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Reactions of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ru(COD) with Lewis bases: Synthesis, structure, and electrochemistry of ruthenium amine, nitrile, carbene, phosphite and phosphine complexes

Yi Sun [a], Hoi-Shan Chan [a], Pierre H. Dixneuf [b], Zuowei Xie [a,*]

[a] *Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong, China*
[b] *Institut de Chimie de Rennes, UMR 6509 CNRS-Université de Rennes, Organométalliques et Catalyse, Campus de Beaulieu, 35042 Rennes, France*

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Abstract

Treatment of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ru(COD) (**1**) with phosphites, phosphines, amines or N-heterocyclic carbene in THF afforded the COD displacement complexes [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ru[$P(OEt)_3$]$_2$ (**2**), [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ru[$PPh_2(OEt)$]$_2$ (**3**), [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ru[$NH_2CH_2CH_2Pr^i$]$_2$ (**4**), [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ru($NH_2Pr^n$)$_2$ (**5**), [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ru ($\eta^2$-$NH_2CH_2CH_2NH_2$) (**6**), [$\eta^5$:$\sigma$-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ru[$\eta^2$-$NH(CH_3)CH_2CH_2NH(CH_3)$] (**7**) or [$\eta^5$:$\sigma$-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ru[NHC]$_2$ (**8**, NHC = 1,3,4,5-tetramethylimidazol-2-yilidene), respectively. Ruthenium–amine complexes were much more labile than **1**. Upon exposure to moisture, **5** was converted into [{η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$}Ru($\mu$-$H_2O$)]$_2$ (**9**). Reactions of **5** with PR_3 (R = PPh_3, Cy), TMEDA (TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) and CH_3CN afforded the corresponding amine replacement products [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ru($NH_2Pr^n$)($PPh_3$) (**10**), [$\eta^5$:$\sigma$-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ru($NH_2Pr^n$)($PCy_3$) (**11**), [$\eta^5$:$\sigma$-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ru(TMEDA) (**12**) and [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ru($NCCH_3$)$_2$ (**13**). These results indicated that the steric factor dominated these substitution reactions. The electrochemical studies showed that the electron richness of the Ru atom decreased in the order $L_2Ru(NHC)_2 > L_2Ru(amine)_2 > L_2Ru(NCMe)_2 > L_2Ru(P)_2$. All of these complexes were fully characterized by various spectroscopic techniques and elemental analyses. The molecular structures of **2**, **3**, **5**–**10**, **12** and **13** were further confirmed by single-crystal X-ray analyses.

Keywords: Carborane; Cyclopentadienyl; Electrochemistry; Ruthenium complexes; Steric effect; Substitution reactions

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1. Introduction

Ruthenium half-sandwich complexes of the type (η^5-C_5R_5)$RuXL_2$ [R = H, Me; X = Cl, Br; L_2 = phosphines, COD (1,5-cyclooctadiene)] are effective catalysts for C–C bond-forming reactions [1]. For example, (η^5-C_5H_5)RuCl(COD) catalyzed a variety of coupling reactions of C≡C and C=C bonds for the production of functional dienes [2]. (η^5-C_5Me_5)RuCl(COD) allowed the head-to-head coupling of alkynes to form dienes and cyclobutenes [3] or the sequential coupling of alkynes generating aromatic compounds [4]. (η^5-C_5Me_5)RuCl(COD) also promoted double addition of carbene to alkynes and to enynes to generate dienes and bicyclo[3.1.0]hexane derivatives [5]. The first step of these catalytic reactions involved the leaving of the COD ligand to form coordinatively unsaturated species.

We recently reported constrained-geometry ruthenium COD complexes incorporating carbon-linked carboranyl–cyclopentadienyl (–indenyl or –fluorenyl) ligands [6]. Reactivity study on [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ru(COD) (**1**) showed that the COD in **1** was unable to be replaced by PR_3 (R = Ph, Cy), CH_3CN, pyridine or TMEDA (TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) even in refluxing THF solutions, but it was able to be displaced by bidentate tertiary phosphines and bipyridine. These results led to an assumption that bidentate ligands with π-accepting ability were necessary to substitute the COD in **1** [6].

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* Corresponding author. Tel.: +852 26096269; fax: +852 26035057.
E-mail address: zxie@cuhk.edu.hk (Z. Xie).

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In the course of reactivity studies, we isolated unexpectedly an amine coordinated ruthenium complex [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ru($NH_2Pr^n$)$_2$ from an attempted reaction of PhC≡CH with ^{n}PrNH_2 using **1** as the potential catalyst. This result indicated that the COD in **1** was able to be replaced by simple ^{n}PrNH_2, and the resultant primary amine–ruthenium complex was stable, which encouraged us to further investigate the displacement reactions of COD in **1** with mono- and bi-dentate Lewis bases. We report herein the synthesis, structure, and electrochemistry of a series of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ru($L_2$) complexes ($L_2$ = amines, diamines, nitrile, carbene, phosphites and phosphines) derived from **1**.

2. Results and discussion

2.1. COD displacement reactions

The COD ligand in **1** was unable to be replaced by PPh_3 or PCy_3 molecules [6]. It, however, was readily substituted by phosphites/phosphines with small cone angles. Treatment of **1** with 2 equiv. of $P(OEt)_3$ or $PPh_2(OEt)$ in refluxing THF afforded the COD displacement complexes [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ru[$P(OEt)_3$]$_2$ (**2**) or [η^5:σ-Me_2C-$(C_5H_4)(C_2B_{10}H_{10})$]Ru[$PPh_2(OEt)$]$_2$ (**3**) in 81–85% isolated yields (Scheme 1). Upon coordination, the ^{31}P NMR chemical shifts of phosphites/phosphines were downfield shifted by ~10 ppm. Therefore, these reactions were closely monitored by the ^{31}P NMR technique. The results indicated that the steric factor dominated the COD displacement reactions. In view of the cone angles of $P(OEt)_3$ (109°), $P(OEt)Ph_2$ (133°), PPh_3 (145°) and PCy_3 (170°) [7], it is anticipated that phosphites/phosphines with the cone angles of $\leqslant 133°$ should be able to displace the COD in **1**.

Unprecedented isolation of a small amount of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ru($NH_2Pr^n$)$_2$ from an attempted catalytic reaction of PhC≡CH with ^{n}PrNH_2 in the presence of **1** prompted us to examine the reaction of **1** with amines. Treatment of **1** with a large excess amount of amines in THF at room temperature afforded the COD displacement complexes [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ru[$NH_2CH_2CH_2$-$Pr^i$]$_2$ (**4**), [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ru($NH_2Pr^n$)$_2$ (**5**), [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ru($\eta^2$-$NH_2CH_2CH_2NH_2$) (**6**) and [$\eta^5$:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ru[$\eta^2$-NH($CH_3$)-$CH_2CH_2$NH($CH_3$)] (**7**), respectively, in 82–88% isolated yields (Scheme 1). Complex **1** reacted also with two equiv. of 1,3,4,5-tetramethylimidazol-2-yilidene (NHC) in refluxing THF to produce [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ru-[NHC]$_2$ (**8**) in 70% isolated yield.

Complexes **2**–**8** were soluble in THF, CH_2Cl_2, toluene and benzene, but insoluble in *n*-hexane. Complexes **4** and **5** were moisture-sensitive, whereas **2**, **3**, **6**–**8** were air- and moisture-stable. The ^{1}H NMR experiments showed that both **4** and **5** reacted rapidly with 1 equiv. of COD in C_6D_6 at room temperature to give **1** quantitatively, indicating that the reactions of **1** with RNH_2 were reversible. Therefore, a large excess amount of RNH_2 was necessary to fully displace the COD in **1**. On the other hand, complexes **2**, **3** and **6**–**8** did not show any reactivity toward COD even in refluxing C_6D_6.

