to olefins.[36]

## EXPERIMENTAL

### Instrumentation

Microanalyses were performed in our analytical laboratory using a Carlo Erba EA1108 microanalyzer. IR spectra were recorded with KBr pellets on a Nicolet 710-FT spectrophotometer. The $^{1}$H and 1H{$^{11}$B} NMR (300.13 MHz), $^{11}$B, $^{11}$B{$^{1}$H} NMR (96.29 MHz) and $^{31}$P{$^{1}$H} NMR (121.5 MHz) spectra were recorded on a Bruker ARX 300 instrument equipped with the appropriate decoupling accessories, at room temperature. All NMR measurements were performed in deuterated solvents at 22 °C. Chemical shift data were referenced to $SiMe_4$ in the $^{1}$H NMR spectra and to external $BF_3{\cdot}Et_2O$ in the $^{11}$B{$^{1}$H} and $^{11}$B NMR spectra (negative values upfield) are given in parts per million, followed by a description of the multiplet (e.g. d = doublet), its relative intensity and observed coupling constants given in hertz. Chemical shift values for $^{31}$P{$^{1}$H} NMR spectra were referenced to external 85% $H_3PO_4$ and are given in parts per million (positive values downfield). The mass spectra were recorded in the negative ion mode using a Bruker Biflex MALDI-TOF mass spectrometer [nitrogen laser; $\lambda_{exc}$ 337 nm (0.5 ns pulses); voltage ion source 20.00 kV (Uis1) and 17.50 kV (Uis2)].

### Materials

All manipulations were carried out under a dinitrogen atmosphere using standard Schlenk techniques. Solvents were purified by distillation from appropriate drying agents before use. Deuterated solvents for NMR (Fluorochem) were freeze–pump–thawed three times under dinitrogen and transferred to the NMR tube using standard vacuum line techniques. $[NMe_4][7\text{-}8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10})]$ was synthesized from $1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_9H_{10}$ as is described in the literature.[37] $[RuH(CH_3COO)(PPh_3)_2]$, $[RuCl_2(PPh_3)_3]$

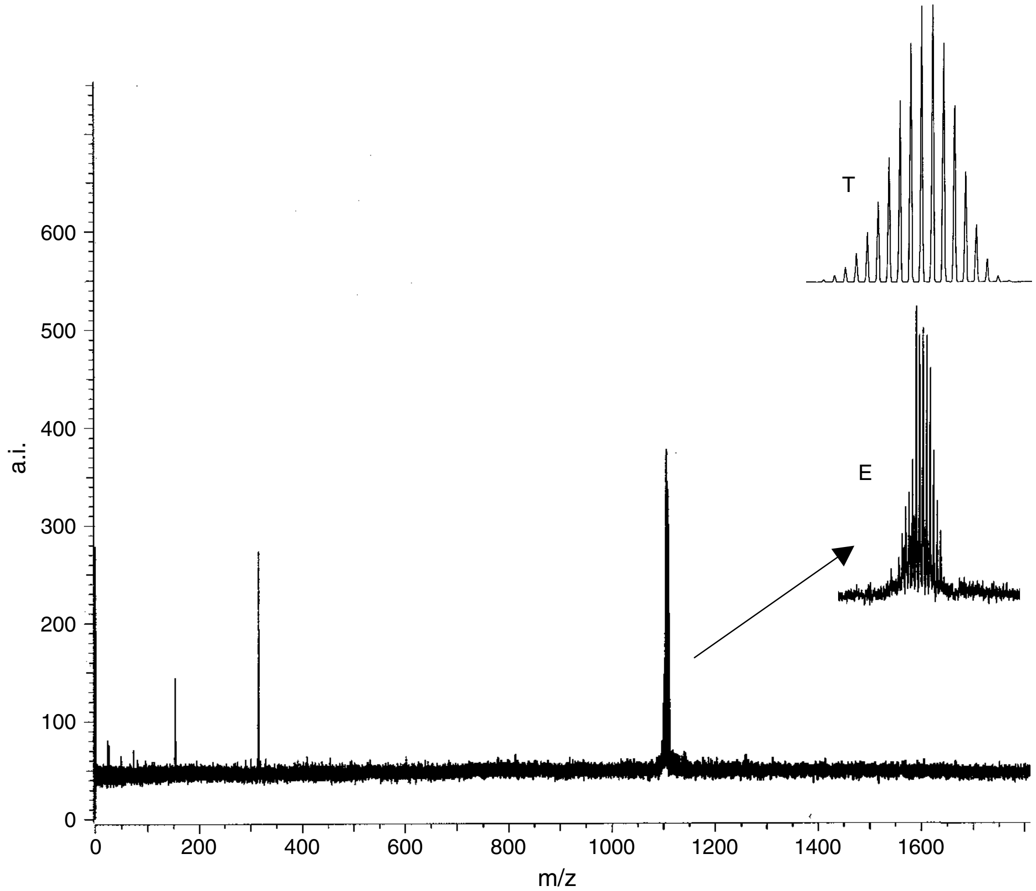


**Figure 8.** MALDI-TOF-MS of **4**: T (theoretical), E (experimental).

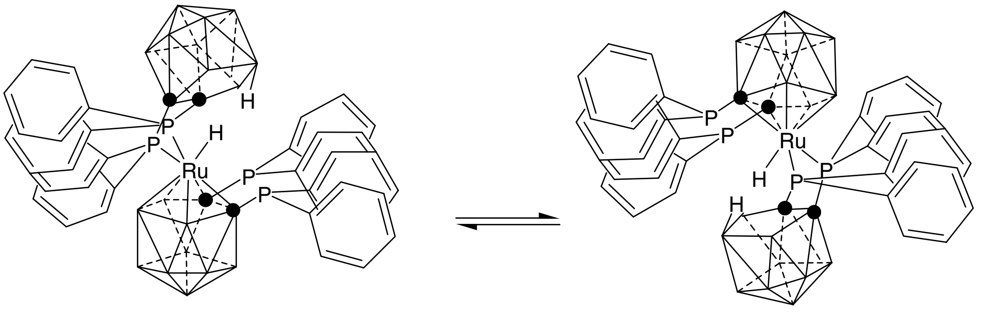


**Figure 9.** Proposed structure for complex **4a**.

and [$RuCl_2(PMePh_2)_4$] were prepared according to the literature.[38–40] All organic and inorganic salts were Fluka or Aldrich analytical reagent grade and were used as purchased. The solvents were reagent grade.

### Preparation of [$RuH(7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10})(PPh_3)_2$] (1)

To 70 ml of hot deoxygenated methanol containing [$NMe_4$][$7\text{-}8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}$)] (127 mg, 0.219 mmol) was added [$RuH(AcO)(PPh_3)_3$] (213mg, 0.219 mmol) and the mixture refluxed for 5 h. The resulting yellow solid was filtered, while hot, washed with hot methanol (20 ml) and vacuum-dried to yield 193 mg (78%). Anal. Found: C, 65.65; H, 5.59. Calc. for $C_{62}H_{61}B_9P_4Ru$: C, 65.99; H, 5.45%. IR (KBr): 2609, 2578, 2561, 2534 [$\nu$(B–H)] $cm^{-1}$. $^1H\{^{11}B\}$ NMR ($CD_2Cl_2$): $\delta$ 7.63 to 6.53 (m, 50H, $-C_6H_5$), −1.81 (s, 1H, B–*H*–Ru), −2.67 (s, 1H, B–*H*–B), −6.55 (d, 1H, $^2J_{PH}$ 28.8 Hz, B–*H*–Ru), −13.78 (td, 1H, $J_{PH}$ 20 Hz, $J_{HH}$ 8 Hz, Ru–*H*). $^1H$ NMR ($CD_2Cl_2$): $\delta$ 7.63–6.53 (m, 50H, $-C_6H_5$), −1.81 (tetrap, 1H, $^1J_{BH}$ 106 Hz, B–*H*–Ru), −2.67 (br, 1H, B–*H*–B,), −6.55 (br, 1H, B–*H*–Ru), −13.78 (br, 1H, Ru–*H*). $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$): $\delta$ 66.28 (dd, $^2J_{PP}$ 38 Hz, $^2J_{PP}$ 27 Hz), 53.61 (dd, $^2J_{PP}$ 248 Hz, $^2J_{PP}$ 27 Hz), 48.97 (ddd, $^2J_{PP}$ 248 Hz, $^2J_{PP}$ 38 Hz, $^3J_{PP}$ 12 Hz), 1.60 (d, $^3J_{PP}$ 12 Hz). $^{11}B$ NMR ($CD_2Cl_2$): $\delta$ 5.1 (1B), −13.5 (1B), −14.9 (1B), −17.3 (d, $^1J_{BH}$ 106 Hz, 1B), −19.9 (1B), −28.7 (3B), −35.9 (1B).