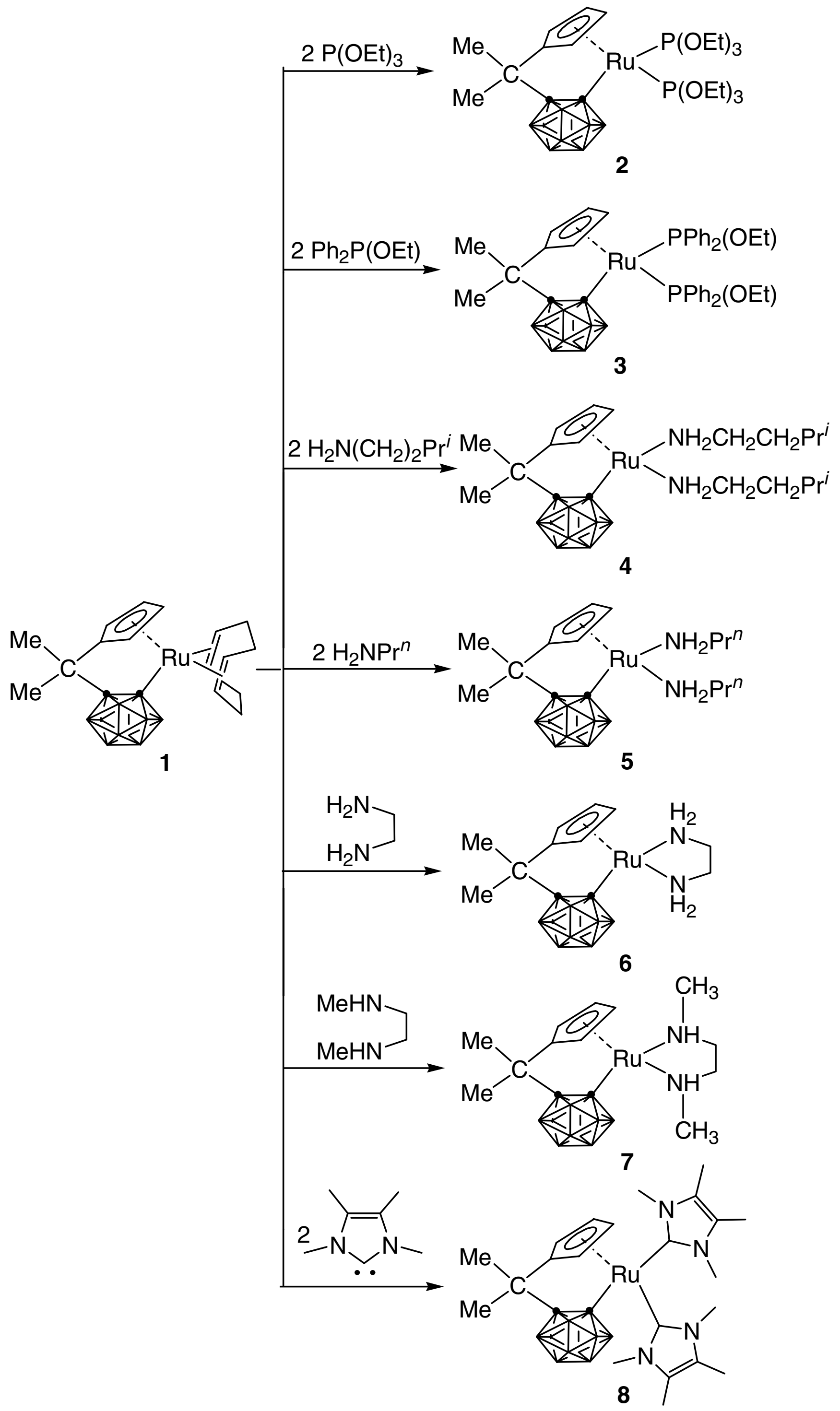
The ^{1}H NMR spectra of **2**–**7** showed two multiplets for Cp protons, one singlet of the Me_2C protons and one set of Lewis base protons, suggesting the *pseudo*-C_s symmetry of these complexes in solution. For **8**, the sterically demanding NHC ligands broke the symmetry, leading to the observation of four resonances for Cp protons, two singlets of the Me_2C group and two sets of NHC protons in the ^{1}H NMR spectrum. The ^{13}C NMR spectra were in line with the ^{1}H NMR data. Different splitting patterns were observed in the ^{11}B NMR spectra depending upon the nature of Lewis bases. The solid-state IR spectra displayed a characteristic terminal B–H absorption at ~2550 cm^{-1} for all complexes.

2.2. Amine displacement reactions

Complex **1** was stable to air and moisture, whereas complex **5** was moisture-sensitive. The color changed from yellow to green upon the exposure of **5** to air for a few minutes. In fact, recrystallization of **5** from a wet CH_2Cl_2/THF solution gave [{η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$}Ru(μ-$H_2O$)]$_2$ · 2THF (**9** · 2THF) as green crystals in 56% isolated yield. The labile nature of coordinated monoamine ligands in **4** and **5** prompted us to further examine the ligand exchange reactions between **5** and other Lewis bases that could not be introduced directly from **1**.

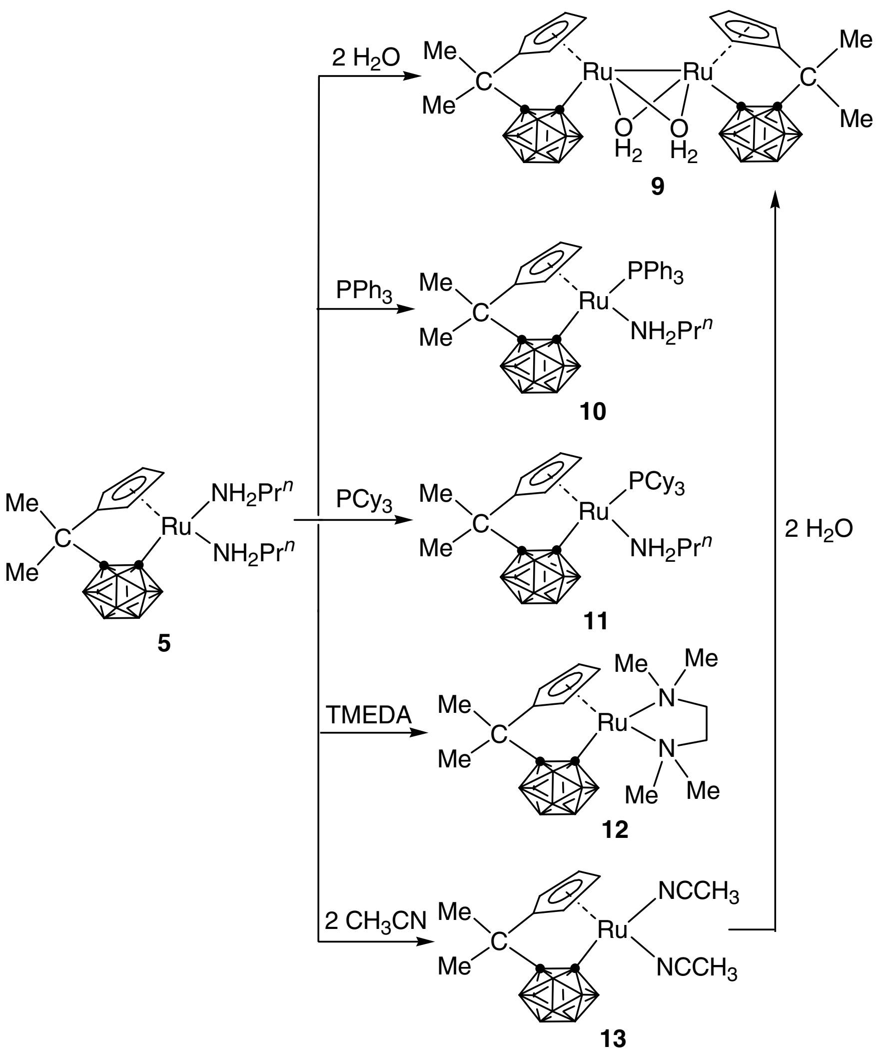
Treatment of **5** with 2 equiv. of PR_3 (R = Ph, Cy) in refluxing THF afforded mono-substituted complexes [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ru($NH_2Pr^n$)($PPh_3$) (**10**) and [$\eta^5$:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ru($NH_2Pr^n$)($PCy_3$) (**11**) in 82% isolated yield, respectively. The complete displacement of amines was not possible even under forced reaction conditions. On the other hand, **5** reacted with excess $P(OEt)_3$ to give di-substituted complex **2**. These results again suggested that the steric factor played a crucial role in these displacement reactions (see Scheme 2).

Complex **5** reacted also with excess TMEDA in refluxing THF afforded [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ru(TMEDA) (**12**) in 77% isolated yield. Complex **12** was not accessible from the reaction of **1** with excess TMEDA. An acetonitrile coordinated complex [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ru-($NCCH_3$)$_2$ (**13**) was isolated in 93% isolated yield by stirring a CH_3CN solution of **5** at room temperature for 2 days. Complex **13** reacted readily with 2 equiv. of ^{n}PrNH_2 in toluene at room temperature to give **5** quantitatively. It was noted that there was no reaction between **1** and CH_3CN even at high temperatures. Complex **13** was extremely moisture-sensitive and converted into **9** as a green compound upon exposure to air. These ligand exchange reactions showed that the lability of complexes followed the order: **13** > **5** > **1**. The presence of amine and acetonitrile in complexes **5** and **13** allowed the introduction of new ligands on the ruthenium site, which is not accessible directly from **1**. In this regards, complexes **5** and **13** may be good candidates as catalyst precursors.



Scheme 1.