## Preparation of [RuCl(7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$)(PPh$_3$)$_2$] (2)

### *Method I*

To 25 ml of hot deoxygenated methanol containing [$NMe_4$][7,8-($PPh_2$)$_2$-7,8-$C_2B_9H_{10}$)] (150 mg, 0.259 mmol) was added [$RuCl_2(PPh_3)_3$] (250 mg, 0.259 mmol) and the mixture was refluxed for 3 h. An orange solid precipitated, which was filtered while hot, washed with hot methanol (10 ml) and vacuum-dried to yield 197 mg (71%). The NMR data indicate a mixture of two species, which we were unable to separate. Anal. Found: C, 63.15; H, 5.31. Calc. for $C_{62}H_{60}B_9ClP_4Ru$: C, 64.04; H, 5.20%. IR (KBr): 2547, 2553 [$\nu$(B–H)] cm$^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$ 7.29–6.40 (m, 50H, –$C_6H_5$), −1.81 (tetrap, 0.63H, $^1J_{BH}$ 106 Hz, B–*H*–Ru, **2a**), −2.67 (br, 1H, B–*H*–B, **2a, 2b**), −3.27 (br, 0.37H, B–*H*–B, **2b**), −6.55 (br, 0.63H, B–*H*–Ru, **2a**), −13.78 (br, 0.63H, Ru–*H*, **2a**), −14.80 (br, 0.37H, B–*H*–Ru, **2b**). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta$ 66.28 (dd, $^2J_{PP}$ 38 Hz, $^2J_{PP}$ 27 Hz, **2a**), 53.61 (dd, $^2J_{PP}$ 248 Hz, $^2J_{PP}$ 27 Hz, **2a**), 48.97 (ddd, $^2J_{PP}$ 248 Hz, $^2J_{PP}$ 38 Hz, $^3J_{PP}$ 12 Hz, **2a**), 45.84 (dd, $^2J_{PP}$ 34 Hz, $^2J_{PP}$ 26 Hz, **2b**), 28.28 (dd, $^2J_{PP}$ 292 Hz, $^2J_{PP}$ 26 Hz, **2b**), 24.27 (ddd, $^2J_{PP}$ 292 Hz, $^2J_{PP}$ 34 Hz, $^3J_{PP}$ 14 Hz, **2b**), 1.60 (d, $^3J_{PP}$ 12 Hz, **2a**), 0.68 (d, $^2J_{PP}$ 14 Hz, **2b**). $^{11}B$ NMR ($CDCl_3$): $\delta$ 8.2, 5.1, −13.5, −14.9, −17.3, −19.9, −21.3, −22.8, −28.7, −35.9.