The ${}^1H$ NMR spectrum of **9** showed only the resonances of the linked cyclopentadienyl–carboranyl ligand which was quite different from its parent complex **5**. Four multiplets of the Cp protons in the range 4.45–3.24 ppm, two singlets of the Me_2C protons at $\delta_H = 1.50$ and 1.45 ppm, one set of PR_3 (R = Ph, Cy) and one set of ${}^nPrNH_2$ protons were observed in the ${}^1H$ NMR spectra of **10** and **11**, respectively. One ${}^{31}P$ resonance was also observed in each of them. On the other hand, the ${}^1H$ NMR spectra of **12** and **13** exhibited only two multiplets and one singlet for the linked ligand and one set of the coordinated Lewis base protons, TMEDA in **12** or CH_3CN in **13**, supporting the C_s symmetry of these complexes in solution. The ${}^{13}C$ NMR spectra of **9**–**13** were line with their ${}^1H$ NMR data.



Scheme 2.

2.3. Molecular structures

Single-crystal X-ray analyses confirmed the molecular structures of **2**, **3**, **5**–**10**, **12** and **13**, shown in Figs. 1–10, respectively. Table 1 compiled their key structural data. Except for **9**, they all adopt monomeric structures in which the Ru atom is η^5-bound to one cyclopentadienyl ring, σ-bound to one cage carbon atom and coordinated to two monodentate ligands or one bidentate ligand in a distorted-tetrahedral geometry. The following trends were observed after carefully examining the bond distances and angles: (1) the sterically demanding ligands are associated with the longer Ru–C(cage), Ru–C(ring) and Ru–X distances, the larger bite angles of X–Ru–X and the smaller Cent–Ru–C(cage) angles and (2) the variations of C(ring)–C(bridge)–C(cage) angles are very small within 2°.

The average Ru–C(cage), Ru–C(ring) and Ru–Cent distances and C(ring)–C(bridge)–C(cage) angles listed in Table 1 are very comparable to the corresponding values observed in **1** and other $[\eta^5:\sigma\text{-Me}_2C(C_5H_4)(C_2B_{10}H_{10})]$Ru(P–P) complexes (P–P = bidentate phosphines) [6]. The average Ru–P

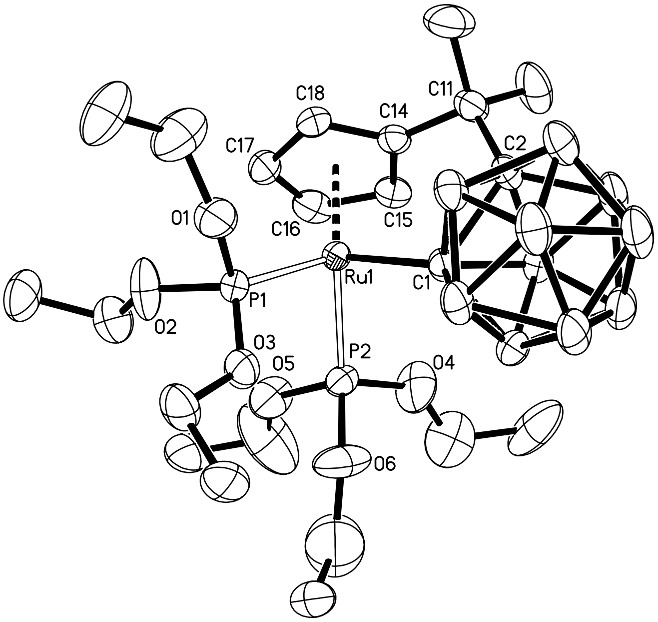


Fig. 1. Molecular structure of $[\eta^5:\sigma\text{-Me}_2C(C_5H_4)(C_2B_{10}H_{10})]Ru[P(OEt)_3]_2$ (**2**).

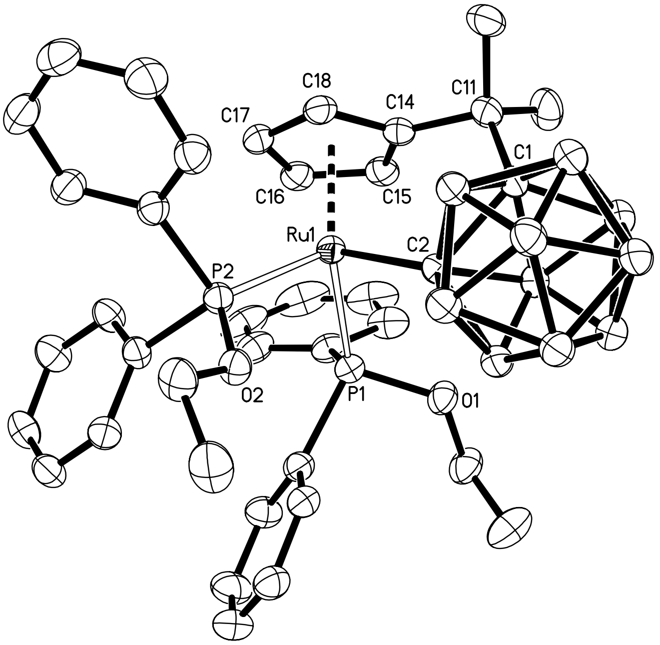


Fig. 2. Molecular structure of $[\eta^5:\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ru[PPh_2\text{-}(OEt)]_2$ (**3**).

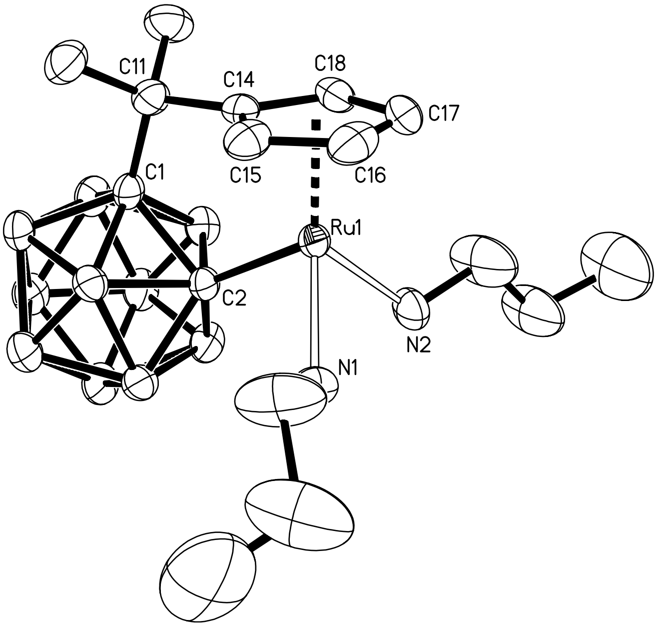


Fig. 3. Molecular structure of $[\eta^5:\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ru(NH_2Pr^n)_2$ (**5**).

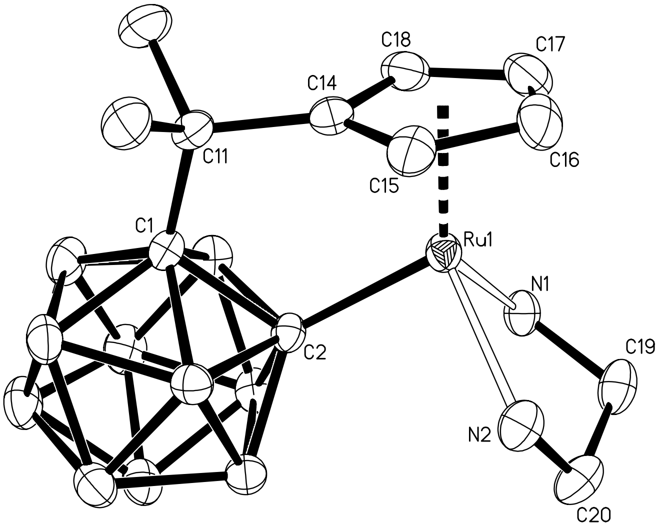


Fig. 4. Molecular structure of $[\eta^5:\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ru(\eta^2\text{-}NH_2CH_2CH_2NH_2)$ (**6**).