### *Method II*

Similar to the above, a 2 : 1 molar ratio of [$NMe_4$][7-8-($PPh_2$)$_2$-7,8-$C_2B_9H_{10}$)] (100 mg, 0.173 mmol) and [$RuCl_2(PPh_3)_3$] (83 mg, 0.087 mmol) yielded 65 mg (64%) of orange solid. IR (KBr): 2547, 2553 [$\nu$(B–H)] cm$^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$ 7.29–6.40 (m, 50H, –$C_6H_5$), −1.81 (tetrap, 0.40H, $^1J_{BH}$ 106 Hz, B–*H*–Ru, **2a**), −2.67 (br, 1H, B–*H*–B, **2a, 2b**), −3.27 (br, 0.60H, B–*H*–B, **2b**), −6.55 (br, 0.40H, B–*H*–Ru, **2a**), −13.78 (br, 0.40H, Ru–*H*, **2a**), −14.80 (br, 0.60H, B–*H*–Ru, **2b**). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta$ 66.28 (dd, $^2J_{PP}$ 38 Hz, $^2J_{PP}$ 27 Hz, **2a**), 53.61 (dd, $^2J_{PP}$ 248 Hz, $^2J_{PP}$ 27 Hz, **2a**), 48.97 (ddd, $^2J_{PP}$ 248 Hz, $^2J_{PP}$ 38 Hz, $^3J_{PP}$ 12 Hz, **2a**), 45.84 (dd, $^2J_{PP}$ 34 Hz, $^2J_{PP}$ 26 Hz, **2b**), 28.28 (dd, $^2J_{PP}$ 292 Hz, $^2J_{PP}$ 26 Hz, **2b**), 24.27 (ddd, $^2J_{PP}$ 292 Hz, $^2J_{PP}$ 34 Hz, $^2J_{PP}$ 14 Hz, **2b**), 1.60 (d, $^3J_{PP}$ 12 Hz, **2a**), 0.68 (d, $^3J_{PP}$ 14 Hz, **2b**).

## Preparation of [Ru(7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{11}$)$_2$] (3)

To 50 ml of hot deoxygenated methanol containing [$NMe_4$][7-8-($PPh_2$)$_2$-7,8-$C_2B_9H_{10}$)] (100 mg, 0.173 mmol) was added [$RuCl_2(PMePh_2)_4$] (170 mg, 0.173 mmol) and the mixture was refluxed for 1 h. An orange solid was separated by filtering while hot. The solid was washed with hot methanol (20 ml) and vacuum-dried to yield 80 mg (84%). Anal. Found: C, 56.25; H, 5.20. Calc. for $C_{52}H_{60}B_{18}P_4Ru$: C, 56.54; H, 5.47%. IR (KBr): 2547 [$\nu$(B–H)] cm$^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$ 7.74–7.00 (m, 40H, –$C_6H_5$), −1.96 (br, 1H, B–*H*–B). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta$ 17.64 (s). $^{11}B$ NMR ($CDCl_3$): $\delta$ −8.2 (3B), −13.3 (4), −27.9 (1B), −33.6 (1B).

## Preparation of [RuH(7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$)$_2$] and [Ru(7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{11}$)$_2$] (4)

To 50 ml of hot deoxygenated methanol containing [$NMe_4$][7-8-($PPh_2$)$_2$-7,8-$C_2B_9H_{10}$)] (100 mg, 0.173 mmol) was added [$RuCl_2(PMePh_2)_4$] (85 mg, 0.086 mmol) and the mixture was refluxed for 1 h. An orange solid was separated by filtering while hot. The solid was washed with hot methanol (20 ml) and vacuum-dried to yield 65 mg. Anal. Found: C, 56.11; H, 5.40. Calc. for $C_{52}H_{60}B_{18}P_4Ru$: C, 56.54; H, 5.47%. MALDI-TOF-MS: $m/z = 1105$. IR (KBr): 2555 [$\nu$(B–H)] cm$^{-1}$. $^1H$ NMR ($CD_2Cl_2$): $\delta$ 7.31–6.63 (m, –$C_6H_5$), −2.25 (br, B–*H*–B), −28.68 (q, $^2J_{PH}$ 18 Hz, Ru–H). $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$): $\delta$ 90.06 (s), 17.64 (s). $^{11}B$ NMR ($CD_2Cl_2$): $\delta$ −12.2 (2B), −17.4 (12B), −32.0 (2B), −37.1 (2B).

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