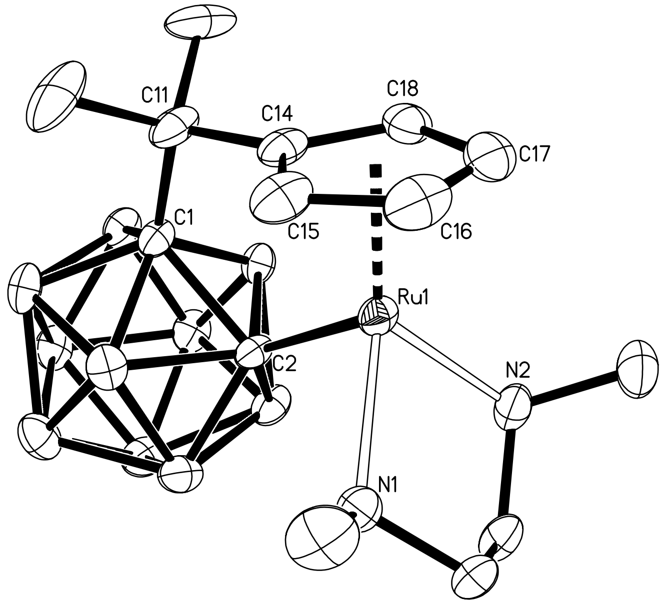


Fig. 5. Molecular structure of $[\eta^5:\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ru[\eta^2\text{-}NH(CH_3)CH_2CH_2NH(CH_3)]$ (**7**).

distances of 2.240(1) Å in **2**, 2.284(1) Å in **3** and 2.328(2) in **10** are close to the corresponding values found in $[\eta^5:\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ru(P–P)$ complexes [6]. The average Ru–N (amines) distances (2.177(2)–2.279(1) Å) are very comparable to the corresponding values observed in $RuCl_2(COD)[Et(H)NCH_2CH_2N(H)Et]$ (2.195(2) Å) [8a], $RuCl_2(COD)(C_6H_{15}N)_2$ (2.174(3) Å) [8b] and $RuCl_2(dppp)(H_2NCH_2CH_2NH_2)$ (2.174(2) Å) [8c]. The average Ru–N (CH_3CN) distance of 2.068(4) Å in **13** is significantly shorter than the Ru–N (amines) distances, but is close to the corresponding values found in $Ru(MeCN)(P^iPr_3)$('$N_2Me_2S_2$') ('$N_2Me_2S_2$' = 1,2-ethanediamine-N,N'-bis(2-benzenethiolate)) (1.990(3) Å) [9a] and $Ru(C_{10}H_8N_2S)_2(CH_3CN)_2(BF_4)_2$ ($C_{10}H_8N_2S$ = di-2-pyridyl sulfide-N,N') (2.022(2) Å) [9b]. The average Ru–C (NHC) distance of 2.073(4) Å in **8** is almost identical with that of 2.040(3) Å in $RuCl_2$ $[\eta^1\text{-}CN\{\eta^6\text{-}C_6H_2Me_3\text{-}2,4,6\}CH_2CH_2N(CH_2C_6H_2Me_3\text{-}2,4,6)]$ and 2.086(3) Å in $RuCl_2\{\eta^1\text{-}CN(CH_2C_6H_2Me_3\text{-}2,4,6)CH_2CH_2N(CH_2CH_2OMe)\}(C_6Me_6)$ [10].

Complex **9** is a dinuclear species with a Ru–Ru distance of 2.657(1) Å (Fig. 7). Comparing this measured value with the Ru–Ru single bond distances of 2.773(1) Å in $(Ph_3P)_4Ru_2(\mu$-

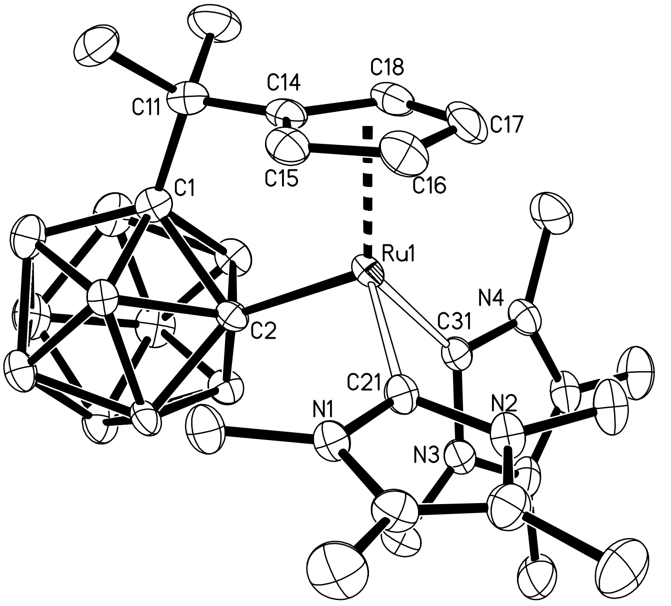


Fig. 6. Molecular structure of $[\eta^5:\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ru\{C[N(Me)C(Me){=}C(Me)N(Me)]\}_2$ (**8**).

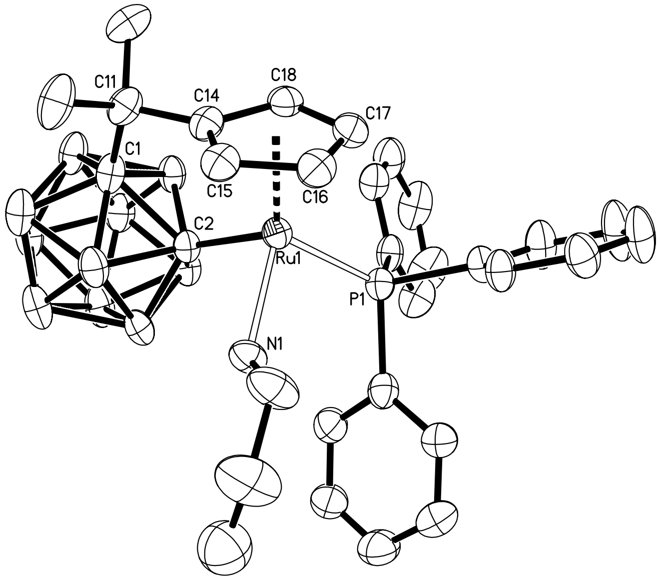


Fig. 8. Molecular structure of $[\eta^5:\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ru(NH_2Pr^n)(PPh_3)$ (**10**) (the solvated toluene molecule is not shown).

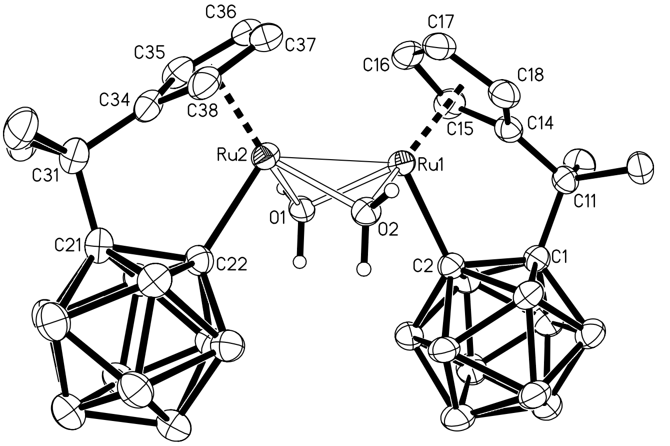


Fig. 7. Molecular structure of $[\{\eta^5:\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})\}Ru(\mu\text{-}H_2O)]_2$ (**9**) (the solvated THF molecules are not shown).

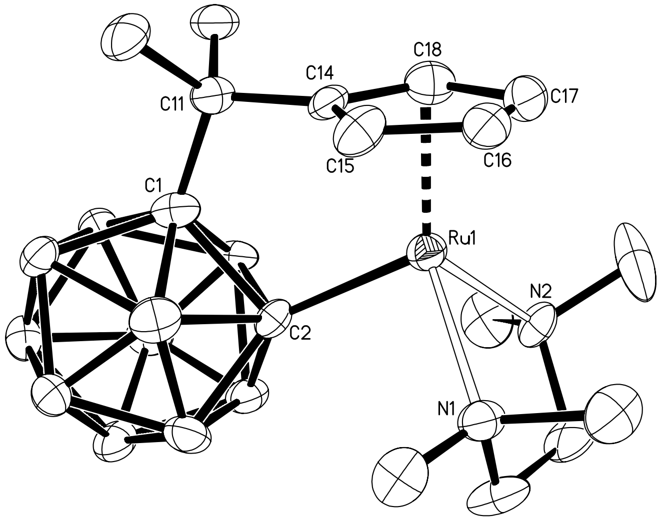


Fig. 9. Molecular structure of $[\eta^5:\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ru(TMEDA)$ (**12**).

$H)_2(\mu\text{-}CF_3SO_2)(CO)_2HC(SO_2CF_3)_2 \cdot CH_2Cl_2$ [11a] and 2.637(1) Å in $(Me_3P)_4Ru(\mu\text{-}CH_2)_2Ru(\mu\text{-}CH_2)_2Ru(Me_3P)_4(BF_4)_2$ [11b], it is better to describe the Ru–Ru interaction in **9** to be the single bond. The Ru–O distances in **9** (2.063(3), 2.070(3), 2.097(3) and 2.116(3) Å) are very comparable to the Ru–OH_2 distances of 2.149(3) and 2.185(3) Å in $Ru_2(C_2H_5)_2(CO)_4(H_2O)_4(CF_3SO_3)_2$, 2.100(5) Å in $Ru(CO)_3(H_2O)_3(BF_4)_2$ [12a] and 2.050(4) Å in $L_{OEt}(H_2O)Ru(\mu\text{-}O)_2Ru\ (OH_2)L_{OEt}$ ($L_{OEt} = CpCo\{(EtO)_2P{=}O\}_3$) [12b]. These measured values are significantly longer than the Ru–O (oxo) distances, e.g. 1.940(9) Å in $(py)_2RuO_2(\mu\text{-}O)_2RuO_2(py)_2$ (py = pyridine) [13a], 1.887(4) Å in $L_{OEt}(O)Ru(\mu\text{-}O)_2Ru(O)L_{OEt}$ [12b] and 1.733(6) Å in $(CH_2SiMe_3)_3Ru(\mu\text{-}O)_2Ru(CH_2SiMe_3)_3$ [13b]. As shown in Table 1, the Ru–C(cage) and Ru–C(ring) distances in **9** are very close to the corresponding values observed in the complexes containing $[\eta^5:\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ru(II)$ moiety [6]. The above data all support **9** to be a divalent Ru aqueous complex.

2.4. Electrochemistry

For all complexes (except for **9**), the electrochemical study revealed that all observed redox processes were one-electron and reversible processes at the scan rate of 100 mV s^{-1}, as indicated by the (i_{Pa}/i_{Pc}) ratios of unity and the ΔE_p peak separations in the range 86–118 mV. The redox potentials $E_{1/2}$ given relative to ferrocenium/ferrocene were compiled in Table 2.

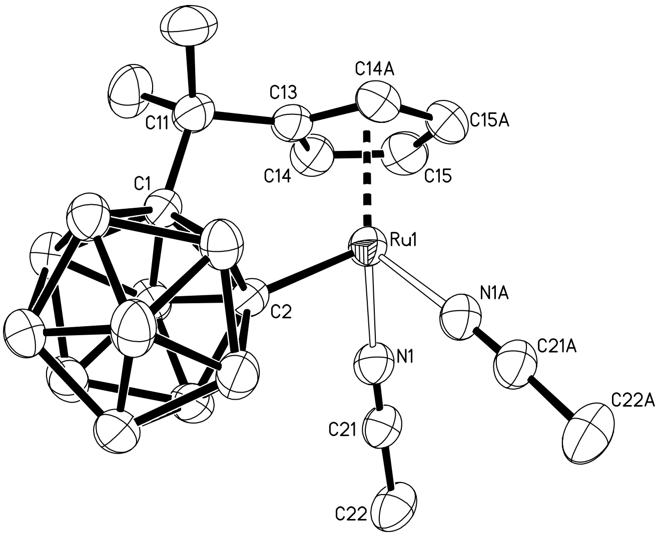


Fig. 10. Molecular structure of $[\eta^5:\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ru(NCCH_3)_2$ (**13**).

All complexes have similar molecular structures with different N- and/or P-ligands or NHC carbenes, thus allowing us to compare the electron-donating ability of the ligands. As shown in Table 2, the electron richness of the Ru atom decreases in the order $L_2Ru(NHC)_2 > L_2Ru(amine)_2 \gg L_2Ru(amine)(phosphine) > L_2Ru(NCMe)_2 > L_2Ru(P)_2$. This trend reflects the net results of the two contrary interactions of σ-donation and π-acception. It is noteworthy that the most electron-rich complex is **8**, due to the fact that NHC carbene exhibits a remarkably strong electron-donating power [14]. It is also obvious that the primary amine complexes (**4**, **5**, **6**) are more electron-rich than the secondary and tertiary amine complexes **7** and **12**. As the most labile complexes are shown to be **4**, **5** and **13**, it is suggested that high reactivity of those complexes is not due to electron-richness (oxidability) of the Ru metal center, but rather to the monodentate and labile nature of the ligands.

Table 2
Redox potentials of ruthenium complexes in CH_2Cl_2[a]

Complex	$E_{1/2}$ (Ru^{III}/Ru^{II}) (V)	ΔE_p (mV)
2	0.305	112
3	0.213	115
4	−0.360	118
5	−0.352	86
6	−0.337	96
7	−0.198	108
8	−0.630	88
10	0.010	115
11	−0.052	102
12	−0.199	90
13	−0.013	117

[a] All potentials were given relative to ferrocenium/ferrocene. Pt working electrode: 100 mV s^{-1}; recorded in CH_2Cl_2 with $n\text{-}Bu_4NPF_6$ (0.15 M) as supporting electrolyte.

3. Conclusion

A series of ruthenium complexes containing carbon-bridged carboranyl–cyclopentadienyl ligands were synthesized via ligand substitution reactions and fully characterized. They are all 18-electron species with a distorted-tetrahedral geometry. The ruthenium–amine complexes are much more labile than the ruthenium–COD ones. For example, **5** is able to react with PR_3 (R = Ph, Cy) and CH_3CN, but the COD in **1** is replaced only by phosphites/phosphines ligands with small cone angles. The less labile complex **1** derived from the classical source of ruthenium moiety $[RuCl_2(COD)]_x$ stands as a key precursor in this Cp–carboranyl ruthenium series. Thus it seems that monoamine and acetonitrile derivatives **5** and **13** constitute substitution intermediates that cannot be overlooked.

The electrochemical studies indicate that the electron richness of the Ru atom decreases in the order $L_2Ru(NHC)_2 > L_2Ru(amine)_2 > L_2Ru(NCMe)_2 > L_2Ru(P)_2$. This work also offers useful information for further investigation of this novel class of ruthenium carborane complexes in both stoichiometric and catalytic reactions.

4. Experimental

All experiments were performed under an atmosphere of dry dinitrogen with the rigid exclusion of air and moisture using standard Schlenk or cannula techniques, or in a glovebox. THF and *n*-hexane were freshly distilled from sodium benzophenone ketyl immediately prior to use. CH_2Cl_2 was

Table 1
Selected bond distances (Å) and angles (°) for **2**, **3**, **5**–**10**, **12** and **13**[a]

Complex	Ru–C_{cage}	Average Ru–C_{ring}	Ru–Cent	Average Ru–X	X–Ru–X	C_{ring}–C_{bridge}–C_{cage}	Cent–Ru–C_{cage}
2	2.142(1)	2.230(1)	1.882	2.240(1) (X = P)	93.6(1)	109.2(1)	115.0
3	2.167(3)	2.232(3)	1.876	2.284(1) (X = P)	95.8(1)	109.4(2)	113.8
5	2.095(5)	2.142(6)	1.771	2.204(5) (X = N)	83.5(2)	108.8(4)	120.1
6	2.098(2)	2.149(2)	1.773	2.177(2) (X = N)	78.1(1)	109.4(1)	120.3
7	2.102(3)	2.157(3)	1.785	2.185(3) (X = N)	78.9(1)	109.2(2)	119.2
8	2.149(4)	2.220(4)	1.864	2.073(4) (X = C)	88.1(2)	109.6(3)	115.2
9	2.141(4)	2.204(5)	1.841	2.084(3) (X = O)	80.0(1)	108.0(4)	110.9
	2.150(5)	2.206(5)	1.843	2.090(3) (X = O)	79.8(1)	109.2(4)	111.2
10	2.105(6)	2.207(6)	1.833	2.176(5) (X = N) 2.328(2) (X = P)	89.3(2)	107.9(5)	116.3
12	2.217(3)	2.171(4)	1.798	2.268(3) (X = N)	77.4(1)	109.2(3)	117.0
13	2.111(5)	2.166(6)	1.799	2.068(4) (X = N)	83.3(2)	109.7(4)	118.7

[a] Cent: the centroid of the cyclopentadienyl ring.

freshly distilled from CaH_2 and P_2O_5, respectively, immediately prior to use. $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ru(COD)$ [6] and 1,3,4,5-tetramethylimidazol-2-ylidene [15] were prepared according to the literature methods. All other chemicals were purchased from either Aldrich or Acros Chemical Co. and used as received unless otherwise noted. Cyclic voltammetric measurements were performed using a BAS CV-50 W Voltammetric Analyzer. The electrochemical cell comprised a platinum-wire working electrode, a silver-wire reference electrode, and a platinum-disk counter electrode. All measurements were made in a dry N_2 atmosphere. All sample solutions (CH_2Cl_2) contained n-Bu_4NPF_6 (0.15 M) as supporting electrolyte and complex (2.0×10^{-3} M). Chemical potentials were internally referenced to the ferrocenium/ferrocene redox system. Infrared spectra were obtained from KBr pellets prepared in the glovebox on a Perkin–Elmer 1600 Fourier transform spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX 300 spectrometer at 300 and 75 MHz, respectively. ^{11}B and ^{31}P NMR spectra were recorded on a Varian Inova 400 spectrometer at 128 and 162 MHz, respectively. All chemical shifts were reported in δ units with references to the residual protons of the deuterated solvents for proton and carbon chemical shifts, to external $BF_3 \cdot OEt_2$ (0.0 ppm) for boron chemical shifts, and to external 85% H_3PO_4 (0.0 ppm) for phosphorus chemical shifts. Elemental analyses were performed by MEDAC Ltd. UK or Shanghai Institute of Organic Chemistry, CAS, China. Melting points were determined on an Electrothermal Digital Melting Point Apparatus M-IA9100 and were uncorrected.

4.1. Preparation of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]$-$Ru[P(OEt)_3]_2$ (**2**)

A THF solution (10 mL) containing $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ru(COD)$ (**1**; 0.23 g, 0.50 mmol) and triethyl phosphite (0.17 g, 1.0 mmol) was heated to reflux for 48 h. After removal of THF, the resulting solid was washed with n-hexane. Recrystallization from THF (10 mL) at room temperature gave **2** as pale yellow crystals (0.29 g, 85%), mp 199–200 °C. ^1H NMR (C_6D_6, δ/ppm): δ 4.88 (m, 2H, C_5H_4), 4.37 (m, 2H, C_5H_4), 3.81 (m, 12H, OCH_2), 1.51 (s, 6H, $C(CH_3)_2$), 1.09 (t, $J = 7.2$ Hz, 18H, CH_2CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6, δ/ppm): δ 80.4, 76.8 (C_5H_4), 60.6 (OCH_2), 40.0 ($C(CH_3)_2$), 31.7 ($C(CH_3)_2$), 16.2 (CH_2CH_3). $^{31}P\{^1H\}$ NMR (C_6D_6, δ/ppm): δ148.2. $^{11}B\{^1H\}$ NMR (C_6D_6, δ/ppm): δ −2.3 (2B), −5.8 (3B), −7.2 (3B), −8.6 (2B). IR (KBr, cm^{-1}): ν 2977vs, 2933s, 2898s, 2584vs, 2537vs, 1442m, 1384s, 1259w, 1044vs, 939vs, 762s. Anal. Calc. for $C_{22}H_{50}B_{10}O_6P_2Ru$: C, 38.76; H, 7.39. Found: C, 38.50; H, 7.35%.

4.2. Preparation of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]$-$Ru[PPh_2(OEt)]_2$ (**3**)

This complex was prepared as yellow crystals from $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ru(COD)$ (**1**; 0.23 g, 0.50 mmol) and ethyl diphenylphosphinite (0.23 g, 1.0 mmol) in THF (15 mL) using the identical procedures reported for **2**: yield 0.33 g (81%), mp 269 °C dec. ^1H NMR (C_6D_6, δ/ppm): δ 7.56–7.03 (m, 20H, *Ph*), 4.13 (m, 2H, C_5H_4), 3.72 (m, 2H, C_5H_4), 3.23 (m, 2H, OCH_2), 3.07 (m, 2H, OCH_2), 1.32 (s, 6H, $C(CH_3)_2$), 0.99 (t, $J = 6.9$ Hz, 6H, CH_2CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6, δ/ppm): δ 139.3, 139.1, 136.3, 133.2, 132.3, 129.9, 129.7, 127.4 (aryl *C*), 84.2, 77.0 (C_5H_4), 63.8 (OCH_2), 39.7 ($C(CH_3)_2$), 31.7 ($C(CH_3)_2$), 16.1 (CH_2CH_3). $^{31}P\{^1H\}$ NMR (C_6D_6, δ/ppm): δ 135.4. $^{11}B\{^1H\}$ NMR (C_6D_6, δ/ppm): δ −3.4 (2B), −7.3 (8B). IR (KBr, cm^{-1}): ν 3051w, 2970m, 2584vs, 2526vs, 1631w, 1438m, 1380m, 1091s, 1025vs, 929s, 740m, 694s. Anal. Calc. for $C_{38}H_{50}B_{10}O_2P_2Ru$: C, 56.35; H, 6.22. Found: C, 56.42; H, 6.77%.

4.3. Preparation of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ru$-$[NH_2CH_2CH_2Pr^i]_2$ (**4**)

A THF solution (10 mL) of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ru(COD)$ (**1**; 0.23 g, 0.50 mmol) and isopentylamine (0.44 g, 5.0 mmol) were mixed at room temperature and stirred for 48 h. After removal of THF and excess isopentylamine, the resulting solid was washed with n-hexane. Recrystallization from THF at room temperature gave **4** as a yellow crystalline solid (0.23 g, 88%), mp 197 °C dec. ^1H NMR (C_6D_6, δ/ppm): δ 3.85 (m, 2H, C_5H_4), 2.95 (m, 2H, C_5H_4), 2.53 (m, 2H, CH_2), 2.35 (m, 2H, CH_2), 2.09 (m, 2H, CH_2), 1.46 (s, 6H, $C(CH_3)_2$), 1.32 (m, 2H, CH_2), 0.98 (m, 2H, CH), 0.78 (d, $J = 3.0$ Hz, 12H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (C_6D_6, δ/ppm): δ 90.3, 75.1 (C_5H_4), 49.7, 43.1 (CH_2), 42.0 ($C(CH_3)_2$), 32.5 ($C(CH_3)$), 26.3 (CH), 23.1, 22.9 ($CH(CH_3)_2$). $^{11}B\{^1H\}$ NMR (C_6D_6, δ/ppm): δ −3.8 (2B), −6.4 (4B), −8.1 (2B), −12.9 (2B). IR (KBr, cm^{-1}): ν 3301m, 2943s, 2557vs, 1589m, 1454m, 1367m, 1058m, 796w. Anal. Calc. for $C_{20}H_{46}B_{10}N_2Ru$: C, 45.86; H, 8.85; N, 5.35. Found: C, 45.51; H, 9.00; N, 5.37%.

4.4. Preparation of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ru$-$(NH_2Pr^n)_2$ (**5**)

This complex was prepared from $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ru(COD)$ (**1**; 0.23 g, 0.50 mmol) and propylamine (0.30 g, 5.0 mmol) in THF (15 mL) using the identical procedures reported for **4**: yield 0.19 g (82%), mp 185 °C dec. ^1H NMR (C_6D_6, δ/ppm): δ 3.79 (m, 2H, C_5H_4), 2.98 (m, 2H, C_5H_4), 2.39 (m, 2H, CH_2), 2.17 (m, 2H, CH_2), 1.46 (s, 6H, $C(CH_3)_2$), 1.02 (m, 4H, CH_2), 0.63 (t, $J = 7.2$ Hz, 6H, CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6, δ/ppm): δ 76.0, 74.4 (C_5H_4), 54.9, 52.6 (CH_2), 41.5 ($C(CH_3)_2$), 32.0 (CH_3), 26.8 (CH_2), 11.0 (CH_3). $^{11}B\{^1H\}$ NMR (C_6D_6, δ/ppm): δ −4.0 (2B), −6.6 (4B), −8.0 (2B), −13.1 (2B). IR (KBr, cm^{-1}): ν 3315s, 3261w, 2961s, 2871m, 2544vs, 1584s, 1461m, 1380m, 1259m, 1041s, 804s, 742w. Anal. Calc. for $C_{16}H_{38}B_{10}N_2Ru$: C, 41.09; H, 8.19; N, 5.99. Found: C, 41.25; H, 8.15; N, 6.00%.

4.5. Preparation of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ru($\eta^2$-$NH_2CH_2CH_2NH_2$) (**6**)

This complex was prepared as yellow crystals from [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ru(COD) (**1**; 0.23 g, 0.50 mmol) and 1,2-diaminoethane (0.30 g, 5.0 mmol) in THF (15 mL) using the identical procedures reported for **4:** yield 0.18 g (88%), mp 133–134 °C. ^{1}H NMR (C_6D_6, δ/ppm): δ 3.57 (m, 2H, C_5H_4), 3.26 (m, 2H, C_5H_4), 2.40 (m, 4H, CH_2), 1.50 (s, 6H, $C(CH_3)_2$). $^{13}C\{^1H\}$ NMR (C_6D_6, δ/ppm): δ 72.3 (C_5H_4), 56.1 (CH_2), 43.9 ($C(CH_3)_2$), 32.0 (CH_3). $^{11}B\{^1H\}$ NMR (C_6D_6, δ/ppm): δ −4.3 (2B), −7.0 (4B), −8.9 (2B), −12.2 (2B). IR (KBr, cm^{-1}): ν 3322vs, 2930s, 2579vs, 2536vs, 1582vs, 1452s, 1360m, 1185w, 1025s, 863m, 800s, 742m. Anal. Calc. for $C_{12}H_{28}B_{10}N_2Ru$: C, 35.19; H, 6.90; N, 6.84. Found: C, 34.93; H, 6.92; N, 6.64%.

4.6. Preparation of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ru[$\eta^2$-$NH(CH_3)CH_2CH_2NH(CH_3)$] (**7**)

This complex was prepared as yellow crystals from [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ru(COD) (**1**; 0.23 g, 0.50 mmol) and *N*,*N*′-dimethylethylenediamine (0.44 g, 5.0 mmol) in THF (15 mL) using the identical procedures reported for **4**: yield 0.19 g (87%), mp 264 °C dec. ^{1}H NMR (C_6D_6, δ/ppm): δ 3.66 (m, 2H, C_5H_4), 3.09 (m, 2H, C_5H_4), 2.17 (s, 6H, NCH_3), 1.64 (m, 4H, CH_2), 1.46 (s, 6H, $C(CH_3)_2$). $^{13}C\{^1H\}$ NMR (C_6D_6, δ/ppm): δ 75.9 (C_5H_4), 54.5, 52.8 (NCH_2), 46.9 (NCH_3), 41.3 ($C(CH_3)_2$), 32.0 (CH_3). $^{11}B\{^1H\}$ NMR (C_6D_6, δ/ppm): δ −3.9 (1B), −5.7 (1B), −6.6 (2B), −7.6 (2B), −8.5 (2B), −13.1 (2B). IR (KBr, cm^{-1}): ν 3718w, 3262w, 2966m, 2911m, 2546vs, 1621w, 1457w, 1373w, 1087s, 1038s, 806s. Anal. Calc. for $C_{14}H_{32}B_{10}N_2Ru$: C, 38.43; H, 7.37; N, 6.40. Found: C, 38.54; H, 7.44; N, 6.29%.

4.7. Preparation of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ru-$(NHC)_2$ (**8**)

This complex was prepared as red crystals from [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ru(COD) (**1**; 0.23 g, 0.50 mmol) and 1,3,4,5-tetramethylimidazol-2-ylidene (NHC; 0.11 g, 1.0 mmol) in THF (15 mL) using the identical procedures reported for **2**: yield 0.21 g (70%), mp 288 °C dec. ^{1}H NMR (C_6D_6, δ/ppm): δ 5.05 (m, 1H, C_5H_4), 4.21 (m, 1H, C_5H_4), 4.20 (m, 1H, C_5H_4), 3.44 (m, 1H, C_5H_4), 4.07, 3.44, 2.51, 2.26 (s, s, s, s, 12H, $C(CH_3)$ of NHC), 1.78 (s, 3H, $C(CH_3)_2$), 1.59 (s, 3H, $C(CH_3)_2$), 1.65, 1.63, 1.45, 1.44 (s, s, s, s, 12H, $N(CH_3)$ of NHC). $^{13}C\{^1H\}$ NMR (C_6D_6, δ/ppm): δ 189.9 ($Ru{=}C$), 83.3, 76.2 (C_5H_4), 67.3, 67.0 ($C{=}C$), 39.8 ($C(CH_3)_2$), 36.1, 35.7 ($C(CH_3)_2$), 34.6, 34.4, 32.2, 32.0 (NCH_3), 9.7, 9.5, 9.4, 9.2 ($CH_3C{=}C$). $^{11}B\{^1H\}$ NMR (C_6D_6, δ/ppm): δ −3.4 (2B), −5.9 (4B), −7.9 (4B). IR (KBr, cm^{-1}): ν 2981w, 2952w, 2919w, 2534vs, 2354m, 2269m, 1554w, 1382m, 1261w, 1091m, 1031w, 800m. Anal. Calc. for $C_{24}H_{44}B_{10}N_4Ru$: C, 48.22; H, 7.42; N, 9.37. Found: C, 48.75; H, 7.42; N, 9.26%.

4.8. Preparation of [{η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$}Ru($\mu$-$H_2O$)]$_2$ · 2THF (**9** · 2THF)

Recrystallization of **5** (100 mg, 0.19 mmol) from wet CH_2Cl_2/THF (1:1, 4 mL) in air give **9** · 2THF as green crystals (57 mg, 56%), mp 154 °C dec. ^{1}H NMR ([D5]pyridine, δ/ppm): δ 5.36 (m, 2H, C_5H_4), 5.17 (m, 2H, C_5H_4), 4.96 (m, 4H, C_5H_4), 3.63 (m, 8H, THF), 1.61 (m, 8H, THF), 1.52 (s, 12H, $C(CH_3)_2$). $^{13}C\{^1H\}$ NMR ([D5]pyridine, δ/ppm): δ 83.2, 79.6 (C_5H_4), 42.3 ($C(CH_3)_2$), 32.5, 31.6 (CH_3). $^{11}B\{^1H\}$ NMR ([D5]pyridine, δ/ppm): δ −3.2 (4B), −4.6 (4B), −8.1 (12B). IR (KBr, cm^{-1}): ν 3490m, 3081w, 2966w, 2561vs, 2341w, 1631w, 1461w, 1384m, 1041m, 845m, 744m. Anal. Calc. for $C_{28}H_{60}B_{20}O_4Ru_2$ · (**9** + 2THF): C, 38.25; H, 6.88. Found: C,38.26; H, 6.85%.

4.9. Preparation of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ru-($NH_2Pr^n$)($PPh_3$) (**10** · 0.5toluene)

Triphenylphosphine (0.26 g, 1.00 mmol) was added to a THF solution (10 mL) of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]-Ru$(NH_2Pr^n)_2$ (**5**; 0.23 g, 0.50 mmol), and the mixture was heated to reflux for 24 h. After removal of the solvent, the residue was recrystallized from THF at room temperature to give **10** · 0.5toluene as yellow crystals (0.29 g, 82%), mp 155–156 °C. ^{1}H NMR (C_6D_6, δ/ppm): δ 7.40 (m, 6H, *Ph*), 7.14 (m, 9H, *Ph*), 4.45 (m, 1H, C_5H_4), 3.80 (m, 1H, C_5H_4), 3.78 (m, 1H, C_5H_4), 3.47 (m, 1H, C_5H_4), 2.42 (m, 2H, CH_2), 1.46 (s, 3H, $C(CH_3)_2$), 1.45 (s, 3H, $C(CH_3)_2$), 0.66 (m, 2H, CH_2), 0.34 (t, $J = 7.2$ Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6, δ/ppm): δ 133.6, 129.7, 129.3, 125.6, 124.1 (aryl *C*), 78.5, 67.4, 59.8, 55.5 (C_5H_4), 40.3 ($C(CH_3)_2$), 32.1, 31.2 ($C(CH_3)_2$), 27.0 (CH_2), 10.4 (CH_3). $^{31}P\{^1H\}$ NMR (C_6D_6, δ/ppm): δ58.1. $^{11}B\{^1H\}$ NMR (C_6D_6, δ/ppm): δ −2.7 (2B), −5.3 (2B), −7.4 (4B), −11.9 (2B). IR (KBr, cm^{-1}): ν 3308s, 3261w, 3046w, 2972s, 2932s, 2571vs, 1579m, 1469m, 1432s, 1180m, 806m, 746s. Anal. Calc. for $C_{32.75}H_{46}B_{10}NPRu$ · (**10** + 0.25toluene): C, 56.69; H, 6.75; N, 2.02. Found: C, 56.62; H, 6.62; N, 1.68%.

4.10. Preparation of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ru-($NH_2Pr^n$)($PCy_3$) (**11**)

This complex was prepared as yellow crystals from [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ru$(Pr^n)_2$ (**5**; 0.23 g, 0.50 mmol) and tricyclohexylphosphine (0.28 g, 1.00 mmol) in THF (15 mL) using the identical procedure reported for **10**: yield 0.28 g (82%), mp 166 °C dec. ^{1}H NMR (C_6D_6, δ/ppm): δ 4.32 (m, 1H, C_5H_4), 4.14 (m, 1H, C_5H_4), 3.87 (m, 1H, C_5H_4), 3.24 (m, 1H, C_5H_4), 2.67 (m, 2H, CH_2), 2.02–1.05 (m, 35H, $Cy + CH_2$), 1.50 (s, 3H, $C(CH_3)_2$), 1.46 (s, 3H, $C(CH_3)_2$), 0.68 (t, $J = 7.2$ Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6, δ/ppm): δ 82.0, 73.9, 65.1 (C_5H_4), 39.0 ($C(CH_3)_2$), 31.1, 30.8 ($C(CH_3)_2$), 27.9, 27.8, 27.5 (*Cy*), 27.0 (NH_2CH_2), 11.0 (CH_2CH_3). $^{31}P\{^1H\}$ NMR (C_6D_6, δ/ppm): δ 36.8. $^{11}B\{^1H\}$ NMR (C_6D_6, δ/ppm): δ −4.2 (2B), −6.1 (2B), −8.1 (2B), −9.9 (2B), −13.1 (2B). IR (KBr, cm^{-1}): ν 3281w, 2925vs, 2844vs, 2549vs, 1585m, 1446s, 1261w, 1043m, 804m. Anal. Calc. for $C_{31}H_{62}B_{10}NPRu$: C, 54.04; H, 9.07; N, 2.03. Found: C, 54.13; H, 8.97; N, 2.07%.

*4.11. Preparation of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ru-(TMEDA) (**12**)*

This complex was prepared as red crystals from [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ru($NH_2Pr^n$)$_2$ (**5**; 0.23 g, 0.50 mmol) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA; 0.12 g, 1.0 mmol) in THF (15 mL) using the identical procedures reported for **10**: yield 0.18 g (77%), mp 240 °C dec. ^1H NMR (CD_2Cl_2, δ/ppm): δ 3.90 (m, 2H, C_5H_4), 3.38 (m, 2H, C_5H_4), 3.10 (s, 6H, NCH_3), 3.00 (s, 6H, NCH_3), 2.43 (m, 4H, NCH_2), 1.37 (s, 6H, $C(CH_3)$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, δ/ppm): δ 75.1 (C_5H_4), 61.5, 60.5 (NCH_2), 54.6, 51.9 (NCH_3), 39.3 ($C(CH_3)_2$), 31.8 ($C(CH_3)_2$). $^{11}B\{^1H\}$ NMR (CD_2Cl_2, δ/ppm): δ −7.7 (2B), −9.4 (2B), −10.7 (2B), −12.3 (4B). IR (KBr, cm^{-1}): ν 3316m, 2958vs, 2877s, 2549vs, 1585m, 1457m, 1376m, 1044s, 806m, 744w. Anal. Calc. for $C_{16}H_{36}B_{10}N_2Ru$: C, 41.27; H, 7.79; N, 6.02. Found: C, 41.14; H, 7.76; N, 6.11%.

*4.12. Preparation of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ru-($NCCH_3$)$_2$ (**13**)*

A CH_3CN solution (10 mL) of [η^5:σ-$Me_2C(C_5H_4)$-$(C_2B_{10}H_{10})$]Ru(NH_2Pr^n)$_2$ (**5**; 0.23 g, 0.50 mmol) was stirred at room temperature for 48 h. After removal of CH_3CN, the resulting solid was washed with *n*-hexane. Recrystallization from CH_3CN at room temperature gave **13** as yellow crystals (0.20 g, 93%), mp 188 °C dec. ^1H NMR (C_6D_6, δ/ppm): δ 4.44 (m, 2H, C_5H_4), 3.67 (m, 2H, C_5H_4), 1.49 (s, 6H, $C(CH_3)_2$), 0.92 (s, 6H, CH_3CN). $^{13}C\{^1H\}$ NMR (C_6D_6, δ/ppm): δ 122.2 (CH_3CN), 77.7, 61.7 (C_5H_4), 41.6 ($C(CH_3)_2$), 31.9 ($C(CH_3)_2$), 2.4 (CH_3). $^{11}B\{^1H\}$ NMR (C_6D_6, δ/ppm): δ −3.6 (2B), −6.7 (2B), −7.9 (2B), −9.1 (2B), −10.5 (2B). IR (KBr, cm^{-1}): ν 3448vs, 2927vs, 2556vs, 2270s, 1658w, 1454s, 1349s, 1060s, 802w. Anal. Calc. for $C_{14}H_{26}B_{10}N_2Ru$: C, 38.97; H, 6.07; N, 6.49. Found: C, 39.15; H, 6.21; N, 6.58%.

4.13. X-ray structure determination

All single crystals were immersed in Paraton-N oil and sealed under N_2 in thin-walled glass capillaries. Data were collected at 293 K on either a Bruker SMART 1000 CCD diffractometer or an MSC/Rigaku RAXIS-II imaging plate using Mo Kα radiation. An empirical absorption correction was applied using the SADABS program [16]. 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 [17]. All hydrogen atoms were geometrically fixed using the riding model. Complexes **9** and **10** showed two THF and half toluene of solvation, respectively. The solvated

Table 3
Crystal data and summary of data collection and refinement for **2**, **3** and **5**–**8**

Complex	**2**	**3**	**5**	**6**	**7**	**8**
Formula	$C_{22}H_{50}B_{10}O_6P_2Ru$	$C_{38}H_{50}B_{10}O_2P_2Ru$	$C_{16}H_{38}B_{10}N_2Ru$	$C_{12}H_{28}B_{10}N_2Ru$	$C_{14}H_{32}B_{10}N_2Ru$	$C_{24}H_{44}B_{10}N_4Ru$
Crystal size (mm)	0.20 × 0.15 × 0.10	0.50 × 0.30 × 0.20	0.50 × 0.40 × 0.20	0.70 × 0.70 × 0.30	0.40 × 0.30 × 0.20	0.40 × 0.30 × 0.20
Formula weight	681.7	809.9	467.7	409.5	437.6	597.8
Crystal system	Orthorhombic	Monoclinic	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group	*Pbca*	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P2_1/n$
a (Å)	20.054(4)	10.787(2)	9.652(1)	9.162(1)	9.052(2)	12.379(5)
b (Å)	16.619(3)	17.859(4)	11.900(1)	11.030(1)	10.344(2)	18.943(8)
c (Å)	20.821(4)	20.942(4)	12.598(1)	18.626(1)	12.538(3)	13.089(5)
α (°)	90	90	63.26(1)	90	79.11(3)	90
β (°)	90	100.82(3)	70.95(1)	96.96(1)	78.16(3)	99.77(1)
γ (°)	90	90	74.94(1)	90	64.80(3)	90
V ($Å^3$)	6939(2)	3962.6(1)	1210.4(1)	1868.4(1)	1032.7(4)	3024.8(2)
Z	8	4	2	4	2	4
D_{calc} ($Mg\ m^{-3}$)	1.305	1.358	1.283	1.456	1.407	1.313
Radiation (λ/Å)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
$2\theta_{max}$ (°)	48.0	50.0	48.0	56.0	50.0	50.0
μ (mm^{-1})	0.577	0.511	0.653	0.835	0.760	0.541
F(000)	2832	1672	484	832	448	1240
Observed reflections	4957	6308	3786	4516	3641	5326
Parameters	370	478	271	242	252	352
Goodness-of-fit on F^2	1.379	1.152	1.127	1.079	1.033	1.043
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.075$, $wR_2 = 0.191$	$R_1 = 0.040$, $wR_2 = 0.114$	$R_1 = 0.057$, $wR_2 = 0.148$	$R_1 = 0.027$, $wR_2 = 0.068$	$R_1 = 0.029$, $wR_2 = 0.070$	$R_1 = 0.043$, $wR_2 = 0.105$

Table 4
Crystal data and summary of data collection and refinement for **9**, **10**, **12** and **13**

Complex	**9** · 2THF	**10** · 0.5toluene	**12**	**13**
Formula	$C_{28}H_{60}B_{20}O_4Ru_2$	$C_{34.5}H_{48}B_{10}NPRu$	$C_{16}H_{36}B_{10}N_2Ru$	$C_{14}H_{26}B_{10}N_2Ru$
Crystal size (mm)	0.50 × 0.50 × 0.40	0.50 × 0.40 × 0.30	0.50 × 0.30 × 0.20	0.50 × 0.30 × 0.20
Formula weight	879.1	716.9	465.6	431.5
Crystal system	Triclinic	Triclinic	Monoclinic	Orthorhombic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	*Pnma*
a (Å)	11.473(2)	10.598(2)	13.694(3)	14.581(3)
b (Å)	12.781(3)	11.424(2)	10.729(2)	13.474(3)
c (Å)	16.952(3)	18.652(4)	16.000(3)	10.660(2)
α (°)	76.88(3)	83.37(3)	90	90
β (°)	74.24(3)	84.72(3)	105.55(3)	90
γ (°)	77.78(3)	80.01(3)	90	90
V (Å^3)	2299.9(8)	2203.0(8)	2264.8(8)	2094.2(7)
Z	2	2	4	4
D_{calc} (Mg m^{-3})	1.269	1.081	1.366	1.369
Radiation (λ/Å)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
$2\theta_{max}$ (°)	50.0	48.0	51.0	51.0
μ/mm^{-1}	0.687	0.414	0.698	0.749
F(000)	896	742	960	872
Observed reflections	7173	5044	7225	1933
Parameters	533	439	268	133
Goodness-of-fit on F^2	1.221	1.281	1.074	1.196
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.053$, $wR_2 = 0.162$	$R_1 = 0.081$, $wR_2 = 0.257$	$R_1 = 0.043$, $wR_2 = 0.130$	$R_1 = 0.046$, $wR_2 = 0.120$

toluene molecule in **10** was highly disordered and only arene ring was located using rigid body refinement. Crystal data and details of data collection and structure refinements are given in Tables 3 and 4.

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Appendix A. Supplementary data

Crystallographic data in CIF format for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, the CCDC reference numbers 289259–289268 for **2**, **3**, **5**–**8**, **9** · 2THF, **10** · 0.5toluene, **12** and **13**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.03.022.

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